

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Surface tension-driven flow in soft porous materials

An investigation of the mechanism of capillary flow in soft hydrophilic microchannels

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Gothenburg, Sweden 2018

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ISBN 978-91-7597-776-8

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Doktorsavhandlingar vid Chalmers tekniska högskola
Ny serie nr 4457
ISSN 0346-718X

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Cover:

Schematic drawing of a liquid droplet, water for example, put in contact with an air-filled capillary in a gel; the liquid will spontaneously fill the capillary only driven by surface tension.

Printed by Chalmers Reproservice
Gothenburg, Sweden 2018

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ABSTRACT

Spontaneous spreading of liquids in porous materials is of great industrial relevance and occurs in, for example, diapers, fabrics, paper or paint. Often, it is necessary to manipulate the spreading rate of liquids to result in the desired mass transport, for example to soak up large liquid volumes, as in a diaper. To do this, it is necessary to know the precise mechanism of surface tension driven flow. However, the process is complex and so are the porous materials in terms of both chemical composition and geometry. The mathematical and physical description of the process is often limited to specific cases – for example, the well-known Lucas-Washburn equation describes the speed of a meniscus in capillaries with circular cross-section in a hard material without interconnections. The objective of this thesis is to deepen the understanding of the mechanism with which a liquid spreads in a soft porous material only driven by surface tension. To this end, the liquid dynamics of water and water-based liquids were investigated in various model systems which are similar to porous 3D materials. In an alginate gel, capillaries with circular cross-sections were produced and the spreading rate of water was determined and compared to existing models. Using a method, which involves 3D printing, it was possible to fabricate open channels with rectangular cross-sections in the same alginate gel. The liquid spreading in these channels in geometries of branched channel systems was investigated. The results revealed that the spreading rate in capillaries of circular cross-sections in soft materials was much slower than that anticipated in existing models, which describe hard materials. In open channels of rectangular cross-sections, the presence of side channels slowed down the meniscus in the main channel; the meniscus stopped when it encountered junctions. The stop duration was longer when the side channels were longer, when they were wider, and when their tilting angle was low with respect to the main channel. An analysis of the volume flow indicated that those geometries that had long side channels but are few in number, resulted in faster volume flow. In a porous 3D material, this suggests that the interconnectivity could decrease the volume flow rate. Finally, a calcium alginate gel with straight-aligned pores was produced and characterised as an example of optimal liquid transport. The outcome of this thesis can be used to adjust the geometrical design of porous materials to result in desired liquid transport properties. The stiffness of the material may influence the liquid transport. The thesis also contributes to the discussion on how the liquid takes selective pathways in porous materials.

Keywords: *Capillary flow, capillary action, alginate gel, wetting on soft materials*

LIST OF PUBLICATIONS

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I. Dynamics of capillary transport in semi-solid channels

Johanna Andersson, Anna Ström and Anette Larsson, *Soft Matter* **13**, (2017) 2562–2570

II. Stick–slip motion and controlled filling speed by the geometric design of soft micro-channels

Johanna Andersson, Anette Larsson and Anna Ström, *Journal of Colloid and Interface Science* **524**, (2018) 139–147

III. Structural design of open microchannels for the highest water volume transport

Johanna Andersson, Tobias Gebäck, Anna Ström and Anette Larsson, *Manuscript*

IV. Microstructural, mechanical and mass transport properties of isotropic and capillary alginate gels

Erich Schuster, Johanna Eckardt (later: Andersson), Anne-Marie Hermansson, Anette Larsson, Niklas Lorén, Annika Altskär, and Anna Ström, *Soft Matter* **10**, (2014) 357–66

Papers not included in this thesis

- i. Long-term frozen storage of wheat bread and dough — effect of time, temperature and fibre on sensory quality, microstructure and state of water**

Johanna Eckardt (later: Andersson), Camilla Öhgren, Ayse Alp, Susanne Ekman, Annika Åström, Guo Chen, Jan Swenson, Daniel Johansson, and Maud Langton, *Journal of Cereal Science* **57**, (2013) 125–33

CONTRIBUTION REPORT

- I.** Responsible for writing, planning the experiments and conducting the experiments under supervision and scientific input of the co-authors.
- II.** Drew the geometrical structures of the mould, designed in collaboration with the co-authors. Responsible for performing all experiments, excluding mathematic modelling. Responsible for writing the major part of the manuscript, interpreting the results together with the co-authors.
- III.** Planned and initiated the geometrical design of the moulds, specified the research question. Responsible for conducting all experiments, evaluating the results. Writing the major part of the manuscript, literature research and interpretation of data in coordination with the co-authors. Mathematic modelling and simulations were done by TG.
- IV.** Responsible for writing certain portions of the manuscript and analysis of the results with the co-authors, as well as for the fabrication of alginate gels and solutions.

