Physicochemical Hydrodynamics of Binary and Ternary Liquids

Ricardo Arturo López de la Cruz

PHYSICOCHEMICAL HYDRODYNAMICS OF BINARY AND TERNARY LIQUIDS

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Front cover: Droplets of oil arranged in a branch-like pattern within an ouzo mixture inside of a Hele-Shaw cell. Back cover: Marangoni rolls evidenced by the different contrast of the ethanol-poor solution. Ouzo droplets are dispersed within the roll.

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DISSERTATION

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on account of the decision of the graduation committee,
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by

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*To my parents,
to my sisters
and
to Víctor Calvillo and Javier Adame*

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Introduction

When thinking of the word *liquid*, it is very probable that the first thing to come to our minds is water (at least this is what happens to the author). Water, as we normally drink it, is a single component liquid, however, for many their drink of preference is not just water, but water with a good dose of caffeine, and perhaps a bit of sweet sugar and –why not?– some milk. This of course means that the drink is no longer a single component liquid, but a multicomponent one. This thesis is concerned with those kind of liquids, and while a Latte might have many components (water, caffeine, milk, sugar), we restrict ourselves to liquids of only two or three components.

As you might have noticed from the title, apart from binary and ternary liquids this thesis is also concerned with physicochemical hydrodynamics. What do we mean by that? In the words of Veniamin G. Levich, “by physicochemical hydrodynamics we understand the aggregate of problems dealing with the effect of fluid flow on chemical or physicochemical transformations as well as the effect of physicochemical factors of fluid flow” [1].

In his book *Physicochemical Hydrodynamics*, Levich covers topics like convective diffusion, diffusion in turbulent flows, heat transfer, coagulation of dispersions, capillary flows, the movement of droplets, bubbles and particles, electrolytic solutions, thin films, wave motion at a liquid surface, and the polarographic method. This is clearly a wide range of topics and many lines of research can start from the ideas of this book as has been recently reviewed [2]. To cite some examples, consider the swimming droplets [3] and particles [4] propelled by interfacial forces that originate from a gradient in temperature [5] or concentration [6] in the surrounding liquid, with such gradients possibly caused by the droplets themselves [7]. We can also think of spontaneous flow at an interface [8,9] or of spontaneous emulsification within a droplet [10]. All these phenomena come about because more than one component is present at the same time in the liquids or the gases, leading to physicochemical transformation with implications on the fluid flow.

Besides the academic interest that one might have in the physicochemical hydrodynamics of multicomponent liquids, different practical application exist that motivate this research. Mixtures of liquids can be found in chemical reactors, in chemical analysis and diagnosis [2], in liquid-liquid extraction [11–13], in pharmaceuticals, for example for drug encapsulation [14, 15], in inkjet printing [2, 16], in emulsions [17], in CO₂ entrapment techniques [18], amongst others.

While clearly this research area is wide, the focus in this thesis is on processes triggered by diffusion. More specifically, we will study the dissolution of droplets and the evaporation of thin films confined by a Hele-Shaw cell (a device consisting of two parallel plates with a small gap in between them, making the system quasi-two-dimensional). In other words, the focus will be on small scale systems that have an interface. By interface we mean the frontier between a liquid and a gas or between two liquids that do not mix. Such frontier will play a central role in the hydrodynamics of the systems studied in this thesis as it will be explained in the following section together with other phenomena that are key to the thesis.

Physical phenomena of interest

Marangoni flow

When two immiscible fluids, like water and oil, are brought into contact, an interface is formed in between them. If we zoom into that interface, it can be realized that the molecules located at the interface are surrounded by molecules of both water and oil ¹. In comparison, in the bulk, the molecules are surrounded only by other molecules of the same kind. As a result, the forces acting on the molecules at the interface are imbalanced, causing an overall tension tangential to the interface. Such force is called surface tension when one of the fluids is a gas and interfacial tension when both the fluids are a liquid.

When the surface tension is not constant along the interface, a flow takes place from regions of lower to regions of higher surface tension. Such flow is

¹In reality an interface is not perfectly sharp. Instead the frontier is *diffuse* and there is a gradual change from one fluid to the other. However, here we are taking a simplification and considering that the interface is actually sharp and infinitesimally thin.

called Marangoni flow after Carlo Marangoni. A short explanation for this phenomenon is as follows. If the surface tension has the same value all over a flat interface, the sum of forces will be zero and the interface would be expected to be at rest (when no other forces are in play). However, if the surface tension is larger at a point on the interface, the sum of forces over the interface will be non-zero. Consequently, the interface should accelerate towards the region of higher surface tension. Equivalently, it can be considered that the regions with lower surface tension get “stretched” by the regions of higher tension, resulting in a flow towards the latter.

Surface tension is a function of temperature and the concentration of solute and surfactants. Therefore, gradients in any of these quantities result in gradients of surface tension and ultimately fluid motion. Such gradients could be intentionally imposed upon a system, by for example warming up one side of an open vessel with a liquid inside, or by adding a drop of soap in the center of a bowl of water, regularly observable when doing the dishes. However, in other cases such gradients are unintentional. For example, when a binary mixture evaporates, if one of the two components is more volatile and also has a different surface tension than the other, small heterogeneities in the evaporation process can result in regions of the interface with different concentration values, thus different surface tensions. In the right conditions, the small changes can grow in time and cause “large” scale flows as it will be discussed in chapter 1.

Phase separation of ternary systems

We might be very familiar with the fact that water and oil do not “like” to mix with each other. However, something that we might not be as familiar with is the fact that if a third player is added, like an alcohol, then water and oil can come to a “truce” and mix as long as there is enough alcohol involved. Leaving the anthropomorphic analogy behind, the message is that alcohols such as ethanol, which is miscible with both water and oil, can increase the solubility of oil in water, and vice versa. The three liquids can thus form a single phase homogeneous mixture when the concentration of ethanol is high enough.

Before explaining how high is “high enough”, it is useful to introduce the ternary diagram, which is a graphical tool used to represent the concentration ratio of ternary systems and their state. Ternary diagrams are based on the

properties of an equilateral triangle. One of those properties is that for any point inside the triangle, the sum of the distances H_i from that point to the three sides is equal to the total height H of the triangle (see figure 1a). Therefore, by taking a triangle with unitary height, any point inside the triangle will indicate the concentration of each of the three components of a ternary system, either as a mass, a volume or a mole fraction. In practice, however, instead of the distance to the sides, the concentration can also be read by tracing a line that passes through the point of interest and that is parallel to one of the sides of the triangle, then the concentration is given by the scale on one of the sides of the triangle. For an example, see the dark green arrow in figure 1a.

Figure 1: a) Example of a ternary diagram with one point marked. The concentration of each component is given by the ratio H_i/H , with $i = 1, 2, 3$. The fraction of a given component can also be read by drawing a parallel line to one of the sides of the triangle, then reading the corresponding scale. In this example, the concentration of component 1 can be read by following the dark green arrow. The arrow is parallel to the side opposite to the corner marked as c_1 . b) Example of a ternary diagram with the binodal and spinodal curves. An example of a tie line is shown and the main regions are labeled.

As mentioned earlier, water, oil and ethanol can form an homogeneous mixture as long as the concentration of the good solvent, ethanol, is high enough. A “high enough” concentration is determined by the thermodynamics of the system, so it depends on the three liquids selected, the temperature and the pressure. The threshold above which the mixture is a single phase is called the binodal. In a ternary diagram it is represented as a line that separates the mixtures that will have a single phase, with those that will create two

phases (see figure 1b). Below the binodal (in terms of alcohol concentration) there is a second threshold called the spinodal. Mixtures with an ethanol (or in general a solvent miscible with the other two components) content below the spinodal are thermodynamically unstable. This means that if three liquids are mixed with a ratio below the spinodal, small fluctuations will cause the mixture to spontaneously separate into two phases by what it is called spinodal decomposition. The two phases will have concentrations that in the ternary diagram are connected by a line segment called the *tie line*. Any mixture laying on the tie line will phase separate into the same two phases whose concentrations are given by the points at the edges of the tie line.

The region in between the binodal and the spinodal curves is a region of meta-stability. It is in this region where a very interesting phenomena takes place, called the “ouzo effect”. The name was coined by Vitale and Katz [19] who borrowed it from a greek liquor called ouzo, which contains a small amount of anise oil. When consumed, it is customary to mix it with water, which transforms it from a clear transparent liquid to a milky white beverage. This is because the addition of water brings the ouzo to the meta-stable state between the binodal and spinodal lines, resulting in the *spontaneous* nucleation of droplets. The droplets of this emulsion are in the micro meter range, resulting in the scattering of light, thus giving the liquid a white color.

The ouzo effect has gained attention because it gives an alternative to create emulsions without the need to spend energy in mixing [17]. Moreover, the emulsions are stable for long periods of time, even months, without the need of stabilizing particles or surfactants [20]. Therefore, it can be useful in processes that require emulsions like the fabrication of micro- and nanoparticles or capsules for drug delivery [14, 15]. A full understanding of the ouzo effect is still lacking which is why the topic of chapter 2 is the evaporation of a ternary system capable of the ouzo effect and how emulsification interacts with a Marangoni instability.

Natural convection

The density of fluids is commonly a function of both temperature and concentration (in the case of mixtures). Therefore, when either of these two parameters changes, it is expected that the density will change too. A very common example is air, which tends to expand with increasing temperature, thus reducing its density. Accordingly, warmed up air experiences a buoyant

force which makes it rise. That is why the second floor of a house tends to be warmer than the ground floor.

The flow caused by changes in density is called natural convection. While this term more commonly refers to a flow caused by temperature changes, in this thesis we will use it for flows caused by changes in concentration. In particular, natural convection will become important in chapter 3. More specifically, the dissolution of a pentanol droplet into water will create an upwards flow (a plume) because a water–pentanol solution has a lower density than pure water.

Systems studied in the thesis

Figure 2: Sketch of the system used in chapters 1 and 2, viewed from a) the side and b) the bottom. A binary or ternary mixture contained in a Hele-Shaw cell is allowed to evaporate into air from one side of the cell. The evaporation of the liquid causes a flow which is assumed to have a Poiseuille profile, as depicted in panel a).

The first system of interest is a Hele-Shaw cell. A cross section of the cell is sketched in figure 2a). The walls of the cell are perpendicular to gravity and they extend from $z = 0$ towards the positive z -direction. The distance δ between the walls is much smaller than the lateral extension of the walls, so that we can assume the system to be semi-infinite. The space between the walls is filled with either a binary or a ternary mixture. The space corresponding to $z < 0$ is filled with air, hence a liquid–air interface forms at $z = 0$. The interface stays pinned at $z = 0$ over time. The liquid inside the cell is volatile, thus evaporation takes place at the interface. The mass loss caused by evaporation and the pinning of the interface causes a flow in the negative z -direction. A replenishing flow is imposed at the right hand side of the cell

Figure 3: Sketch of the system used in chapter 3. Two droplets vertically aligned dissolve into a bath of a denser liquid. Each droplet is held in place by a capillary.

to compensate for the flow caused by evaporation. At the solid walls we will consider a no-slip boundary condition and as the simplest approximation to the flow a Poiseuille (parabolic) profile will be assumed.

In chapters 1 and 2 we will observe at the system from below (in the y -direction), therefore, the images that will be presented will look as sketched in figure 2b) focusing mainly on the liquid side. Because one of the components of the mixtures will be more volatile, a concentration gradient perpendicular to the interface will build up. For modeling, it will be assumed that the concentration of vapour at the interface on the air side is given by the local saturation value c_{sat} , which depends on the local concentration at the interface on the liquid side via Raoult's law. Far away from the interface as $z \rightarrow \pm\infty$ the concentration will tend to the initial concentrations $c_{\text{initial}}^{\text{liquid}}$ and $c_{\text{initial}}^{\text{air}}$ in the liquid and air, respectively. In the air, the concentration of the most volatile liquid will be set to zero to promote its evaporation.

Figure 3 shows a sketch of the system under study in chapter 3. Two droplets will be left to dissolve in a bath of a denser liquid. The droplets will be held in place by two capillaries that are also used to infuse the droplets. The dissolution of the droplets will cause the liquid around them to become less dense resulting in natural convection in the form of a plume moving upwards. The system will be assumed axisymmetric. In experiments the size of the

U	characteristic velocity	L	characteristic length
D	diffusion coefficient	μ	dynamic viscosity
ρ	density	ν	kinematic viscosity
g	gravity	c	mass fraction
$\langle \dot{m} \rangle_A$	surface averaged mass flux	A	surface area
R	radius of a droplet	γ	surface tension
β	solutal expansion coefficient		

Table 1: Variables used in the definitions of the non-dimensional numbers.

container will be about 10 times the diameter of the droplets, so we will ignore the effects of the walls and assume that the concentration far away from the droplets tends to zero. In simulations, the lateral side and the bottom will be assumed to have no slip boundary conditions and the top will have an open flow.

Non-dimensional numbers and the physical regimes in this thesis

Non-dimensional numbers compare the importance of pairs of physical mechanism, for example, by taking the ratio between the force caused by gravity and the force caused by viscosity. The values taken by these numbers determine which of the two physical mechanisms is dominant, thus dictating the behavior of the system under study. There are a few non-dimensional numbers that are important for the thesis and they will be introduced in this section. For each number we will present its definition, its physical meaning and the typical values it takes in the systems studied in the thesis. Table 1 lists the variables used in this section.

Marangoni number. This number compares the rate of advective transport due to gradients in surface tension to the rate of transport due to diffusion. It is defined as $Ma = -(d\gamma/dc)L\Delta c/(\mu D)$, with γ the interfacial tension, c the concentration of one component in a mixture, Δc a change in that concentration, L a characteristic length, μ the dynamic viscosity and D the diffusion coefficient. In chapter 1 and 2, this number will arise when evaluating the stability of the liquid–gas interface. For a large enough Marangoni number the interface will be unstable, evidenced by the emergence of flows parallel to the interface. In the systems in chapters 1 and 2, one of the components will

be considerably more volatile than the others, so its evaporation will cause a large value for Δc , bringing the value of the Marangoni number up to 10^4 , and casting the interface unstable. In chapter 3, while we do not use this number to determine the stability of the liquid–liquid interface, its large values ($Ma \sim 10^3$ to 10^4) indicate that when a gradient in interfacial tension appears, it will result in a flow at the interface.

The **Schmidt number** is given by the ratio of diffusive momentum transport to diffusive mass transport, which reduces to $Sc = \nu/D$, with $\nu = \mu/\rho$ the kinematic viscosity. In chapter 1, this number will also come up when calculating the stability of the interface, however we will show that it has a minor effect. Additionally, this number gives an indication of the relative size of the velocity boundary layer to the concentration boundary layer. In our systems the Schmidt number goes from 10^3 to 10^4 . Therefore, the velocity boundary layer caused by the Marangoni effect or by natural convection will be wider than the concentration boundary layer.

Péclet number. This number compares the rate at which a quantity is transported by fluid motion (advection) to the rate of transport by diffusion. It is defined as $Pe = UL/D$, where U is the characteristic velocity scale of the system under study. When $Pe \ll 1$, the system is dominated by diffusion. This is normally the case for small scale systems, like in this thesis. However, in the presence of a Marangoni flow or natural convection the characteristic velocity can become sufficiently large to bring the Pe number above 1 in certain regions of the system, for instance close to an interface. Since we are concerned both with Marangoni flows and natural convection, the Péclet number will have a wide range that goes from below 1 to above 1 at different locations and times. Therefore, in the following chapters, both advective and diffusive effects will be taken into account. More specifically, we will have to make use of the advection diffusion equation to model the concentration field of our mixtures, instead of the simpler diffusion equation. This will become evident in the corresponding sections of chapters 1 and 3. Furthermore, in chapter 1, the Péclet number will hint towards the mechanism behind the transport of dye within our system.

Archimedes number. It determines how strong is the force caused by buoyancy as compared to the force caused by viscosity. It is defined as $Ar = gL^3\rho\Delta\rho/(\mu)^2$, where $\Delta\rho$ is the maximum density difference attainable in our systems, and g is the acceleration due to gravity. For chapters 1 and 2, where the system is a thin film normal to the direction of gravity (see figure 2a)), the relevant length scale will be the thickness of the film. Since this

length is very small, the Archimedes number will be small too, in the order of $\sim 10^{-3}$. Therefore, the buoyancy forces that could arise due to fluctuations in the density along the direction of gravity will be much smaller than the viscous forces in the same direction. Consequently, the buoyant forces can be ignored in the momentum equation. However, in chapter 3, the characteristic length is the radius of the droplets, resulting in $Ar \sim 1$, meaning that the buoyancy forces will have to be taken into account.

In chapter 3, where the focus changes to the dissolution of droplets, the **Sherwood number** will become central. This non-dimensional number will be defined as $Sh = \langle \dot{m} \rangle_A L / (\Delta c D)$, with $\langle \dot{m} \rangle_A$ the mass flux averaged over a surface area. This number naturally appears in the context of natural convection in a vertical wall, as a non-dimensional mass flux. In the case of the dissolution of droplets, L will be substituted by the radius R of the lower droplet. As a result, the Sherwood number will compare the measured mass flux per unit area in contact with the bath, with the mass flux caused solely by diffusion in the case of a perfectly spherical droplet suspended freely in a stagnant bath. In this way we can assess the impact that other mechanisms have in the dissolution process. For example, if $Sh > 1$ it would mean that the dissolution is faster than in the case of pure diffusion, indicating that there are other mechanisms aiding the mass transfer, like natural convection.

Very closely related to the Sherwood number is the **mass transfer Rayleigh number**. It can be considered as the ratio between the characteristic time for mass transport by diffusion to the characteristic time of mass transport by natural convection. Its definition is $Ra = g\beta\Delta c L^3 / \nu D$ with $\beta = (\partial\rho/\partial c)/\rho$ the solutal expansion coefficient. Like the sherwood number, the Rayleigh number also arises when calculating the mass flux caused by natural convection next to a vertical wall. The Rayleigh number will be translated to the system of dissolving droplets, where again the radius R of the lower droplet will be the characteristic length, like it has been done in Reference [21]. Since the radius of the droplet changes over time, the Rayleigh number will change too, going from approximately 1000 to 0. Therefore, gravity will play a prominent role for the majority of the life time of the dissolving droplets. In other words, the dissolution rate will be determined mainly by the transport caused by natural convection, affecting the value of the Sherwood number.

Reynolds number. This number compares inertial forces to viscous forces and it is defined as $Re = UL/\nu$. In the systems treated in this thesis $Re \ll 1$, except for flows caused by the Marangoni effect, in which case $Re \sim 1$. More importantly, in chapter 3, this number will be calculated considering the

velocity caused by natural convection and the radius of the lower droplet. It will be corroborated that the Reynolds number is dependent on the Rayleigh number when natural convection is active.

Bond number. It compares the strength of gravity forces with those of surface tension and it is defined as $Bo = gL^2\Delta\rho/\gamma$. In the context of droplets, it gives an indication of the deviation of the shape of a droplet away from a sphere. Given that in our experiments this number is in the order of $Bo \sim 0.05$, it means that the surface tension is dominant, hence the shape of the droplets will be closely a sphere.

A guide through the thesis and the questions it tackles

As already hinted by the description of the systems in a previous sections, this thesis has two parts, the first one (chapters 1 and 2) looks at the evaporation of mixtures within a Hele-Shaw cell, hence a quasi-2-D system in cartesian coordinates. The second part (chapter 3) deals with the dissolution of droplets in a three-dimensional bath, but with cylindrical symmetry. In a broad sense, in this thesis I explore what kind of phenomena can be triggered by the geometry and the composition of a multicomponent system. Then I identify, to the best of my abilities and aided by my supervisors and collaborators, the basic mechanisms at play and how their interactions results in the observed phenomena.

In Chapter 1, I tackle an old problem, namely a Marangoni instability at an air-liquid interface. This chapter is based on experiments and theoretical work that goes back all the way to Henry Bénard at the beginning of the 1900's [22]. I study the evaporation of an ethanol–water mixture contained in a Hele-Shaw cell, as already sketched in figure 2. To study this system I made use of experimental, numerical and theoretical techniques that support each other. The main questions to answer in this chapter are: i. *How does the flow caused by the Marangoni instability inside the Hele-Shaw cell evolve over time?* ii. *Under which conditions will a Marangoni instability arise?* and iii. *How does the presence of the walls of the cell affect these conditions?*

In Chapter 2, the same experimental system is used, but the mixture is made more complex by adding a third component, namely, trans-anethole. As a result, the phenomena become richer. With a ternary mixture, phase separation can take place in the form of the ouzo effect or spinodal decomposition, while the Marangoni instability is also present. Given the wide variety of phenom-

ena than can arise, I limit myself to qualitatively describe *how the temporal evolution of the system changes when we change the initial composition of the mixture*. I also offer a rationale to explain *why the different phenomena happen, according to the ternary phase diagram of the mixture and the existing literature*.

In Chapter 3, I study the dissolution of droplets of alcohols in water, both a single droplet and a pair of droplets. A sketch of the system is shown in figure 2b), for the case of two vertically aligned droplets. While in chapters 1 and 2 gravity is disregarded, in this chapter it plays a role in the form of natural convection. The plumes arising from the dissolution of the droplets affect back the dissolution process. Moreover, when the upper droplet is of a different liquid than the lower one, gradients in concentration result in an oscillatory Marangoni flow. In the first part of the chapter I study two reference cases, namely a single and a pair of droplets of the same liquid. Then I explore *how changing the liquid of the upper droplet affects the dissolution process of the lower droplet?* and *how the plume created by the lower droplet affects the dissolution of the upper one?* Finally, I shift focus to the Marangoni flow. I use both experiments and numerical simulations to describe and understand the interplay between the Marangoni and the gravitational flow and to answer *why the flow becomes oscillatory?*

Before moving on to the main content of the thesis, I would like to add some words about how the work put into the thesis was distributed, although I would like to stress that it was the result of team work. In all chapters, the experiments, the data processing and analysis were done by Ricardo López. Dr. Yanshen Li helped me with the initial design of the microfluidics chips used as a Hele-Shaw cell. In chapter 1, I performed the linear stability analysis based on the work by Yibo Chen *et al.* [23]. Yibo Chen and Dr. Steven Chong gave me very useful input during the process. In chapter 2, Noor Schilder performed preliminary experiments that helped in the understanding of the system. The numerical simulations in chapters 1 and 3 were set by Dr. Christian Diddens who shared the code with me so I could perform some of the simulations myself. I performed the numerical data processing and analysis with constant input from Dr. Christian Diddens. The writing process was shared between Dr. Christian Diddens, Prof. Dr. Xuehua Zhang, Prof. Dr. Detlef Lohse, and me. For the three chapters, Prof. Dr. Xuehua Zhang and Prof. Dr. Detlef Lohse constantly gave input and supervised the work.

1.1 Introduction

The stability of an interface is important for processes where mass or heat transfer between two phases take place, e.g. drying of paint, coating, distillation, absorption and extraction. In the particular case of a Marangoni instability, variations of temperature or concentration along the interface give rise to surface tension gradients that trigger convection. The study of interfacial instability goes back to the pioneering work of H. Bénard in 1901 [22]. Although in that work natural convection was considered to be the cause of the instability, Pearson [8] showed by means of linear stability analysis that some of the observations could be explained by gradients in surface tension caused by variations in temperature (thermal Marangoni instability). Soon after, Sternling & Scriven [9] showed, by a linear stability analysis too, that the same effect could be driven by gradients of concentration (solutal Marangoni instability).

Since then, a large body of studies has extended and generalized the works by Sternling & Scriven [9], for example, to three dimensions with deformable interfaces [25, 26] and gravity waves [27]. Also the effects of chemical reactions [28], finite domains [29], finite domains with binary mixtures and the Soret effect [30] and modified geometries (such as spherically symmetric [31]) have been considered. Exponential concentration profiles and surfactant accumulation at the interface were studied by Sørensen *et al.* [32, 33]. More recently, Bratsun & De Wit [34] studied the instability between two liquids inside a Hele-Shaw cell where a chemical reaction takes place at the interface. Picardo *et al.* [35] considered the case of evaporation coupled with a Poiseuille flow, and Machrafi *et al.* [36] looked at the stability of an evaporating ethanol–water mixture in two dimensions taking evaporative cooling and the Soret effect into account. This list is by no means extensive, the reviews by Levich & Krylov [37], Sanfeld & Steinchen [38] and Kovalchuk & Vollhardt [39] present a more comprehensive overview, including cases where heat transfer is also considered. We refer to the reviews of Linde *et al.* [40] and Schwarzenberger *et al.* [41] for further experimental and numerical work. While a considerable part of the experimental work has focused on extended interfaces [40, 42], there has also been quite some work on binary systems confined within a Hele-Shaw cell. Employing this kind of cell has the advantage that it allows us to have visual access to the effects that the instability has in the bulk of the two phases. Furthermore, the system can be consid-

ered as quasi-two-dimensional (quasi-2-D). Many of the papers that make use of a Hele-Shaw cell have focused on liquid–liquid interfaces where chemical reactions take place, including experimental [43–48], numerical [49, 50] and theoretical [34] approaches. In particular, Köllner *et al.* [51] performed both experiments and numerical simulations, showing good qualitative agreement between them, though the Marangoni rolls in experiments grew faster than in simulations.

Following the criteria established by Sternling & Scriven [9], Linde *et al.* [52] studied the stability of liquid–gas interfaces of binary systems, where either selective evaporation or adsorption triggered a Marangoni instability. Linde *et al.* [52] pointed out that both thermal and solutal instabilities were at play simultaneously. By looking at the evaporation of pure liquids to isolate the thermal instability, they observed that the flow was weaker than when the solutal Marangoni instability was also present. In this way they were able to suggest that solutal Marangoni was the strongest mechanism. However, in that paper, the quantitative description of the phenomena was limited.

More generally, great efforts have been devoted to the understanding of the physicochemical hydrodynamics of multicomponent systems [1], especially of multicomponent droplets, due to their importance in many fields such as chemical diagnosis, inkjet printing or nanotechnology, to mention a few. For a recent review on this subject we refer to the work of Lohse & Zhang [2]. In many of these systems, mass transfer through interfaces causes gradients in chemical concentration that in turn result in a Marangoni flow. Such a flow can then lead to quite rich phenomena; for example, it can participate in the segregation of evaporating binary droplets [53], make a droplet inside a bath jump against the pull of gravity [6, 54], and more generally cause the self-propulsion of droplets [2, 3, 7]. These Marangoni flows can also assist the emulsification of evaporating ternary droplets [10, 55], or drive the so-called Marangoni bursting [56]. In some cases Marangoni forces compete with gravity, leading to unexpected flow directions inside evaporating sessile and pendant droplets [57, 58]. Clearly, these phenomena are closely connected with the presence of instabilities at interfaces where mass transfer and evaporative cooling take place. However, the three-dimensional (3-D) shape of the droplet which changes in time makes the geometry complicated. Therefore, the Hele-Shaw geometry is a good candidate to further understand the Marangoni convection present when selective evaporation takes place. Moreover, the very common use of microfluidic devices in research nowadays makes it important to understand the influence that the confinement has on the Marangoni con-

vection. Indeed, Marangoni flow in microfluidic devices can be used to enhance mixing [59].

The aim of this work is to revisit one of the systems studied by Linde *et al.* [52], namely a binary solution of ethanol–water confined by a Hele-Shaw cell evaporating into air. In particular, we study the evolution of the instability in time by means of confocal microscopy and microparticle image velocimetry (μ PIV) (section 2). In section 3, this system is modelled and numerical simulations of the model equations are performed. This model is quasi-2-D and takes into account the drag caused by the walls of the cell [34, 51, 60]. The simulation results are able to reproduce our experimental observations quite well, even though we do not consider the effects of evaporative cooling. In section 4, inspired by a previous work [23], we present a linear stability analysis of a simplified version of the quasi-2-D model equations. We compare the results of the linear stability analysis with those from numerical simulations at early times, showing not perfect, but close agreement. Finally, in section 5 we conclude and give an outlook on future work with ternary systems.

1.2 Experimental methods and results

1.2.1 Materials and methods

Design of Hele-Shaw cell

A microfluidic chip (Beijing First Mems Co., Ltd) was used as a Hele-Shaw cell. In figure 1.1a) a cross-section of the chip is shown. The black region was made of an edged silicon wafer, while the light blue plate was made of glass to allow for optical visualization. The gap between the two plates was of 20 μm and kept constant by means of a series of pillars depicted as thin vertical lines in figure 1.1a). Further details can be seen in appendix 1.6.1. At the back of the chip (right-hand edge in figure 1.1b) and c)), a channel 50 μm in depth was used to fill the chip with the binary liquid. Three sides of the chip were closed and one was open to allow for evaporation (left-hand side in figure 1.1b) and c)). The surface of the chip was made hydrophobic as described in appendix 1.6.1.

Figure 1.1: Sketch of the experimental setup from a) frontal, b) bottom and c) side views. The main component was a microfluidic chip made of an edged silicon wafer and a glass plate for observation. The gap between both plates was $20\text{ }\mu\text{m}$. To maintain a homogeneous gap, a matrix of pillars was placed between the wafer and the glass, represented as thin vertical lines in panel a) and as circles in panel b) (not to scale). Additionally, two walls divided the cell in three different parts. At the back of the chip a channel of $50\text{ }\mu\text{m}$ in depth was used to continuously refill the cell and compensate for mass losses due to evaporation. As depicted in panel a), the whole chip was surrounded by a chamber where the humidity was monitored and controlled with a flow of dry and humid nitrogen. In panel b), the gap region is represented in grey and the red rectangle indicates the region of observation. In panel c), the meniscus is drawn (solid green line) to indicate a slightly wetting liquid. The dimensions are not to scale for better visualization. The silicon wafer is $400\text{ }\mu\text{m}$ thick without edging and the glass plate is $500\text{ }\mu\text{m}$ thick. The holder cap was approximately $170\text{ }\mu\text{m}$ above the chip.

Experimental setup

We visualized the evaporation process at a region around the open edge (red square in figure 1.1b)) with a confocal microscope (Nikon Confocal Microscopes A1 system). As opposed to the liquid, the gas phase was not contained by the Hele-Shaw cell; instead it was a 3-D volume of approximately 3000 cm^3 . This volume was created by covering part of the microscope with plastic wrap (see the appendix 1.6.1). The relative humidity (RH) in this chamber was maintained within a desired range using a negative feedback. Every time the RH was outside the desired range, a flow of either humid or dry nitrogen was gently blown in. As long as the RH was within the range, the nitrogen flow was turned off. Humidity and temperature sensors (HIH6130, Honeywell) were used to monitor these two quantities. The readings were taken with an Arduino board (Arduino Nano) which also controlled the valves of the humid and dry nitrogen accordingly. The range over which there was no flow was either $50 \pm 1\%$ or $51 \pm 1\%$, depending on the RH in the room. This resulted in an overall range between 48% – 52% for all our experiments. Examples of

the time series of the RH in the chamber and extra details on the chamber can be found in the appendix.

In the case of the temperature of the air in the chamber, we only measured it during each experiment, but did not control it. Due to the heating caused by the electronics, the temperature was constantly rising at approximately 2 K h^{-1} . In the majority of our experiments the focus was on the first 100 s, during which the variations in temperature stayed within 0.3 K. The initial temperature of different experiments ranged from 294 to 298 K, with the majority starting around 297 K. We did not observe a strong effect on the main evolution of the instability and the velocity field. Examples of the temperature time series can be found in the appendix.

We assumed that at the beginning of each experiment the concentration of ethanol in the gas phase was negligible. We did not introduce ethanol into the chamber intentionally besides that coming from evaporation of the liquid inside the cell. Between each experiment, the chamber was opened to change the chip, allowing the ethanol that had evaporated during the experiment to escape.

In each experiment, the solution was delivered from a syringe connected through a capillary tube to the back channel of the chip (see figure 1.1b)). The flow rate was controlled with a motorized syringe pump (Harvard Instruments, PHD 2000). In each experiment the chip was filled within a minute at a rate of $15 \text{ } \mu\text{L min}^{-1}$. After the chip was filled, we had a delay of approximately 30 s to 60 s before a replenishing flow was started to compensate the mass loss due to evaporation. This flow was kept constant throughout the rest of the experiment (the direction of the flow is depicted with blue arrows in figure 1.1b)). Despite the hydrophobicity of the chip, the ethanol–water mixture slightly wets the chip. The contact angle with the glass wall is within 75° to 80° and 75° to 95° with the silicon wall (see the appendix for more details on the estimations of the contact angle). Therefore, as long as there was liquid at the back channel, the Hele-Shaw cell would remain filled. The replenishing flow would then prevent the back channel from emptying. We found the right volumetric flow by slightly underfilling the chip such that a meniscus was visible at the back channel (figure 1.1b). A volumetric flux of approximately $0.43 \text{ } \mu\text{L min}^{-1}$ kept the meniscus stationary. In experiments with dye, we used a slightly larger flow, $0.5 \text{ } \mu\text{L min}^{-1}$, which resulted in the chip eventually getting fully filled. However, there was no noticeable overflow at the observation region. Furthermore, the edge of the chip helped to keep the interface pinned. The pressure at the inlet of the chip was estimated to be approximately 19

Pa higher than at the evaporating edge. This pressure is smaller than the pressure drop across the meniscus at the evaporating edge (10^2 to 10^3 Pa), in accordance with no overflow (see the appendix for details on the calculation of the pressure drop).

We used rhodamine 6G (SigmaAldrich, dye content 99%) and $1\text{ }\mu\text{m}$ particles (FluoSpheres, carboxylate modified, Life Technologies) for visualization and for μPIV (30 fps), respectively. Further details on the μPIV experiments can be found in appendix 1.6.2.

After each experiment the chip was cleaned by immersing it in a bath of acetone, isopropyl alcohol and ethanol, sequentially. In-between each bath we used a flow of nitrogen for drying.