NOMENCLATURE

γ	Surface Tension (without indices referring to liquid-air)
η	Viscosity
θ	Contact angle
θ^*	Apparent contact angle
κ^{-1}	Capillary Length
ρ	Density
σ	Cutoff length
Δ	Fraction of energy dissipated
ϵ	Aspect ratio h/w of a channel cross-section
A	Area
Ca	Capillary number
dl/dt	Velocity
$\dot{E}$	Energy
F	Force
g	Gravity on earth
G	Elastic (shear) modulus
G'	Storage modulus
G''	Loss modulus
h	Height
l	Travelled distance of a meniscus
l_s	Length of side channel
n	Fitting parameter for material characteristics
P_c	Laplace or capillary pressure
P_e	External pressure
r	Radius
r_W	Wenzel roughness
Re	Reynolds number
t	Time
U	Speed at which the triple line moves
U_0	Fitting parameter for material characteristics
w_s	Width of side channel

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CHAPTER 1

INTRODUCTION

In our daily life, as well as in the industry, we constantly make use of the autonomous movement of liquids in porous materials. Wiping away spilled liquids, the capillary flow in a diaper, the printing on paper and the liquid uptake in wound patches are all based on surface tension-driven flow. Other examples are the movement of liquid in drying paint or the capillary bridges in a sand castle that make it stand as it was built. All these systems can be optimised if the phenomenon of surface tension-driven flow is known in detail, which explains why it has been studied for a long time. However, the process is complex and so are the porous materials in terms of both the chemical composition and geometry. The role of surface tension-driven flow is reflected by the following statement made by Karin Glasmästar at Mölnlycke Health Care, a wound care company:

‘A wound care swab put in contact with a bleeding wound can easily absorb the blood. In order to improve product properties there is a need to understand the influence of capillary forces.’

Further, it has been discussed in diverse fields, as expressed by the following quote by Mats Stading at the Research Institutes of Sweden (RISE):

‘In porous food products the spontaneous liquid uptake is especially important during food oral processing. When we masticate and process a food, saliva enters the progressively smaller pieces to finally form a bolus suitable to swallow. During the process we perceive textural changes (consistency) as well as exchange of volatiles (aroma and taste), which both are strongly influenced by the saliva flow in a porous food product.’

In order for surface tension-driven flow to occur, or also referred to as capillary flow, two main conditions must be fulfilled. First, the liquid has to wet the surface of the capillary, that is, when it has a contact angle of less than 90° with the solid. Second, the capillary diameter must be sufficiently small [1], which is the case when it is much smaller than the capillary length [2]; this describes the balance between gravitational forces and capillary effects [3], which is explained in section 2.1. Connecting

a thin glass tube with a water reservoir results in the rise of the water level up to an equilibrium height. In a vertical capillary, this height has been described by [Jurin](#) as early as in 1718; the equation is still used today and is known as *Jurin's height* [4]. It balances hydrostatic pressure arising from the liquid mass and capillary pressure and is inversely proportional to the capillary radius. However, only knowing the final height does not provide information on how fast the liquid actually travels during the process. Approximately one century later, [Lucas](#) and [Washburn](#) independently published a mathematical description of the dynamics a liquid undergoes in a capillary tube of arbitrary inclination [5, 6]. The law encapsulated in this description, referred to as the Lucas-Washburn (LW) equation, combines the capillary pressure caused by a curved meniscus and the opposing Hagen-Poiseuille flow, which is the pressure loss due to the viscosity of the liquid. Accordingly, the position of the meniscus is proportional to the square root of elapsed time. This relationship has been confirmed by numerous studies in microchannels [1, 7–10] and nanochannels [11–13]. Today, another century later, an effect referred to as *wetting ridge* has increasingly been attracting the attention of researchers. According to this effect, a droplet on a soft substrate will deform the underlying solid at the three-phase contact line due to the vertical component of the surface tension [14–18]. The effect significantly increases the time of establishment of the equilibrium contact angle of the droplet [19]. The viscous dissipation within the solid has been proposed to slow down the moving meniscus in a channel if the capillary wall is a soft solid compared to a hard material, but has only been modelled mathematically and not been experimentally proven [20]. Despite the anticipated large impact on the surface driven flow in a variety of different products, this delay caused by the modulus of the capillary walls has not been experimentally confirmed thus far.

The liquid dynamics in single capillaries can usually be related to the dynamics of an entire 3D porous structure. Often LW is used to describe the flow in porous materials, where the material is modelled as a bundle of straight capillaries with an effective capillary radius [21, 22]. However, the material's pores usually have an entirely different shape and cannot be compared to straight capillaries without interconnections. The pores can be the voids between packed beads, such as in soil or paint, or the porous material can comprise fibres, isotropically or anisotropically ordered, like in paper, where the pores adopt an entirely different shape. It has been shown that water spreads differently on paper, depending on the direction of the fibres [23]. There are other modelling approaches as well, which describe the flow in one phase, such as Darcy's law, applied for surface tension-driven flow in porous materials. Further, multiphase flows are another approach, that, for example, employ a more generalised form of Darcy's law with mass-balance equations; in addition, an unsaturated flow model can be used as a derivative of the multiphase flow [24]. However, these models do not describe the capillary force causing the liquid to flow into single capillaries, as the LW equation does. These models could be advantageous for the flow description of an existing porous material and the prediction for the dynamics of other liquids, but the models are not suitable for optimising the porous material in order to tailor mass transport. It has been reported that during liquid imbibition, some pores are filled faster while other pores

are by-passed [25–27], and entrapment of air may occur [28]. In this manner, the liquid takes a selective pathway. From the LW equation it becomes clear that large capillaries are filled fast, while smaller ones are filled at a slower speed, despite the driving capillary pressure being higher in smaller diameters. Similarly, in porous materials, it could be assumed that larger pores are filled first, and then smaller pores drain the larger ones. However, some authors anticipate that smaller pores are filled first in a porous system [29–31]. Owing to these different actions, it is not easy to predict the pathway of a liquid in a porous structure. The experimental investigation of such flow mechanisms is challenging. This is partially due to the fact that the process is fast and often porous materials are not transparent; thus the tracking of single menisci is only possible on the surface. Another difficulty might be that many porous materials swell. Therefore, this thesis investigates model systems in which the liquid can be easily tracked to allow for determination of flow and identify pore geometries that facilitate spreading of liquid. In this thesis, the objective is to answer the following research questions:

- Do the dynamics of liquid spreading in soft channels follow the LW model? And how does the velocity, termed as spreading rate in this thesis, in soft capillaries relate to the transport in capillaries with stiff walls?
- What influences a penetrating liquid to take a selective pathway in a porous material, for example in paper, and leave other channels unfilled?
- How does the geometrical design of the pores facilitate enhanced liquid volume flow driven only by capillary forces?

The study does not include the effect of chemical modifications of the porous material and focusses on water-based wetting liquids with Newtonian flow behaviour. It is done on horizontal capillaries and does not include capillary rise. Figure 1.1 summarises the experimental outline of this thesis. A model system is created with one straight capillary of micrometre size and circular cross-section in a soft material. The dynamics of spontaneous liquid transport are recorded and described. The results are compared to the LW model, and other potential factors influencing the dynamics of the liquid are evaluated. However, porous materials usually do not consist of straight capillaries, but have complex networks of interconnected capillaries. Therefore, I have selected to systematically investigate a model system containing branched channels. This was done in open and soft channels with rectangular cross-sections. The water-spreading rate in the main channel was characterised depending on the existence of side channels on either one or two sides and how their tilting angles influenced the flow. Further, the number, width and length of the side channels was varied to study the effect on the spreading rate in the main channel. The volume flow in the entire branched channel system was measured and related to the geometrical structure. Finally, a porous capillary alginate gel with a large number of straight cylindrical capillaries was created, which is believed to facilitate mass transport, and possible applications are discussed.