The solutions were made at a 50 wt% ratio between Milli-Q water (produced by a Reference A+ system (Merck Millipore) at $18.2\text{ M}\Omega\text{cm}$ (at 25°C)) and ethanol (Boom; 100%(v/v), technical grade), prepared by measuring the mass of each component using a balance (Secura 224-1S, Sartorius). The solution was not degassed before experiments.

1.2.2 Evolution of the instability from the interface into the cell

In one set of our experiments, we dyed the ethanol–water solutions with a trace amount of rhodamine 6G (R6G). As evaporation takes place, non-volatile R6G accumulates close to the edge, resulting in brighter regions, as can be seen in figure 1.2a) (these snapshots were taken at the region marked with a red square in figure 1.1b)). These regions are shaped as arches of approximately the same sizes, suggesting the presence of an instability [51, 52]. If this were not the case, we would expect the accumulation of R6G to be distributed uniformly all along the edge (white vertical dashed line), but not in specific regions.

Over time, the arches grow and merge with each other as seen in figure 1.2a), where their number has gone from three to one over a few seconds. This kind of coarsening behaviour is expected for Marangoni instabilities [41]. Such a phenomenon was also observed in evaporation experiments inside a Hele-Shaw cell by Linde *et al.* [52].

We measured the distance $z_F^d(t)$ that the accumulated dye penetrated towards the inside of the cell as a function of time (see the third subpanel of figure 1.2a) for an example of z_F^d). Here the superscript d indicates a dimensional quantity. To measure z_F^d , we took the vertical average of the intensity field, resulting in an intensity profile as a function of z^d . Then we took the derivative of this

Figure 1.2: a) Snapshots taken at the region marked with a red square in figure 1.1b) at three different times. The snapshots show an evaporating 50 wt% ethanol–water solution dyed with rhodamine 6G (see movie 1 of appendix 1.6.8 for the whole time evolution). The dye accumulates in regions shaped as arches that grow and merge with each other over time. We have added the time t_0^d because the solution can start to evaporate even before it reaches the edge. The vertical white dashed lines indicate the position of the edge of the chip and the interface between air (left) and liquid (right). b) Height z_F^d of the arches (see last subpanel of panel a) for a definition) as a function of time. Different independent realizations of the experiment are shown in grey, while a single case is highlighted in red. The black dashed line corresponds to the power law $z_F^d \propto (t^d)^{0.50 \pm 0.04}$. All the realizations were fitted omitting the data for which $t^d < 1$ s. *Inset*: same plot, but with linear axes.

profile with respect to z^d . Finally, we looked for the distance from the edge where the derivative was zero within noise level and we assigned this value to z_F^d . This process was then repeated for every time frame.

In figure 1.2b), we show some examples of $z_F^d(t)$ on a double logarithmic scale. A close inspection of the plots shows that during a merging event z_F^d accelerates and then slows down. However, as an overall trend, z_F^d grows effectively as a power law. Fourteen independent runs were fitted to $\propto (t^d)^\alpha$. An average exponent of $\alpha = 0.50 \pm 0.04$ suggests that z_F^d effectively grows in a diffusive-like manner. A similar behaviour has been observed in liquid–liquid systems with Marangoni instabilities [51]. Figure 1.2b) includes cases with two different mass fractions of R6G: 10^{-4} and 10^{-5} . There are no considerable changes in the exponent (see the appendix for a plot with all cases).

We defined the time $t^d = 0$ s to be the moment at which the solution reached the edge within our field of view. Although evaporation can take place while the chip gets filled, we expect its effect to be negligible as long as the liquid is far away from the edge. Nevertheless, it can trigger the instability already some time before the liquid reaches the edge. For the fits, data for which

Figure 1.3: Long-time flow dynamics for the same experiment as in figure 1.2. In panel a) we highlight how the dye flows back at the centre of an arch in a meandering way (marked with a white arrow). In panel b) secondary arches are clearly visible. They last for just a few seconds and travel towards the tip of the principal arch. For these two images we adjusted the contrast for visibility. In panel c) the arches have grown to a size comparable to the width of the central part of the chip marked by the red square in panel d). The semiarch visible in the first subpanel of c) is in contact with the upper wall. The white dashed line indicates the edge of the chip. The images in panel c) were made by stitching smaller pictures (taken over 20 s).

$t^d < 1$ s was omitted to minimize the effects of our uncertainty on the initial time. The rest of the time series was included in the fit.

As the arches get bigger, interesting phenomena take place inside them. We show in figure 1.3a) how the dye flowed back into the chip in a meandering way, and in figure 1.3b) short-lived secondary arches. The latter travelled towards the tips of the arches in a few seconds while changing in size, as also observed by Linde *et al.* [52] and Schwarzenberger *et al.* [48]. In movie 2 in appendix 1.6.8 the secondary arches are clearly visible for a case where the liquid was seeded with tracer particles.

Eventually, the lateral size of the arches becomes comparable to the width of the central part of the chip, as shown in the first subpanel of figure 1.3c). The area shown corresponds to the red square in the sketch of figure 1.3d). We did not observe arches spanning over this whole area. Instead the arches eventually start to reduce in size (second subpanel of figure 1.3c)), sometimes

causing the remaining ones to start traveling along the edge. Overall, after 10-25 min the instability fades away and the dye is swept to the interface (third subpanel of figure 1.3c)). Then a narrow bright stripe parallel to the edge forms, suggesting that the gradient of surface tension is not strong enough to drive the flow anymore.

A possible reason for the instability stopping is a reduced evaporation of ethanol. Indeed, after taking the chip out from the chamber, we observed that the instability can start again. Therefore, as the chip was moved to an environment without any ethanol vapour, evaporation of ethanol can be restarted and the instability triggered again.

1.2.3 Visualization of the bulk flow by μ PIV

To visualize the flow caused by the instability, the solution was seeded with 1 μ m fluorescent particles at a very small volume fraction. In figure 1.4a) we show the streak lines made by the particles over a period of 1 s around 1.63 s after the solution reached the edge. Clearly shown by this figure, the arches in the previous section are the result of advected dye (a typical movie can be seen in movie 2 of the appendix 1.6.8).

The direction of the flow can be read from figure 1.4b) where we have plotted the corresponding normalized velocity vector field (averaged over 30 frames of a single experiment). The colour code in this image corresponds to the horizontal component of the velocity, while the vertical component and the magnitude can be seen in the appendix. We did not measure the velocity close to the edge for two reasons. One is the “shadow” caused by the edge of the glass plate. The other is the limited frame rate of the confocal system used for imaging, while closer to the edge the flow becomes too fast.

We would expect the flow to be as depicted in figure 1.4c), where the velocity at the interface is directed towards the centre of the arches. Then the fluid recirculates back to the tips of the arches. This kind of flows is typical for Marangoni-driven systems [41, 44, 51, 52]. Therefore, we can conclude that the flow changes direction at a distance smaller than the closest distance to the edge at which we can still see particles (~ 50 μ m from figure 1.4a)).

The effect of the interfacial flow is quite dramatic as can be seen from figure 1.4d), where we show the mean velocity profiles (averaged over 30 frames and along the x -direction) for different times. From these plots we can see the huge difference in the velocity close to the edge as compared with the velocity far

Figure 1.4: Flow characterization while the instability is active. a) Streak lines formed by tracer particles obtained by averaging the intensity of 31 frames, allowing to see the same arches as with dye. The white vertical line indicates the edge. b) The μ PIV measurement averaged over 1 s around $t^d = 1.63$ s after the solution reached the edge. The measurement was taken inside the white square marked in panel a). The colour code shows the horizontal component u_z of the velocity to highlight the periodicity of the flow. The arrows were normalized to clearly show the direction (the vertical component and the total magnitude are shown in the appendix 1.6.2). The black dotted line indicates the position of the edge. c) Sketch of the flow around and inside the arches. The gradient in concentration of ethanol produces a gradient in surface tension that drives a flow at the interface, resulting in convective rolls which cause the arch-like shape. d) Profiles of the velocity magnitude at different times in a semilogarithmic scale. The profiles were obtained as a spatial average over the x -direction of the velocity fields. Different symbols represent different realizations to show reproducibility. One of the blue lines corresponds to the case at $t = 1.63$ s shown in panel b). All cases were obtained from velocity fields averaged over 1 s around the time indicated by the legend.

away, going from some hundreds to approximately $20 \mu\text{m s}^{-1}$. In particular, this decay of the velocity seems to occur exponentially as can be seen from the approximately linear character of the velocity profiles when plotted in a semilogarithmic scale. With ongoing time, the velocity decays over longer distances, indicating that the arches are growing. Therefore, the slope of the linear regime (in the semi-logarithmic scale) also decreases. Moreover, we noticed that the change in time of the slope is more drastic at earlier times than at longer times, reflecting the fact that $z_F^d \sim t^{1/2}$. At longer times the arches are bigger than our field of view, so the profiles were obtained as an average over a fraction of an arch. Additionally, for the yellow curves we have masked the region inside the arch as the density of particles was too high for a correct measurement of the velocity (an example of a frame with the mask can be found in the appendix).

With the measured velocity we can now calculate a Péclet number, $\text{Pe} = U^d L^d / D_{\text{R6G}}^d$, with U^d and L^d the typical velocity and length of the flow, and D_{R6G}^d the diffusion coefficient of R6G in ethanol ($D_{\text{R6G}}^d = 2.9 \times 10^{-10} \text{m}^2/\text{s}$ [61]). For the typical velocity we can consider the maximum velocity (that we can measure) inside the rolls, which is of the order of $10^{-4} - 10^{-3} \text{m s}^{-1}$. The typical size of the arches is of the order of $10^{-4} - 10^{-3} \text{m}$. This results in a range of $\text{Pe} \sim 10 - 10^3$, clearly meaning that advection overcomes diffusion. Therefore, the dyed arches should result from the Marangoni rolls. As a last note, if we take the velocity far away from the arches ($\sim 20 \mu\text{m s}^{-1}$) as the typical velocity caused by evaporation and the size of the arches just after the stability is over, namely approximately 2 mm, then we obtain $\text{Pe} \sim 100$. The dye should indeed accumulate very close to the edge as advection overcomes the diffusion of the dye.

1.3 Model equations and their numerical simulations

1.3.1 Model equations

In the following, the governing equations modelling the evaporation of a confined ethanol–water solution into humid air as used for numerical simulations are described. A schematic of the simulated system confined by two walls is shown in figure 1.5.

Figure 1.5: Schematic of the numerical simulation. a) The small distance δ^d between the plates of the Hele-Shaw cell allows for the assumption of a parabolic flow profile in y -direction, which effectively reduces the problem to two spatial dimensions (x, z) . b) Sketch of considered domains, fields and boundary conditions. Notice that the quantities are non-dimensional.

The equations are made non-dimensional by using the distance between plates δ^d as a length scale, the initial mass density of the liquid ρ_0^d as a mass per volume scale, and the initial kinematic viscosity $\nu_0^d = \mu_0^d / \rho_0^d$ to construct the viscous time scale $(\delta^d)^2 / \nu_0^d$. Therefore, the non-dimensional space coordinates, time and velocities are given by $\mathbf{r} = \mathbf{r}^d / \delta^d$, $t = t^d \nu_0^d / (\delta^d)^2$ and $\mathbf{v} = \mathbf{v}^d \delta^d / \nu_0^d$, respectively. Due to the presence of a binary solution in the liquid phase, the mass density $\rho = \rho^d / \rho_0^d$, the dynamic viscosity $\mu = \mu^d / \mu_0^d$, the diffusion coefficient $D = D^d / \nu_0^d$ and the surface tension $\gamma = \gamma^d(c_e) / (d\gamma_0^d / dc_e)$ of the liquid are dependent on the local ethanol mass fraction $c_e(\mathbf{r}, t)$. The surface tension is made non-dimensional using its derivative with respect to the mass fraction at $t = 0$. It is the derivative and not the absolute value of the surface tension what determines the strength of the tangential stress. The non-dimensional mass transfer rate is given by $j_\alpha = j_\alpha^d \delta^d / (\nu_0^d \rho_0^d)$ for $\alpha = e, w$. As mentioned before, we use the superscript d in case we want to make reference to a dimensional variable. The subscript 0 indicates the value of a quantity at $t = 0$.

This gives rise to the 3-D Navier-Stokes equations with varying density and viscosity

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (1.1)$$

$$\rho (\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) = -\nabla p + \nabla \cdot [\mu (\nabla \mathbf{v} + \nabla \mathbf{v}^t)], \quad (1.2)$$

along with the convection–diffusion equation of the ethanol mass fraction c_e with the composition-dependent diffusivity D ,

$$\rho(\partial_t c_e + \mathbf{v} \cdot \nabla c_e) = \nabla \cdot (\rho D \nabla c_e). \quad (1.3)$$

In the above equations we have neglected the effects of gravity, given the small distance between the plates δ^d (20 μm), which is the relevant length for gravity in a horizontally oriented cell. In particular if we calculate the Galilei number $\text{Ga} = g(\delta^d)^3(\rho_0^d/\mu_0^d)^2$ and the Archimedes number $\text{Ar} = g(\delta^d)^3\rho_0^d\Delta\rho_0^d/(\mu_0^d)^2$ based on the plate distance, the density difference between pure ethanol and water (207.7 kg/m^3 at 293.15 K and 211.3 kg/m^3 at 298.15 K), the dynamic viscosity (3.1 mPas at 293.15 K and 2.4 mPas at 298.15 K) and the density (0.918 kg/m^3 at 293.15 K and 0.911 kg/m^3 at 298.15 K) at 50 wt%, we obtain $\text{Ga} \sim 0.01$ and $\text{Ar} = 0.0016 - 0.0026$. In both cases, their magnitude is much smaller than one, meaning that we can neglect gravity effects [57, 62].

As schematically depicted in figure 1.5a), the 3-D flow inside the cell is strongly confined in the y -direction and enclosed by no-slip boundary conditions at the top and bottom plate. To the lowest non-trivial order compatible with these boundary conditions, a parabolic velocity distribution in the y -direction can hence be assumed, i.e. $\mathbf{v}(x, y, z, t) = f(y)\mathbf{u}(x, z, t)$ with $f(y) = (by)(1-y)$ (see 1.5a)). The 2-D velocity $\mathbf{u}$ is defined in the (x, z) -plane, i.e. $\mathbf{u} \cdot \mathbf{e}_y = 0$, and the constant b is set to $b = 6$ in the numerics so that the lateral velocity $\mathbf{u}$ coincides with the height average of the 3-D velocity $\mathbf{v}$. With these assumptions and by taking the an average in the y -direction, the 3-D Navier-Stokes equations (1.2) are simplified to two dimensions, resulting in a factor 6/5 for the nonlinearity and a drag term $-12\mu\mathbf{u}$ stemming from the shear of the parabolic flow profile [34, 60]:

$$\partial_t \rho + \nabla_{\parallel} \cdot (\rho \mathbf{u}) = 0 \quad (1.4)$$

$$\rho \left(\partial_t \mathbf{u} + \frac{6}{5} \mathbf{u} \cdot \nabla_{\parallel} \mathbf{u} \right) = -\nabla_{\parallel} p + \nabla_{\parallel} \cdot [\mu (\nabla_{\parallel} \mathbf{u} + \nabla_{\parallel} \mathbf{u}^t)] - 12\mu \mathbf{u}. \quad (1.5)$$

Here, $\nabla_{\parallel} = (\partial_x, \partial_z)$ is the 2-D nabla operator. The resulting equation 1.5 is in a sense a Darcy equation with the Brinkman [63] and inertial [64] corrections. The liquid properties ρ , μ and D are still allowed to depend on the local ethanol mass fraction, which is now also considered in its 2-D height-averaged projection, i.e. $c_e(x, z, t)$, which is subject to the 2-D convection–diffusion equation

$$\rho(\partial_t c_e + \mathbf{u} \cdot \nabla_{\parallel} c_e) = \nabla_{\parallel} \cdot (\rho D \nabla_{\parallel} c_e). \quad (1.6)$$

Considering only the 2-D projection of the concentration field c_e does not take into account diffusion processes in y -direction, which can, in cooperation with the parabolic flow profile, contribute to an effectively enhanced projected 2-D diffusivity (cf. Taylor–Aris dispersion). However, due to the non-trivial and time-dependent flow, this effect cannot be taken into account within this model, the full 3-D equations would be needed to take this effect into account. The gas phase is modelled as a mixture of air, ethanol and water, for which we assume quasi-stationary vapour diffusion, i.e. we only consider the Laplace equations

$$\nabla^2 c_e^g = 0 \quad \text{and} \quad \nabla^2 c_w^g = 0 \quad (1.7)$$

for the vapour mass fractions c_e^g and c_w^g of ethanol and water, respectively. The superscript g indicates the gas phase. Then the mass fraction of air is given by $c_a^g = 1 - c_e^g - c_w^g$. The assumption of a quasi-stationary model has been validated previously for evaporating ethanol–water sessile droplets. In particular, the consideration of convection [65] or the full diffusion equation [66] in the gas phase resulted in negligible differences in the evaporation rates or tangential velocities at the surface of the droplets. Given that the velocities in our experiments are smaller or of the same order as in the droplet case, we have decided to follow the same approach.

Opposed to the experimental set-up, the gas phase in the numerics is considered in a 2-D projection as well. To mimic the evaporation in a 3-D space, the length of the gas domain in the z -direction is adjusted until the typical evaporation velocity matches the experimentally observed one.

The boundary conditions for the velocity and for c_e are shown in figure 1.5b), namely an open stress-free inflow at the liquid boundary far away from the liquid–gas interface and no-slip boundary conditions at the sidewalls. Alternatively, when only a section of the cell with some distance to the sidewalls is of interest, periodic boundary conditions in the x -direction can be used (if so, this will be mentioned in the text). At the liquid–gas interface, ethanol and water evaporate with local non-dimensional mass transfer rates j_e and j_w , respectively. These, together with the assumption of a static interface, yields the kinematic boundary condition

$$\rho u_z = -(j_e + j_w), \quad (1.8)$$

where we have neglected the solubility of air in the binary solution, such that the air flux at the interface is zero. The negative sign arises because we have defined the fluxes as positive when directed away from the liquid.

Due to the small viscosity ratio of the gas phase with respect to the liquid phase, the varying interfacial tension induces a Marangoni shear stress only on the liquid phase, i.e.

$$\mu (\partial_z u_x + \partial_x u_z) = \frac{\text{Ma}_s}{\text{Sc}} \frac{d\gamma}{dc_e} \partial_x c_e, \quad (1.9)$$

where we have introduced the solutal Marangoni number [36]

$$\text{Ma}_s = -\frac{\delta^d}{\mu_0^d D_0^d} \frac{d\gamma_0^d}{dc_e}, \quad (1.10)$$

and the Schmidt number

$$\text{Sc} = \frac{\nu_0^d}{D_0^d}, \quad (1.11)$$

with D_0^d the diffusion coefficient of the liquid at time zero. The introduction of these two non-dimensional numbers is in preparation for the linear stability analysis to be done in the following section.

In the following section, for linear stability analysis we will introduce linear mass fraction profiles close to the edge, with slope E . Therefore, a characteristic change in mass fraction $\Delta c_\delta = E^d \delta^d = E$ over a distance equal to δ^d is obtained. Then a “modified” Marangoni number [36]

$$\text{Ma}_s^* = \text{Ma}_s \Delta c_\delta = -\frac{(\delta^d)^2 E^d}{\mu_0^d D_0^d} \frac{d\gamma_0^d}{dc_e} \quad (1.12)$$

can be introduced, which determines the stability of the system. Notice that dispersion can result in an enhanced effective diffusion coefficient, and reduce the value of the Marangoni number. But as mentioned before, the determination of this effect is not trivial for our flow.

Due to the preferential evaporation of ethanol and the mass transfer taking place at the interface, the convection–diffusion equation (1.6) is subject to the boundary condition

$$\rho D \partial_z c_e = (1 - c_e) j_e - c_e j_w, \quad (1.13)$$

which considers the effects of both diffusion and convection on the flux of ethanol. The far-field boundary condition of the gas composition is set to that of ambient air, plus an optional RH. At the liquid–gas interface, vapour–liquid equilibrium is imposed, i.e.

$$c_e^g = c_e^{g,\text{VLE}}(c_e) \quad \text{and} \quad c_w^g = c_w^{g,\text{VLE}}(c_e), \quad (1.14)$$

where the equilibrium is calculated by Raoult's law generalized by activity coefficients, i.e.

$$c_{\alpha}^{\text{g,VLE}}(c_e) = \mathcal{A}_{\alpha}(c_e) n_{\alpha}(c_e) \frac{p_{\alpha,\text{sat}}^{\text{d}}(T) M_{\alpha}^{\text{d}}}{R^{\text{d}} T^{\text{d}} \rho^{g,d}}. \quad (1.15)$$

Here, $\mathcal{A}_{\alpha}$ are the activity coefficients, n_{α} the liquid mole fractions, M_{α}^{d} the molar masses, and $p_{\alpha,\text{sat}}^{\text{d}}$ the saturation pressures of the pure components, whereas R^{d} is the universal gas constant, T^{d} is the temperature of the system, $\rho^{g,d}$ is the density of the gas and the superscript d indicates dimensional quantities. Notice that the equilibrium mass fraction changes in time through $n_{\alpha}(c_e(z = 0, x, t))$ and $\mathcal{A}_{\alpha}(c_e(z = 0, x, t))$. The evaporation rates are finally given by the diffusive vapour flux at the interface, i.e.

$$j_e = \rho^{\text{g}} D_e^{\text{g}} \partial_z c_e^{\text{g}} / \text{Sc} \quad \text{and} \quad j_w = \rho^{\text{g}} D_w^{\text{g}} \partial_z c_w^{\text{g}} / \text{Sc}, \quad (1.16)$$

where $\rho^{\text{g}} = \rho^{g,d} / \rho_0^{\text{d}}$ and $D_{\alpha}^{\text{g}} = D_{\alpha}^{\text{g,d}} / D_0^{\text{d}}$ are the gas to liquid density and diffusivity ratios. Recalling that we have neglected the flow in the gas phase. As we mentioned in the introduction, we do not consider thermal effects, which in the experiments can take place by means of evaporative cooling. In order to justify this assumption we refer to Linde *et al.* [52] and Machrafi *et al.* [36], who found that the solutal effect is dominant. In particular, Machrafi *et al.* [36] showed that the ratio between solutal and thermal Marangoni numbers is large for their ethanol–water solutions. We can obtain the same ratio in our case considering the thermal Marangoni number as

$$\text{Ma}_{\text{th}} = \frac{\delta^{\text{d}} \Delta T^{\text{d}}}{\mu_0^{\text{d}} D_{0,T}^{\text{d}}} \frac{d\gamma_0}{dT^{\text{d}}}, \quad (1.17)$$

where T^{d} is the temperature, ΔT^{d} is a characteristic temperature change along the interface and $D_{0,T}^{\text{d}}$ is the thermal diffusion coefficient. The specific values used are shown in table 1.2.

We do not have the values of the characteristic temperature change, but when assuming the range is between 1 K and even as unrealistically high as 10 K, the ratio $\text{Ma}_{\text{s}}^* / \text{Ma}_{\text{th}} \sim 10^3 - 10^4$. Therefore, the solutal Marangoni effect is much stronger than the thermal one. This is consistent with the case of evaporating sessile ethanol–water droplets, where thermal Marangoni effects could be neglected as long as the ethanol has not yet fully evaporated [65].

1.3.2 Numerical simulation implementation

For the numerical simulation we used a finite element method implemented on the basis of the finite element package oomph-lib [67]. The liquid in the Hele-Shaw cell and the adjacent gas domain are discretized by a rectangular mesh, using triangular Taylor–Hood elements for the degrees of freedom of the velocity and pressure space and linear shape function for the composition in both domains. The composition dependence of the liquid and gas properties are obtained by models or fits of experimental data (see [65] for details). The general numerical technique is described in more detail and compared with various experiments in, for example, references [6, 57, 65, 68]. In the present case, however, the method is generalized by considering the drag term in the momentum equation (1.5).

In all simulations the number of triangular elements was the highest close to the interface and then reduced continuously the farther away from the interface. More details on the meshes used for different simulations can be found in the appendix.

For the simulation used for comparison with experiments (section 1.3.3) the domain size was selected to be the same as the observation area in experiments in the vertical direction. This was already quite demanding computationally, so we used a reduced resolution such that the simulation time would not be exceedingly long. However, this came at the price that the boundary condition (1.13) was not fully satisfied due to the steep gradient at the edge which could not be captured by our linear elements. Nonetheless, we were able to observe a good agreement with experiments. More details can be seen in the appendix. In the case of simulations used for comparison with linear stability analysis, we made use of three different configurations of the mesh which we describe in the appendix.

In all simulations the initial mass fraction was $c_e = 0.5$, the RH far away was taken equal to 50% and the temperature was set to 295.15 K. The instability was triggered by numerical noise in all cases. To process the data, we linearly interpolated the mass fraction and velocity fields from the unstructured mesh used for simulations into a regular rectangular mesh.

Figure 1.6: a) Ethanol mass fraction field on the liquid phase c_e obtained from a simulation with periodic boundary conditions. The times are the same as in figure 1.2a). The normalized velocity vector field is plotted on top of the concentration field. As in experiments, with progressing time, the arches merge with each other. Close to the edge, smaller secondary arches become visible (the whole time evolution can be seen in movie 3 in appendix 1.6.8). b) Averaged velocity profiles at two different times. The curves with markers show the same profiles as in figure 1.4d) where different markers indicate different runs. The solid lines are results from the simulation. For the blue curves, we took the closest time obtained from simulation. c) Height z_F of the arches as a function of time. The grey dotted lines show all the experimental realizations up to $t = 6.85 \times 10^4$ ($t^d = 10$ s). The dark red line with squares shows the results from the simulation. c) Surface tension γ along the edge for the three times shown in panel a). The small scale jumps in the curves originate from the smaller secondary rolls. Notice that the variables with out superscript d are non-dimensional.

1.3.3 Numerical results and comparison with experiments

In figure 1.6 we show results obtained from a simulation using periodic boundary conditions and a simulation with a domain size equal to the field of view that we had for experiments. Other conditions can be found in table 1.2 in Appendix 1.6.3. The three snapshots in figure 1.6a) show the evolution of the instability over three different times. As opposed to experiments, this time we can directly observe the ethanol concentration field, and on top the normalized velocity vector field. It is clear that Marangoni rolls advect ethanol-depleted fluid into the arch-shaped regions. As in experiments, the arches merge and grow over time.

After the arches are large enough we can see secondary arches too. From movie 3 in the the appendix 1.6.8 it can be seen that initially only the principal arches are present. Inside the arches, “pockets” of rich ethanol solution are present. Secondary rolls can appear from these pockets. We can think of this as if locally the concentration field is back to the initial state when no instability was present and the gradient of concentration just builds up. Therefore, besides the fact that now there is a flow along the interface, locally a second instability can be triggered as described by Köllner *et al.* [69] for 3-D simulations of a liquid–liquid interface.

The length of the gas domain in the z -direction was selected such that the velocity far away from the interface would be close to the velocity measured in experiments. We show this matching in figure 1.6b). We plot non-dimensional averaged velocity profiles obtained at two different times, both from experiments and from the simulation. The curves with markers are experimental results, corresponding to the two earliest cases that were already shown in figure 1.4d). The solid lines represent the results obtained from a single simulation, a single time and averaging along the x -direction (for the blue curve, we took a profile at the closest time obtained from the simulation). Notice that the complete profiles agreed quite well with the experimental measurements, despite the fact that we only matched the velocity far away from the edge.

It is important to note that the merging between arches did not take place at the same times between simulations and experiments, causing a discrepancy between the experimental and numerical velocity profiles during certain periods of time. In figures 1.19 and 1.20 in appendix 1.6.6, we make more detailed comparisons of the velocity between experiments and simulations. We have noticed that the velocity increases sharply during a merging event, but

changes slowly otherwise. This is in agreement with the faster growth of z_F during merging. Moreover, as long as single arches have similar sizes, the local velocity is approximately the same. In figure 1.20 in appendix 1.6.6, we compare the experimental velocity profiles of arches of similar size at different times or from different realizations. The velocity profiles match with each other. The velocity profiles obtained from a simulated arch with a similar size compare well, too. On the other hand, the local velocities did not match between experiments and simulations if the arches had different sizes.

For $t = 6.85 \times 10^4$, the velocity far away from the interface is smaller than in experiments. This could be the result of the comparable size of the arch with the simulation domain. Nevertheless, the main features stay similar as in experiments with a region of exponential decay until the velocity reaches the far end value. Furthermore, we can now see that the velocity close to the edge (i.e., small values $z \lesssim 2$) can reach much larger values than those measured experimentally, approximately two orders of magnitude larger.

We tracked the height z_F as in experiments by measuring the distance from the edge at which the vertically averaged profile of the mass fraction had reached the far-field mass fraction. The result of this process is shown in figure 1.6c). Both experimental and simulation results are plotted together, again showing a good match despite our uncertainty in the initial time in the experiments. Note that there is no adjustable parameter, we only matched the initial far-field velocities in the liquid.

From the simulations we can also have access to the local surface tension $\gamma(x)$ as can be seen in figure 1.6d). We show the surface tension $\gamma(x)$ corresponding to the three snapshots in figure 1.6a). The curves confirm the presence of gradients going from the centre of the arches to their meeting points. Overall, the gradient in surface tension seems to stay approximately constant over the time span shown here. The small scale jumps in the curves originate from the secondary rolls.

Before a merging event, both in simulations and in experiments, the stagnation point at the summit of the arches displaces towards one side. Therefore, the flow towards the edge in-between two arches reduces. In turn, the supply of ethanol-rich solution also decreases. A similar situation was observed by Köllner *et al.* [69], where the bulk flow caused by the Marangoni rolls hindered the flow towards the interface. Afterwards, the two adjacent rolls merged into one.

1.4 Linear stability analysis

1.4.1 Simplified model

In this section we will perform a linear stability analysis of a simplified version of the model equations described in section 1.3.1. In this way we will be able to obtain analytical solutions that are very close to those obtained by Sternling & Scriven [9], with the addition of the drag term which originates from the wall friction.

In this simplified version of our model equations we will take the density, dynamical viscosity and diffusion coefficients as constants with respect to mass fraction in order to be able to obtain analytical solutions. This approach has been taken before for different systems with good results [34, 36, 60]. Furthermore, we will assume that surface tension is a linear function of the mass fraction such that the derivative of the surface tension with respect to the mass fraction is constant. In particular we will take the values at time zero such that $\rho^d = \rho_0^d$, $\mu^d = \mu_0^d$, $D^d = D_0^d$ and $d\gamma^d/dc_e = d\gamma_0^d/dc_e$. In other words $\rho = \mu = d\gamma/dc_e = 1$ and $D = 1/Sc$, which results in the simplified model equations for the liquid phase

$$\nabla_{\parallel} \cdot \mathbf{u} = 0 \quad (1.18)$$

$$\partial_t \mathbf{u} + \frac{6}{5} \mathbf{u} \cdot \nabla_{\parallel} \mathbf{u} = -\nabla_{\parallel} p + \nabla_{\parallel}^2 \mathbf{u} - 12\mathbf{u} \quad (1.19)$$

$$\partial_t c_e + \mathbf{u} \cdot \nabla_{\parallel} c_e = \frac{1}{Sc} \nabla_{\parallel}^2 c_e \quad (1.20)$$

and for the gas phase

$$\nabla^2 c_e^g = 0 \quad \text{and} \quad \nabla^2 c_w^g = 0. \quad (1.21)$$

Similarly, the boundary condition for the tangential stresses at the interface (equation (1.9)) is simplified to

$$\partial_z u_x + \partial_x u_z = \frac{Ma_s}{Sc} \partial_x c_e. \quad (1.22)$$

We will neglect the velocity caused by evaporation such that $u_z(x, 0, t) = 0$. This assumption has been validated by comparing simulations with and

without making the normal velocity at the edge equal to zero. The results for both cases were virtually the same. Therefore, for the linear stability analysis we kept $u_z(x, 0, t) = 0$, while for the simulations $u_z(x, 0, t) \neq 0$. In the experimental section we obtained Péclet numbers larger than unity in odds with this assumption, however, for the onset of instability a more proper length scale to be consider is δ^d (the gap of the Hele-Shaw cell), which gives $Pe \sim 1$, meaning that we are in the limit where we could actually neglect this velocity.

After neglecting the normal velocity, from equation (1.8) we get $j_e + j_w = 0$ at the interface, and equation (1.13) simplifies to $j_e = \partial_z c_e / Sc$. Therefore, introducing this expression for the mass transfer rate of ethanol into equation (1.16), we get

$$\partial_z c_e = \rho^g D_e^g \partial_z c_e^g, \quad (1.23)$$

recalling that $D_e^g = D_e^{g,d} / D_0^d$.

Raoult's law is simplified by taking a Taylor expansion of the molar fraction around $c_e(t = 0) \equiv c_{e,0} \neq 0$, such that $n_e = (1 + (1/c_e - 1)M_e^d/M_w^d)^{-1} \approx a_0(c_{e,0}, M_e^d/M_w^d) + a_1(c_{e,0}, M_e^d/M_w^d)c_e + O(c_e^2)$. The previous step allows us to keep the equations linear. Finally, if we take the activity coefficient $\mathcal{A}_\alpha = 1$ we are left with

$$c_e^{g,VLE}(c_e) \approx c_{sat}(a_0 + a_1 c_e), \quad (1.24)$$

where $c_{sat} = p_{e,sat}^d(T)M_e^d / (R^d T^d \rho_0^{g,d})$. An analogous expression can be found for water.

1.4.2 Linear stability of 2-D equations

For the base case we will consider no flow in the liquid phase, i.e. $\mathbf{u}_0 = 0$, which results in a constant pressure p_0 . While for the mass fraction linear profiles close to the edge will be taken, in the same spirit as Sternling & Scriven [9],

$$c_{e,0} = Ez + \mathcal{C}_0, \quad (1.25)$$

$$c_{e,0}^g = E^g z + \mathcal{C}_0^g, \quad (1.26)$$

with E and E^g made non-dimensional with δ^d . A more complete model would consider a time evolving base state with an error-function-like shape, however, then the equation has to be solved numerically. Here we consider that close to the edge the profiles can be approximated as linear. We also assume that the

changes in concentrations at the edge are small around the time the instability takes place. By focusing our analysis on the region close to the interface, our analysis corresponds to the small wavelength regime.

We considered small perturbations in the standard way for the velocity, pressure and mass fraction fields,

$$\mathbf{u} = \epsilon \hat{\mathbf{u}}_1(z) e^{i\kappa x + \sigma t} \quad (1.27)$$

$$p = p_0 + \epsilon \hat{p}_1(z) e^{i\kappa x + \sigma t} \quad (1.28)$$

$$c_e = c_{e,0}(z, t) + \epsilon \hat{c}_{e,1}(z) e^{i\kappa x + \sigma t} \quad (1.29)$$

$$c_e^g = c_{e,0}^g(z, t) + \epsilon \hat{c}_{e,1}^g(z) e^{i\kappa x + \sigma t}, \quad (1.30)$$

where ϵ is a small non-dimensional number, κ is the non-dimensional wavenumber of the perturbation, σ its non-dimensional growth rate and $\hat{\mathbf{u}}_1(z)$, $\hat{p}_1(z)$, $\hat{c}_{e,1}(z)$ and $\hat{c}_{e,1}^g(z)$, the amplitudes of the corresponding perturbations in velocity, pressure and mass fraction in the liquid and gas, respectively. These perturbed quantities can be used to linearize equations (1.18) to (1.21), resulting in the following dispersion relation (see appendix 1.6.4 for further details):

$$\begin{aligned} \text{Ma}_s^* = \kappa^2 & \left(c_{\text{sat}} a_1 \rho^g D_e^g + \sqrt{1 + \frac{\sigma}{\kappa^2} \text{Sc}} \right) \left(1 + \sqrt{1 + \frac{12}{\kappa^2} + \frac{\sigma}{\kappa^2}} \right) \\ & \left(1 + \sqrt{1 + \frac{\sigma}{\kappa^2} \text{Sc}} \right) \left(\sqrt{1 + \frac{12}{\kappa^2} + \frac{\sigma}{\kappa^2}} + \sqrt{1 + \frac{\sigma}{\kappa^2} \text{Sc}} \right). \end{aligned} \quad (1.31)$$

Notice that this is a simplified version of equation (30) from Sternling & Scriven [9], but with the addition of the drag term and a Marangoni number Ma_s^* based on the plate distance δ^d .

From this equation we can obtain the condition of marginal stability by setting $\sigma = 0$, resulting in

$$\kappa_{\sigma=0} = \sqrt{\frac{\text{Ma}_s^*}{8\mathcal{M}}} - 3\sqrt{\frac{8\mathcal{M}}{\text{Ma}_s^*}}, \quad (1.32)$$

where $\mathcal{M} = 1 + c_{\text{sat}} a_1 \rho^g D_e^g$. This relation is independent of Sc , which was expected from the results of Sternling & Scriven [9]. Their results can be recovered in the limit of large Ma_s^* , i.e. $\kappa_{\sigma=0} = (\text{Ma}_s^*/8\mathcal{M})^{0.5}$ where the dependence on δ^d is not present anymore, because $\kappa_{\sigma=0} \propto \delta^d$ as well as $\sqrt{\text{Ma}_s^*} \propto \delta^d$. This is equivalent to making the gap between plates large enough so that the limit of an unbounded system is reached [70].

Figure 1.7: Phase diagram of the growth rate σ for different values of κ and a) Ma_s^* , with constant $Sc = 7.51 \times 10^3$, and different values of b) Sc , with constant $Ma_s^* = 1.54 \times 10^5$. The vertical white dashed line in panel a) marks $Ma_c^* = 121.2$, below which the system is always stable, while the dotted line corresponds to the limit $\kappa_{\sigma=0} = (Ma_s^*/8\mathcal{M})^{0.5}$. In both panels a) and b) we have clamped negative values of σ to zero to facilitate visualization (grey region). The solid white curve indicates $\sigma = 0$, while the solid red line indicates $\max(\sigma)$. The black region in panel a) indicates where we did not find solutions for the dispersion relation. c) The growth rate σ as a function of κ corresponding to the red vertical dashed line shown in panels a) and b).

We can now find a critical Marangoni number $Ma_c^* \equiv 24\mathcal{M}$ for which $\kappa_{\sigma=0} = 0$. Below this critical value, the right hand side of equation (1.32) becomes negative, while κ has to be positive. Therefore, for $0 < Ma_s^* \leq Ma_c^*$ the system should become stable for all wavelengths. Furthermore, the Marangoni number can become negative if either the gradient E or the derivative of surface tension with concentration $d\gamma_0^d/dc_e$ change in sign. Of course this is not possible as the wavenumber has to be a real positive quantity. However, this does not exclude the possibility of an oscillatory instability, which could be expected for negative Marangoni numbers considering the results from Sternling & Scriven [9]. Given that the evaporating ethanol–water system results in positive Marangoni numbers, we will restrict ourselves to this regime.

1.4.3 Numerical solution of the dispersion relation

Equation (1.31) was solved numerically to obtain σ as a function of κ and Ma_s^* for $Sc = 7.51 \times 10^3$, and the properties shown in table 1.2 in appendix 1.6.3 corresponding to an ethanol–water solution at 50 wt% and 295 K. The results can be seen in figure 1.7a), where we have clamped negative σ to zero to facilitate visualization. Equation 1.32 is plotted as a solid white line, while the purely 2-D limit, $\kappa_{\sigma=0} = (Ma_s^*/8\mathcal{M})^{0.5}$ is highlighted by a dotted line. The

red solid line corresponds to the locations where σ is maximum for a given Ma^* , i.e. the fastest growing modes.

Indeed, for $\text{Ma}_s^* < \text{Ma}_c^* = 121.2$ the system is expected to be stable, as $\sigma < 0$ for every value of κ . However, we must notice that for regions where $\sigma < -\kappa^2/\text{Sc}$, we did not find solutions (marked as a black region). This region corresponds to where three of the radicals become purely imaginary. We looked for imaginary solutions of σ , without success. While our search was not exhaustive, we are in the region where Sternling & Scriven [9] only found real solutions for the purely 2-D case so we think it is reasonable not to find complex solutions.

Once a particular liquid–gas system has been fixed (with a given mass fraction gradient E), the Marangoni number Ma_s^* indicates the effect of the gap between the walls of the Hele-Shaw cell. By comparing the solid and dotted lines in figure 1.7 we can observe that the effect of the confinement as compared to the purely 2-D case is only visible for $\text{Ma}_s^* \lesssim 1000$. Meaning that for larger values the purely 2-D model of Sternling & Scriven [9] should be enough to calculate the critical wavelength. In other words, for a given set of properties, as long as δ^d is large enough, but not so large that gravity starts to play a role, the use of the purely 2-D model is sufficient.

According to Sternling & Scriven [9], if the conditions $D^d/D^{g,d} < 1$, $\nu^d/\nu^{g,d} < 1$ and $d\gamma^d/dc_e < 0$ are satisfied, while solute transfer occurs from the liquid to the gas, the system should be unstable. However, consideration of the drag of the walls for an evaporating binary liquid introduces the possibility of stability as long as $\text{Ma}_s^* < \text{Ma}_c^*$.

We also looked at the effect of the Schmidt number, Sc , as shown in figure 1.7b) for a fixed $\text{Ma}_s^* = 1.54 \times 10^5$. As mentioned by Sternling & Scriven [9], varying Sc shows only a minor effect which was already suggested by the fact that $\kappa_{\sigma=0}$ is not a function of this parameter. Only for $\text{Sc} \lesssim 50$ there is a slight increase on the value of the fastest growing wavenumber.

A plot of σ as a function of κ is displayed in figure 1.7c). This case corresponds to the dashed red line in both panels a) and b) of figure 1.7 ($\text{Ma}_s^* = 1.54 \times 10^5$ and $\text{Sc} = 7.51 \times 10^3$). We have selected this particular case, because it corresponds to the simulated case in section 1.3.3. In order to know the correct value of E , we conducted simulations in a smaller domain such that the mismatch of the boundary condition was not present. If we then assume that this corresponds to the same conditions as in experiments (for which we do not know the actual gradient), it would be in accordance with the presence of an instability, as the Marangoni number is above the critical value.

Figure 1.8: a) Ethanol mass fraction c_e averaged over the x coordinate as a function of the position z in a log-log axis for a simulation at very early times. The curves were shifted by subtracting the mean mass fraction at $z = 0$ to show that close to the edge the profile is actually linear. Different curves represent different times (see legend). b) Mass fraction profile as a function of position z on the gas phase for the same times as shown in panel a). The changes are so small that the curves practically overlap with each other. (c) Evolution in time of the averaged mass fraction along the edge $z = 0$. d) Mass fraction profile along the edge $z = 0$. All curves were shifted by the corresponding averaged mass fraction at the edge. The colours correspond to the same times as those shown in panel a). Movie 4 in appendix 1.6.8 shows the whole concentration and velocity vector fields as a function of time.

With respect to the term $c_{\text{sat}} a_1 \rho^g D_e^g$, it affects the range over which the system becomes stable, as clearly seen from equation (1.32). In particular, it increases the value of Ma_c^* , while in the extreme case, in which it is equal to zero, one gets $\text{Ma}_c^* = 24$, which corresponds to completely ignoring the gas phase and just setting a constant solute flux at the interface. Additionally, we noticed that the values of σ decrease with increasing values of the factor $c_{\text{sat}} a_1 \rho^g D_e^g$.

One of the simplifications that we took for the linear stability analysis was to consider the solution as ideal by setting the activity coefficient $\mathcal{A}_e = 1$. If this is not the case, an increase or decrease of the activity coefficient would affect the value of c_{sat} correspondingly. Therefore, changes in the activity coefficient would come into effect through c_{sat} . In particular for ethanol–water mixtures with activity coefficients above one, consideration of the activity coefficient would cause the growth rate σ to decrease.

1.4.4 Comparison of linear stability analysis with numerical simulations

Experimentally, we were not able to observe the onset of the instability since at that moment the accumulation of dye or particles was too low to create a large enough contrast. Furthermore, given that the arches merged with each other, it is possible that by the time we are able to observe them, they are already the result of different merging events, which is what we observe from simulations. Therefore, we relied on the latter for comparison with theory. To do so, we performed simulations over short times, such that merging had not taken place, and in domains at least five times larger than the fastest growing wavelength. To test different Marangoni numbers we varied the evaporation rate by changing the size of the gas domain.

In figure 1.8 we show the mass fraction of ethanol c_e as a function of space and time. In particular, these are results for a case of $Ma_s^* = 1.55 \times 10^5$. In figures 1.8a) and b) we show the averaged mass fraction profiles on the liquid and gas side, respectively. In both cases the average was taken along the x -direction and we display the profiles over five different times. In the case of the gas profiles, the changes are so small that they lie on top of each other almost indistinguishably. Notice that we have plotted the liquid profiles on a double logarithmic scale and we have shifted them by subtracting the averaged mass fraction at the interface, i.e. $\langle c_e(z = 0) \rangle_x$ (shown in figure 1.8(c)). In this way we can see that close to the interface the profiles are approximately linear, while of course far away they reach the far-field value. As in the work by Köllner *et al.* [69] we observed a local minimum that results from the mixing zone caused by the Marangoni rolls, indicating that at those times the instability has already developed and that ethanol depleted liquid has already been advected back into the bulk.

In figure 1.8d) we show the mass fraction profiles along the edge at different times. These profiles were shifted by their corresponding mean values for visibility. Clearly, the instability has not grown very much after approximately seven viscous times, while at $t = 10.3$ it has dramatically increased. The presence of the instability is also suggested by the increase of the averaged mass fraction at the edge (figure 1.8(c)) and the standard deviation of the surface tension in figure 1.9. Furthermore, at $t = 17.1$ merging has already started, showing the very early onset of nonlinear effects.

From the profile at $t = 27.4$ it can be seen that more than one wavelength is still present at the same time, which can be expected since the perturba-

Figure 1.9: Average diffusive flux $\langle \partial_z c_e \rangle_x$ at the edge and standard deviation of the surface tension $\text{std}(\gamma)$ as a function of time, corresponding to the same simulations as shown in figure 1.8.

tion comes from numerical noise combined with the non-uniform shape of the mesh, meaning that more than one mode can be excited at the same time. Furthermore, certain modes could be excited again, given that at these early times merging takes place by the displacement (along the edge) of the formed rolls, leaving free space for new ones to be generated, as can be seen close to the end of movie 4 of appendix 1.6.8. In fact, we tried cases where we intentionally introduced a perturbation with one particular wavelength, but other wavelengths developed too. Since the results were quite similar, here we present only the cases with random noise.

The presence of many wavelengths at the same time makes it difficult to determine which one grows the fastest just from looking at the mass fraction profiles, especially since merging starts very soon. In order to answer this question, we calculated the Fourier transform of the edge profiles (figure 1.8d)) at each time.

The corresponding plot of growth rate σ versus wavenumber κ is shown in figure 1.10 for different Ma_s^* . In each case, the curves are the average over different realizations and the error bars represent one standard deviation on each side. We have included cases using the different kinds of meshes described in section 1.3.2. We varied the size of the domain in the x - and z -directions, but always keeping the domain at least five times the size of the fastest growing

wavelength in the x -direction. We only show cases where we did not impose any initial perturbation and the instability started from numerical error.

Given that in simulations we control the evaporation rate through the size of the gas domain, in order to determine the modified Marangoni number Ma_s^* of each case, we obtained E from the average diffusive flux at the boundary $\langle \partial_z c_e \rangle_x$. Figure 1.9 shows the evolution in time of $\langle \partial_z c_e \rangle_x$. For the first time steps the mass fraction gradient increases very quickly from zero up to the value determined by the boundary condition (1.23), then it increases slowly until merging takes place and the gradient slightly decreases. In all cases, we took the average value over the same period for which we fitted the growth rate of the power (see appendix 1.6.5). This average mass fraction gradient $\bar{E} \equiv \overline{\langle \partial_z c_e \rangle_x}$ was then used to calculate Ma_s^* together with material quantities corresponding to $c_e = 0.5$. The corresponding values of $\bar{E}$ and Ma_s^* obtained for each different run are shown in the appendix. The values of $\langle \text{Ma}_s^* \rangle$ shown in figure 1.10 are the average of the modified Marangoni number over all the different runs.

With the Marangoni number known, we calculated the theoretical growth rates as a function of wavenumber for each case. The results are plotted as solid red lines in figure 1.10. The prediction tends to underestimate κ by a factor of approximately 0.5, and for smaller modified Marangoni numbers, the growth rate is underestimated too. Furthermore, we would expect that the inclusion of the activity coefficient would shrink the theoretical curves. However, the agreement is still fairly good considering all the simplifications done for the linear stability analysis, and the fact that in the simulations nonlinear terms and water evaporation are taken into account.

Notice that for large values of κ , the growth rate calculated from the simulations does not keep on decreasing. This could be a result of the higher resolution needed to better resolve the corresponding wavelengths. Moreover, it can be seen from figure 1.18a) that the power of large values of κ ($\kappa > 100$ in that example) is quite small. Therefore, above a given value of κ we cannot trust anymore the obtained values of the growth rate.

On top of each of the plots from figure 1.10 we have indicated the corresponding values of the dimensional wavelength $\lambda^d = 2\pi\delta^d/\kappa$. Note that for the two largest Ma_s^* the fastest growing wavelength is smaller than the gap between the plates of the cell ($\delta^d = 20\text{ }\mu\text{m}$). Bratsun & De Wit [34] also found that for large Marangoni numbers their predicted fastest wavelength was smaller than the gap of their cell, which led them to disregard those solutions. A reason for this is that the Hele-Shaw model relies on the assumption that variations of the

Figure 1.10: Comparison of the normalized growth rate σ versus normalized wavenumber κ obtained from linear instability theory (solid line) and from simulations (*). The upper horizontal axis shows the corresponding wavelength $\lambda^d = 2\pi\delta^d/\kappa$. The mean $\langle Ma_s^* \rangle$ indicated in each plot corresponds to the average value over different realizations (see the appendix for a table with the values of Ma_s^* of individual simulations).

velocity in the direction parallel to the plates of the cell are much smaller than variations in the directions normal to the plates [64]. Therefore, a wavelength smaller than the gap of the cell would result in changes of velocity that would be stronger in the plane of the cell.

In fact, from equation (1.32) we can obtain a value for Ma_s^* for which $\kappa = 2\pi$, meaning that $\lambda^d = \delta^d$. This implies that $Ma_s^* = 8\mathcal{M}(\pi + \sqrt{(\pi^2 + 3)})^2$, meaning that for Marangoni numbers larger than this quantity, there will be at least one wavelength smaller than the gap. This is already the same regime over which the model becomes close to the purely 2-D case (from the point of view of linear stability analysis) suggesting that for large Marangoni numbers a 3-D model would be more suitable in order to look at the onset of the instability, even if the gap is as small as 20 μm . Nevertheless, as time goes on and coarsening takes place by means of merging, this restriction is not in play anymore, explaining the good agreement between simulations and experiments

at much longer times. Furthermore, if the properties of the fluids or the evaporation rate result in a low enough Marangoni number, then equation (1.31) could be used as a first estimation of the growth rate of long wavelengths at onset.

1.5 Summary, conclusions and outlook

We have investigated by means of experiments, numerical simulations and linear stability analysis the evaporation of a solution of ethanol and water confined in a Hele-Shaw cell. The selective nature of the evaporation process, due to the larger volatility of ethanol, resulted in the appearance of a Marangoni instability at the liquid–air interface. This instability results in the appearance of convective rolls in the bulk of the liquid phase, which caused the accumulation of dye in arch-like regions. With ongoing time, we observed the rolls to grow and merge until they reached the lateral size of the cell. Eventually, the instability stopped and the flow ceased.

Qualitatively, such phenomena were observed before in experiments by Linde *et al.* [52] for different evaporating binary mixtures confined inside a Hele-Shaw cell, however, here we measured and analysed the growth of the rolls in a quantitative way by means of confocal microscopy, μ PIV, and numerical simulations. We found that the size of the arches increases following an overall square root of time dependence, similarly to other multicomponent liquid–liquid systems [51]. Furthermore, by looking at averaged velocity profiles, we found that the velocity in the rolls decays exponentially towards the bulk of the liquid.

For numerical simulations and linear stability analysis we considered a quasi-2-D model which results from an average over the direction normal to the walls, assuming a parabolic profile for the velocity and a constant mass fraction in that direction. In this way we took into account the drag caused by the walls without having to use the full 3-D equations. In spite of these simplifications, simulations and experiments showed a good quantitative agreement supporting the applicability of the quasi-2-D model at long enough times.

Due to the merging process that characterizes the evolution of the instability, which also slows down with time, we cannot be sure if the first rolls that we observe experimentally represent the onset of the instability. In fact, from simulations we were able to corroborate that the merging process can start at shorter times than those accessible experimentally. Therefore, for comparison

with linear stability theory, we relied only on the results from simulations.

By looking at the perturbation of the mass fraction at the interface at early times, we were able to calculate the growth rate of the perturbation as a function of the different wavenumbers present in it. This allowed us to compare these calculations with the predictions that we made by linear stability theory. The results are in reasonable agreement, taking into account that simulations consider the complete nonlinear equations with material properties that depend on mass fraction, while for linear stability analysis we (i) made use of a simplified model with constant material properties, we (ii) disregarded the velocity caused by the evaporation of both ethanol and water, we (iii) did not include the evaporation of water and we (iv) did not consider a time evolving base state.

The consideration of the drag of the walls of the Hele-Shaw cell in our analysis resulted in the possibility of stability for conditions that would be considered unstable under the purely 2-D model of Linde *et al.* [9]. More specifically, for $\text{Ma}_s^* < \text{Ma}_c^* = 24\mathcal{M}$ the system is expected to be stable for all values of the wavenumber κ . For large Marangoni numbers the quasi-2-D model tends to the purely 2-D model, making it unnecessary to consider the drag of the walls, at least in terms of the linear stability prediction. However, at the same time at large Marangoni numbers, the model predicts wavelengths that can be smaller than the gap of the cell, suggesting that the full 3-D equations need to be considered in order to account for the onset of the instability. Nevertheless, as long as $\text{Ma}_s^* \leq 8\mathcal{M}(\pi + \sqrt{(\pi^2 + 3)})^2$, the wavelengths predicted by the Hele-Shaw model become smaller than the cell thickness. Therefore, the dispersion relation given by equation (1.31) could be used as a first estimate for the initial size of the instability, as long as thermal effects stay small. Moreover, as time goes on and coarsening takes place, the restriction which the gap size imposes is overcome, and, as we mentioned before, the numerical results show good agreement with experiments, even at large values of the Marangoni number. It would be interesting to further test the predictions of the stability analysis using systems with lower solutal Marangoni numbers.

In the next chapter we will apply our results to evaporating ternary systems, also confined in a Hele-Shaw cell. In those cases the Marangoni instability will determine the location of spontaneous emulsification (ouzo effect) and could compete with other mechanisms of pattern formation. In particular, this competition could preclude the formation of branch-like structures, composed of emulsion droplets, that were observed for a ternary miscible liquid–liquid system [71].

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1.6 Appendix

1.6.1 Appendix A. Further experimental details

Pillars and walls inside the chip

The small gap size (μm) compared with the lateral dimensions (cm) of the Hele-Shaw cell caused a large overhang between the silicon and glass plates. This made the cell prone to collapse at the centre during the fabrication process. Therefore we divided the cell into three channels of 1 cm width each by adding two walls, shown in figure 1.1b) as horizontal black stripes. For additional support and to keep a homogeneous gap, a matrix of pillars, 50 μm in diameter, was added in-between the walls. In figure 1.1a), the pillars are represented as thin vertical lines, while in figure 1.1b) the gap region is coloured grey, and the pillars are shown as black circles (their size is exaggerated).

Surface coating

The surface of the chip was made hydrophobic by depositing a layer of Trichloro (octadecyl) silane (OTS, Sigma-Aldrich) by chemical liquid deposition in a similar way as in Reference [72]. To activate the surface, we dipped the chip in a bath of piranha solution (30% of hydrogen peroxide and 70% sulphuric

Figure 1.11: Disposition of chip, nitrogen inlets and sensors. a) Sketch of the side view of the confocal microscope, showing the inlets of dry and humid nitrogen (N_2) and their location with respect to the chip. The humidity and temperature sensor (green rectangle) is placed inside the gas volume, approximately at the same height as the chip. b) View from the horizontal dashed line drawn in panel a). The distances between the inlets, sensor and chip are shown. c) Photograph showing the actual setup to show the wrapping around the microscope. Gas was able to escape from small spaces all around the microscope.

acid) for 40 min at 75°C . We then washed it with plenty of Milli-Q water and ethanol. The chip was kept in an oven at 120°C for 2 h to eliminate traces of water. After cooling down, the chip was dipped in a solution of 0.5% OTS in toluene for 17 h. Finally the chip was sonicated for 10 min in chloroform and 15 min in each of the following solvents one after the other: toluene, acetone, isopropyl alcohol, ethanol and water. Finally, the chip was dried under a nitrogen flow.

Extended setup

In figure 1.11 we show in more detail the position of the chip, the dry and humid nitrogen inlets, and the humidity and temperature sensor. The gas flow was not directed to the chip, but to the side. The plastic wrapping was not hermetically sealed, therefore the gas was able to escape from different places around the gas phase volume (see figure 1.11a, c)). Notice that the gas phase is not confined by the Hele-Shaw cell. Instead the gas phase is a large 3-D volume. Because the ethanol vapor is denser than air, it can sink away from the edge of the chip. However, we do not have a quantification of this effect.

Figure 1.12: Examples of a) the relative humidity (RH) and b) the temperature over a period of 900 s for two experiments with rhodamine 6G and two μ PIV experiments. For each kind of experiment we show cases where the flow was turned on or off. The temperature changes during each experiment because of the heating caused by the electronics. The majority of our experiments are between 296 and 298 K.

Humidity and temperature time series

Four examples of the relative humidity time series are shown in figure 1.12a). Two of them correspond to experiments with rhodamine 6G (R6G) and two for μ PIV experiments. For each pair, we show examples with the flow turned on and off. For the latter, the relative humidity was inside the desired range throughout the experiment. In the realization shown with R6G, the humid flow was turned on every time the relative humidity was below 49%. In the μ PIV example, the dry flow was turned on every time the relative humidity was above 50%. We adjusted the thresholds at which the flow was active to keep the average value close to 50%. The flow rates were in the range of 1 ± 0.1 L/min.

The corresponding temperatures are shown in figure 1.12b). As it can be seen, in three cases the temperature increased about half a degree over 15 min because of the heating of the electronics. Therefore, the temperature for a new experiment was higher than in the previous case.

Figures 1.2b), 1.4d), and 1.14 include the realizations corresponding to the conditions in figure 1.12. The impact on the results from the variations of the conditions inside the chamber seem to be relatively small. However, the lifetime of the instability could be affected by such variations.

Contact angle inside the chip

In order to get an estimation of the contact angle, we took volumetric scans of the meniscus formed at the back channel of the chip. We adjusted the flow so the meniscus would stay in place during the scan. In figure 1.13a) we show an example of one of the horizontal planes. The inset shows a zoom to the back channel of the chip. A red square indicates the approximate position where the scan was taken. The distance between planes was of $1.1\text{ }\mu\text{m}$ or $2\text{ }\mu\text{m}$ for different repetitions.

By taking a slice along the x^d direction we could obtain the vertical profile of the meniscus as shown in figure 1.13b). The left side of the picture shows the data obtained from the fluorescent channel while the right side shows data obtained from the reflection channel. From the reflection data we get the location of the walls. In figure 1.13c) we show the same image but the liquid side (fluorescent channel) has been corrected for the different refractive index inside the mixture (1.36 [73]).

Figure 1.13: Example of contact angle measurement. a) Horizontal slice showing the interface between air and the ethanol–water mixture dyed with rhodamine 6G. The image was taken at the back channel. *Inset*: Sketch showing a portion of the chip. The red square gives and indication of the measurement location and the green curved line represents the meniscus. b) Reconstructed slice (normal to the walls of the chip) taken at the horizontal red line marked in a). We have mixed the image obtained from the fluorescent channel (left half) and the reflection channel (right half). c) Same as in b) but the liquid side has been corrected for the different refractive index (1.36). The red dots indicate the interface. d) Vertical profile of the meniscus at different slices. Two different repetitions at 2 different locations in the back channel are shown. The contact angle was obtained by making linear fits in the ranges marked. e) The contact angle measured at each slice (different z^d locations) for repetition 1.

	θ_{Bottom}	θ_{Top}
Rep 1	$79^\circ \pm 2$	$75^\circ \pm 4$
Rep 2	$78^\circ \pm 3$	$89^\circ \pm 5$
Rep 3	$76^\circ \pm 3$	$86^\circ \pm 4$

Table 1.1: Average contact angle and standard deviations for 3 repetitions. Repetitions 2 and 3 are two consecutive measurements at the same location but different from the location of repetition 1.

To find the interface we made use of the fact that the intensity at a given y^d position behaves closely to a step function. The intensity is approximately constant with respect to x^d before and after the step. We determined the mean intensity before the step, I_0 , and after the step, I_1 . The location of the interface was assumed to be where the intensity was given by $0.5 \cdot (I_0 + I_1)$. The red dots in figure 1.13c) show the found interface.

In figure 1.13d) we show a few meniscus profiles obtained at different vertical slices of the same repetition (Rep 1). Each profile was translated horizontally by subtracting the mean x^d position to show the profiles on top of each other. A second set of vertical profiles taken at a different location inside the chip is shown for comparison (Rep 2).

The contact angle was finally obtained by fitting a line to the data in a range of $10 \mu\text{m}$ as indicated in figure 1.13d). The resulting angles for all the slices are shown in figure 1.13e) for repetition 1. The results from 3 different measurements are shown in table 1.1.

From these contact angles we can have an estimation of the pressure drop across the meniscus at the evaporating edge in the Hele-Shaw cell, by considering a meniscus between parallel plates and two different contact angles, $\Delta p^d = \gamma(\cos \theta_{\text{Bottom}} + \cos \theta_{\text{Top}})/\delta^d$. This implies that the pressure drop is between 10^2 and 10^3 Pa.

Estimation of pressure drop inside the chip

In order to keep the chip filled, we kept a continuous flow from the inlet of the chip. This flow requires an over-pressure at the inlet of the chip. In order to have an estimate of the pressure drop from the back channel to the open edge we have assumed a perfectly rectangular channel with dimensions $w^d = 1 \text{ cm}$ and $\delta^d = 20 \mu\text{m}$, meaning that the aspect ratio is given by $\delta^d/w^d = 0.002$. This small aspect ratio allowed us to make use of the limiting equation for the

Figure 1.14: Height z_F^d over time for different mass fractions of rhodamine 6G with a) linear and b) logarithmic scales.

pressure drop [74] :

$$\Delta p^d = \frac{12\mu_0^d L^d Q^d}{w^d (\delta^d)^3 (1 - 0.63 \frac{\delta^d}{w^d})}, \quad (1.33)$$

where Δp^d is the pressure drop along the channel, $\mu_0^d = 2.5$ mPas is the viscosity of the fluid, $Q^d = 2.8 \times 10^{-12}$ m³ s⁻¹ is the volumetric flow, and $L^d = 1.8$ cm is the length of the channel. Then, the pressure drop is $\Delta p^d = 19$ Pa. Therefore, the pressure caused by the replenishing flow is very small compared with the pressure drop at the meniscus, calculated in the previous section. Deformations of the interface due to this pressure are hence not expected.

Effects of the Rhodamine 6G concentration

Figure 1.14b) shows measurements of z_F^d for two different rhodamine 6G concentrations, namely 10^{-4} (0.1 g/L) and 10^{-5} (0.01 g/L). The variation for a fixed concentration (blue curves), specially after 7 s, are larger than those caused by changing the concentration. The large variations are caused, in part, by the non-sharp boundary between the arches and the bulk. Over time this boundary becomes even more diffuse, thus the position of the summit is not as easy to track. The time at which merging takes place can also affect the value of z_F^d , given that the growth is faster just after merging. This is evidenced by the sudden jumps in z_F^d . Therefore, if a merging event takes

place at different times for different experiments, z_F^d will be different. Despite this larger variability, the match of z_F^d between experiments and simulations is reasonably good given that simulations were performed for up to 10 s. Furthermore, as shown by figure 1.14b), the overall trend for z_F^d stays close to a square root dependence with time besides the accelerated growth during the merging events.

1.6.2 Appendix B. Further observations from μ PIV

μ PIV conditions

A suspension of fluorescent particles (FluoSpheres, Life Technologies, 1 μ m, carboxilate-modified, 2% solid in aqueous solution, with 2 mM of sodium azide) was added at 0.9 wt% to the ethanol–water solution. This resulted in an initial volume fraction of particles of 0.016 % and mass fraction of sodium azide of 1.2×10^{-4} wt%, meaning that we can disregard any effects from the latter even after 30 min of evaporation.

We recorded images with a confocal microscope (Nikon Confocal Microscopes A1 system) at 30 fps using a 488 nm laser and a pinhole size of 26.8 μ m. This settings resulted in a vertical resolution of 8 μ m. We made measurements at a single position in the y direction, approximately in the middle of the cell. By translating the position of the focal plane along the gap of the cell, we observed that the visible particles were always the same, but with different intensities. Therefore, despite the vertical resolution of 8 μ m all the particles inside the gap were visible at the same time. Different particles moved at different speeds, which we attribute to the Poiseuille flow. Therefore, the velocity results shown in this work represent a weighted average of the velocity, where the dominant peak during the correlation step in the PIV process determines the velocity at a given position.

The recorded images were processed with PIVLab for Matlab [75–77]. We used interrogation windows of 40 pixels $\times$ 40 pixels (100 μ m $\times$ 100 μ m) with a 50% overlap.

We calculated the relaxation time according to [6, 78],

$$t_0^d \equiv \left(1 + \frac{\rho_{\text{sol}}^d}{2\rho_p^d}\right) \frac{(d_p^d)^2 \rho_p^d}{18\mu_{\text{sol}}^d}, \quad (1.34)$$

where $\rho_{\text{sol}}^d \approx 910.73$ kg/m³ and $\mu_{\text{sol}}^d \approx 2.5$ mPa s are the density and dynamic viscosity of the ethanol–water solution, and $\rho_p^d = 1050.00$ kg/m³ and $d_p^d = 1\mu$ m

Figure 1.15: a) Vertical component of the velocity and b) the total velocity magnitude corresponding to the same case as in figure 1.4b) in the main text. The size of the arrows was kept constant to highlight the direction.

are the density and diameter of the tracer particles. Then the Stokes number is estimated to be $St = t_0^d u_{\max}^d / z_F^d$, with $u_{\max}^d$ the maximum velocity at a given time and z_F^d the roll height at that time. The velocity ranges from $\sim 10^{-4} - 10^{-3}$ m/s while the roll height goes from 0.1 mm – 1 mm, resulting in a Stokes number of at most $St \sim 10^{-7}$. If we consider that from simulations we observed that the velocity at the edge reaches up to 0.01 m/s and we combine this with the smallest roll that we can observe experimentally, then we get $St \sim 10^{-6}$, meaning that in any case the particles should follow the flow properly.