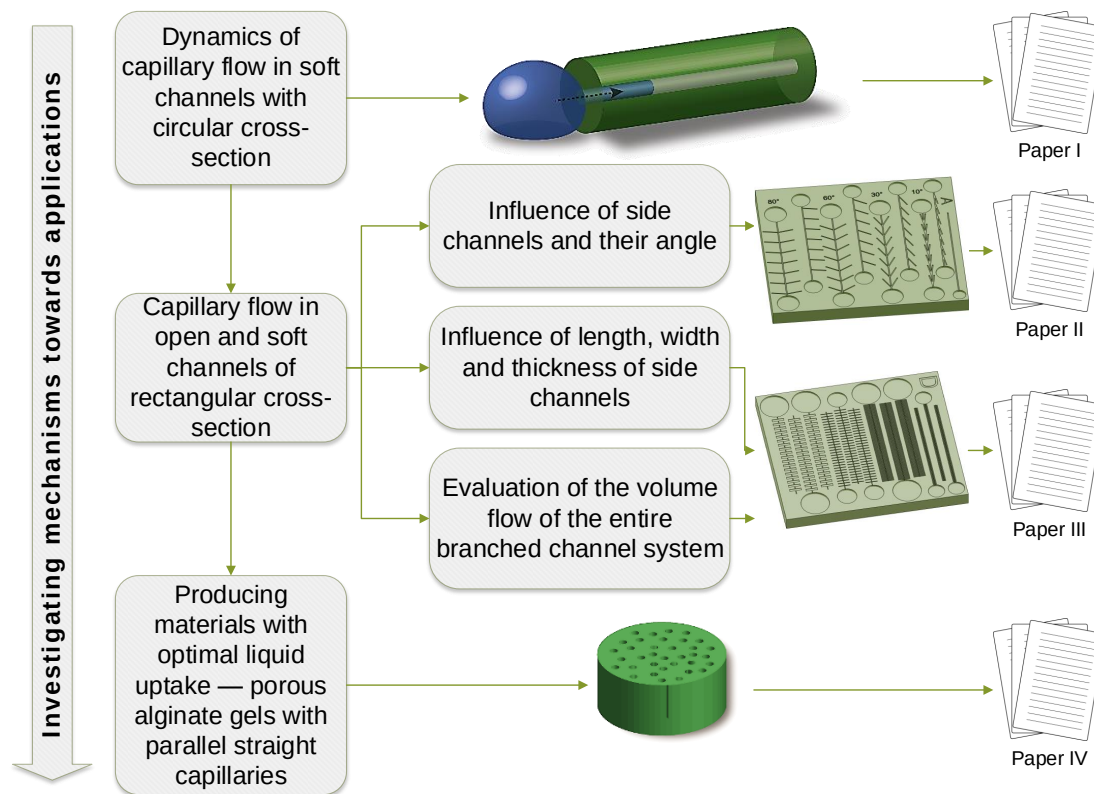


Figure 1.1: Experimental outline of the thesis.

CHAPTER 2

WETTING AND CAPILLARY FLOW

2.1 WETTING

For capillary flow to occur, the liquid needs to wet the solid. If not, no spreading will occur. To quantify the degree of wetting, the contact angle, θ , is often measured, which is formed by a droplet deposited on a flat solid at the contact line between solid, liquid and gas (see Figure 2.1). If the liquid completely covers the surface, full wetting occurs and $\theta = 0^\circ$. In a capillary with a circular cross-section, the meniscus would form a perfect half sphere when gravity is neglected. If $0^\circ < \theta < 90^\circ$, then partial wetting occurs and if $\theta > 90^\circ$, the liquid does not wet the surface [3]. If the contact angle with water is very large, usually above 120° , the surface is referred to as superhydrophobic, as described later. A hydrophobic surface can be realised by the chemical character of the solid material in that a very hydrophobic substance is used or by the topological structure of the solid surface, which will be further described in section 2.1.3. Figure 2.1(d) depicts the forces acting on the three-phase contact line, that is, the surface tensions between the different phases, γ_{LG} , γ_{SL} and γ_{SG} , where the subscripts S, L and G stand for the solid material, the liquid phase and the gas phase, respectively. Young's equation describes the equilibrium contact angle, where the resultant force is zero and no spreading occurs [32]:

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta. \quad (2.1)$$

This illustrates that the contact angle is a result of the the surface tension, which is the free energy of the surface and is further described in the next section.