Vertical component and magnitude of velocity

Figure 1.15 shows the vertical component (figure 1.15a)) and the magnitude (figure 1.15b)) of the velocity corresponding to the field shown in figure 1.4b) in the main text. The black dotted vertical line indicates the position of the edge of the chip.

Evaporation velocity

During the first 10 seconds over which we compared experiments with simulations, the velocity away from the edge stays approximately constant as shown by figure 1.16a). The velocities shown were obtained as a spatial average taken over the area enclosed by the black rectangle plotted in figure 1.16b), where we also show the velocity field at 10 s. At longer times, we expect the evapo-

Figure 1.16: a) Time series of the velocity far away from the edge. The values shown were obtained as a spatial average over the area A marked by the rectangle in b). b) Velocity field obtained from a single frame at $t = 10$ s. The size of the arrows was kept constant to highlight the direction.

ration rate to reduce as the gradient of ethanol reduces. Once the instability is vanishing, the velocity caused by evaporation reduces to about $10 \mu\text{m/s}$.

Mask used for μPIV at 100s

Figure 1.17 shows an example of a frame used in the μPIV measurements. The blue region is the mask used to avoid taking measurements inside the Marangoni rolls once the density of particles was too high. This was the case for the yellow curves in figure 1.4d) in the main text. At the moment shown in figure 1.17 it might seem that the mask is larger than needed, however later the high density region extends to occupy the masked region.

1.6.3 Appendix C. Values of different properties used for simulations and theoretical calculations

In table 1.2 we show the initial dimensional values of the different properties of the fluids used in the simulations. As mentioned in section 1.3.1, the generalized form of Raoult's law (equation 1.15) was used in simulations, for which the activity coefficient was calculated by the thermodynamic model AIOMFAC [79, 80]. On the other side, as also mentioned before, a Taylor expansion around an initial mass fraction of $c_{e,0} = 0.5$ was used for the the-

Figure 1.17: Example of a frame used to obtain the velocity field at $t^d = t_0^d + 100$ s. The blue region was masked.

oretical calculations. The corresponding coefficients were calculated according to $a_0(c_{e,0} = 0.5) = (1 + M_e^d/M_w^d)^{-1} - 2(M_e^d/M_w^d)(1 + M_e^d/M_w^d)^{-2}$ and $a_1(c_{e,0} = 0.5) = 4(M_e^d/M_w^d)(1 + M_e^d/M_w^d)^{-2}$. Their numerical values are displayed in table 1.2.

The thermal diffusion coefficient was obtained from Yano *et al.* [81], corresponding to $c_e = 0.494$ at 288 K. The gradient of surface tension with respect to temperature was obtained by fitting data from Vazquez *et al.* [82].

For the case of E , as discussed in the main text, we did not use the value at $t = 0$ as there is no gradient initially. Instead, we used the mean value $\overline{E}$ calculated over the same period used for calculating the growth rate σ in appendix 1.6.5. The corresponding values for each simulation can be seen in the appendix 1.6.7.

1.6.4 Appendix D. Derivation of dispersion relation

Here we show in more detail the derivation of the dispersion relation (1.31). Introduction of the perturbed quantities (1.27)–(1.30) into equations (1.18)–(1.21) yields the following ordinary differential equations after neglecting non-linear terms in ϵ ,

$c_{e,0}$		0.5	$c_{e,0}^g$		0
D_0^d	$[\text{m}^2 \text{s}^{-1}]$	3.65×10^{-10}	$D_{e,0}^{g,d}$	$[\text{m}^2 \text{s}^{-1}]$	1.35×10^{-5}
ρ_0^d	$[\text{kg m}^{-3}]$	9.11×10^2	$\rho_0^{g,d}$	$[\text{kg m}^{-3}]$	1.2
μ_0^d	$[\text{kg m}^{-1} \text{s}^{-1}]$	2.49×10^{-3}	$\mu_0^{g,d}$	$[\text{kg m}^{-1} \text{s}^{-1}]$	1.80×10^{-5}
$\frac{d\gamma_0^d}{dc_e}$	$[\text{kg s}^{-2}]$	-1.85×10^{-2}	$D_{w,0}^{g,d}$	$[\text{m}^2 \text{s}^{-1}]$	2.45×10^{-5}
p_{sat}^d	$[\text{kg m}^{-1} \text{s}^{-2}]$	6.57×10^3	T^d	$[\text{K}]$	2.95×10^2
M_e^d	$[\text{kg mol}^{-1}]$	4.61×10^{-2}	M_w^d	$[\text{kg mol}^{-1}]$	1.80×10^{-2}
RH	$[\%]$	50	δ^d	$[\text{m}]$	2.00×10^{-5}
a_0		-1.23×10^{-1}	a_1		8.08×10^{-1}
$D_{0,T}^d$	$[\text{m}^2 \text{s}^{-1}]$	8.74×10^{-8}	$\frac{d\gamma_0^d}{dT}$	$[\text{kg s}^{-2}]$	-8.99×10^{-5}

Table 1.2: Dimensional values used in simulations for the two phases at $t = 0$ and for the thermal Marangoni number estimation.

$$\left(\frac{d^2}{dz^2} - \kappa^2\right) \hat{p}_1 = 0, \quad (1.35)$$

$$\left(\frac{d^2}{dz^2} - \kappa^2 - 12 - \sigma\right) \hat{\mathbf{u}}_1 = \left(\frac{d}{dz} \hat{z} + i\kappa \hat{x}\right) \hat{p}_1, \quad (1.36)$$

$$\left(\frac{d^2}{dz^2} - \kappa^2 - \sigma \text{Sc}\right) \hat{c}_{e,1}(z) = E \text{Sc} \hat{u}_{z,1}(z) \quad (1.37)$$

$$\left(\frac{d^2}{dz^2} - \kappa^2\right) \hat{c}_{e,1}^g(z) = 0, \quad (1.38)$$

Equation (1.35) was obtained in the regular way of applying the divergence to the Navier-Stokes equation in combination with the continuity equation. It has for its solution

$$\hat{p}_1 = f_p e^{-\kappa z}, \quad (1.39)$$

where f_p is a constant and we have kept $\hat{p}_1$ finite. Substituting equation (1.39) into equation (1.36) leads to the solutions

$$\hat{u}_{z,1} = -\frac{\kappa f_p}{\kappa^2 - \beta^2} \left(e^{-\kappa z} - e^{-\beta z}\right), \quad (1.40)$$

in the z -direction, and

$$\hat{u}_{x,1} = \frac{if_p}{\kappa^2 - \beta^2} \left(\kappa e^{-\kappa z} - \beta e^{-\beta z}\right) \quad (1.41)$$

in the x -direction, with $\beta^2 = \kappa^2 + 12 + \sigma$. In these solutions we have already considered that the velocity should stay finite, assumed $u_{z,1}(x, 0, t) = 0$ as described in the main text, and took into account continuity $\nabla_{\parallel} \cdot \mathbf{u} = 0$.

Introduction of equation (1.40) into equation (1.37) leads to

$$\hat{c}_{e,1} = \frac{B_0}{\kappa^2 - \zeta^2} e^{-\kappa z} - \frac{B_0}{\beta^2 - \zeta^2} e^{-\beta z} + B_1 e^{-\zeta z}, \quad (1.42)$$

where $\zeta^2 = \kappa^2 + \sigma \text{Sc}$, $B_0 = -E \text{Sc} f_p \kappa / (\kappa^2 - \beta^2)$ and B_1 is a constant. Again we took a finite perturbation far away from the edge.

The solution of equation (1.38) is given by

$$\hat{c}_{e,1}^g = B_1^g e^{\kappa z}, \quad (1.43)$$

with B_1^g a constant. Once more, we have consider that the perturbation tends to zero far away from the edge.

The expanded Raoult's law (1.24) for the base case results in

$$\mathcal{C}_0^g = c_{\text{sat}}(a_0 + a_1 \mathcal{C}_0), \quad (1.44)$$

meaning that for the perturbed mass fraction the condition reads

$$\hat{c}_{e,1}^g(0) = c_{\text{sat}} a_1 \hat{c}_{e,1}(0), \quad (1.45)$$

thus

$$B_1^g = c_{\text{sat}} a_1 (I(0) + B_1), \quad (1.46)$$

where $I(0) = \frac{B_0}{p} - \frac{B_0}{q}$, with $p = \kappa^2 - \zeta^2$ and $q = \beta^2 - \zeta^2$.

On the other side, the mass conservation of solute at the interface (1.23) for the base case results in

$$E = D_e^g \rho^g E^g, \quad (1.47)$$

while for the perturbed mass fraction we have

$$I'(0) + \zeta B_1 = -D_e^g \rho^g \kappa B_1^g, \quad (1.48)$$

with $I'(0) = \frac{\kappa B_0}{p} - \frac{\beta B_0}{q}$ and $D_e^g = D_e^{g,d} / D_0^d$.

In this way we can obtain B_1 and B_1^g in terms of B_0 , but more importantly the mass fraction at the edge, which in the liquid side reads

$$\hat{c}_{e,1}(0) = \frac{\zeta I(0) - I'(0)}{\kappa c_{\text{sat}} a_1 D_e^g \rho^g + \zeta}. \quad (1.49)$$

As a last step we apply boundary condition (1.22),

$$\frac{d\hat{u}_{x,1}(0)}{dz} = i\kappa \frac{Ma}{Sc} \hat{c}_{e,1}(0), \quad (1.50)$$

where again we have taken into account that $u_{z,1}(x, 0, t) = 0$. In this way, the dispersion relation is expressed as

$$EMa_s = \kappa^2 \left(c_{\text{sat}} a_1 D^g \rho^g + \frac{\zeta}{\kappa} \right) \left(1 + \frac{\beta}{\kappa} \right) \left(1 + \frac{\zeta}{\kappa} \right) \left(\frac{\beta}{\kappa} + \frac{\zeta}{\kappa} \right), \quad (1.51)$$

which becomes equivalent to equation (30) from Sternling & Scriven [9], provided that we neglect surface viscosity, and consider that $\mu^{g,d} \ll \mu^{l,d}$, $\rho^{g,d} \ll \rho^{l,d}$ and $D^{l,d} \ll D^{g,d}$, with the superscripts g and l referring to the gas and liquid phases, respectively. We solved the complete equation from Sternling & Scriven [9] for a few cases and compared it with its simplified counterpart (1.51), which resulted in negligible differences when taking into account the material properties of ethanol and water and keeping the surface viscosity term equal to zero.

Finally, if we notice that $Ma_s^* = EMa_s$, then equation (1.51) leads to equation (1.31) in the main text.

1.6.5 Appendix E. Calculation of the growth rate

In this appendix we show typical plots used for the calculation of the growth rate σ as a function of wavenumber κ . In figure 1.18a) we show the power density function (PDF) as a function of the normalized wavenumber κ . This PDF corresponds to the mass fraction profile at $t = 10.3$ from figure 1.8d). By calculating the PDF over different times, we can look at the evolution in time of the power for every single wavenumber (not only those for which the power has a peak). In figure 1.18b) we show four examples corresponding to the vertical dashed lines in figure 1.18a).

If plotted in a semilogarithmic scale, there is a region where the power can be approximately fitted by a straight line (shadowed region in figure 1.18b)), reflecting exponential growth. The growth rate was obtained from a straight line fit in the shadowed region. We did not apply the fit at earlier times to avoid the period over which the concentration gradient is building up (transients, see figure 1.9). Later times were also avoided because eventually either nonlinear coupling or spectral bleeding causes all the wavelengths to grow at the same rate as the fastest wavelength. As an example, one can see that both the

Figure 1.18: a) Power density function obtained from the fast Fourier transform of the mass fraction profile at $t = 10.3$ from figure 1.8d) as a function of the normalized wavenumber κ . b) Same power as in panel a) but now as a function of time in a semilogarithmic scale. The four curves correspond to the vertical dashed lines in panel a). The shadowed area represents the section over which a linear fit (in semilogarithmic scale) was used to calculate the growth rate σ .

blue line with circles and the green line with right triangles in figure 1.18b) eventually start growing at a faster rate before reaching a saturation value. Nevertheless, in some cases we used a wider fitting period in order to have enough fitting points for the smallest wavenumbers, even if that implied that we included a small part of the regions of nonlinear growth for the largest wavenumbers. This is the reason for the noisy behaviour observed in figure 1.10 at larger values of κ .

Figure 1.10 shows the average over different runs, for which we have changed the mesh kind (see appendix 1.6.7 for a description of the different kinds of meshes), the resolution and the size of the simulation domain. The use of different resolutions and different domain sizes, resulted in different values of κ after taking the Fourier transform for simulations. In order to obtain an average curve of $\sigma(\kappa)$, we interpolated the values of σ at values of κ common to every different run.

From figure 1.18b) it is evident that the power is quite small in the region over which we made the fit (notice that the power represents variations on the

mass fraction). However, by the time the value becomes large, either merging has already taken place or the fastest wavelength has already shadowed the growth rate of the others. Therefore, we made the fit at early times when different wavelengths have different growth rates. In movie 5 of appendix 1.6.8 we show the evolution in time of the mass fraction variation showing that merging already takes place before the variations in mass fraction becomes large. This early merging makes it hard to observe the onset of the instability in experiments.

In some of our simulations the instability was triggered first in certain regions of the interface, while it started later in others. We discarded those simulations.

1.6.6 Appendix F. Velocity comparison between experiments and simulations

Here we discuss in more detail the comparison of the velocity between experiments and simulations. In figure 1.19a) we show velocity profiles $\langle |u| \rangle_x$ as function of z for four different times. The solid lines correspond to simulations and the crosses to experiments. If we take $t_1 = 6.85 \times 10^3$, then the other times correspond to $t_2 = 3t_1$, $t_3 = 7t_1$, and $t_4 = 9t_1$. In the case of experiments, the first three velocity profiles have a strong change, while the last profile is very similar to the third one. In simulations, there is a strong change from the first profile to the second, and from the third to the fourth profile, while the second and third profiles are quite similar. These changes are easier to see from figure 1.19b) where we show the evolution of the averaged velocity at fixed z positions. It is clear that the velocity evolves in a staggered manner with three steps visible in both experiments and in simulations. Therefore, we can expect that if we look at velocity profiles that correspond to the same step in figure 1.19b), they will be very similar, while if we look at velocity profiles at different steps, then they will look quite different.

Figures 1.19c) and d) show snapshots of the experiment and simulation respectively (in experiments we averaged 31 frames to make it easier to see the arches). Two merging events took place over time, reducing the number of arches to one, both in experiment and in simulation. However, the merging events took place at different moments in time. By comparing the times on the snapshots with the times at which the velocity has changed into a new step, we can see that a new step corresponds with a merging event. During the time between merging events the velocity stays approximately constant,

Figure 1.19: Velocity comparison between experiments and simulations at different times and positions. a) Average velocity profiles at four different times obtained from simulation and from experiments. The profiles correspond to a single frame, while in the main text the profiles were obtained from velocity fields which were already an average over 31 frames. b) Average velocity as a function of time at three different distances from the edge. Since the resolutions are not the same between experiments and simulations, we took the closest positions for comparison. c) Evolution of the instability obtained from experiments seeded with particles. Each image was obtained as an average over 31 frames centered at the indicated time. The times correspond to those shown in a). The white vertical lines in each panel, indicate the position of the edge of the chip. d) Mass fraction fields obtained from simulations for the corresponding times.

therefore, as we already mentioned, if we look back at the profiles from figure 1.19a), they do not change very strongly until a merging event takes place.

When we compare experiments and simulations, we can see that although the simulation has a slightly smaller velocity, as long as both have gone through the same number of merging events, the profiles coincide quite well. Furthermore, in both cases, the distance where the velocity reaches the far-end value coincides quite well as can be seen from figure 1.19a).

One reason for the mismatch between the times for merging comes from our uncertainty in the initial time in experiments. However, the time zero uncertainty should not affect the duration between merging events, which is not the same between experiments and simulation. This could come from irregularities at the edge of our chip, which are not present in simulations. However, further investigation is needed to determine what initiates a merging event.

The steps in the velocity in figure 1.19b), suggest that as long as the arches have a similar size, the velocity field should be approximately the same. In figure 1.20 we compare velocity measurements both from experiments and simulations at multiple positions, times, and realizations for arches with a similar size.

The velocity fields u_z in figure 1.20a,b) correspond to the same realization but at two different times, while no merging event has taken place (second step in figure 1.19b)). We will focus on the larger arch of about 40 length units in the x -direction. In figure 1.20c) a different realization is shown at the same time as in figure 1.20a) where an arch of half-width of 20 length units is visible. Finally, figure 1.20d) shows a velocity field obtained from simulations at the same time as in figure 1.20b) where the central arch is also close to 40 unit lengths. In the later plot we have made the velocity equal to zero in the region where we cannot measure in experiments, otherwise the much larger velocity close to the edge would make it difficult to make a comparison with experiments.

From each of the four velocity fields, we have taken a profile at approximately the same z position, namely $z = 6.75, 6.75, 5.56, 6.29$ corresponding to fields a–d) (these positions are marked with vertical black lines). Figures 1.20e) and g) show the profiles for both u_z and u_x . The x coordinate was shifted such that the maximum in u_z is placed at $x - x_1 = 0$, allowing us to compare the velocity of the large arch. The comparison is reasonably good, indicating that for a given arch size, the velocity is approximately the same despite the time, or the realization. Furthermore, the velocity from the simulations agrees quite well.

Figure 1.20: Velocity field comparison for similar sized arches. a,b) Velocity fields for a single realization at two different times without merging taking place. c) Velocity field of a different realization at the same time as in panel a) where an arch of similar half-size is visible at the top-left corner. d) Velocity field obtained from simulations at the same time as in panel b) with the central arch about the same size as in panels a) and b). Velocity profiles were taken at the place marked by the solid vertical black lines. Panel e) shows u_z and panel g) shows u_x . The profiles were displaced to align the centres of the arches, with x_1 the position of the centre of the arch in the x -direction. Velocity profiles along z are shown in panels f) and h). They were taken at positions marked with solid horizontal black lines on top of the velocity fields and correspond to the maxima and minima marked with black circles and squares in panels e) and g). *Inset:* Time series of u_z obtained at the centre of single arches. The blue curve is from experiments and the purple heavier line is from simulations. The arches tracked are such that they were one of the parents merging into the following arch.

Profiles along z are also plotted in figure 1.20f) and h) at the x positions marked in figure 1.20e, g) with black circles and black squares. This indicates that if at a single time the arches visible are of approximately the same size, the averaged velocity profiles should give approximately the same information as compared to profiles at a single position.

Finally, the inset of figure 1.20f) shows the time series of $u_z(t)$ obtained at the centre of a single arch and $z = 6.75$. The arches that we tracked can be seen in figure 1.19c). In the first two snapshots, we measured the velocity at the centre of the lowest arch. In the last two snapshots we followed the only visible arch. In this way, the arches we followed are “parents” from the new ones appearing. The step like behavior is obtained again as in figure 1.19b), indicating that indeed the velocity mainly increases during merging events.

The same procedure was applied to the simulated velocity field. The corresponding time series is also shown in the inset of figure 1.20f). Notice that the first step of the experimental velocity has a value in between two steps of the velocity from the simulation. We associate this with the fact that the arches in experiments have an intermediate size. In experiments, the arches are about 20 length units, while in simulations the arches go from about 10 length units before merging to about 40 length units after merging. Although in simulations the change in velocity from the second to third step is not as abrupt as in experiments, the velocities compare quite well.

1.6.7 Appendix G. Further details on simulations

Simulation meshes and domain size

We used three different kinds of mesh configurations for the different simulations we performed. Examples of the meshes are shown in figure 1.21 with definitions of different length scales needed to determine the mesh. The numerical values of these length scales are shown in table 1.3. The simulation numbers corresponds with those shown in table 1.4.

Mesh 1 was used for the large size simulation presented in section 3.3 of the main text. These kind of meshes consisted of triangular elements with a higher density close to the interface, where a higher resolution is needed. The number of elements reduces with distance from the interface. This is the kind of mesh that was used for the gas domain in all simulations. While setting up the simulations, we determined the size at the gas–liquid interface Δx^i , at the far edge in the liquid $\Delta x^{l,\infty}$, and at the far edge in the gas $\Delta x^{g,\infty}$ (see figure 1.21

for a graphical definitions of these quantities). These length scales determine the resolution. The corresponding values are shown in table 1.3.

Mesh 2 included a layer on the liquid side where the triangular elements were arranged to create a rectangular mesh (see second and third columns of figure 1.21). This layer extended from the interface up to a distance L_{BL} , then the mesh would behave as Mesh 1, with the number of elements decreasing the further away from the interface.

Mesh 3 was divided in three stages: first the rectangular layer up to L_{BL} (as in Mesh 2), then a section of increasing element size over a distance L_{BL2} (as in Mesh 1) and finally a section of coarser resolution. In this last section a blending factor was used to determine if the element size would be homogeneous and given by the size of $\Delta x^{1,\infty}$ (blending factor equal to 1), or if the resolution would linearly increase up to $\Delta x^{1,\infty}$ (blending factor smaller than 1). This would then affect how fast the resolution would decrease over the distance L_{BL2} .

Mismatch of boundary condition

As mentioned in the main text, for the simulation used for comparison with experimental results, we reduced the resolution in order to avoid exceedingly long simulation times. This came at the cost of a mismatch of the boundary condition between fluxes, meaning that

$$\rho D \partial_z c_e \neq (1 - c_e) j_e - c_e j_w. \quad (1.52)$$

In figure 1.22 we show both the left and the right hand sides of equation (1.52). In figure 1.22a) both quantities are shown as function of the coordinate x at $t = 1.37 \times 10^4$. In figure 1.22b) we show the same quantities over time, but this time averaged along the x coordinate. The gradient in mass fraction that is imposed by the flux in the gas, cannot be captured properly by the low resolution used in the liquid side. In fact, no matter how small the resolution is chosen, it is not possible to perfectly satisfy (1.52), the convection-diffusion equation and the conservation of mass on the linear shape functions used for the composition space. Hence, this type of error needs to be accepted, i.e. the mass is conserved at the expense of not perfectly reproducing the imposed normal composition gradient due to preferential evaporation directly at the interface. Nevertheless, since for this simulation we are more interested on the phenomena that takes place in the bulk, this mismatch does not seem to represent a big problem at distances larger than the concentration boundary layer.

Figure 1.21: Examples of the three kind of meshes used in the liquid phase for comparison with linear stability analysis. For each case, we show two levels of zoom of the lower left corner. We also marked the definitions of the different distances reported in table 1.3. In the case of the gas phase we only used meshes of kind 1, but mirrored horizontally. The left edge corresponds to the gas–liquid interface.

#	L^g	L^l	W	$\Delta x^{g,\infty}$	$\Delta x^{l,\infty}$	Δx^i	Mesh kind ^a	L_{BL}	L_{BL2}	Blending factor	BC^b
1	500	12.5	17.5	17.5	1.75	0.175	1	-	-	-	P
2	500	12.5	20	20	1	0.05	1	-	-	-	P
3	500	12.5	25	25	2.5	0.125	1	-	-	-	P
4	500	12.5	17.5	17.5	1.75	0.175	2	1.05	-	-	P
5	500	25	25	25	2.5	0.25	2	0.5	-	-	NP
6	500	37.5	50	50	25	0.25	2	0.5	-	-	NP
7	500	12.5	20	20	1	0.05	3	0.75	4	1	P
8	500	12.5	20	20	1	0.05	3	0.75	8	0.5	P
9	125	5	10	10	0.5	0.025	1	-	-	-	P
10	125	5	10	10	0.5	0.025	1	-	-	-	NP
11	125	10	10	10	0.5	0.025	1	-	-	-	P
12	125	15	10	10	0.5	0.025	1	-	-	-	P
13	125	5	15	15	0.75	0.0375	1	-	-	-	P
14	125	15	15	15	0.75	0.0375	1	-	-	-	P
15	125	2.5	10	10	0.5	0.05	2	1	-	-	P
16	125	5	10	10	0.5	0.025	3	0.5	2	1	P
17	5	1	5	5	0.25	0.025	1	-	-	-	P
18	5	5	5	5	0.25	0.0125	1	-	-	-	P
19	5	1	7.5	7.5	0.375	0.0375	1	-	-	-	P
20	5	7.5	7.5	7.5	0.375	0.01875	1	-	-	-	P
21	5	1	10	10	0.5	0.05	1	-	-	-	NP
22	5	7.5	10	10	0.5	0.025	1	-	-	-	NP
23	5	5	5	5	0.25	0.0125	3	0.05	1	1	P
24	3.5	0.5	2	0.4	0.08	0.008	1	-	-	-	P
25	3.5	0.5	2	0.5	0.1	0.005	1	-	-	-	P

26	3.5	0.5	2	0.5	0.1	0.01	1	-	-	-	P
27	3.5	1.5	2	0.5	0.1	0.01	1	-	-	-	P
28	3.5	2	2	2	0.1	0.005	1	-	-	-	P
29	3.5	2	2	0.5	0.1	0.01	1	-	-	-	P
30	3.5	2.5	2	0.5	0.1	0.01	1	-	-	-	P
31	3.5	0.5	3	0.75	0.15	0.015	1	-	-	-	NP
32	3.5	0.5	3.5	3.5	0.0875	0.00875	1	-	-	-	P
33	3.5	0.5	5	5	0.125	0.0125	1	-	-	-	P
34	3.5	0.5	2	2	0.1	0.01	2	0.025	-	-	P
35	3.5	0.5	2	2	0.1	0.01	2	0.014	-	-	P
36	3.5	0.5	2	2	0.1	0.02	2	0.025	-	-	P
37	3.5	2	2	0.5	0.1	0.005	3	0.1	0.8	0.5	P
38	3.5	2	2	2	0.1	0.01	3	0.1	0.4	0.5	P
39	2.25	1	2	1	0.1	0.005	1	-	-	-	P
40	2.25	2	2	1	0.1	0.005	1	-	-	-	P
41	2.25	2	3	1.5	0.15	0.0075	1	-	-	-	P
42	2.25	2	2	1	0.1	0.005	3	0.1	0.8	1	P
43	2.25	60	60	60	6	0.6	1	-	-	-	P

Table 1.3: Domain characteristics of the simulations used for linear stability comparison. Quantities are normalized using the chip height $\delta^a = 20 \text{ }\mu\text{m}$. Simulation #43 corresponds to the case shown in figure 1.6 in the main text.
^b Kind of boundary condition, either periodic (P) or non periodic (NP).

Figure 1.22: Example of the mismatch between the left and right hand side in the boundary condition given by equation (1.13) in the main text. a) Fluxes along the interface at $t = 1.37 \times 10^4$. b) Average fluxes over time.

On the other side, the kinematic boundary condition (equation 3.10 in the main text) is properly captured despite the low resolution. Furthermore, by comparing with simulations with a smaller simulation domain and higher resolutions, we confirmed that the values of the velocity in the z direction at the interface $u_z(z = 0)$ reached the same order of magnitude as in the larger simulation. Therefore, the velocity field should only be affected weakly by the mismatch. This explains why there is a good comparison with experiments. However, we can not expect that the exact values of mass fraction observed in simulations represent those in experiments. It can then be questioned how the growth of the front agreed with experiments. We consider that this suggests that it is the velocity field, by means of the size of the Marangoni rolls, which determines the penetration depth z_F . Since we only look at the position z where the mass fraction reaches the far field value, it is not as important how much ethanol has been lost. Instead, what is more important is up to which position has the ethanol-poor solution been advected back into the bulk by the Marangoni rolls.

Values of $\overline{E}$ and Ma_s^* obtained from simulations

In table 1.4 we show the corresponding time limits and the values of $\overline{E}$ and Ma_s^* for each simulation used to obtain figure 1.10 of the main text.

#	$t_{\text{fit},1}$	$t_{\text{fit},2}$	$\overline{E}$	Ma_s^*
1	6.85×10^2	1.37×10^3	1.56×10^{-3}	6.33×10^2
2	1.71×10^3	2.40×10^3	1.73×10^{-3}	7.03×10^2
3	1.03×10^3	1.71×10^3	1.63×10^{-3}	6.64×10^2
4	2.05×10^3	2.74×10^3	1.75×10^{-3}	7.13×10^2
5	1.37×10^3	2.05×10^3	1.74×10^{-3}	7.08×10^2
6	1.71×10^3	2.40×10^3	1.74×10^{-3}	7.09×10^2
7	2.40×10^3	3.42×10^3	1.76×10^{-3}	7.16×10^2
8	2.40×10^3	3.42×10^3	1.76×10^{-3}	7.16×10^2
9	2.05×10^2	4.11×10^2	6.87×10^{-3}	2.79×10^3
10	2.05×10^2	4.11×10^2	6.87×10^{-3}	2.79×10^3
11	2.05×10^2	4.11×10^2	6.88×10^{-3}	2.79×10^3
12	3.42×10^2	4.79×10^2	6.91×10^{-3}	2.81×10^3
13	1.37×10^2	2.74×10^2	6.68×10^{-3}	2.71×10^3
14	1.37×10^2	2.74×10^2	6.70×10^{-3}	2.72×10^3
15	2.05×10^2	3.42×10^2	6.56×10^{-3}	2.66×10^3
16	2.05×10^2	4.11×10^2	6.96×10^{-3}	2.83×10^3
17	6.85×10^1	1.37×10^2	1.68×10^{-2}	6.82×10^3
18	2.74×10^1	6.85×10^1	1.71×10^{-2}	6.94×10^3
19	4.11×10^1	9.59×10^1	1.58×10^{-2}	6.40×10^3
20	3.42×10^1	6.85×10^1	1.68×10^{-2}	6.82×10^3
21	5.48×10^1	1.37×10^2	1.51×10^{-2}	6.12×10^3
22	3.42×10^1	6.85×10^1	1.64×10^{-2}	6.65×10^3
23	1.23×10^2	1.92×10^2	1.73×10^{-2}	7.05×10^3
24	3.42	6.85	2.35×10^{-1}	9.56×10^4
25	3.42	6.85	2.43×10^{-1}	9.86×10^4
26	3.42	6.85	2.29×10^{-1}	9.31×10^4
27	3.42	6.85	2.31×10^{-1}	9.40×10^4
28	3.42	6.85	2.44×10^{-1}	9.91×10^4
29	3.42	6.85	2.33×10^{-1}	9.46×10^4
30	3.42	6.85	2.33×10^{-1}	9.46×10^4
31	3.42	6.85	2.15×10^{-1}	8.73×10^4
32	3.42	6.85	2.33×10^{-1}	9.47×10^4
33	3.42	6.85	2.24×10^{-1}	9.10×10^4

34	3.42	6.85	2.42×10^{-1}	9.81×10^4
35	3.42	6.85	2.22×10^{-1}	9.00×10^4
36	3.42	6.85	2.41×10^{-1}	9.81×10^4
37	3.42	6.85	2.01×10^{-1}	8.16×10^4
38	3.42	6.85	2.28×10^{-1}	9.25×10^4
39	3.42	5.82	3.79×10^{-1}	1.54×10^5
40	3.42	6.85	3.81×10^{-1}	1.55×10^5
41	3.42	5.48	3.69×10^{-1}	1.50×10^5
42	3.42	6.85	3.89×10^{-1}	1.58×10^5

Table 1.4: Time limits $t_{\text{fit},1}$ and $t_{\text{fit},2}$ over which the values of the mass fraction gradient $\bar{E}$, and the growth rate σ were calculated. The corresponding values of $\bar{E}$ and the modified Marangoni number Ma_s^* (calculated using $\bar{E}$) are shown too.

1.6.8 Appendix H. QR-code for videos

Figure 1.23

2.1 Introduction

Evaporation from multicomponent liquid mixtures is ubiquitous in fundamental and applied processes [2], such as inkjet printing [16, 84], microencapsulation by spray drying [85, 86], concentration of an analyte in chemical diagnosis [87], extraction and purification of pharmaceutical ingredients from solutions [88], and fabrication of functional materials by droplet templating methods [89–94]. For example, recent work demonstrates the potential application of evaporating multicomponent droplets in the fabrication of supraparticles [95, 96]. Briefly explained, oil formed from liquid-liquid phase separation creates a ring around the drop boundary and acts as a self-lubricating layer to overcome the coffee ring effect. As the evaporating droplets shrink with a freely moving boundary, nanoparticles dispersed inside the drop get assembled into supraparticles of different shapes. [95, 96]

Following the pioneering works of Sternling and Scriven [9], and Linde, Pfaff and Zirkel [52], our recent work from [24] showed that evaporation of a binary solution from an open side of a Hele-Shaw cell can trigger complicated flow dynamics, in particular a Marangoni instability. In this case, selective evaporation creates a gradient in concentration normal to the gas-liquid interface. If the concentration field is perturbed, concentration gradients along the interface can appear, ultimately leading to the Marangoni instability. It has been shown that enhanced mixing, fast mass transfer, [41, 50] or a fast propagation of chemical fronts [44] may occur when a Marangoni instability is present at an interface.

Evaporation can also result in the spontaneous emulsification of ternary solutions consisting of ethanol, water, and anise oil, namely by the so called ouzo effect. Here the ouzo effect refers to the spontaneous microdroplet formation in ternary liquid mixtures with compositions between the spinodal and the binodal curves in the solubility phase diagram [19, 97, 98]. These ternary solutions are the favored model systems for understanding evaporation of multicomponent mixtures coupled with liquid-liquid phase separation [2, 10, 55]. In general, depending on the composition in the ternary solution, liquid-liquid phase separation can take two routes. It may form two macroscopic subphases via spinodal decomposition [99, 100], or form microdroplets via the ouzo effect [19, 101] with the relative decrease in the concentration of the good solvent. When confined in a 2D micro-chamber, surface microdroplets nucleated due to the ouzo effect can self-arrange into intriguing branch-like patterns with a

characteristic angle between the merging branches [71]. Such patterns are a signature of diffusion-dominated nucleation and growth of droplets confined in a 2D space, with a mechanism similar to the ramification of underground rivers over a much larger length scale [102, 103]. Furthermore, the sharp gradient of chemical concentration caused by the phase separation, can result in the autonomous motion of the microdroplets due to diffusiophoresis. [104, 105]

In the paper mentioned above [71, 104, 105], phase separation of the ternary mixtures was triggered by diffusive mixing with a poor solvent supplied from a deep side channel adjacent to the main 2D chamber. No gas-liquid interface was responsible for the phase separation or for droplet formation in the chamber. To the best of our knowledge, the study of phase separation induced by evaporation of a ternary mixture confined in 2D space remains scant. The fundamental questions to be answered are: how does the interfacial tension gradient caused by solvent evaporation affects the mass transfer and liquid-liquid phase separation confined in the 2D chamber? How is the evaporation-induced behaviour correlated with the composition of the solution?

To address those questions, in the present work we will follow the evaporation of ternary mixtures from a Hele-Shaw cell. As the good solvent evaporates from an opening at the side of the cell, we found that regardless of the initial composition of the ternary solution, a Marangoni instability occurs at the early stage of evaporation, with a mechanism similar to that in the evaporation of binary solutions. However, with time, the processes of mass transfer in the liquid mixture, and the formation and evolution of droplets from phase separation display distinct features, according to the composition of the initial ternary solution. The oil-rich liquid from phase separation can self-seal the opening of the cell and slow down evaporation. The notable droplet patterns suggest that after self-sealing all subsequent processes become dominated by diffusion.

The organization of the paper is as follows: in the next section we will present the system and materials used. Afterwards, we discuss the Marangoni instability, its evolution in time and the conditions under which it is triggered. The following four sections are dedicated to describe the four groups in which the mixtures were classified according to the way they phase separate. A rationale for the different ways of phase separation is given in each section. We close with a summary and conclusions.

Tag	$c_e \times 100\%$	$c_w \times 100\%$	$c_{tA} \times 100\%$
a	45.8	53.4	0.8
b	54.9	43.1	2.0
c	60.7	35.2	4.1
d	63.7	30.0	6.3
e	66.1	21.9	12.0
f	66.5	16.0	17.5
g	60.0	10.0	30.0
h	51.1	7.3	41.6
i	35.6	4.5	59.9
j	20.0	2.0	78.0
k	14.0	1.0	85.0

Table 2.1: Initial mass fraction c_α of the different mixtures used in experiments, where α is e, w, and tA, standing for ethanol, water, and trans-anethole, respectively. The tags are also displayed in the ternary diagram in figure 2.1a.

2.2 Experimental

2.2.1 Chemicals and solutions

The ternary mixtures in our experiments were made out of water (produced by a Reference A+ system, Merck Millipore, at 18.2 M cm and 25°C), ethanol (Boom, 100%(v/v), technical grade), and trans-anethole (Aldrich, 99%). Initial mass fraction c_α of the different mixtures is listed in table 2.1, where α refers to ethanol (e), water (w), and trans-anethole (tA). For solutions of the same mass fraction, the error is of 0.1 wt% as prepared for different runs of experiments. Figure 2.1a shows the same mass fractions in a ternary solubility phase diagram. The mixtures were classified in four groups: low (blue), intermediate-low (red), intermediate-high (yellow), and high (green) oil concentrations (see figure 2.1a), according to the characteristics of the phase separation. The error in the concentration values is of 0.1wt%.

Figure 2.1: a) Ternary diagram of ethanol, water and trans-anethole. The solid lines represent the binodal (black and grey) and the spinodal (red) limits calculated as described in Ref [106]. The initial concentrations used in our experiments are labelled with color-coded circles. Each color represents the solutions that exhibit similar dynamic behavior induced by evaporation and correspond to the same group. Double-colored circles (c,d, and i) are for solutions that have features of two groups. b) Sketch of the experimental set up showing a frontal view of the Hele-Shaw cell. Black region: silicon frame; light blue region: glass plate for visualization. Thin and thick vertical lines: micropillars and walls to maintain the spacing between the two plates (not to scale). c) Bottom view of the chip showing the internal structure. Gray areas represent the sections with a gap. The micropillars are depicted as circles and the walls as horizontal stripes. The two plates are bonded in the black areas. The left edge is open to air so evaporation can take place. On the right, a channel of 50 μm depth was used to fill the chip and keep the volume constant during the experiment. d) Cross section of the chip with the dimensions of the gap. The position of the meniscus between air and liquid is also sketched.

2.2.2 Configuration of the Hele-Shaw cell for evaporation

A microfluidic chip (Beijing First Mems Co., Ltd) was used as a Hele-Shaw cell in all of our experiments. Figure 2.1b shows a cross section of the chip. The gap in between the two plates was 20 μm , so the space inside the cell can be considered as quasi 2D. As shown in figure 2.1b, a set of micropillars of 50 μm in diameter (thin vertical lines in the sketch) and intermediate walls of 0.5 mm width (thick vertical lines in the sketch) were placed inside the cell to stabilize the top and bottom plates during the fabrication process.

The chips were sealed, except for one side left open to allow for evaporation (left side in figure 2.1c and d). Along the opposite side of the chip there was a sub-channel with 50 μm in depth, acting as a reservoir to keep the chip filled with the solution (see figure 2.1c and d). The surface of the chip was hydrophobilized by depositing a layer of trichloro (octadecyl) silane (OTS, Sigma-Aldrich) by a procedure of solution deposition [72]. In brief, the chip was cleaned in a bath of piranha solution (30% of hydrogen peroxide and 70% sulfuric acid) (caution: piranha solution is highly corrosive and acidic!) for 40 min at 75 $^{\circ}\text{C}$. The chip was then taken out and rinsed with plenty of water (Mill-Q, 18.2 m Ω) and then with ethanol. The chip was then kept in an oven at 120 $^{\circ}\text{C}$ for 2 h to eliminate excessive water on the surface. After cooling down, the chip was soaked in a solution of 0.5% OTS in toluene for 17 h. Finally, the chip was sonicated for 10 min in chloroform and 15 min in toluene, acetone, isopropyl alcohol, ethanol and water, sequentially. After each experiment the chip was cleaned in a bath of acetone, isopropyl alcohol, and ethanol sequentially. In between each bath, the chip was dried with a flow of nitrogen.

2.2.3 Experimental procedure and evaporation conditions

We followed the evaporation process in a region near the open edge as depicted in figure 2.1c, by using an inverted microscope (Olympus GX51) with a 5X objective (Olympus, MPlan FL N, 5X/0.15) in line with a 0.5X lens for observation and recorded with a CCD camera (MD061MU-SY, Ximea). A CMOS camera (MQ013MG-ON, Ximea) was also used in several experiments. To stitch images we used a plugin in ImageJ [107]

Fluorescent images were taken with a Nikon Confocal Microscopes A1 system.

Perylene (Sigma-Aldrich, $\geq 99\%$) was used to dye two of the oil-rich solutions. For mixture h, the mass fraction of perylene was $c_p = 4 \times 10^{-4}$. For mixture j we had $c_p = 5 \times 10^{-5}$. Experiments with the confocal microscope were made in laboratory conditions without relative humidity control. To visualize the flow of some of the mixtures, the solution was doped with tracer particles (FluoSpheres, Life Technologies, $1\ \mu\text{m}$ in diameter carboxylate-modified, 2% solid in aqueous solution with 2 mM of sodium azide).

During the experiments, the solution was delivered from a syringe connected through a capillary tube to the chip. The flow rate was controlled by using a motorized syringe pump (Harvard Instruments, PHD 2000). In each experiment the chip was filled within 1 min at a rate of $15\ \mu\text{L min}^{-1}$. After 20-30 s the flow was reduced to a value ranging from 0.005 - $0.5\ \mu\text{L/min}$ to keep the chip filled and compensate the liquid loss from evaporation. Generally, a solution with a higher oil concentration required a slower rate of the replenishing flow. The direction of the flow is depicted with blue arrows in figure 2.1c. Because the gap of the Hele-Shaw cell ($20\ \mu\text{m}$) is smaller than the gap of the reservoir channel ($50\ \mu\text{m}$), capillary forces keep the cell filled, compensating evaporated liquid with liquid from the reservoir. To ensure that the capillary pressure was enough to compensate the evaporation, the outlet was exposed to ambient pressure.

The chip was placed inside a closed environmental chamber where the humidity was controlled by a flow of humid or dry nitrogen. This chamber was created by covering part of microscope with plastic wrap. The relative humidity was maintained to be within 50% and 52 %. When the relative humidity was outside that range, there was a delay before it was back to the desired value, resulting in a larger effective range from approximately 48% and approximately 53%, depending on the outside humidity. A humidity and temperature sensor (HIH6130, Honeywelle) was used to monitor these two quantities. An Arduino board (Arduino Nano) was used to read the signal from the sensor and to control a pair of valves that controlled the flow of humid and dry nitrogen, according to the readings of the sensor. The temperature of the gas surrounding the chip was only monitored but not controlled, varying within $20\ ^\circ\text{C}$ and $25\ ^\circ\text{C}$, for different experiments. Due to the lamp of the microscope, the gas temperature in a single experiment varied approximately at $1\ \text{K/h}$ to $2\ \text{K/h}$. A figure with the location of the nitrogen inlets and the sensor with respect to the chip are shown in the appendix.

2.3 Results and discussion

Evaporation of the most volatile component (ethanol) in the ternary mixture takes place at the gas-liquid interface that was aligned with the open edge of the chip in figure 2.1c. In the next section, we will investigate the interesting and complex dynamic phenomena induced by evaporation and the dependence on the initial composition of the ternary solution. The initial solutions were classified in four groups: low, intermediate-low, intermediate-high, and high oil concentrations (see figure 2.1a), according to the main characteristics of the phase separation. The differences between groups are not sharp and the solution labelled with two colors show characteristics of two adjacent groups.

2.3.1 Initial Marangoni instability

At the beginning of the evaporation process, a Marangoni instability was triggered for all cases. The instability was evident in the growth and merging of arch-like region as shown in figure 2.2a. The flow inside the arches is depicted with black arrows and shown with streak-lines in figure 2.2b for the case of $c_{tA} = 0.416$. Such a flow with pairs of convective rolls is typical of Marangoni instabilities [24, 41, 51, 52]. In our case, the presence of the air-liquid interface and the lower surface tension of volatile ethanol are the origin of the instability [9, 24]. For further details in the conditions needed for the instability to be triggered see the SI.

The horizontal size x_F of the arches increases in time as shown in figure 2.2c. Similarly to binary ethanol-water mixtures, x_F increases approximately as a power law while the instability is active. For low oil contents (blue group), the exponent of the power law is close to $1/2$, as in the binary case [24]. For the rest of the cases the exponent is larger, up to 0.7 (see the appendix). Therefore, it seems that the third component (oil) can help accelerate the arch growth. Furthermore, the life-time of the Marangoni instability reduces with increasing oil concentration, as shown by the time at which x_F reaches a plateau.

The strong flow at the air-liquid interface makes our evaporating system different from systems where phase separation is induced solely by diffusive mixing [71]. The flow confines the phase separation inside the arches and prevents surface droplets from self-arranging into branch-like patterns close to the in-

Figure 2.2: a) Snapshots showing the area in the Hele-Shaw cell along the open side. The time t_0 is defined at the moment when the ternary solution covers the edge in the field of view. The initial mass fraction of trans-anethole is labelled below the images. When phase separation takes place, it happens inside of the arch-like regions. The black arrows indicate the general direction of the flow caused by a Marangoni instability. In the first panel, the vertical white dotted line indicates the location of the air-liquid interface. b) Composite image obtained from 31 frames for a solution of initial oil mass fraction $c_{tA} = 0.416$ seeded with tracer particles. The arrows indicate the direction of the flow. The vertical black dotted line indicates the position of the air-liquid interface. Movie 1 in appendix 2.5.6 corresponds to this figure. c) Double logarithmic plots showing the distance x_F from the edge of the chip up to the summit of the biggest arch at a given time. The insets in each plot give examples of x_F . Each different plot corresponds to one of the four different groups marked in figure 2.1a. Curves of same color represent different repetitions of the same case. For $c_{tA} \geq 0.120$, x_F dramatically slows down after the Marangoni instability stops. Lines indicating a $1/2$ power law are added for comparison.

terface, in contrast to previous observations [71]. However, in regions where the flow is slow or after the instability has stopped, diffusion can become dominant and branch-like patterns are recovered. We will discuss in more detail the differences in the spatial distribution of phase separation and droplet nucleation in the following sections.

2.3.2 Group 1: Low oil concentration in the ternary solution

The solutions in this group are labelled in figure 2.3a and also listed in table 2.1 as Tag (a-d). Ethanol evaporation reduces the concentration of ethanol in the solution while the loss of water and oil is negligible. With progression of evaporation the ratio of water and oil remains constant before liquid-liquid phase separation and the mixture composition follows the path in the phase diagram. The compositions of all four solutions in this group go through the ouzo region with ethanol loss from evaporation. Therefore spontaneous emulsification is expected. [19, 97] Indeed, the common features of this group is droplet nucleation and growth. The distribution of the droplets is in part associated with the flow caused by the Marangoni instability. Furthermore, away from the gas-liquid interface, groups of surface droplets can arrange themselves into finger-like patterns as it will be described in more detail in the rest of this section. See figure 2.3b for examples of the finger-like patterns. The snapshots in figure 2.3b show the first 10 min of a typical experiment with $c_{tA} = 0.020$. Initially, oil droplets nucleate from the gas-liquid interface along the open edge of the chip and are distributed inside the arches by the convective rolls as depicted in the first panels of figure 2.3b and c. Other locations of initial droplet formation within the arches are attributed to the influence of the Marangoni instability on the local composition of the solution. Water-rich solution with less ethanol at the gas-liquid interface is transported inside the arches by recirculation, leading to quick depletion of ethanol inside the arches. Therefore, a large concentration gradient normal to the perimeter of the arches (blue dashed line in figure 2.3c) builds up, causing the oversaturation of oil and, after tenths of seconds, surface droplets nucleation. The surface droplets at the perimeter of the arches are shown in the second and third panels of figure 2.3b and sketched in figure 2.3c. As the surface droplets become dominant, some of them coalesce into small oil-rich regions that accumulate at the stagnation points between consecutive convective rolls (see figures 2.3b and 2.3c).

In parallel to the advective flow caused by the Marangoni instability, the

Figure 2.3: Main characteristics of droplet formation induced by evaporation of ternary solutions with low concentrations of oil c_{tA} . a) Ternary diagram showing the initial mass fractions in the group. The dashed lines are composition paths for which only ethanol evaporates, while the ratio of water and oil remains constant. b) Snapshots showing the temporal evolution of a typical evaporating-emulsification process over the first 10 min for an initial concentration ratio $c_{tA} = 0.020$. Movie 2 in appendix 2.5.6 correspond to this case. Evaporation takes place from the left side of each snapshot. c) Sketch showing the main characteristics observed in the evaporation-emulsification process inside a Marangoni arch over time. The qualitative change in the ethanol concentration c_e and surface tension γ is signaled with the superscripts $(++,+,-)$. The solid arrows with open heads indicate the direction of flow. The yellow circles in the left sketch represent bulk droplets. The yellow circles in the right sketch indicate surface droplets, some of which arrange into finger-like patterns.

presence of concentration gradients around the droplets can result in diffusio-phoretic (non-charged solute) and Marangoni effects at the droplet interface [4, 108]. In some cases we observed that the surface droplets displace in a direction approximately perpendicular to the perimeter of the arches (see movie 3 in appendix 2.5.6). As we already mention, we suspect that a strong gradient is present in the direction perpendicular to the perimeter of the arches. Given that both the Marangoni and diffusio-phoretic propulsion depend on the existence of a concentration gradient around the droplet, it is possible that these effects are in play here [104]. However, the direction of displacement can change over time, making it complicated to conclusively determine what is the cause behind droplet displacement once they have nucleated (see movie 3). Collective effects could also play a role [109].

In movie 3 some bulk droplets move in the opposite direction of the surface droplets, possible indicating the position of the binodal concentration [101]. However, it is not easy to decouple such displacement from the advective flow caused by the Marangoni instability or due to the flow caused by displacement of other droplets or larger oil regions. In some cases, we can also observe that bulk droplets or tracer particles flow in circles around surface droplets, further indicating local Marangoni flows. We refer to the work of Zhang *et. al* [104] for a closer look into such an interaction between surface and bulk droplets in a ternary system.

Over time, droplet formation inside the cell become more and more dominated by diffusion rather than by transport inside the Marangoni arches. It is evident as the droplets self arrange into finger-like droplet patterns (i.e. signature of diffusion-dominated process [71]) at the summit of the arches. The fingers are marked in figures 2.3b and sketched in figure 2.3c as an elongated group of droplets. The fingers grow approximately in the radial direction with respect to the center of a given arch. However, the finger-like patterns are not long-lived and eventually droplets nucleate in between them (see movie 2 in the appendix), indicating that advection is still present. As the arches become larger, new finger-like patterns appear (third panel of figure 2.3b) and get blurred again.

Eventually, the arches become comparable in size with the width of the chip and the surface droplets can nucleate virtually everywhere. In figure 2.4 we show two stitched images obtained about 30 min after the evaporation process started for two different initial concentration ratios. Finger patterns are visible at the frontier (marked with blue dashed lines) between the area with surface droplets and the one-phase area. For the higher oil case, the fingers are more

Figure 2.4: Stitched snapshots showing a larger field of view. In a) $c_{tA} = 0.020$ and the image corresponds to the same series of snapshots shown in figure 2.3 b). Finger patterns are visible at the lower right and upper right corners. In b) we show an example of $c_{tA} = 0.041$ with ramified fingers. In that case, the snapshots were taken at the middle compartment of the chip (see figure 2.1c). In both cases, the blue dashed lines qualitatively indicate the frontier between the two-phase and one-phase areas considering where oil droplets are visible.

evident and they have ramified into branch-like patterns.

The mechanism for the self arrangement of the surface droplet in a quasi-2D chamber is explained in the work by Lu *et al.* [71]. In their case, the emulsification was induced by diffusive mixing with the poor solvent (water), and self arrangement into branch-like patterns occurred in the entire chamber. In contrast, in our experiments emulsification is caused by the loss of the good solvent (ethanol), and finger-like patterns only appear locally at the summit of the arches, close to a stagnation point (see figure 2.3c). The decrease in velocity around the stagnation point can cause that locally diffusion is more important than advection. For $c_{tA} = 0.041$ and $c_{tA} = 0.063$, a thin layer of oil can form along the edge. The layer can hinder both the evaporation and the Marangoni flow, supporting our hypothesis that branches and fingers mainly grow due to diffusion.

The formation of the oil layer is in accordance with the composition path of the mixture at $c_{tA} = 0.041$ and $c_{tA} = 0.063$. For the former the path passes very close to the spinodal line, and for the later, the path actually crosses the spinodal limit. We marked mixtures c and d with two colors in figure 2.1a because a larger accumulations of oil-rich phase is the main feature of the next

Figure 2.5: Main characteristics of phase separation induced by evaporation of the solutions with intermediate-low trans-anethole concentrations c_{tA} . a) Ternary diagram with the initial concentrations corresponding to the group of intermediate-low oil concentrations. The straight dashed lines correspond to processes for which only ethanol evaporates. Points e' and e'' indicate two possible compositions after bulk phase separation. b) Snapshots at increasing times of a typical example of $c_{tA} = 0.120$. Movie 4 in appendix 2.5.6 corresponds to this case.

group.

2.3.3 Group 2: Intermediate-low oil concentration

Figure 2.5a shows a ternary diagram with the composition paths corresponding to the group at intermediate-low oil concentration (Tag e to f in table 2.1). Since the paths cross a small section of the ouzo region before reaching the spinodal line, it can be expected to observe bulk phase separation and areas with non-coalescing droplets simultaneously. Indeed, evaporation-induced behaviour for this group of ternary solutions is characterized by a combination of bulk phase separation and emulsification as shown in figure 2.5b for $c_{tA} = 0.120$.

While the simple straight line evaporation paths are consistent with our observations, a second process might aid to the appearance of non-coalescing droplets. Spinodal decomposition results in two phases with compositions on the binodal line. For the sake of argument, consider compositions e' and e''

plotted in figure 2.5a. The latter indicates the composition of the oil-rich agglomerates and the former gives the composition of the surrounding areas. Since ethanol is continuously evaporating, composition e' can enter into a larger portion of the ouzo region, with the corresponding nucleation of new oil droplets. Additionally, notice that e'' is just above the inverse ouzo region, therefore the composition of the oil-rich agglomerates can enter the inverse ouzo region, as ethanol is lost. From figure 2.5b we can confirm that, indeed, water-rich droplets form inside the oil-rich regions.

The early stage of phase separation is influenced by Marangoni arches as shown in figure 2.5b. However, this time the oil droplets that nucleate inside the arches coalesce into large domains of oil-rich phase with a sharp interface. The oil-rich domains are very mobile, continuously coalescing with each other. Sometimes the movement is so violent that the oil-rich domains split into two before coalescing again (see movie 4 in appendix 2.5.6). This behavior is probably a consequence of the nonuniform concentration field around the oil-rich regions, like in the case of droplets inside a nonuniform vapour field. [109] Both, gradients in interfacial tension along the liquid-liquid interface, and differences in wetting behavior, together with the hydrophobicity of the walls, could result into motion.

At about 300 s, there are no detectable Marangoni arches any more and all oil-rich domains have merged into a continuous zone that covers the entire open edge of the cell. It is possible that the oil-rich region reduces the overall surface energy as a mixture of ethanol and trans-anethole has a lower surface tension than a water rich-solution. Moreover, the interfacial tension between trans-anethole and ethanol-water mixtures is also relatively low (below 25 mN/m [6]). In fact, as shown by the fourth panel in figure 2.5b, the oil-rich region eventually flattens, further reducing the interfacial area, although this could also be an effect of the pressure caused by the replenishing flow. Such a barrier brings the flow to a halt and evaporation is strongly reduced. Without the Marangoni flow to bring “fresh” solution to the edge, phase separation cannot happen as quickly. However, adjacent to the oil-rich domains, some new droplets can still form and stay on the surface. They are oil-rich droplets, stable in the surrounding water-rich liquid.

Along the boundary of the oil-rich region, droplet fingers form on both sides. Short fingers of water-rich droplets form in the oil-rich region while fingers of oil-rich droplets extend towards the solution in the inner cell (see the last panel of figure 2.5b). The fingers of oil-rich droplets ramify with time, extending to the whole width of the cell over about 10 h. The emergence of fingers suggests

Figure 2.6: a) Ternary diagram showing the initial concentrations corresponding to the yellow group (points g, h, i). The dashed lines correspond to processes for which only ethanol evaporates. b) Snapshots at increasing times of a typical example of case h ($c_{tA} = 0.416$). Movie 5 in appendix 2.5.6 corresponds to this case. c) Ternary diagram with the proposed composition path $h - h' - h'' - h'''$, corresponding to the black line in the last panel in b). The dashed line indicates the initial composition path due to evaporation before bulk separation. The black line connecting h and T is tangent to the binodal. In both a) and c) the open red circle indicates the position of the plait point.

that after the establishment of the oil-rich zone, the mass transfer in the cell becomes dominated by diffusion [71]. In other words, the solvent evaporation along the opening of the cell is a self-sealing process, creating an oil-rich zone that damps the Marangoni instability, stops moving violently, and reduces the rapid mass loss from the cell. Notice that the slow nucleation of new droplets (to form fingers) indicate that ethanol transport across the oil-rich region and evaporation should continue but at a much slower rate.

2.3.4 Group 3: Intermediate-high oil concentration

The mixtures in group 3 are labelled in the ternary diagram shown in figure 2.6a and in table 2.1 with tags g to i. The composition path of the ternary mixtures in this group does not intersect with the ouzo region as the ethanol concentration reduces. The composition of the oil-rich subphase from spinodal decomposition is given by a point in the gray side of the binodal line. However, further loss of ethanol can result in the inverse ouzo effect, forming water droplets in the oil-rich phase.

The main features induced by evaporation of the mixtures in group 3 are bulk phase separation at early times and the formation of droplet fingers in both the oil-rich and the water-rich regions at late times. As shown in figure 2.6b for $c_{tA} = 0.416$, large domains of oil-rich phase have already appeared at time $t = t_0 + 6$ s, which is much quicker than in group 2 due to the higher initial concentration of oil in group 3. At $t = t_0 + 300$ s, the opening of the cell is fully blocked by the oil-rich phase (figure 2.6b). On both sides of the liquid-liquid interface, surface droplets form. Oil droplets nucleate in the water-rich phase from the ouzo effect and water droplets nucleate in the oil-rich phase from the inverse ouzo effect.

Ethanol evaporation leads to the emergence of a configuration where an oil-rich phase is in contact with a water-rich phase. Ruschak and Miller [110] studied a similar configuration, where two different mixtures of the same ternary system were put into contact and allowed to inter-diffuse. In the cases where the composition path crossed the two-phase region in the ternary diagram, droplet formation was observed, like in our experiments.

To explain our observations of droplet formation, in figure 2.6c we have sketched a possible composition path by following the analysis of Ruschak and Miller [110]. First, we considered that the mixtures on each side of the liquid-liquid interface are locally in equilibrium. The corresponding compositions are then connected by a tie-line in the ternary diagram. Since water droplets nucleate inside the oil-rich phase, the physical path $h''' - h''$ should cross the inverse ouzo region when mapped into the ternary diagram. While the line $h''' - h''$ is closely parallel to the binodal, it can go inside the inverse ouzo region. On the other side of the interface, the composition should change from an oil depleted value h' at the interface, up to the original composition h far away inside the chip. In order for the composition path $h' - h$ to cross the two-phase region, point h' should lie to the left of the tangency point T [110]. While we do not

have the exact values of the concentration field and we have assumed straight lines for the composition paths, the constructed path is consistent with nucleation on both sides of the interface. In the appendix we show results with a dyed mixture that seem to support the proposed diffusion path. Nevertheless, further work, possibly in the form of numerical simulations, is needed to confirm our hypothesis.

It is interesting to note that from the liquid-liquid interface water-rich droplets form in “packs”. The position of the droplet packs shifts towards the air-liquid interface with time (see movie 5 in appendix 2.5.6). The way the shift takes place is by formation of new droplets at one end of the pack closer to the air-liquid interface and simultaneous dissolution of the droplets at the other end. Such shift may be due to the concentration of ethanol always being lower near the air-liquid interface, although the transient nature of the shift (nucleation and dissolution) suggests that there are more mechanisms at play. Some of the packs grow into long-lived branch-like patterns that extend between the liquid-liquid and the air-liquid interfaces, as shown in the last snapshot of figure 2.6b. We suspect that the droplet branches are the consequence of the diffusion-dominated mass transfer in the oil-rich region, similarly to the fingers formed at the summit of the arches in group 1. Like in group 2, notice that despite the oil-rich phase covering the edge, ethanol transport must continue to take place in order to trigger phase separation.

The motion of individual water-rich droplets supports the presence of an ethanol concentration gradient in the oil-rich zone. Those droplets move towards the liquid-liquid interface, and join the water-rich liquid on the other side of the interface. We suspect that Marangoni flows at the interface of the droplets drive them towards regions of lower surface energy [6, 101, 111]. The droplet motion is similar to the self-propulsion of droplets in the work by Zhang *et. al* [104] where a concentration gradient is created by liquid-liquid phase separation. On the water-rich side of the liquid-liquid interface, oil-rich droplets appear as shown in the last two snapshots in figure 2.6b. Analogously to their water-rich counterparts, some of the oil-rich droplets displace towards the liquid-liquid interface. While moving, the droplets coalesce with those they encounter in their way, leaving the path temporarily free of surface droplets. Later new droplets nucleate and grow in the freed space. As in group 1, diffusiophoresis [108] and a nonuniform concentration field, thus nonuniform wetting, [109] could also play an important role in the displacement of the droplets. For the initial concentration $c_{tA} = 0.598$, the dynamics of the droplets are more complicated and more details are provided in the SI.

Figure 2.7: Temporal evolution of the fingers composed by oil-rich droplets. a) Graphical definition of the quantities used to characterize the fingers. b) Length d_f of each finger as function of time. Different colors indicate different fingers. *Inset*: Same data with a double logarithmic scale. Power laws $t^{1/2}$ and t are plotted for a comparison with the data to guide the eye. t_f is defined by the moment the first finger appeared. c) Vertical position y_f of the two-dimensional centroid of the fingers as function of time. The colors correspond with those in b). Time zero in both main plots corresponds to the moment at which the mixture reached the edge of the chip for the first time.

Diffusion-dominated characteristics of fingers of oil-rich droplets within a water-rich phase

A number of fingers of oil-rich droplets is shown in the last two panels of figure 2.6b. Their temporal evolution is more clearly seen in figure 2.7, which shows plots of the length d_f and the vertical position y_f of the fingers over time. A graphical definition of these quantities can be seen in figure 2.7a. Figure 2.7b shows that initially all the fingers grow, but eventually some shrink and disappear. Therefore, the overall distance between adjacent fingers increases over time as shown in figure 2.7c.

In the inset of figure 2.7b the length d_f of the droplet fingers that last the longest is plotted on a double logarithmic scale. The time axis is shifted by the moment at which the first finger is visible. There is an indication that initially d_f grows roughly as $\sim t^{1/2}$, and then it accelerates into a linear regime. The growth mechanism of individual fingers of droplets might be similar to that of the branches observed by Lu *et. al* [71] In that study, the process was diffusion dominated, which can be associated with the initial regime shown in the inset of figure 2.7b.

Lu *et. al* [71] concluded that the presence of an already nucleated droplet promoted the formation of new adjacent droplets, due to an enhancement in local oversaturation. Moreover, it was observed that adjacent branches grew

Figure 2.8: Main characteristics of the evaporation process for high trans-anethole content mixtures. a) Ternary diagram showing the mixtures corresponding to the green group. The dashed lines correspond to processes for which only ethanol evaporates, while water and oil remain constant. *Inset*: Zoom to the lower-right corner of the diagram. b) Snapshots at increasing times of a typical example of mixture j ($c_{tA} = 0.780$). Movie 6 in appendix 2.5.6 corresponds to this case. *Inset*: Confocal image of a similar mixture dyed with perylene (non-soluble in water).

towards each other, which suggested that there was a long range interaction between them. We do not observe formation of branches in our experiments (fingers connecting with each other), possible because of the displacement of the droplets towards the liquid-liquid interface. However, the connection of two branches into one, in the work by Lu *et. al* [71], can be seen as a kind of coarsening, as the number of nucleation points decreases. Therefore, the increasing distance between fingers of droplets could be the result of a long range interaction between fingers. Such coarsening can also be seen in the development of fingering instabilities [43, 112–116]. Additionally, the fingers could compete for oversaturated oil in analogy to the nucleation and growth of droplets in confinement [117], the formation of dew [118], or in two dimensional Ostwald ripening [119].

Finally, the reducing number of fingers might result in more oversaturated oil available per finger, thus favoring a transition to a faster growth. However, an explanation for the change into a linear growth regime must be left for future work.

2.3.5 Group 4: High oil concentration

The ternary diagram in figure 2.8a shows the initial concentration corresponding to group 4. As before, the evaporation path is plotted, assuming only ethanol loss. Both paths may cross into the inverse ouzo region, which for $c_{tA} = 0.780$ is in accordance with the nucleation of water droplets (figure 2.8b). However, on the contrary, for $c_{tA} = 0.850$ there is no phase separation at all. This difference might be explained by the fact that the path is almost parallel to the binodal line. Therefore, the solution may not undergo phase separation.

Snapshots of the first 10 min of the evaporation process for $c_{tA} = 0.780$ are shown in figure 2.8b. Initially, the Marangoni arches are the predominant feature and for a short period of time some emulsion droplets are visible. For both $c_{tA} = 0.780$ and $c_{tA} = 0.850$, a diffused interface (slightly darker line in figure 2.8b) forms at the perimeter of the arches. However, once the Marangoni instability stops, such interface is not visible anymore. Instead, the intensity of light changes continuously as shown at 60 s in figure 2.8b. The lack of an interface indicates that the liquid close to the edge is miscible with the bulk liquid.

For $c_{tA} = 0.780$, fingers of water-rich droplets form as indicated in figure 2.8b. We confirmed that the droplets were water-rich by adding a small amount of fluorescent dye that dissolves in ethanol and oil but not in water. The snapshot in the inset of figure 2.8b shows an example. The fluorescent color (yellow) stays outside of the droplets, indicating that they are water-rich. The length of the fingers increases over time, and they present some ramifications as shown at time 600 s. The ramifications grow from the principal branch, instead of two fingers meeting with each other as mainly observed by Lu *et al* [71]

The droplets that compose the fingers increase in size and, eventually, those closer to the tip, drift towards the bulk (third panel in figure 2.8b and movie 6 in appendix 2.5.6). While drifting, the droplets dissolve again, indicating that they have reached a high ethanol content environment. Like in the yellow group, the water-rich droplets move up the ethanol gradient in the direction that lowers their surface energy. On their way, coalescence with other growing droplets frees the space behind them. Later on, nucleation and growth takes place again in the free space, suggesting that the mixture along the fingers is constantly in the inverse ouzo region.