2.1.1 SURFACE TENSION

Surface tension does not only describe a single phase, but is actually an interfacial tension of a material in contact with another material. It is a measure of how strong the intermolecular forces are in the bulk of a material in respect to the interaction of the molecules of another material [32]. One can also refer to the relation of cohesive and adhesive forces. High surface tension stands therefore for high intermolecular forces,

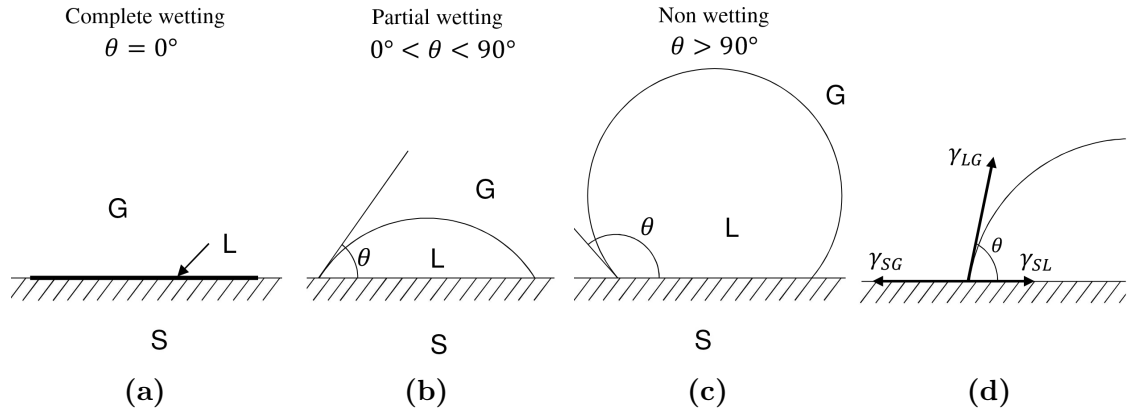


Figure 2.1: A drop deposited on a surface can adopt different shapes depending on the surface tension in the interfaces between the phases liquid (L), solid (S) and gas (G). (a) A droplet is (a) considered complete wetting when $\theta = 0$, (b) partial wetting when $0^\circ < \theta < 90^\circ$, (c) non wetting when $\theta > 90^\circ$. (d) illustrates the forces acting on the three-phase contact line.

that is, high cohesive forces, and less interaction with the surrounding phase, that is, less adhesive forces. In physical terms the surface tension is equal to the surface free energy expressed as a force per unit length N/m or equally as the surface energy per unit area J/m². Pure water in air has, for example, a relatively high surface tension ($\gamma = 72$ mN/m at 25°), which can be explained by its strong hydrogen bonds between the water molecules. If a small amount of surfactant is added, the value significantly drops since surfactants enrich at the interfaces, due to their molecular structure with a polar and non-polar part [32]. The surface tension is reduced while all surfaces are covered with surfactants, and when saturation of surfactant molecules is reached, the number of surfactants at the interface stays the same upon adding more surfactant. This is defined as the critical micelle concentration. The addition of electrolytes increases γ somewhat and organics slightly decrease the surface tension [32].

2.1.2 CONTACT ANGLE

As introduced above, the contact angle is a result of the surface forces of the involved phases. It is a sensitive and relatively simple method to characterise the first molecular layers of a material. A distinction between the static and dynamic contact angles is useful since the time it takes to establish the equilibrium contact angle depends on the nature of the three involved phases. In this context, contact angle hysteresis is a term often used referring to the difference of a larger advancing θ_{ad} and a lower receding θ_{re} contact angle. Just depositing a droplet on a surface will always result in a value between θ_{ad} and θ_{re} [3, 33]. It is useful to measure both values, which is an indication of how rough the surface is, and larger differences between θ_{ad} and θ_{re} are an indication of rougher materials [33]. More comprehensive descriptions of how moving contact angles form and behave can be found elsewhere [34, 35].