2.4 Conclusion

We have investigated dynamical flow phenomena in ternary mixtures of ethanol, water, and trans-anethole confined in a Hele-Shaw cell as evaporation takes place from one side of the cell. Based on the experimental measurements by using optical microscopy, a Marangoni instability occurs at the early stage of the evaporation process, regardless of the initial composition of the solutions. The instability and the induced convective rolls are in accordance with linear stability predictions for binary solutions in two-dimensional [9] and quasi-two dimensional [24] models. Depending on the initial concentration of the ternary mixtures, the duration and the effect of the Marangoni instability on the subsequent liquid-liquid phase separation varies significantly. When droplets have already nucleated, they can be transported by the flow caused by the Marangoni instability, but the nonuniform concentration field can also result in propulsion by a Marangoni flow at the interface of the droplets or by diffusiophoresis [4, 108]. When the initial oil concentration in the ternary mixtures is large, a zone of oil-rich phase forms along the open side of the chip. When the whole edge is covered, the Marangoni instability induced by ethanol evaporation stops. The nucleation of droplets from phase separation, and the interactions and evolution of patterns formed both by water-rich and oil-rich droplets in their insoluble surroundings suggest that diffusion-dominated processes take place after the opening is self-sealed by the oil-rich zone.

Our results show that the dynamical behaviour induced by evaporation of a ternary system affects how and where phase separation takes place. On the other side, bulk phase separation in combination with the quasi two dimensional geometry can eventually hinder advection. Furthermore, the concentration gradient caused by evaporation is coupled with phase separation, too. We find it stunning how rich the flow dynamics in a ternary liquid in such a simple geometry as the Hele-Shaw cell can be. Often beyond our ability to theoretically and quantitatively explain the observed phenomena. However, we hope that nonetheless our study opens paths for further studies, focusing on certain aspects of the different ways in which phase separation can take place, and its interplay with advection and wetting.

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2.5 Appendix

2.5.1 Appendix A. Geometry of the setup

Figure 2.9: Sketch of the a) side and b) bottom views of the experimental setup. The approximate distance between the chip holder and the nitrogen inlets are shown. A paper cylinder, used to prevent the nitrogen flow from directly impacting on the chip, is indicated with a dashed contour.

Figure 2.9 shows two sketches of the experimental setup with the locations of the nitrogen inlets and the sensor. To prevent the flow from impacting directly on the chip, a cylinder made out of paper was placed around the objective used

for observation. The sensor was inside the cylinder. To isolate the chip from the surroundings we used plastic wrap around the microscope. The plastic wrap prevented strong air currents, but it did not provide an hermetic seal. Therefore air was still able to escape from different places around the gas volume. As a result, the pressure around the chip would still be atmospheric pressure.

2.5.2 Appendix B. Marangoni instability

Conditions for the appearance of the Marangoni instability

The spontaneous appearance of advective rolls at the beginning of the evaporation process suggests the presence of an instability [24, 41, 51, 52]. More specifically, a Marangoni instability given the preferential evaporation of ethanol and its lower surface tension. Sternling and Scriven [9] predicted an unstable interface when a solute that decreases surface tension is transferred between two fluids. Specifically, transfer from a fluid of lower diffusion coefficient and kinematic viscosity, into another fluid of larger values of both quantities. This conditions are satisfied by our system since the transfer is from a liquid to a gas, in accordance with the presence of an instability, like in the case of ethanol–water mixtures [24].

Sternling and Scriven [9] considered a purely two-dimensional system, however the drag caused by the walls of the Hele-Shaw cell have a stabilizing effect [24]. The stability depends on a Marangoni number defined as

$$\text{Ma}^* = -\frac{E_l \delta^2}{D_l \mu_l} \frac{\partial \gamma}{\partial c_e}, \quad (2.1)$$

where δ is the gap size between the walls, E_l the gradient in solute concentration normal to the interface, γ the surface tension, c_e the mass fraction of solute, D_l the diffusion coefficient of the solute, μ_l the dynamic viscosity, and l indicates the liquid.

The Marangoni number given by (2.1) corresponds to an evaporating binary mixture. Therefore, strictly speaking, it does not apply to ternary mixtures as used in our experiments. However, in many cases the initial concentration of either water or *trans*-anethole is small as compared to that of the other two components, in particular for the blue and green groups.

We will assume the mixtures in the blue group to be approximated by an ethanol-water solution and those in the green group by an ethanol–*trans*-

anethole solution. The former case was already studied before [24], in particular for a 50 wt% solution. The corresponding value of the Marangoni number was $\text{Ma}^* \sim 10^5$. In table 2.2 we present the values of the different properties corresponding to the ethanol–water solution as used by Lopez *et al* [24]. Those values were originally obtained by interpolating experimental data reported in the literature [82, 120, 121].

The properties of ethanol–*trans*-anethole mixtures are not available in the literature, however we can estimate their order of magnitude. For viscosity, we consider the value of pure *trans*-anethole given that it is the most viscous of the two components. The diffusion coefficient of ethanol in *trans*-anethole was estimated using the Stokes-Einstein equation

$$D = \frac{k_B T}{6\pi r_e \mu_l}, \quad (2.2)$$

where k_B is the Boltzman’s constant, T is the temperature of the solution, r_e is the radius of the ethanol molecule, and μ_l is the viscosity of the surrounding liquid (*trans*-anethole). The derivative of the surface tension with respect to the ethanol mass fraction was estimated by the difference in surface tension between the pure components, namely $\partial\gamma/\partial c_e \sim \gamma_{tA} - \gamma_e$.

Finally, the gradient of ethanol concentration normal to the interface E_l was estimated from the volume flux $Q_{\text{mix}} = 0.005 \text{ }\mu\text{L/min}$ to $Q_{\text{mix}} = 0.5 \text{ }\mu\text{L/min}$ needed to keep the chip filled. Assuming that only ethanol evaporates, that there are no volume changes with concentration, and using Fick’s law, the normal gradient is estimated as $\partial c_e / \partial x \sim -Q_{\text{mix}} / (D_l A)$, where A is the area where evaporation takes place, given by the gap thickness δ times the size of the open side of the chip of 29 mm. The corresponding values used for the estimation of the Marangoni number are shown in table 2.2.

The resulting Marangoni number ranges from $10^3 - 10^5$ depending on the volumetric flux considered. For the green group the flux needed to keep the chip filled was of $Q_{\text{mix}} = 0.005 \text{ }\mu\text{L/min}$, corresponding to $\text{Ma}^* \sim 10^3$.

Critical Marangoni number

A critical Marangoni number was obtained by means of a linear stability analysis, [24] based on previous works [9, 23]. It is defined by

$$\text{Ma}_c^* = 24 \left(1 + \frac{c_{\text{sat}} a_1 \rho_g D_g}{\rho_l D_l} \right), \quad (2.3)$$

with ρ the density, and the subscript g indicating the gas phase. The saturation concentration of ethanol was obtained as $c_{\text{sat}} = p_{e,\text{sat}}(T)M_e/(RT\rho_g)$, with

$p_{e,\text{sat}}(T)$ the saturation pressure of ethanol at temperature T , M_e the molar mass of ethanol, and R the universal gas constant. The constant a_1 results from taking a Taylor expansion of the molar fraction $n_e = n_e(c_e)$ around $c_e(t=0) \equiv c_{e,0} \neq 0$, such that $n_e = (1 + (1/c_e - 1)\mathcal{M})^{-1} \approx a_0(c_{e,0}, \mathcal{M}) + a_1(c_{e,0}, \mathcal{M})c_e + O(c_e^2)$. Then $a_0 = c_{e,0}(c_{e,0} + \mathcal{M}(1 - c_{e,0}))^{-1} - c_{e,0}\mathcal{M}(\mathcal{M}(c_{e,0} - 1) - c_{e,0})^{-2}$, and $a_1 = \mathcal{M}(\mathcal{M}(c_{e,0} - 1) - c_{e,0})^{-2}$, where $\mathcal{M} = M_e/M_s$ with M_s the molar mass of the second component, either water or *trans*-anethole. The values of the different properties are shown in table 2.2. For the gas phase, the density of air at 50 % relative humidity and the diffusion coefficient of ethanol in air were used as shown in table 2.2.

For the ethanol–*trans*-anethole mixture, the liquid density was estimated by $\rho_l = c_{e,b}\rho_e + c_{tA,b}\rho_{tA}$, with the subscript b indicating a binary solution. We consider a case of $c_{e,b} = 0.14$ which is close to the mixture with the highest oil content in the ternary mixtures. Finally, $c_{tA,b} = 1 - c_{e,b}$.

For both ethanol–water and ethanol–*trans*-anethole mixtures $\text{Ma}_c^* \sim 10^2$. This value is below the estimated Marangoni numbers for both mixtures. Therefore, a Marangoni instability is to be expected, which is indeed what we observe in experiments. For the groups with intermediate values of the three components, this analysis is not valid anymore, however, it seems that as long as one of the three components is present at a low concentration, the results of the binary analysis could be use as a first approach to determine if a Marangoni instability could arise.

2.5.3 Appendix C. Power law exponents during the Marangoni instability stage

Figure 2.10 shows the average exponent of the power law fitted to the initial arch growth, before x_F reaches the plateau. The error bars correspond to one standard deviation, obtained from fitting different realizations at the same initial oil mass fraction c_{tA} .

For the group 1, the exponent is close to 0.5, however for larger oil concentrations the exponent goes up to 0.7. This corresponds to the cases for which bulk phase separation takes place, except for the last two points. This suggests that the extra interface could accelerate the growth process. For the two points with the highest oil mass fraction, we only have a small period over which to make the fit, therefore the value obtained might not properly reflect the growth rate of the initial period.

Property	Ethanol–water	Ethanol– <i>trans</i> -anethole
D_l [$\text{m}^2 \text{s}^{-1}$]	3.65×10^{-10}	$3.90 \times 10^{-10,a}$
D_g [$\text{m}^2 \text{s}^{-1}$]	1.35×10^{-5}	1.35×10^{-5}
μ_l [$\text{kg m}^{-1} \text{s}^{-1}$]	2.49×10^{-3}	$2.45 \times 10^{-3,b}$
ρ_l [kg m^{-3}]	9.11×10^2	$9.61 \times 10^2,a$
ρ_g [kg m^{-3}]	1.2	1.2
$\frac{d\gamma}{dc_e}$ [kg s^{-2}]	-1.85×10^{-2}	$-1.37 \times 10^{-2,a}$
p_{sat} [$\text{kg m}^{-1} \text{s}^{-2}$]	6.57×10^3	6.57×10^3
M_e [kg mol^{-1}]	4.61×10^{-2}	4.61×10^{-2}
M_s [kg mol^{-1}]	1.80×10^{-2}	1.48×10^{-1}
a_1	8.08×10^{-1}	1.88
T [K]	2.95×10^2	2.93×10^2
R [$\text{kg m}^2 \text{K}^{-1} \text{mol}^{-1} \text{s}^{-2}$]	8.31	8.31
γ_e [kg s^{-2}]	-	2.18×10^{-2}
γ_{tA} [kg s^{-2}]	-	3.55×10^{-2}
k_B [$\text{kg m}^2 \text{K}^{-1} \text{s}^{-2}$]	-	1.38×10^{-23}
r_e [m]	-	$4.5 \times 10^{-10,c}$
A [m^2]	-	5.80×10^{-7}

Table 2.2: Values of the properties used to calculate the Marangoni number and its critical value for two binary mixtures. For the ethanol–water mixture we did not estimate the diffusion coefficient, therefore we added a hyphen (-) in the properties needed for the calculation of D_l . ^aEstimated values. ^bValue for pure *trans*-anethole at 20 °C. ^cObtained from Song *et al* [122]

Figure 2.10: Power law exponent of x_F versus the initial oil mass fraction.

2.5.4 Appendix D. Confocal images and intensity profiles of case h, $c_{tA} = 0.417$

One repetition of case h (specifically $c_{tA} = 0.417$) was dyed with perylene to highlight the regions of higher oil concentration. Figure 2.11 shows average intensity profiles taken close to the air–liquid interface once phase separation has taken place and the oil-rich phase has covered the whole edge. Figure 2.11a was obtained shortly after the visible arches merged. A sharp interface is present only in the region where the merging took place. Figure 2.11b was obtained when the sharp liquid–liquid interface has extended over the whole field of view.

In the averaged intensity profiles of both cases, marked with a red arrow, a minimum in intensity is visible to the right of the interface. While perylene might not perfectly follow the concentration of oil, the dip in intensity suggests that there is a local decrease in oil mass fraction. The minimum in intensity is in agreement with our hypothesis that the concentration just to the right of the liquid–liquid interface has a lower oil mass fraction than the original mixture far away from and to the right of the interface.

Figure 2.11: Intensity profiles obtained from a realization of case h ($c_{tA} = 0.417$) dyed with perylene. a) Shortly after the arches have merged. A sharp interface is still developing. b) Once a sharp interface has formed and flattened. The insets in both cases show the intensity field from which the profiles were obtained. Note that the snapshot in b) was rotated to make the liquid-liquid interface vertical. The profiles are averages taken in between the red horizontal lines shown in the insets. In both cases, a red arrow points to a minimum in the intensity just after the liquid-liquid interface, suggesting a lower oil concentration. The scale bars correspond to 500 μm . The black region to the left corresponds to air phase.

2.5.5 Appendix E. Description of case i, $c_{tA} = 0.599$

In this section we show an example of case i (yellow group) because it presents some extra interesting characteristics that are not seen in cases g and h. In figure 2.12a a series of snapshots taken at increasing times are shown. Like in all cases, the initial stage presents the Marangoni instability with growing and merging arches. Inside the arches water rich droplets nucleate, but eventually disappear. Once the oil rich phase has covered the whole edge, a series of fingers appear to the right of the liquid-liquid interface. As in the case shown in the main text, the finger grow in length and reduce in number over time. From the snapshot at 999.5 s it is clear that there is a change in the light intensity at the areas that separate the fingers. Such a change in intensity indicates a change in the composition of the liquid. More specifically, given that the oil-rich phase has a darker color, it is possible that the lighter areas in between fingers have a lower oil mass fraction. Such a depletion of oil to the right of the liquid-liquid interface further supports the scenario proposed in the main text with regards to the composition changes in the mixture along the x direction.

Figure 2.12b-d show zooms to the fingers at the three different times. One

Figure 2.12: Main characteristics of case i ($c_{tA} = 0.599$). (a) Snapshots taken at increasing times. The scale bar at 1 s is 500 μm in length and applies to all the snapshots in the time series. In all cases, the gas phase is to the left of the image. (b) Zoom (4x) to two fingers taken from the snapshot at $t = 499.5$ s. Bulk droplets travel away from the interface. (c) Zoom (4x) to two fingers taken from the snapshot at $t = 999.5$ s showing surface droplets pinching from fingers and traveling towards the interface. (d) Zoom (4x) to one finger taken from the snapshot at $t = 2499.5$ s. Surface droplets have grown into columnar droplets which also travel to towards the interface.

difference with cases g and h of the yellow group is that initially the fingers are not formed by surface droplets, but by a continuous stream of new phase. Close to the liquid–liquid interface, bulk droplets nucleate, which once large enough travel *away* from the liquid–liquid interface. On the contrary, at later times, surface droplets pinch off from the streams and travel *toward* the liquid–liquid interface. Even later, the surface droplets become large enough to span through the whole gap of the cell (from the glass plate to the silicon plate), creating columnar droplets, which from the bottom look like circles with a sharp interface. The columnar droplets also travel *toward* the interface. Since bulk droplets travel to the right, while surface droplets travel to the left, we can conclude that the interaction with the wall has a strong effect on the direction of the droplet displacement.

2.5.6 Appendix F. QR-code for videos

Figure 2.13

3.1 Introduction

Droplet dissolution, and more generally mass transfer between droplets and the surrounding liquid, are important processes for a variety of technical technologies. For instance, any process industry in which emulsions are part of the processes will be concerned with droplet dissolution. One example is within contactor columns where mass transfer can affect the coalescence of the droplets of the emulsion [123]. As another example, many foods and cosmetics are in the form of emulsions; thus stabilizing these emulsions is important for the shelf life of the products [88, 124]. Yet another example is in the pharmaceutical industry where emulsions are used as a way to create drug delivery systems [14]. In ecology, the dissolution of CO₂ droplets deep in the ocean has been seen as a way to reduce the concentration of this gas in the atmosphere [18]. Finally, for chromatography the mass transfer of a solute into a small droplet by liquid-liquid microextraction has been considered as a way to obtain high concentrations of the solutes needed [11–13, 125].

The examples listed above show how important droplets are for the process industry. Therefore, it is not strange that many efforts have been undertaken to understand the diffusive dynamics of droplets, see e.g. our reviews [2, 125, 126]. On the theoretical front the classical diffusion based model for bubble dissolution of Epstein and Plesset [127] has been extended to the dissolution of spherical pure [128], and binary [129] droplets. Moreover, very recently, a more accurate binary droplet dissolution model was developed by Chu and Prosperetti [130] for the diffusion dominated regime. Instead of approximating the equilibrium conditions of the dissolving entities at the interface, it explicitly makes use of the equality of chemical potentials and considers non-ideal solutions. Moreover, it has been suggested that it could also be applied to translating droplets. Simultaneously, experimental and numerical work for the dissolution of pure [21, 39, 131–136], binary [128, 137], and multicomponent droplets [2, 78, 138] have been developed.

In the absence of an external flow, the dissolution of a droplet is determined by diffusion. The Epstein-Plesset like model has been shown to be successful in capturing experimental observations for such pure diffusive situations [128]. However, once either forced or natural convection is present, models based only on diffusion obviously fail to properly predict the dissolution time of droplets [21, 136, 137]. Dietrich *et al.* [21] showed that when natural convection is present, the dissolution time of a pentanol droplet was reduced to 3 h instead

of the 11 h predicted by the Epstein-Plesset model. The reason being the emergence of a low density plume of dissolved liquid on top of the droplet which accelerates the mass transport from the droplet into the host liquid.

We now come to the situation of two or more droplets next to each other. Then, besides the effect of flow around the droplet on the dissolution dynamics, also the interaction between them can affect the dissolution time [136, 139, 140]. Chong *et al.* [136] showed that when multiple droplets are dissolving collectively in a diffusive regime, their dissolution time is increased because of shielding, as the dissolution of neighboring droplets reduces the concentration gradient experienced by the droplets. Moreover, if the droplets are arranged in a rectangular 3×3 lattice, due to shielding the central droplet takes longer to dissolve than those at the edges of the array. On the contrary, in the convective regime, the plumes created by each droplet can merge into one big centered plume provided they are close enough, causing the dissolution time to be shorter than for a single droplet in the diffusive regime. But still the central droplet dissolves slower than those at the edges. Bao *et al.* [140] showed that if instead of natural convection there is an externally imposed flow, the dissolution of a lattice of droplets also displays the shielding effect and the droplets at the center of the lattice are the last to dissolve, while those which are upstream dissolve first. Additionally, it was shown that not unsurprisingly higher flow velocities and a larger spacing between the droplets resulted in shorter dissolution times.

Alongside the phenomena described so far, the presence of non-uniform temperature [5] or concentration fields [6, 54, 141] can further complicate the dynamics of a dissolving droplet by giving rise to Marangoni flows. If the droplet is not fixed in place, the forces caused by the Marangoni flow can propel the droplet against its own weight. Depending on the properties of the system this can result in the droplets being suspended at a higher location than where a buoyancy balance would suggest or even more surprisingly make the droplet repeatedly jump. In other cases, even without externally imposing a non-uniform field, the dissolution of the droplet can create gradients in concentration around the droplet that result in self-propulsion [3, 7, 23, 142, 143].

In the present work we study the simultaneous dissolution of two droplets in the natural convection regime. Different to the case of Chong *et al.* [23], one of the droplets is placed above the other, such that the plume of the lower one rises towards the upper one. In this way we further study the effects of convection on the dissolution of droplets, but also the effect of having solute already dissolved in the host liquid. Moreover, by changing the liquid of the

upper droplet, gradients in the interfacial tension can arise together with a Marangoni flow that, as will be shown, can become oscillatory.

This chapter is structured as follows. In the next section (3.2) we describe our experimental methods. Afterwards, in section 3.3.1 we discuss two reference systems consisting of an individual 1-pentanol droplet and a pair of 1-pentanol droplets dissolving in water, respectively. We compare the reference systems with the results of Dietrich *et al.* for a single dissolving droplet [21], showing that indeed we are in the convective regime and we confirm the scaling laws previously found [21, 136]. Then, in section 3.3.2 we show experimental results for the system of two vertically aligned droplets with the liquid of the top droplet changed for alcohols with longer carbon chains. Following, in section 3.4, we focus on the flow that arises when the top droplet consists of 1-heptanol or 1-octanol and surprisingly observe oscillations. To further elucidate the observed oscillatory phenomena, we numerically simulate the flow. We first describe the numerical setup in section 3.4.1. Then, in section 3.4.2 we compare the numerical results with the experimental ones. We make use of the numerical results to describe in detail one cycle of the oscillatory flow. In section 3.5 we discuss what are the mechanisms behind the observed oscillatory flow. The chapter ends with the conclusion in section 3.6.

3.2 Experimental methods

3.2.1 Experimental setup

A cuvette (flow-trough cell, Suprasil quartz cuvette, Hellma) was used as a container, see figure 3.1a). The cuvette had a square base and rectangular sides. The inner dimensions of the square were 10 mm $\times$ 10 mm. The total volume was 3300 μ L. Both at the bottom and top there were inlets through which two fused silica capillaries were inserted (Polymicro Technologies, nominal inner diameter 150 μ m, nominal outer diameter 360 μ m). The lower capillary passed through the straight section of a T junction. A third capillary was connected to the perpendicular arm of the T junction and was used to fill the cuvette with water. The upper inlet of the cuvette was not sealed so that we could move the top capillary for alignment. During the experiments, a small amount of evaporation took place at the top, but this was normally in the order of 3 μ L to 6 μ L ($\sim$ 0.1% the total volume). In figure 3.1a) we also include a sketch of the capillaries and connectors.

Figure 3.1: a) Sketch of the cuvette and the capillaries connected to it. The bottom capillary passes through a T junction and wide-enough connectors into the cuvette. From the third leg of the T junction water is supplied into the cuvette. The water flows around the capillary inside the wide connectors. b) Typical example of two droplets just after infusion with tracer particles. The definitions of three length scales are shown. The laser sheet comes from the right. c) Sketch of the experimental setup from a top view. The glass cuvette was illuminated from the back (from the right in the image) with a white light source. A diffuser was used to have an approximately homogenous illumination. A laser sheet illuminated the central plane perpendicular to the direction of the rays of white light. A long distance microscope was used to observe the droplets. Each capillary was connected to a syringe mounted to a syringe pump. A cage of acrylic wall was built around the cuvette to reduce air currents and heat exchange with the surroundings. The top of the cage was open.

The capillaries were connected to two glass syringes (Hamilton) controlled by a syringe pump (Harvard Instruments, PHD 2000). With the pump, droplets of 0.2 μL were infused and left to dissolve in a bath of water (see figure 3.1b) for an example of the two droplets). For some experiments either the top or bottom capillary were removed in order to observe the dissolution of a single droplet.

The cuvette was held in front of a long distance microscope (Navitar 12x) and illuminated from behind with light that passed through a diffuser as depicted in figure 3.1c). Videos were recorded with a CCD camera (MD061MU-SY, Ximea). To measure the velocity field in the bath, a laser sheet was created using a La Vision system and a 532 nm laser of 0.1W. For our first set of experiments the power was set to 55 % and for the second at 60 %. The width of the laser sheet was measured using thermal paper. The size of the mark left by the laser sheet was measured using a calibrated picture. The width was measured to be $900 \mu\text{m} \pm 180 \mu\text{m}$ in our first set of experiments and $270 \mu\text{m} \pm 90 \mu\text{m}$ in the second. Fluorescent particles (Fluoro Max, red fluorescent polymer microspheres 6 μm) were used to seed the flow. The weight percentage of particles in the majority of our experiments was 3×10^{-4} , but for two repetitions with 1-heptanol the weight percentage was 1.5×10^{-4} . The Stokes number for a pentanol-in-water solution and the employed tracer particles is of the order of $St \sim 10^{-6}$ to 10^{-5} , taking the initial radius of the droplet as length scale and the velocity of the plume or the velocity at the Marangoni interface (as obtained from simulations as will be shown in section 3.4) as characteristic velocity. Since the value is much smaller than 1, we can be sure that the particles are faithful tracers.

For the majority of the experiments shown in this work, a cage made of acrylic panels was built around the cuvette. We noticed that when the experimentalist was standing close to the cuvette, a small flow inside the cuvette was started. Therefore we used the cage to reduce such thermal effect and the experimentalist stood away from the setup once an experiment started. In all our experiments the temperature and humidity around the cuvette were monitored with a sensor (HIH6130, Honeywell) placed a few centimeters from the cuvette as shown in the sketch in figure 3.1c).

For the cases of a single droplet dissolution and one set of experiments with double droplet dissolution (1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol at the top droplet), the acrylic cage was not used. They correspond to our first set of experiments. In the second set of experiments (1-pentanol, 1-heptanol, and 1-octanol at the top droplet) we used the acrylic cage.

3.2.2 Liquids used

The bath consisted of Milli-Q water (produced by a Reference A+ system (Merck Millipore) at 18.2 MΩcm (at 25°C)). 1-Pentanol (ACS reagent $\leq 99\%$), 1-Hexanol (reagent grade, 98%), 1-Heptanol (98%), and 1-Octanol (anhydrous $\leq 99\%$) were bought from Sigma-Aldrich and used as received. The properties of the liquids can be consulted in Table 3.1.

3.2.3 Experiment preparation

The capillaries were plasma cleaned for 10 min before a set of experiments. After one experiment, about 0.5 mL of water was pumped to reduce the amount of pentanol dissolved. The water used in experiments was left at least 1 hour in the laboratory before use. When a different liquid was used the cuvette was sonicated in a mixture of water and acetone for 10 min, then dried. The connectors were sonicated in water for 10 min and dried.

3.3 Results

3.3.1 Reference case, dissolution of pentanol droplets

We first investigated the dissolution of pentanol droplets. We looked at the three different configurations shown in figure 3.2a). In the first case we placed an individual droplet with the capillary below it, in the second case the capillary was above the droplet and in the third case two droplets dissolved simultaneously, one above the other. The initial distance L_0 (see figure 3.1a for a definition) between the two droplets was $L_0 \sim 2R_{e,0}$, with $R_{e,0} = (3V_0/(4\pi))^{1/3}$ the initial equivalent radius.

The droplet was assumed to be a spherical cap, thus to calculate its volume we fitted a circle to the edge of the two-dimensional projection of the droplet. The radius of the circle is the same as the radius of the spherical cap under the axysimmetric assumption. We found the intersection between the fitted circle and the edge of the capillary to determine the base of the droplet, hence the volume (the procedure is explained in more detail in appendix 3.7.1).

Liquid	ρ [$\frac{\text{kg}}{\text{m}^3}$]	D [$\frac{\text{mm}^2}{\text{s}}$]	c_{sat} [wt %]	$\Delta\rho$ [$\frac{\text{kg}}{\text{m}^3}$]	μ [mPa s]	γ [$\frac{\text{mN}}{\text{m}}$]	$\partial\gamma/\partial c$ [$\frac{\text{mN}}{\text{m}}$]	Bo
1-pentanol	811 ^a	888 ^b	2.2 ^c	3.42 ^a	3.52 ^d	4.4 ^e	—	0.05
1-hexanol	815 ^a	830 ^b	0.6 ^c	0.92 ^a	4.40 ^d	6.8 ^e	-11.7	0.03
1-heptanol	819 ^a	800 ^b	0.17 ^c	0.29 ^a	6.00 ^d	7.7 ^e	-20.4	0.03
1-octanol	822 ^a	780 ^a	0.049 ^c	0.07 ^a	7.60 ^d	8.52 ^e	-30.9	
water	997 ^f	—	—	—	0.89 ^f	—	—	
water saturated with pentanol	994 ^f	—	—	—	0.98 ^f	—	—	

Table 3.1: Properties of the liquids used in experiments for a temperature of 25 °C. ρ is the density, D is the diffusion coefficient, c_{sat} is the saturation mass fraction of the alcohols in water, $\Delta\rho$ is the difference in density between pure water and water saturated with the alcohol, μ is the dynamic viscosity, γ is the interfacial tension with water, and $\partial\gamma/\partial c$ is the change in interfacial tension with mass fraction of pentanol as measured by the pendant droplet method (see appendix 3.7.6 for the details). The Bo number is obtained for $R = 363$ μm and the density difference between pure water and the corresponding alcohol.

^a Obtained from Reference [21].

^b Obtained from Reference [144].

^c Obtained from Reference [145].

^d Obtained from Reference [146].

^e Obtained from Reference [147].

^f Obtained or extrapolated from Reference [148].

Figure 3.2: Dissolution of pentanol droplets. a) Diagrams showing the three configuration used in this figure. A single droplet down (SD), a single droplet up (SU), and double droplets down (DD) and up (DU). b) Volume versus time of four 1-pentanol droplets in the three configuration described in a). The curves of the volume of the double droplet case are nearly on top of each other. The horizontal black line indicates the volume of a hemisphere with a radius equal to the radius of the tubes. Inset: Rate of volume change over time showing a local maximum. c) Sherwood number compensated with $Ra^{1/4}$ versus the Rayleigh number Ra . The vertical lines indicate the moment when the radius of curvature of the droplet is smaller than the radius of the tubes. The horizontal dashed black line is a guide to the eye to compare with the data. Data below $Ra = 100$ have been omitted as the influence of the tube increases the noise significantly (the complete data set can be found in appendix 3.7.4).

The deviation of the projected edge from a circle was small and only noticeable at the beginning. The Bond number $Bo = gR_{e,0}^2\Delta\rho/\gamma$ for the droplets is much smaller than 1 as shown in Table 3.1. Those small values are in agreement with a small deformation of the droplet. As dissolution takes place, the radius, and consequently the Bond number, becomes smaller, making the deviation from the spherical shape even smaller.

The experimentally observed droplet volumes for the three configurations considered are plotted in figure 3.2b). As can be seen, the single droplet at the bottom dissolves slightly faster than those of the other cases. This is presumable due to the “free space” above the droplet. For the upper droplet, in all cases the upper capillary acts as an obstacle for convection which can affect the dissolution time. From the inset in 3.2b), we observe that the rate of change of the volume over time is actually not that different between the various cases. There is an initial period over which the dissolution rate first increases, it reaches a maximum and then decreases. It is during this initial stage that the single droplet down reaches a larger dissolution rate, i.e., the volume decreases more than in the other cases.

For the size of the droplets used in our experiments, it is expected that convec-

tion dominates the dissolution process, given that the solutal Rayleigh number is high [21, 136]. The solutal Rayleigh number compares the time scales for transport of solute due to buoyancy to that due to diffusion, and is defined as

$$Ra = \frac{g\beta\Delta c R_e^3}{\nu D}, \quad (3.1)$$

where ν is the dynamic viscosity of the bath, D the diffusion coefficient of the solute in the bath, c the concentration of solute, $\Delta c = c - c_\infty$ the excess concentration at a given position with respect to the bath at infinity (assumed to be pure water), and $\beta = (\partial\rho/\partial c)/\rho_b$ the solutal expansion coefficient, with ρ_b the density of the bath.

For the conditions in our experiments, and assuming that $\Delta c = c_{\text{sat}}$, the Rayleigh number starts above 1000 and decreases over time. It has been shown that for sessile droplets with $Ra > 12$, their dissolution is dominated by convection because of the formation of a plume above the droplet [21, 136]. Therefore, we can expect that natural convection dominates the dissolution process in our experiments and that a plume arises. Moreover, when an obstacle is above the droplet, the plume will not be able to rise freely, affecting the dissolution process [149].

It has also been shown that the non-dimensional dissolution rate in the form of the Sherwood number follows a power law when plotted against the Rayleigh number. The Sherwood number is given by

$$Sh = \frac{\langle \dot{m} \rangle_A R}{D \Delta c}, \quad (3.2)$$

where $\langle \dot{m} \rangle_A$ is the mass transfer flux, averaged over the surface area of the droplet in contact with the bath. In the convection dominated regime the Sh number should increase as $\sim Ra^{1/4}$ [21]. In figure 3.2c) we have plotted the Sh number compensated with $Ra^{-1/4}$ versus the Ra number. We can see that for the range plotted the data is approximately flat, indicating that indeed we are in a convection dominated regime, at least while the droplet is larger than the size of the capillary (vertical solid lines in figure 3.2c)) and after an initial transient. We notice that the derivation of the scaling law is originally based on the results of steady natural convection next to a vertical wall with the Boussinesq approximation. While the density of the liquid in the bath must change as the droplet dissolves, the fact that the data approximately follows the predicted trend gives evidence, *a posteriori*, that the Boussinesq approximation is reasonably valid. However, the exact details behind this result are still to be addressed rigorously.

We have also compared our data to the predictions of the diffusion dominated Epstein-Plesset model [127] without success. The dissolution times for those models are much larger than the times observed experimentally, as expected from the value of $Ra \gg 12$ [21].

We have also measured the velocity field of the liquid surrounding the droplets. In figure 3.3a) we show the velocity field for the single lower droplet and the double droplet ($L_0 \sim 2R_{e,0}$). Two times are shown, first a few seconds after the droplets were infused and later when the droplets are the same size as the capillary. In both cases, above the bottom droplet, the velocity is maximum and pointing upwards away from the lower droplet, indicating that indeed there is a plume. Clearly, in the case with two droplets the plume is deflected around the upper droplet and the velocity cannot increase as much as for the single droplet at the bottom, but the scaling laws are roughly the same.

We measured the velocity over time at about one radius above the lower droplet and plotted it in figure 3.3b). The velocity first quickly goes up as the plume builds up (first ~ 10 s) and eventually reaches an approximately constant value. However, eventually the velocity has to decrease as the droplet and its Rayleigh number become smaller. According to our data the velocity of the individual lower droplet is at first larger than in the double droplet case, but eventually becomes smaller. The sudden decrease in velocity for the single lower droplet is caused by a background side flow that deflected the plume away from our measurement point. It is important to notice that the plume is present up to the end of the life time of the droplet because there is always 1-pentanol inside the capillary. The plume only disappears once some of the 1-pentanol inside the tube has dissolved (a few inner tube diameters).

We have also included the velocity measured one radius below the single upper droplet in figure 3.3b). Clearly, the velocity is much smaller and is not very different from the existing background flow. We can conclude that the dissolved 1-pentanol does not have time to travel downwards by diffusion, instead, it is all carried upwards by buoyancy.

Dietrich, et al. [21] also found a scaling law between the Reynolds number of the bath $Re = UR/\nu$ and the Ra number, with U the velocity measured about one initial radius above the droplet and on the axis of symmetry. In figure 3.3c) we have plotted the Re number versus the Ra number in a double logarithmic plot. We found the same scaling, at least for an intermediate range of Ra numbers. In the double droplet case for high Ra there is a deviation from the power law which we think is the result of the blocking effect that the upper droplet and capillary cause. Here the noise of our data is smaller

Figure 3.3: Velocity caused by natural convection. a) Velocity fields close to a single 1-pentanol droplet (upper two panels) and two vertically aligned 1-pentanol droplets (lower two panels). Two times are shown: the first time is a few seconds after the droplets were infused and the plume has already developed. The second time corresponds to a moment at which the droplets have a radius of curvature close to the radius of the capillaries (160 μm). The velocity fields are averaged over a few frames, equivalent to 1 s. b) Velocity versus time taken approximately one initial radius above the summit of the lower droplet for the cases of a single droplet down (SU) and double droplets (D). The velocity time series for a single droplet up (SU) is also shown for comparison, in which case the velocity was taken one initial radius below the droplet. For the SD and D cases, the locations where the velocity was obtained are marked with a green star in the velocity fields of panel a). The vertical black arrows indicate the approximate times at which the velocity fields were obtained. c) Reynolds number versus Ra number for the single down and double droplets cases. The power law $Re \sim Ra^{5/8}$ is recovered for an intermediate range. For the two droplets case, at large Ra number, the Re number deviates from the power law. The deviation indicates the influence of the upper droplet which should decrease as the droplets become smaller.

Figure 3.4: Volume versus time for a 1-pentanol droplet dissolving below a second droplet of 1-pentanol or a different alcohol (1-hexanol, 1-heptanol or 1-octanol). The initial separation is $L_0 \sim 2R_{e,0}$, except for 1-hexanol for which $L_0 \sim 1.6R_{e,0}$. In a) we show the volume of the lower droplet. The dissolution of the bottom 1-pentanol droplet is hardly affected by changing the alcohol used for the upper droplet. The horizontal black line in a) indicates when the diameter of the droplet is equal to the diameter of the capillary. The top-right inset in panel a) shows the compensated Sh number versus Ra number, calculated with the volume of the lower droplet. For large values of Ra the curve is approximately flat, reflecting the scaling $Sh \propto Ra^{1/4}$, previously predicted [21,136]. The vertical colored lines in the inset indicate when the droplet diameter is equal to the one of the capillary. For low Ra numbers the data strongly varies because the droplet is always connected to the liquid inside the tubes and variations in temperature or pressure inside the tube become more evident once the droplet is small. b) Volume of the top droplet as function of time. When the top droplet is made of a different alcohol, its volume first increases before decreasing by dissolution, contrary to the bottom droplet. The increase in volume is more prominent and lasts for a longer time for a longer carbon chain. The diagrams in both a) and b) indicate from which droplet the volume is plotted.

because we do not have to take a derivative, therefore we can see the trend down to lower values of Ra . As opposed to Dietrich, et al. [21], we do not observe a strong decrease in the Re number at low Ra because the plume persists for the whole life time of the droplet.

3.3.2 Effect of changing the liquid of the upper droplet

With the dissolution of 1-pentanol droplets as a reference, we can now look at the effects of changing the liquid of the top droplet to 1-hexanol, 1-heptanol, and 1-octanol. In figure 3.4a) we show that the effect in the evolution of the

volume of the bottom droplet is not very strong. While there seems to be a slight decrease in the dissolution time for the 1-hexanol case, this is within the variations we observed for repetitions of the same case.

We have also plotted the non-dimensional numbers (based on the lower droplet) in the inset of figure 3.4a). As before, for $Ra > 100$ the data is approximately flat, while for lower values of Ra the variation in the Sh number are too large to see any clear trend. If we focus our attention to the time when the droplet is larger than the capillary, we can conclude that changes in the liquid of the top droplet do not seem to affect the mechanism behind dissolution, namely convection dominated dissolution.

On the contrary, as can be seen from figure 3.4b) once the liquid of the top droplet is different from 1-pentanol, an initial increase in volume for the three cases takes place, specially for 1-heptanol and 1-octanol. This is an indication that some of the 1-pentanol that is transported by the plume dissolves into the upper droplet. To corroborate that this increase in volume is not a result of residual pressure in the tube we looked at the dissolution of single droplets in water held at the top position. In the single droplet cases there can be indeed a small increase in volume at the beginning, which is actually close in magnitude to the increase observed in figure 3.4b) for 1-hexanol, however it is considerably smaller than in the cases of 1-heptanol and 1-octanol (we show a comparison of the volume time series between the single and double droplet cases in appendix 3.7.3).

The volume increases for a longer time the longer the carbon chain, as clearly shown by figure 3.4b). One possible explanation can be found in the decreasing solubility of the carbon chain (cf. table 3.1), which means that the saturation concentration at the interface, and in turn the dissolution rate, will be smaller for a longer carbon chain. Since there is no alcohol of the top droplet already dissolved in the bath, dissolution still has to happen even if 1-pentanol is diffusing into the droplet. Thus the volume change of the droplet will be given by the sum of both fluxes, and since the flux out is stronger for the smaller carbon chain, the volume increases only for a small time. However, as we will show next, for 1-heptanol and 1-octanol, there is a Marangoni flow at the top droplet taking place at the start of the dissolution process which could also play a role on the time over which the droplet grows in size.

In figure 3.5a) we show the velocity measured one radius above the bottom droplet when the liquid of the top droplet is changed from 1-pentanol to 1-octanol. For the case of 1-hexanol the overall behavior is very similar to the 1-pentanol case, with the small difference that, when the plume reached

Figure 3.5: Velocity related data for pairs of droplets dissolving simultaneously at an initial separation of $L_0 \sim 2R_{e,0}$, except for 1-hexanol for which $L_0 \sim 1.6R_{e,0}$. a) Velocity magnitude taken at the middle point between the two droplets. When the upper droplet is made of 1-heptanol or 1-octanol the velocity starts to oscillate once the plume created by the lower droplet reaches the upper droplet. *Inset*: zoom to the first 100s. During the oscillations, the velocity reaches up to 1 mm/s, and then goes down close to 0 mm/s during each cycle. For the first cycles the vertical velocity can even become negative momentarily. Eventually the oscillations stop and the velocity starts to decrease as the lower droplet dissolves. The time in the inset was displaced so that all curves coincide during the first 5 s to show that before the oscillations start, the velocity is almost the same for all cases. b) Reynolds number compensated with $Ra^{-5/8}$ versus Ra number. In all cases, there is a region over which the data is approximately flat. Notice that this flat region is around the time the droplet is close in size to the size of the tube as indicated by the short vertical solid colored lines. The horizontal flat dashed lines are only used as references. The initial deviation indicates the influence of the upper droplet, which becomes less important as the lower droplet dissolves. The inset shows a sketch of the two droplets. The black star indicates the position where the velocity was measured.

the upper droplet, there is a small increase in the velocity around the upper droplet. However, for 1-heptanol and 1-octanol, the velocity surprisingly starts to oscillate once the 1-pentanol plume reaches the top droplet (see the inset of figure 3.5a)). Later the oscillations stops and the velocity decreases over time.

The oscillatory behavior of the velocity is reminiscent of other oscillatory systems like the flows around droplets in a density stratified bath [6, 141], the up and down movement of a bubble inside a binary bath close to a heated surface [150], or the intermittent kicking of a pendant droplet of water surrounded by a binary gas [151]. In all systems just mentioned, there is a concentration or temperature gradient in the fluid surrounding the droplet, thus gradients of density and surface tension. The competition between these gradients or against other mechanisms drive the oscillatory flows. In our case, given that the 1-pentanol plume creates a gradient in concentration around the upper droplet, we can expect that a similar competition is at place in our experiments.

More precisely, we can imagine that when the plume touches the upper droplet, there is a local dip in the interfacial tension at the bottom of the top droplet. As a consequence, a Marangoni flow develops and pulls liquid from the bottom to the top of the droplet. We indeed see that the velocity suddenly increases in magnitude when the plume reaches the top droplet. In the case of the jumping droplets in a stratified flow [6], the oil droplet suddenly jumped because of the Marangoni flow caused by the surrounding concentration gradient. Later on, the same flow causes the homogenization of the liquid inside the boundary layer around the droplet, stopping the Marangoni effect itself. Afterwards, the droplet moves down due to gravity until diffusion allows the far field stratification to get in contact with the droplet once more, triggering the Marangoni flow again. In a similar way, one could assume that in our system the Marangoni flow transports the pentanol-rich liquid all around the droplet until a homogeneous layer is created around the top droplet. Later, the lower density of the pentanol-rich water as compared to pure water would advect the concentration boundary layer away, bringing the system to the initial state, where the plume could cause a concentration gradient along the interface. However, in the following section we will see, with the help of numerical simulations, that this view is slightly too simplistic and that in fact there is an extra step in which the lower plume detaches from the top droplet, and it is this step which actually causes the oscillatory behavior.

In figure 3.5b) we show the corresponding compensated Re numbers as function of the Ra number. Again, the data is flat for intermediate values of the

Figure 3.6: a) Schematic with the boundary conditions used in simulations, with $j = 2, 3$ and $k = 1, 3$. b) Vertical velocity at the middle point between the two droplets for 100 s. The initial separation between the droplets is $L_0 \sim R_{e,0}$. In the simulation the oscillations are present for all the life time of the lower droplet. c) Comparison of the central velocity between simulations (upper) and experiments (lower). The qualitative behaviour is satisfactorily recovered in the numerics. The order of magnitude of the velocity is in good agreement. The period of one cycle in experiments is slightly longer than in simulations, which we attribute to the simplifications taken in the numerics (see text). The six times marked in the upper plot of panel c) correspond to the times of the snapshots shown in figure 3.7.

Ra number, further suggesting that the 5/8 scaling law becomes applicable only after the droplets have dissolved for some time. In this compensated version we can also see that for low Ra numbers the data go up, suggesting that the capillaries and the liquid within them start to have an effect.

3.4 Numerical simulations of the oscillatory regime

3.4.1 Numerical setup

We performed numerical simulations for the case of a 1-pentanol droplet at the bottom and a 1-octanol droplet at the top. We used a finite element

method implemented on the basis of the finite element package oomph-lib [67]. The liquids inside the droplets and the surrounding bath are discretised using triangular Taylor-Hood elements for the degrees of freedom of the velocity and pressure space, and a linear shape function for the composition in the three domains. The general numerical technique is described in detail in [68], however, in that work the droplet was assumed as a spherical cap while here the full interface dynamics are solved, thus the interface can deform and deviate from the form of a spherical cap. Comparison with various experimental cases for benchmarking of the code can be found in [6, 57, 65].

The cylindrical symmetry of the system allows us to use an axisymmetric simulation as shown in figure 3.6. The chosen domain is 8 mm in height and 3 mm in diameter. Two solid cylinders are placed at the top and bottom along the axis of symmetry. As opposed to the experiments, the cylinders are not capillaries, thus the droplets are not connected to a reservoir of 1-pentanol. The base of the droplets is pinned to the cylinders. No-slip boundary conditions, a zero normal velocity and no mass transfer were considered at the edges of the cylinders as depicted in figure 3.6a).

Apart from the cylinders, the domain was divided in three regions: 1 the bottom droplet, 2 the top droplet, and 3 the bath. In the three regions we considered the continuity equation for incompressible fluids and the Navier-Stokes with the Boussinesq approximation,

$$\nabla \cdot \mathbf{v} = 0, \quad (3.3)$$

$$\rho_\alpha (\partial_t \mathbf{v}_\alpha + \mathbf{v}_\alpha \cdot \nabla \mathbf{v}_\alpha) = -\nabla p_\alpha + \nabla \cdot [\mu_\alpha (\nabla \mathbf{v}_\alpha + \nabla \mathbf{v}_\alpha^T)] - \rho_\alpha g \mathbf{e}_z, \quad (3.4)$$

where $\mathbf{v}_\alpha$ and p_α are respectively the velocity and pressure in each region $\alpha = 1, 2, 3$. The density and viscosity are functions of the mass fraction of 1-pentanol c , i.e. $\rho_\alpha = \rho_\alpha(c)$, and $\mu_\alpha = \mu_\alpha(c)$. The reason behind the use of the Boussinesq approximation for the continuity equation lays in the numerics. While the complete equation considers density variation accurately, the partial masses are not perfectly conserved within the numerical scheme. However, when considering a divergence free fluid, this is not an issue, so we have decided to choose the Boussinesq approximation.

Inside the bottom droplet and the bath the advection diffusion equation is solved,

$$\rho_\alpha (\partial_t c + \mathbf{v} \cdot \nabla c) = \nabla \cdot (\rho_\alpha D \nabla c), \quad (3.5)$$

where D is the diffusion coefficient of either pentanol in water (in the bath) or of water in pentanol (inside the lower droplet). Solving for either the mass

fraction of 1-pentanol c (in the bath) or of water c_w (inside the droplet) is enough as they are coupled by the relationship $c_w + c = 1$. One simplification we make is that the top droplet is considered insoluble in water, thus there is no need to solve for the concentration inside the top droplet, and there is no third component going into the bath. We will later discuss the implications of this simplification.

The boundary conditions for the tangential and normal stresses at the interfaces of both droplets are given by

$$\mathbf{e}_n \cdot [\mu_i(\nabla \mathbf{v}_i + \nabla \mathbf{v}_i^T) - \mu_3(\nabla \mathbf{v}_3 + \nabla \mathbf{v}_3^T)] \cdot \mathbf{e}_t = \mathbf{e}_t \cdot \nabla_t \gamma \quad (3.6)$$

$$\mathbf{e}_n \cdot [\mu_i(\nabla \mathbf{v}_i + \nabla \mathbf{v}_i^T) - \mu_3(\nabla \mathbf{v}_3 + \nabla \mathbf{v}_3^T) + (p_3 - p_i)\mathbf{I}] \cdot \mathbf{e}_n = \kappa \gamma, \quad (3.7)$$

where $\mathbf{e}_n$ and $\mathbf{e}_t$ are unit vectors in the normal and tangential direction with respect to the interface of each droplet. The symbol ∇_t indicate the gradient in the tangential direction. The subscript $i = 1, 2$ indicates that a quantity is inside the respective droplet. The superscript T indicates the transpose, $\mathbf{I}$ is the identity matrix and κ is the curvature of the interface.

For both droplets the tangential velocities are continuous across the interface

$$(\mathbf{v}_3 - \mathbf{v}_i) \cdot \mathbf{e}_t = 0. \quad (3.8)$$

Given that the top droplet is considered insoluble in water, no flux takes place across its interface $\partial_n c = 0$, resulting in the kinematic condition

$$(\mathbf{v}_j - \mathbf{v}_{\text{interf}}) \cdot \mathbf{e}_n = 0. \quad (3.9)$$

where $\mathbf{v}_{\text{interf}}$ is the velocity of the interface and $j = 2, 3$. On the contrary, the bottom droplet is allowed to dissolve. Therefore its corresponding kinematic condition is

$$\rho_k(\mathbf{v}_k - \mathbf{v}_{\text{interf}}) \cdot \mathbf{e}_n = j_p + j_w, \quad (3.10)$$

with $k = 1, 3$. The fluxes of 1-pentanol j_p and water j_w are also subject to the boundary conditions

$$\rho_3 D_{p,w} \partial_n c = (1 - c)j_p - c j_w, \quad (3.11)$$

$$\rho_1 D_{w,p} \partial_n c_w = (1 - c_w)j_w - c_w j_p, \quad (3.12)$$

where ∂_n indicates a partial derivative in the direction normal to the droplet interface. The concentrations at the interface were assumed to be the corresponding saturation values on both sides of the interface of the bottom droplet,

$$c_{\text{interf}} = c_{\text{sat}}, \quad \text{bath side}, \quad (3.13)$$

$$c_{\text{interf},w} = c_{\text{sat},w}, \quad \text{drop side}, \quad (3.14)$$

with the saturation values obtained from literature [145, 152].

Finally, at the bottom and right edge of the domain we consider no-slip boundary conditions and an open inflow for the top edge.

3.4.2 A more detailed description of the oscillatory cycle

In figure 3.6b) we have plotted the vertical velocity obtained at the middle point between the simulated 1-pentanol and 1-octanol droplets ($L_0 \sim R_{e,0}$). The oscillatory behavior of the velocity is satisfactorily recovered. In figure 3.6c) we show a zoom to the first two cycles and compare them to the first two cycles obtained experimentally ($L_0 \sim R_{e,0}$). It can be seen that the maximum velocity in both simulations and experiments are of the same order of magnitude, with the velocity in simulations being slightly larger. As for the period of oscillation, while it is longer in experiments, both have the same order of magnitude. The fair agreement lets us conclude that the diffusion into and from the upper droplet is not a key element for the appearance of the oscillatory behavior.

From the simulations we can further verify the mechanism behind the oscillations proposed in the previous section. We have selected six different moments during the first oscillation cycle from the simulation, as marked in figure 3.6c). The corresponding snapshots are shown in figure 3.7.

As we already concluded from experiments, initially (at time 1) the dissolution of pentanol causes an accumulation of pentanol rich liquid around the bottom droplet, resulting in the creation of a convective plume. In the snapshot at time 1 the plume is just starting to move up. A couple of seconds later, the plume gets in contact with the top droplet as shown in snapshot 2. It is clear that the velocity at the section of the interface where the plume has contacted the upper droplet is much higher than at the region of the interface where the plume has not arrived. Furthermore, we can clearly see that there is a gradient in concentration along the interface with the higher concentration at the bottom of the droplet. Therefore the interfacial tension increases from the bottom towards the top of the droplet. Just a fraction of a second later, at time 3, the Marangoni flow extends along the whole droplet and the pentanol-rich liquid has been transported to the top of the droplet.

From our hypothesis in the previous section, the Marangoni flow could help to homogenize the pentanol-rich liquid around the top droplet, therefore stopping itself. However, from the snapshot at time 4, we can see that before

Figure 3.7: Snapshots of the numerical results at 6 different moments during one oscillation cycle. At 1, the plume is building up and moves towards the top droplet. At 2, the plume has reached the top droplet, creating a gradient in interfacial tension and triggering an upwards Marangoni flow. At 3, the Marangoni flow has brought pentanol rich liquid all around the droplet in a relatively thin concentration boundary layer. At 4, pentanol rich liquid has accumulated close to the contact line between the top droplet and the top capillary, causing a secondary Marangoni flow. A zoom to the upper droplet shows the accumulation. At 5, the secondary Marangoni flow has created a thicker concentration boundary layer all around the droplet. The velocity in between the droplets points down, causing the plume to “detach” from the upper droplet. At 6, buoyancy competes with the secondary Marangoni flow. Eventually the plume is able to get in contact with the upper droplet again and the process restarts.

homogenization takes place, a contrary gradient in 1-pentanol is created at the top part of the droplet (see the zoomed region). Therefore an adversary Marangoni flow appears (see the velocity field inside the droplet). Such an opposing flow brings back down the pentanol-rich liquid and increases the thickness of the concentration boundary layer around the top droplet. Eventually, the velocity inside the droplet completely reverses and the secondary Marangoni flow takes over (time 5). The downward flow pushes the plume away from the top droplet letting the secondary Marangoni flow dominate. Notice that by bringing down pentanol-rich fluid and increasing the thickness of the boundary layer, the result is similar to the homogenization caused by diffusion in the bouncing droplet case [6].

Despite the downward flow caused by the secondary Marangoni flow, the pentanol-rich fluid is less dense than water, thus buoyancy starts to take over and, as shown in time 6, the flow starts to move upward once more. This causes that outside the top droplet and very close to its interface the velocity points down, but after a small distance it points up (look at the equator of the droplet at time 6 in figure 3.7). Eventually, the plume is able to reach the top droplet again and the whole process repeats.

When we look closely at our experiments, we can see that indeed there is a momentary downward flow at each cycle (at least for a few first cycles) in accordance with what we see in the simulations. We point at the negative flow in figure 3.6c) with red arrows.

3.5 Discussion

A possible explanation for the accumulation of 1-pentanol at the top of the droplet is the no-slip boundary condition on the top capillary. As we can see from the simulations, at time 3, the pentanol-rich solution does not go up parallel to the tube wall, but instead it is advected at an oblique angle due to the velocity boundary layer created at the wall. The concentration then takes the shape of a horn. Along this “horn” the gradient of pentanol mass fraction is much smaller than the radial gradient in other lower locations of the interface. Therefore, diffusion in the direction normal to the interface is smaller at the location of the horn, which over time can cause that the concentration at the horn is higher than at another point on the interface below the horn. Once this happens, the contrary Marangoni flow appears and the thicker concentration boundary layer starts to propagate down the interface.

One can then wonder if the oscillatory behavior would take place if the capillary was removed, because the no-slip boundary condition would not be present. We can still expect that a stagnation point would form on the top of the droplet and advection could still create a “horn” but this time on the top of the droplet. Therefore, we can speculate that even without the capillary the oscillatory behavior would appear. Moreover, if the Reynolds number were to be larger, and a pair of standing eddies were to appear behind the droplet, they would serve as a way to accumulate pentanol-rich solution on top of the droplet and trigger the secondary Marangoni flow. However, for the moment this only remains as a speculation.

As opposed to the experiments, for this particular simulation, the oscillations lasted for the whole life of the lower droplet. This suggests that some of the simplifications taken in the simulation play a role in determining the time during which the oscillatory behavior is active. First of all, we did not consider the dissolution of 1-pentanol into the 1-octanol droplet, which is clearly happening in experiments. At the same time, 1-octanol can also dissolve into the bath. Both mass transfer processes can affect the concentration at the interface and thus the Marangoni flow. Moreover, it is known that mass transfer of a solute that affects the interfacial tension can destabilize an interface [39]. Additionally, the liquids in the simulation are pure, while in experiments there can always be some contamination that could stop the flow. Some other possible effects that are not taken into account in the simulations are temperature variations, 1-pentanol inside the capillaries and pressure perturbations coming from the capillaries and the syringes.

We have performed a few experiments and corresponding simulations with modified initial distance between the droplets, namely $L_0 \sim R_{e,0}$, $L_0 \sim 2R_{e,0}$, $L \sim 4R_{e,0}$. The general trend is that for larger spacing, the number of oscillations is smaller. In a simulation the oscillations were reduced to only 3 cycles when the distance was increased to $L_0 \sim 2R_{e,0}$, while in experiments the number of oscillations was between 6 and 20 for different repetitions at the same spacing. Therefore we can conclude that the initial spacing is important for triggering the oscillatory behavior. Possibly this is a consequence of weaker concentration gradients inside the plume after traveling for a longer distance. A smaller gradient results in a smaller Marangoni flow. Within the same line of reasoning, when the liquid is changed to a shorter carbon chain alcohol, the derivative of the surface tension with respect to the concentration of 1-pentanol ($\partial\gamma/\partial c$) is reduced (cf. Table 3.1). As we saw in the previous section, oscillations did not happen for 1-pentanol and 1-hexanol in the top

droplet, indicating that indeed a strong enough interfacial tension gradient is needed to have oscillations.

Additionally, different geometries at the contact line seems to have an effect on the total number of cycles too, as we discuss in appendix 3.7.5. Clearly, there are many parameters to be considered, but making a exhaustive exploration of the parameter space is beyond the scope of the present work.

3.6 Conclusion

We have studied the dissolution of droplets of alcohols of different carbon chains inside a water bath, mainly focusing in a system of two vertically aligned droplets dissolving simultaneously. As reference cases, we looked at the dissolution of an individual droplet of 1-pentanol and of two vertically aligned 1-pentanol droplets. Then we built up from these base cases and changed the liquid of the top droplet to alcohols with longer carbon chains. In all the cases, for the dissolution of the lower droplet we recovered the scaling $Sh \sim Ra^{1/4}$ for high Rayleigh numbers for which the droplets are larger than the capillary used to hold them. This is in agreement with the results obtained previously for the dissolution of sessile droplets [21, 136]. Furthermore, we have also confirmed the scaling $Re \sim Ra^{5/8}$ for the velocity of the plume, although for the two droplets the data deviates from this scaling at the beginning of the dissolution process, indicating that the presence of the upper droplet affects the dynamics of the plume.

For two vertically aligned droplets, when the top droplet consisted of 1-heptanol and 1-octanol, we observed an oscillatory behavior both experimentally and numerically. The interaction of the top droplet with the pentanol plume coming from the bottom droplet triggered an oscillatory Marangoni flow around the top droplet. During one cycle, the Marangoni flow pulls the liquid upwards, in the same direction as natural convection. However, the presence of the top capillary and the no-slip condition at its walls result in an inversion of the concentration gradient along the interface of the droplet. Consequently, an adverse secondary Marangoni flow appears, which competes with the primary Marangoni flow and natural convection. The secondary flow hinders the flow of the 1-pentanol plume and detaches it from the top droplet, until buoyancy takes over and brings the plume back into contact with the upper droplet again.

By comparing our experimental and numerical results we could conclude that

the diffusion of 1-pentanol into the top droplet and the dissolution itself of the top droplet into the bath do not play a prominent role in the appearance of the oscillations in velocity. However, mass transfer can affect the total duration of the oscillatory regime and causes a temporary increment in the volume of the top droplet. While the parameter space is large, we were able to recognize that for a larger spacing between the droplets the oscillatory behavior lasts less time. Additionally, a reduction on the value of the derivative of interfacial tension with respect to concentration can also eliminate completely the oscillatory behavior. In future works, it would be interesting to further explore the parameter space by including more values of the distance L_0 between the droplets and of the initial radii. Also, it would be instructive to change the density difference between the plume and the bath and the viscosity of the liquids. In addition, it would be very interesting to see whether the oscillations persist if for example the capillary holds the top droplet from the side and not from the top, or if in simulations the capillary is completely removed.

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3.7 Appendix

3.7.1 Appendix A. Image analysis for volume calculation and error estimation

Image processing

In figure 3.8 we show a series of images summarizing the process used to detect the edge of the droplets and the capillaries from the side view using a home made code in Matlab. Figure 3.8a) shows the original image I from which we obtained the most common intensity, $\text{mode}(I)$, which would correspond to

Figure 3.8: Sequence of images showing different steps of the image processing. a) Original image of the lower droplet with tracer particles. b) Image after subtracting the image from the mode of the intensity and readjusting the contrast. c) Binary version of the image. d) Filled and dilated version of the binary image. e) Filled and eroded version of the binary image. f) Masked version of the image in panel b) using the eroded and dilated versions of the binary image. g) Zoom to the region marked with a white rectangle in panel f). Only a region of a few pixels around the edge is not masked. The red lines mark the limits of the masks. The green dots indicate the detected edge using the canny method. h) Edge of the droplet and the capillary.

the intensity in the background (here we have cropped the image for visualization but the background occupies a bigger area). We subtracted the image from the most common intensity, $\text{mode}(I) - I$, and readjusted the contrast by remapping the intensity values so that the new minimum corresponds to 0 and the maximum to 255. The result is shown in figure 3.8b). The adjusted image is then binarized using the function *imbinarize* from Matlab. In some cases we used Otsu's method, but if we considered necessary we included a threshold ourselves. In some cases, we applied the morphological operation of opening the image to delete small specks left after binarization, resulting in figure 3.8c). The binary image was then filled to delete holes. Following, the image was dilated and a copy was created as shown in figure 3.8d). Then the binary image was eroded more than it was dilated and another copy was created, (see figure 3.8e)). With the dilated image we created a mask of the outside of the droplets, and with the eroded image a mask of the inside of the droplets, which we show in figure 3.8f). In this way only the region around interface of the droplets and the capillaries is considered in the next steps. To better illustrate the effect of masking we show in figure 3.8g) a zoom to

Figure 3.9: Sequence of images showing different steps of the droplet detection. a) Image of the capillaries without infused droplets after subtracting the most common pixel intensity and adjusting the contrast. The detected contour is shown in green. b) Image after subtracting the most common pixel intensity and adjusting the contrast. The detected contour is shown in green. c, d) Zoom to the upper and lower droplets respectively. A circular fit is shown in white. The contour of the capillary is shown in red. The base of the droplet is highlighted in yellow. f, g) Zoom to one side of the contact line of the upper and lower droplets. The detected contour is shown in green and magenta. For the fit we only used the magenta part of the contour. The yellow star marks the intersection with the capillary.

the region marked with a white square in figure 3.8f). The contours were obtained using the function *edge* from Matlab with the Canny method with two limits, which we adjusted manually for each experiment, but were left the same for all the images of the same experiment. The edge can be seen as green points in figure 3.8g) and the complete edge in figure 3.8h) as a white line. Sometimes the edge was not connected into a single region, so we applied another morphological closing function followed by a bridging function *bwmorph* with bridges of 1 pixel. Finally, in case some specks survived the whole process, we selected the largest regions in the image which corresponds to the contour of the droplet.

Droplet detection and volume calculation

To obtain the volume of the droplets we used the detected edge and assumed them to be axisymmetric. Since the droplets were connected to the capillaries we first detected the contour of the capillaries as shown in figure 3.9a). We dilated the contour of the capillaries 4 to 6 pixels and subtracted the dilated contour from the contour with droplets shown in figure 3.9b). In some

situations the capillary drifted slightly during the dissolution process, when this was the case, we applied a cross-correlation between the contour of the capillaries alone and the contour of the droplets with the capillaries. In some cases we found it better to cross correlate the binary images instead of only the contours. From the cross correlation we obtained the amount of displacement of the capillary, and in this way we shifted the contour of the capillaries alone so that we could subtract it from the contour with both capillaries and droplets. In the case of figures 3.9 there was no drift so the correlation step was omitted. Figure 3.9c, d) show the superposed contour of the capillary on top of the image with both capillaries and the droplet.

A fit to a circle [153] was made to the contour of the droplets after subtracting the contour of the capillaries. The fit is shown in white in figures 3.9c, d). The contact points of the droplet were obtained by getting the intersection [154] between the circle and the contour of the capillary, highlighted with yellow stars. After taking the first fit, we further eliminated the points of the edge that were within another circle of radius $0.95R$ to $0.99R$. Similarly points outside a circle of radius $1.01R$ were neglected. In this way, we could avoid the irregularities introduced to the edge by the presence of the tracer particles, or in some cases by changes in the light. An example of this can be seen in figures 3.9e, f), where we show a zoom to the contact line. The magenta points are the points used in a second fit, while the green points are the points omitted after considering the threshold. Particularly in figure 3.9f) it can be seen that the edge was affected by a tracer.

Despite the small Bond number of our system, there is a slight deformation of the droplets. In figure 3.9e) it can be seen that for the droplet held from the top, the circular fit over-estimates the position of the contact line by a few pixels. For the lower droplet in figure 3.9f) the fit under-estimates the position of the contact line. This is in accordance with the upper (lower) droplet being pushed (pulled) against (from) the capillary by buoyancy. This effect can also be seen in other parts of the contour, however, we have estimated that this error is at most 5% of the total volume. This estimation was made by calculating the volume between the fit and the real edge assuming a revolution body. In the worst cases, the error volume is in the order of 10^5 pixels³ while the volume is in the order of 10^7 pixels³. As the droplets become smaller, the effect of buoyancy reduces. Moreover, for the upper droplet the effect is further reduced when the liquid is changed to longer carbon chain alcohols with a smaller density difference.

The reason not to use the detected edge itself to obtain the volume is that

Figure 3.10: Example of the original and the interpolated volume series. We point with a green arrow to one data point for which the edge detection failed. *Inset*: zoom to the region marked with the green rectangle. Notice that the original data does not have a homogeneous time step because we changed the recording frame rate after the velocity oscillations stopped causing a small time lag. The interpolations ensures an homogeneous time step for when the derivative is taken.

in many occasions the presence of the tracer particles affects the shape of the contour. Moreover, because we kept the intensity of light source low (to increase the contrast of the tracer particles) some times we do not detect the whole edge, therefore, if we were to use the edge instead of the fit the error would be greater in those cases.

3.7.2 Appendix B. Data cleaning

We automated the edge detection process described in the previous section. The detection method gave successful results most of the time, however in some occasions either the cross correlation or the edge detection were not accurate. Therefore, we cleaned our data by linearly interpolating the volume at the frames when the detection was incorrect. An example of the original volume time series and the interpolated one is shown in figure 3.10. We marked with a green arrow one particular point where the detection was incorrect.

In some cases we changed the rate at which we recorded to reduce the amount of data collected. For the case with a 1-pentanol droplet at the bottom with a 1-octanol droplet at the top, we recorded at 30 frames per second (fps) while

Figure 3.11: Volume series of the top droplet when it is made of a) 1-hexanol, b) 1-heptanol, and c) 1-octanol. The thin lines correspond to 3 different repetitions of a single droplet up (SU). The thick lines correspond to the upper droplet of a double droplet dissolution case (DU). The inset in a) shows schematics of the corresponding experimental configurations.

the oscillations were active, and then reduced the recording rate to 10 fps. As a result, there was a small time lag as can be seen in the inset of figure 3.10. Additionally, sometimes the camera we used dropped a few frames, effectively reducing the frame rate temporarily and making the time resolution non-homogeneous. Therefore, we interpolated the data using a homogeneous time step, which was required to get a derivative using a convolution with the derivative of a Gaussian function. Notice that the volume was measured only every 1 s, while the actual frame rate was larger for the velocity measurement. By comparing the original and the interpolated data series we could corroborate that the effect of the interpolation should be small. When an original data point has the exact same time as the interpolated time series, the resulting volume is exactly the same, and when there is a time lag the interpolation effectively smooths the signal.

3.7.3 Appendix C. Dissolution of individual droplets

In order to better assess the effect of the plume on the dissolution of the top droplet, we measured the volume of single droplets of 1-hexanol, 1-heptanol, and 1-octanol. We used the configuration of a single upper droplet (SU), meaning that the capillary was above the droplet. The volume versus time series are shown in figure 3.11 for the three alcohols. Three repetitions are shown to give an indication of reproducibility. For comparison, we have plotted one example of the volume of the upper droplet in the double droplet configuration (DU).

Figure 3.12: Sherwood number compensated with $Ra^{-1/4}$ versus Ra . The vertical colored lines indicate the moment when the radius of curvature of the droplet is equal to the radius of the tubes. The horizontal dashed black line is a guide to the eye to compare with the data. Same data as shown in figure 3.2, but including the whole range of Rayleigh numbers measured.

For the 1-hexanol case the effect of the plume on the volume is small. There seems to be a small increase in volume, but it is only slightly different from the cases of the single droplet. In some of the SU cases there is actually a small increase in volume which could come from residual pressure in the capillary, thermal expansion or water dissolution into the droplet. However, that increase is not always present while in all the repetitions of the DU we observe the volume increase.

The volume increase is clearer in the case of 1-heptanol and even more for 1-octanol. It is possible that the oscillatory Marangoni flow contribute to this volume increase, but it cannot be the only explanation because the volume continues to grow even after the oscillations stop. In particular, for the 1-octanol case, the volume reaches a maximum approximately at 500 s, while the oscillations last at most 200s. Therefore, the decreasing solubility might be a more plausible explanation.

3.7.4 Appendix D. Complete data set of the non-dimensional numbers of the 1-pentanol cases

Figure 3.12 shows the complete range of Rayleigh numbers measured during the dissolution of single and double 1-pentanol droplets. For low Rayleigh numbers, the data becomes quite noisy, because of fast variations in the droplet size. One possible reason for this behaviour is the coupling of the droplet with the liquid inside the capillary. Variations in the temperature of the capillary

Figure 3.13: a) Velocity measured at the middle point between the two droplets for the 1-pentanol–1-octanol case for 3 different initial distances L_0 . The arrows indicate the approximate time t_{osc} at which the oscillations have stopped. b) Time over which oscillations take place versus the initial distance between the droplets L_0 for 1-heptanol and 1-octanol droplets at the top. Each symbol is one repetition of the experiment. The error bars are of 10 s, a little bit more than the oscillation period. We chose this error bar because the last oscillation is not always easy to recognize.

can cause the liquid to expand and compress slightly, and because the capillary is small, the variations are perceptible. This could be more important for the single droplet experiments for which the acrylic cage was not used. However, it is also possible that a small air bubble was trapped at any part of the capillary, the syringe or the connectors, despite our efforts to prevent this. If that was the case, variations in the pressure could cause the bubble to oscillate and make the droplets increase and reduce in size accordingly.

3.7.5 Appendix E. Small study of the parameter space

We did a small exploration of the parameter space of our system, including a few variations in the initial distance L_0 between the droplets for both the 1-heptanol and the 1-octanol cases. In figure 3.13a) we show three time series of the velocity measured at the middle point between the droplets for the 1-pentanol–1-octanol case. As can be seen, as the distance is reduced the time over which the oscillations take place t_{osc} increases. In figure 3.13b) we plot t_{osc} versus L_0 , for both 1-heptanol and 1-octanol. In both cases, it is clear that t_{osc} increases with a decrease in L_0 . The effect of changing the liquid of the

Figure 3.14: a) Velocity measured at the middle point between the two droplets for the 1-pentanol–1-heptanol case comparing the effect of the presence or absence of a cavity between the droplet and the capillary. The reason for the difference in velocity magnitude is that for the case without a cavity the recording frame rate was not high enough to capture the high speed peaks. b) Two snapshots showing how for one case the droplet is in contact with the capillary tube, while in the other case there is a cavity between the droplet and the capillary.

droplet is not that clear as for the smallest L_0 , the oscillations last longer for 1-heptanol, while for the intermediate values of L_0 the oscillations last longer for 1-octanol. Understanding this transition will be left for future research.

Additionally, there is some evidence that the geometry at the contact line could have an effect on t_{osc} . In figure 3.14a) we plot two examples of the velocity at the middle point between the droplets. In one case the base of the droplet extends over the whole capillary, while in the second case the base of the droplet is smaller and there is a cavity between the droplet and the capillary as depicted in figure 3.14b). We suspect that such a cavity could promote the accumulation of pentanol-rich liquid, hence triggering the secondary Marangoni flow more easily. Nevertheless, we should point out that the experiments in which there is no cavity were performed without the acrylic cage around the setup, so there could also be a small thermal effect. Finally, the fact that in simulations the oscillations last for the whole life time of the droplet without a cavity, indicates that there are other parameters at play, besides the geometry, affecting the time over which the oscillations occur.

Figure 3.15: Interfacial tension between alcohols and a bath of 1-pentanol in water solution as function of the mass fraction of pentanol c in the bath. The solid lines are linear fits to each data set. The open symbols indicate literature values of the interfacial tension between the alcohols and pure water as reported in [21].

3.7.6 Appendix F. Interfacial tension measurements

We measured the interfacial tension between the alcohols and solutions at different concentration of 1-pentanol in water. The measurements were done using the pendant droplet method, with a contact angle system OCA 15 Pro (Dataphysics) and the software SCA20 U. The bath was prepared by measuring the weight of 1-pentanol and water. A saturated mixture was initially prepared and then diluted to have smaller mass fractions. The droplets of alcohols were dispensed using a glass syringe (Hamilton, 100 μ L, 1710 TLL, no stop) and a general purpose stainless steel needle with a blunt end (Precision Tips, 7018336, outer diameter 0.52 mm, inner diameter 0.25 mm). The needle was curved into a hook shape to dispense droplets of the less dense alcohols into the host solution.

In figure 3.15 we show the measured interfacial tensions at four different concentrations. The vertical error bars are 1 standard deviation obtained from at least three repetitions at each concentration, while the horizontal error bars are the estimated error of the mass fraction of 1-pentanol. The interfacial tensions depends linearly on the concentration of pentanol. Therefore, we obtained the gradient of interfacial tension with respect to mass fraction by making linear fits (solid colored lines in figure 3.15). The corresponding values are shown in Table 3.1 of the main text. As a reference we show the literature values of the interfacial tension between the alcohols and pure water [21].

Conclusions

This thesis investigates the physicochemical hydrodynamics of binary and ternary liquids in three different projects. In the first two chapters the focus was on the evaporation of a liquid contained in a Hele-Shaw cell. In chapter 1 the liquid was a binary mixture of ethanol and water, while in chapter 2 trans-anethole was added into the mixture making it a ternary system. Chapter 3 studies the dissolution of alcohols (from 1-pentanol to 1-octanol) in water. In particular we looked at the simultaneous dissolution of two droplets, one placed above the other.

Chapter 1 focuses on the Marangoni instability that arises at the gas-liquid interface due to the higher volatility of ethanol and the fact that ethanol has a lower surface tension than water. When the instability is active, convective rolls are created in the bulk of the liquid inside the cell. We followed the size of the rolls over time and found experimentally and numerically that they grow as $\sim t^{1/2}$, indicating a diffusion like process. While growing, the rolls merge with each other and reduce their number until eventually only one or two are visible. Eventually the instability ceases and the flow comes to a halt, we speculate this is due to a high ethanol concentration in the gas phase.

We were able to show that the numerical scheme developed by Dr. C. Diddens [68] was able to capture fairly well the main characteristics of the flow over time. The equations solved by the simulations used a Hele-Shaw model in which an average in the direction normal to the plane of the cell results in a quasi-2-D version of the Navier-Stokes and the advection-diffusion equations. Comparisons between the simulations and the experiments were only possible after the instability was already active and much later than the minimum viscous time needed for the Hele-Shaw cell to be applicable. Therefore, we were able to show that for the late time regime the simulations properly reflect the experimental results and thus the Hele-Shaw cell model is indeed applicable. We also performed a linear stability analysis for which we used a simplified version of the quasi-2-D model equations. From the analysis we were able to

obtain the stability region of the system as function of a modified Marangoni number that depends on the thickness of the cell. Therefore, once a system has been set with its corresponding physical properties, the Marangoni number indicates the effect of the size of the gap between the walls.

We found that below a critical Marangoni number the system should be stable. We attribute this stability region to the dissipation due to the drag caused by the walls, which is introduced as a permeability term in the quasi-2-D equations. The estimated value of the Marangoni number in the experiments and calculated in simulations was always above the critical threshold, thus explaining why we always observed the instability. From the theoretical analysis we obtained the rate at which perturbations at the interface should grow. The growth rates measured from simulations compared well with the theoretical ones despite the simplifications and assumptions taken in order to have an analytical prediction. While some of our theoretical results are outside the limits of the Hele-Shaw model we were able to conclude that as long as the Marangoni number is small enough, but still larger than its critical value, our results can serve as a first approximation to know if a system will be unstable and which wavelength sizes could be expected to grow with time. Quite surprisingly, despite the very small gap used in our cell (20 μm), it seems that the ethanol–water system requires the full 3-D version of the equations in order to calculate the onset of the instability, given that the quasi 2-D model used predicts wavelengths that are smaller than gap.

Further studies could include the use of a different system with values of the Marangoni number in the neighborhood of its critical value to further test the validity of our theoretical predictions. Additionally, a theoretical explanation is lacking for the observed power law for the growth of the convective rolls. This would required a more careful study of the merging events. Since we have corroborated that the simulation can reproduce the experimental observations it would be worth exploiting such a tool to find a complete explanation.

As we showed in chapter 2, the addition of trans-anethole to the mixture did not prevent the Marangoni instability from happening. Instead, parallel to the Marangoni instability, the initially single-phase ternary mixture phase separates as evaporation takes away the good solvent, ethanol. The phase separation took place both as emulsification due to the ouzo effect, and as bulk separation from spinodal decomposition. This was concluded by assuming that only ethanol evaporates, allowing us to draw composition paths in the ternary phase diagram. Such paths and the binodal and spinodal curves of the system allowed us to deduce the state of the system over time depending

on the initial composition of the mixture. By comparing the deduced states with our experimental observations we were able to offer a rationale for the different phenomena observed. For low oil mixtures we observed emulsification and surface droplet nucleation inside the Marangoni rolls, in accordance with a larger metastable region in the ternary diagram. At intermediate oil content mixtures, bulk separation overtook emulsification due to the vanishing gap between the binodal and spinodal lines. At high oil content mixtures, water droplets in an oil rich solution formed, which is a signature of the inverse ouzo region.

In some cases, the surface droplets tended to nucleate in lines that could evolve into more complicated patterns that looked like the branches of a tree. Such patterns appear either at regions of weak flow or after the Marangoni instability ceased, suggesting that they are part of a diffusion dominated regime, like it was concluded in the previous work by Lu *et al.* [71].

In general, the surface droplets where subjected to concentration gradients that in many cases caused the droplets to displace. For some cases this movement seemed to be related to the direction of the gradient in ethanol concentration, however, for some droplets their direction changed abruptly over time making it clear that the situation is complicated, with possible more than one mechanism at play. The mechanisms are not easy to deduce solely from our experimental observation. Therefore, it is clear that further studies are needed to fully understand all the phenomena that take place when droplets are formed from phase separation in a system that is far from equilibrium. In particular, despite the fact that a Hele-Shaw cell was used with the intention to simplify the geometry, the introduction of solid walls implies the introduction of solid-liquid interactions that bring their own complications. Certainly, such interactions and the observed phenomena deserve more attention, together with more careful and detailed experiments and simulations. Like in the case of a swimming droplet in a linear concentration gradient [6] or of sessile droplets in a non-uniform vapour field [109], studying a sessile droplet inside a bath with a controlled concentration gradient and the influence of neighboring droplets would be key to understand the displacement of the droplets.

In chapter 3, the number of droplets was reduced to either one or two. Given the large Ra number of the system, we stayed in the convection dominated regime, in which the low density of 1-pentanol as compared to the density of water results in the formation of a solutal plume. Therefore, the dissolution of the droplets was much faster than if diffusion was the dominant process.

From the dissolution of the bottom droplet, it was corroborated that the non-dimensional mass flux in the form of the Sherwood number scales with the Rayleigh number as $Sh \sim Ra^{1/4}$, like already found for sessile droplets [21,136]. Similarly, it was corroborated that the Reynolds number of the plume scales as $Re \sim Ra^{5/8}$ after the droplets have dissolved for some time. The same behavior was observed when the liquid of the upper droplet was changed. Deviations from the scaling law at the beginning of the process possibly stem from the interaction of the two droplets when they are close together.

When the liquid of the top droplet was changed to less soluble alcohols, the volume of the top droplet first increased before starting to decrease. In comparison, when the top droplet was left to dissolve alone, the volume only decreased over time. This indicated that some of the 1-pentanol dissolved in the plume diffused into the top droplet, given that the alcohols are miscible.

When the liquid of the upper droplet was changed to either 1-heptanol or 1-octanol, a Marangoni flow was triggered by the non-uniform concentration field created by the solutal plume around the top droplet. The Marangoni flow was oscillatory and only occurred for a limited amount of time at the beginning of the dissolution process. The oscillations were a consequence of the no-slip condition at the capillary used to hold the top droplet. The velocity boundary layer around the capillary caused a low concentration gradient at the top of the droplet and ultimately the accumulation of pentanol-rich liquid. Such accumulation reverses the concentration gradient along the interface of the droplet and with that an adversary Marangoni flow emerges. The secondary Marangoni flow homogenizes the liquid around the droplet, stops the solutal plume from rising and, even more, detaches the plume from top droplet. Eventually the buoyant force felt by the pentanol-rich solution restores the upward flow and restarts the process. This leaves as an open question if by taking away the top capillary the oscillatory flow could be hindered.

A final comment on to the scaling between the Reynolds and Rayleigh numbers is that the Marangoni flow would undoubtedly eliminate such scaling. This is because a Marangoni flow was not considered at all in the analysis that lead to the scaling in the first place. However, once the oscillatory Marangoni effect has ceased, the scaling is eventually recovered.

We were able to recover the oscillatory behavior in simulations and, in fact, they allowed us to notice the secondary Marangoni flow. The simulations used a very similar numerical scheme as in chapter 1, thus we further corroborated its capabilities to reproduce experimental results.

Given that in the numerical simulations the mass transfer from and into the

top droplet was turned off, we can conclude that the dissolution of the droplet or the diffusion of pentanol into the droplet are not necessary to observe the oscillatory behavior. Instead, they might play an important role in determining the time over which the oscillations are active given that in numerics the oscillations did not stop over the whole life of the bottom droplet. However, once the spacing was increased the oscillations only lasted for a short time. Definitely studying the parametric space of the system would be necessary to fully understand under which conditions the flow becomes oscillatory.

In future studies it would be very interesting to study if the presence of pentanol in the top droplet already from the beginning of the process would hinder the oscillatory behavior of the Marangoni flow. However, it could also be possible that a binary droplet becomes unstable on its own due to differences in the dissolution rates of the two components, like it happened in the first two chapters, or like it has already been observed for evaporating [53] and dissolving droplets [78]. Such instability would then interact with the flow of the plume, making the scenario even more complicated.

As we saw in chapter 3, the top droplet grows when it is made of a different liquid than the bottom droplet, therefore, it would be interesting to observe if this could be useful to extract an analyte dissolved in the bath. In the spirit of liquid–liquid micro-extraction, if the analyte has a low solubility in the bath, but the liquids of the droplets are good solvents, the analyte might accumulate inside the droplets. In regular liquid–liquid micro-extraction the accumulation would happen by diffusion, but it is possible that the plume created by the lower droplet helps to bring more of the solute into the top droplet, improving the extraction efficiency. Of course, as the lower droplet dissolves, the solubility of the analyte in the bath could increase (just as trans-anethole becomes soluble in water with the addition of ethanol) and eventually the process could become counterproductive. Therefore, there could be a set of conditions in which the extraction becomes optimized. While this remains speculative, this could be one potential direction of research inspired by the lessons learned in this thesis.

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Summary

Multicomponent liquids are an important part of both nature and process industry. They are inside our bodies, in our drinks and food, in chemical reactors, in medicines, in cosmetics, and in ink, to mention some examples. The multicomponent aspect of the liquids make them very rich in terms of the phenomena they can display. In this thesis we are concerned with the physicochemical hydrodynamics of binary and ternary liquids, in other words, with the effects that physical and chemical properties have in the flow within the liquids and vice versa.

The focus of chapter 1 is on the simplest multicomponent liquid, a binary liquid. We study the evaporation of an ethanol–water solution confined in a Hele-Shaw cell, making the system quasi-two-dimensional. The higher volatility of ethanol, results in its preferential evaporation causing a concentration gradient normal to the air–liquid interface. In addition, the lower surface tension of ethanol makes the interface unstable to small perturbations. Specifically, a Marangoni instability is triggered, resulting in a flow tangential to the interface which propagates inside the cell in the form of convective rolls. We studied experimentally and numerically the time evolution of such rolls with a fairly good agreement between both approaches. Furthermore, we performed a linear stability analysis to a simplified version of the model equations. According to the results of the linear stability analysis there is a critical Marangoni number above which the system should be unstable. The Marangoni numbers in experiments and simulations were above the critical value, in agreement with the presence of the instability. Comparison between the results from the simulations and the linear stability analysis were also in reasonable agreement, suggesting that the linear stability analysis could be used as a first approach to predict if a binary system evaporating inside a Hele-Shaw cell is stable or not.

In chapter 2 we studied the evaporation of a ternary mixture, namely, ethanol, water, and trans-anethole, also confined in a Hele-Shaw cell. We investigated

how variations in the initial concentration of the three components affected the temporal evolution of the system. Like for the binary system in chapter 2, a Marangoni instability was observed, regardless of the initial concentration. However, additionally, phase separation took place in different ways depending on the initial concentration. For low amounts of trans-anethole, we observed emulsification due to the "ouzo effect", with oil droplets in a water-rich solution. At intermediate oil contents, both emulsification and bulk phase separation took place. For high oil concentrations we observed the inverse ouzo effect, with water droplets in an oil-rich solution. The different behaviors were explained by means of the ternary phase diagram of the system together with the assumption that only ethanol evaporates, given that it is the most volatile component. Additionally, we observed the nucleation of surface droplets which self-arrange into lines, one droplet after the other, but also into patterns that looked like branches. Those patterns predominantly appeared in regions where the flow was small, indicating that diffusion was one of the mechanism behind the formation of such patterns.

In chapter 3 we studied the dissolution of two vertically aligned droplets. More specifically, the dissolution of alcohols with different carbon chain lengths. The liquid of the droplets was less dense than that of the host bath, therefore, the dissolution resulted in the formation of a solutal plume that raised from the lower droplet up. When both droplets were of the same liquid, the effect of the rising plume on the dissolution of the upper droplet was small. However, when the liquid of the upper droplet was different than that of the lower droplet, some of the solute dissolved in the plume was transferred into the upper droplet, causing it to grow temporarily before shrinking. Moreover, for the two alcohols with the longest carbon chain, an oscillatory flow around the top droplet was observed. We were able to identify by means of experiments and simulations that the oscillatory behavior was the result of a competition between Marangoni and buoyancy flows. We concluded that the diffusion of solute into the top droplet is not necessary for triggering the oscillatory flow, but it affects the time over which the oscillations occur. Additionally, we were able to corroborate previously found scaling laws between the Sherwood number and the Rayleigh number ($Sh \sim Ra^{1/4}$) and between the Reynolds number and the Rayleigh number ($Re \sim Ra^{5/8}$) taking into account the properties of the lower droplet and the velocity of the plume.

Resumen

Los líquidos multicomponentes (como el café, una limonada o el jabón líquido) son una parte importante tanto de la naturaleza como de la industria de procesos. Están dentro de nuestros cuerpos, en nuestras bebidas y alimentos, en reactores químicos, en medicamentos, en cosméticos o en la tinta con que escribimos, por mencionar algunos ejemplos. El hecho de estar formados por más de un componente hace que estos líquidos presenten una gran variedad de fenómenos. En esta tesis nos limitamos a los líquidos formados por dos o tres componentes. Más específicamente, el enfoque está en los efectos que tienen las propiedades físicas y químicas de los líquidos en el flujo que ocurre dentro de ellos, y viceversa. En otras palabras, el enfoque está en la hidrodinámica físicoquímica de los líquidos multicomponentes.

El capítulo 1 se centra en el líquido multicomponente más simple, un líquido binario. Estudiamos la evaporación de una mezcla de etanol y agua confinada dentro de una celda Hele-Shaw, lo que hace que el sistema sea aproximadamente bidimensional. La volatilidad del etanol resulta en su evaporación preferencial, provocando un gradiente de concentración normal a la interfaz entre el aire y el líquido. Además, la baja tensión superficial del etanol hace que la interfaz sea inestable a pequeñas perturbaciones. Específicamente, se desencadena lo que se conoce como una inestabilidad de Marangoni. Como resultado surge un flujo tangencial a la interfaz y se propaga hacia adentro de la celda en forma de rollos convectivos. En este capítulo, estudiamos experimental y numéricamente la evolución temporal de dichos rollos. Los resultados de ambos enfoques coincidieron satisfactoriamente. Más aún, se realizó un análisis de estabilidad lineal a una versión simplificada de las ecuaciones del modelo numérico. Según los resultados del análisis de estabilidad lineal, existe un número de Marangoni crítico por encima del cual el sistema debería ser inestable. El número de Marangoni en experimentos y simulaciones tienen un valor por encima del valor crítico, lo que concuerda con la presencia de la inestabilidad. Los resultados de las simulaciones y el análisis de estabilidad

lineal coincidieron razonablemente. Por ende, el análisis de estabilidad lineal podría usarse como un primer enfoque para predecir si un sistema binario en evaporación dentro de una celda de Hele-Shaw es estable o no.

En el capítulo 2 estudiamos la evaporación de una mezcla ternaria, a saber, etanol, agua y trans-anetol, también confinada en una celda de Hele-Shaw. Investigamos cómo las variaciones en la concentración inicial de los tres componentes afectan la evolución temporal del sistema. Al igual que para el sistema binario, en el capítulo 2 se observó una inestabilidad de Marangoni, independientemente de la concentración inicial de la mezcla. Sin embargo, además de la inestabilidad de Marangoni, observamos separación de fases. Dicha separación ocurrió de diferentes maneras dependiendo de la concentración inicial. En el caso de una concentración inicial de trans-anetol baja, observamos emulsificación espontánea debido al “efecto ouzo”, en donde las gotas de la emulsión estaban hechas de aceite y sumergidas en una solución con una alta concentración de agua. Cuando la concentración inicial de aceite tenía valores intermedios, ocurrieron tanto la emulsificación como separación de fases de bulto. Cuando la concentración inicial de aceite era alta, observamos el efecto ouzo inverso, con gotas de agua sumergidas en una solución rica en aceite. Los diferentes comportamientos se explicaron usando el diagrama de fases ternario del sistema aunado al supuesto de que solo se evapora el etanol (dado que es el componente más volátil). Además, observamos la nucleación de gotas sésiles en las paredes de la celda de Hele-Shaw. Las gotas se acomodaron espontáneamente en líneas, una gota tras otra, pero también en patrones que parecen ramas. Esos patrones aparecieron predominantemente en regiones donde el flujo era pequeño, lo que apunta a que los mecanismos detrás de la formación de tales patrones son procesos difusivos.

En el capítulo 3 estudiamos la disolución de dos gotas alineadas verticalmente. Las gotas estaban formadas por alcoholes con cadenas de carbono de diferentes longitudes. El líquido en las gotas era menos denso que el líquido en el que estaban sumergidas. La disolución de las gotas resultó en la formación de una columna de líquido con densidad baja (una pluma hidrodinámica). Dicha columna de baja densidad se elevó debido a la fuerza boyante, viajando desde la gota inferior hasta la gota superior. Cuando ambas gotas eran del mismo líquido, el efecto que la columna ascendente tuvo en la disolución de la gota superior fue pequeño. Sin embargo, cuando el líquido de la gota superior era diferente al de la gota inferior, parte del soluto disuelto en la columna de baja densidad se transfirió a la gota superior. Consecuentemente, la gota superior creció en volumen temporalmente antes de encogerse. Además, en los casos

en los que la gota superior estaba hecha por alguno de los dos alcoholes con la cadena de carbono más larga, se observó un flujo oscilatorio alrededor de la gota superior. Pudimos identificar mediante experimentos y simulaciones que el comportamiento oscilatorio es el resultado de una competencia entre flujos causados por el efecto Marangoni y flujos causados por la fuerza boyante. Concluimos que la difusión del soluto en la gota superior no es necesaria para desencadenar el flujo oscilatorio, pero afecta el tiempo durante el cual ocurren las oscilaciones. También pudimos corroborar leyes de escala encontradas previamente entre el número de Sherwood y el número de Rayleigh ($Sh \sim Ra^{1/4}$) y entre el número de Reynolds y el número de Rayleigh ($Re \sim Ra^{5/8}$) teniendo en cuenta las propiedades de la gota inferior y la velocidad de la columna de baja densidad.

Samenvatting

Vloeistoffen die bestaan uit meerdere componenten zijn een belangrijk onderdeel van zowel de natuur als de procesindustrie. Zij bevinden zich in ons lichaam, in ons eten en drinken, in chemische reactoren, in geneesmiddelen, in cosmetica, en in inkt, om maar enkele voorbeelden te noemen. Juist het feit dat deze vloeistoffen bestaan uit meerdere componenten, maakt dat ze zeer diverse fenomenen kunnen vertonen. In dit proefschrift houden we ons bezig met de fysisch-chemische hydrodynamica van binaire en ternaire vloeistoffen, met andere woorden, met de effecten die de natuurkundige en scheikundige eigenschappen hebben op de stroming in de vloeistoffen en vice versa.

De focus van hoofdstuk 1 ligt op de eenvoudigste vloeistof die uit meerdere componenten bestaat, een binaire vloeistof. We bestuderen de verdamping van een ethanol–water oplossing opgesloten in een Hele-Shaw cell, waardoor het systeem quasi-tweedimensionaal is. De hogere vluchtigheid van ethanol resulteert in zijn preferentiële verdamping die een concentratie gradiënt veroorzaakt loodrecht op het grensvlak tussen lucht en vloeistof. Bovendien maakt de lagere oppervlaktespanning van ethanol het grensvlak instabiel bij kleine verstoringen. In het bijzonder wordt er een Marangoni instabiliteit teweeggebracht, wat resulteert in een stroom die tangentieel is aan het grensvlak en zich binnen de Hele-Shaw cell voortzet in de vorm van convectieve rollen. Wij hebben de tijds evolutie van dergelijke rollen zowel experimenteel als numeriek bestudeerd met een vrij goede overeenkomst tussen beide benaderingen. Bovendien hebben wij een lineaire stabiliteitsanalyse uitgevoerd op een vereenvoudigde versie van de model vergelijkingen. Volgens de resultaten van de lineaire stabiliteitsanalyse is er een kritisch Marangoni getal waarboven het systeem onstabiel zou moeten zijn. De Marangoni getallen in zowel de experimenten als de simulaties lagen boven de kritische waarde, in overeenstemming met de aanwezigheid van de instabiliteit. De resultaten van de simulaties en de lineaire stabiliteitsanalyse waren ook in redelijke overeenstemming, wat suggereert dat de lineaire stabiliteitsanalyse gebruikt kan worden als een eerste

benadering om te voorspellen of een binair systeem dat verdampt in een Hele-Shaw cell stabiel is of niet.

In hoofdstuk 2 bestudeerden we de verdamping van een ternair mengsel, zijnde ethanol, water, en trans-anethol, eveneens opgesloten in een Hele-Shaw cel. We onderzochten hoe variaties in de begin concentratie van de drie componenten, de temporele evolutie van het systeem beïnvloedden. Net als bij het binaire systeem uit hoofdstuk 2, werd een Marangoni instabiliteit waargenomen, ongeacht de begin concentratie. Echter vond de fase-scheiding op verschillende manieren plaats, afhankelijk van de begin concentraties. Bij lage hoeveelheden trans-anethol zagen we een emulsie ontstaan als gevolg van het "ouzo effect", wat leidt tot olie druppels in een waterrijke oplossing. Bij tussengelegde oliegehalten vond zowel de formatie van een emulsie als fase scheiding van de bulk plaats. Bij hoge olie concentraties werd het omgekeerde ouzo-effect waargenomen, met waterdruppels in een olierijke oplossing.

De verschillende gedragingen werden verklaard aan de hand van het ternaire fasediagram van het systeem, samen met de veronderstelling dat alleen ethanol verdampt aangezien dit de meest vluchtige component is.

Bovendien zagen we druppels ontstaan aan het oppervlakte die zichzelf rangschikken in lijnen, de ene druppel na de andere, maar ook in patronen die leken op vertakkingen. Deze patronen verschenen voornamelijk in gebieden waar de stroming klein was, wat erop wijst dat diffusie een van de mechanismen was achter de vorming van dergelijke patronen.

In hoofdstuk 3 bestudeerden we het oplossen van twee verticaal uitgelijnde druppels. Specifieker, het oplossen van alcoholen met verschillende koolstofketen lengtes. De vloeistof van de druppels had een lagere dichtheid dan die van het gastheerbad, daarom resulteerde het oplossen van de druppels in de vorming van een oplospluim die vanuit de onderste druppel omhoog steeg. Wanneer beide druppels uit dezelfde vloeistof bestonden, was het effect van de opstijgende pluim op het oplossen van de bovenste druppel gering. Wanneer de vloeistof van de bovenste druppel echter anders was dan die van de onderste druppel, werd een deel van de in de pluim opgeloste stof overgebracht naar de bovenste druppel, waardoor deze tijdelijk groeide alvorens te krimpen. Bovendien werd voor de twee alcoholen met de langste koolstofketen een oscillerende stroming rond de bovenste druppel waargenomen.

Door middel van experimenten en simulaties konden wij vaststellen dat het oscillerende gedrag het resultaat was van een competitie tussen Marangoni en opwaartse stromingen.

Wij concludeerden dat de diffusie van de opgeloste stof in de bovenste druppel

niet noodzakelijk is voor het op gang brengen van de oscillerende stroming, maar wel de duur van het oscillerende gedrag beïnvloedt. Daarnaast konden we eerder gevonden schalingswetten tussen het Sherwood getal en het Rayleigh getal ($Sh \sim Ra^{1/4}$) en tussen het Reynolds getal en het Rayleigh getal ($Re \sim Re^{5/8}$) bevestigen, rekening houdend met de eigenschappen van de onderste druppel en de snelheid van de pluim.

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ronment to PoF. You helped me with my experiments and taught me how to use different devices. Also, you invited me to join the archery group which I enjoyed quite a lot and it was great to go climbing with you. Even more importantly, you listened to me many times, invited me for dinners or had a drink with me. I am sorry I could not join you to Japan. I hope we can meet again soon.

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Diana, we met during the master, I am happy I have met you. We have done many things together, from studying to dancing in Rico Latino, and even carrying a fridge on a bike from the city center to your place. Now we are office mates and we are finishing almost at the same time. Thank you for your friendship. ¡Venga con todo al final del camino!

Olinka, you also started the master with us. Back then with *Diana*, we were a small Latin American group. I am happy to have met you here in Enschede and that we could meet a few times in Germany during our PhDs. I am thankful for your friendship. I know you are soon to be a doctor too, so I wish you the best in the final stretch.

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as persons and as a PhD. I was happy to listen to what you learn so you could consolidate your knowledge. Thank you for recommending me many books and for inviting me to Kangoo Jump, I always enjoyed it. You had to repeat so many times how to say "provecho" in Cantonese, thanks for your patience. I wish you the best on your career whatever path you take. Wherever we go, lets keep in touch.

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Bio

Ricardo Arturo López de la Cruz was born on December 31st, 1991 in San Luis Potosí, Mexico. As a kid, he dreamed of exploring nature like Steve Irwin or David Attenborough. He later changed his mind and stuck with the idea of paleontology for a long period. During secondary and high school his interest wandered into arts and fancied the idea of becoming a graphic designer. However, after learning more about mathematics, chemistry, and physics, his attention got fixed on science. On an evening, when thinking about what bachelor's program to choose, with some advice from his mother, Ricardo decided that physics seemed more interesting than chemistry. In 2010, he enrolled to the program of engineering in industrial physics at the *Instituto Tecnológico de Estudios Superiores de Monterrey* (ITESM). During a seminar at the Department of Physics of his university, Ricardo met Dr. Gabriel Caballero Robledo, with whom he worked for his bachelor's project, performing numerical simulations of granular materials. In the winter of 2014, Ricardo obtained his bachelor's degree and continued to work with Dr. Caballero for 6 more months. In August of 2015, Ricardo started his master's degree in applied physics at the University of Twente under the supervision of Dr. Adeline Pons, Dr. Sissi de Beer, and Prof. Dr. Devaraj van der Meer. His thesis was entitled "Exploring cornstarch suspensions: from a classical to a polymer point of view". During the last three months of his masters, he did an internship

at the University of Chicago with Dr. Nicole James and Prof. Dr. Heinrich Jaeger, where he continued to study cornstarch suspensions. In September of 2017, Ricardo started his doctoral studies at the Physics of Fluids group from the University of Twente. The topic of his Ph.D. was on the physicochemical hydrodynamics of mixtures, under the supervision of Prof. Dr. Detlef Lohse and Prof. Dr. Xuehua Zhang. The result is in the book you have now in your hands or perhaps on your screen. Nowadays, Ricardo still enjoys visiting art museums and looking at the paintings of old and new artists.

Physics of Fluids

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