2.1.3 WETTING ON TEXTURED SURFACES

The contact angles on a textured surface and a perfectly smooth surface of the same material can vary. Since the difference between the advancing and receding contact angle is higher on textured surfaces than on smooth ones and an apparent contact angle θ^* on a rough surface can be defined [36]. To account for the difference in the contact angle caused by the topography, Wenzel introduced a roughness factor, r_W , (also termed *Wenzel roughness*), defined as the ratio between the true surface area compared to the apparent one [37]:

$$\cos \theta^* = r_W \cos \theta. \quad (2.2)$$

If $r_W = 1$, then $\cos \theta^*$ becomes $\cos \theta$, which implies a perfectly smooth surface. For rough surfaces, r_W has a value larger than one. Equation (2.2) reveals that surfaces with roughness and $\theta < 90^\circ$ will appear as more hydrophilic, whereas rough surfaces with $\theta > 90^\circ$ will appear more hydrophobic. Two aspects must be noted here: First, that Wenzel roughness is not an absolute measurable value and it can only be used as a comparison between surfaces. Second, Equation (2.2) tends to be wrong when very high contact angles are reached. On smooth chemically hydrophobic surfaces, the maximum value a contact angle can reach is $\theta \approx 120^\circ$ [38, 39]. If a surface with the same chemical composition is rough, it can exhibit contact angles up to almost 180° [33, 40]. These high contact angles can only be realised if air is trapped on the rough surface, thereby making it more hydrophobic. In nature, this phenomenon can be seen, for example, on the leaves of the plant *Lotus* or on *Salvinia*, which have a hairy surface [41].

When their leaves are submerged into water, air pockets remain on the surface of the leaves indicated by a silvery shine. Hence, Cassie and Baxter developed the Wenzel equation further to account for two different contact phases [42]:

$$\cos \theta^* = f_1 \cos \theta - f_2, \quad (2.3)$$

where

$$f_1 = \frac{\text{area in contact with liquid}}{\text{projected area}}, \quad f_2 = \frac{\text{area in contact with air}}{\text{projected area}}. \quad (2.4)$$

The two states are illustrated in Figure 2.2, where (a) is a droplet on a rough surface without air pockets, as described by Wenzel and Equation (2.2) and (b) shows a droplet with trapped air and solid parts at the contact line, which is described by Cassie and Baxter and Equation (2.3). In the case of no trapped air, f_1 is equal to the Wenzel roughness r_W ; then f_2 becomes zero and the equation becomes Equation (2.2). The smaller the contact with the solid parts, the higher the resulting contact angle. In this manner, it is possible to fabricate superhydrophobic surfaces. Plants use these surfaces for self-cleaning purposes, since a droplet rolling off the surface takes up dust, spores or bacteria [41]. In the same manner, surfaces can be artificially produced, with self-cleaning capability [33]. For example Choi and Kim showed that it is possible to fabricate such surfaces with very small solid content in contact with the droplet [43].

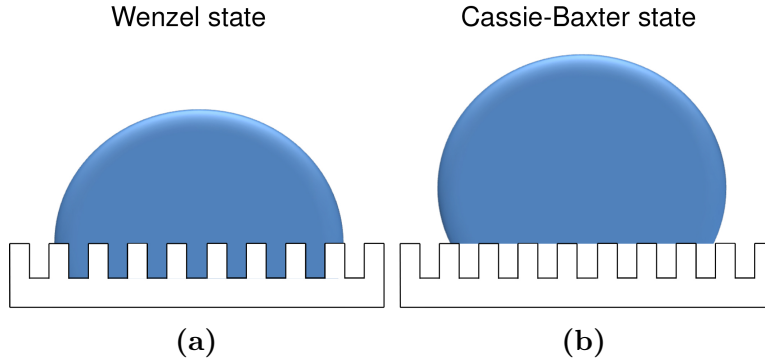


Figure 2.2: A water droplet sunk into the structure representing the Wenzel state (a) and repelled by the structure showing the Cassie-Baxter state (b).

Using microfabrication techniques, cones are produced on a surface where only the tip is touched by the droplet. Then, very little force is needed to move the droplet over such surfaces, thereby indicating that a droplet can easily roll off at low tilting angles.

2.1.4 WETTING ON SOFT SURFACES

Thus far, the emphasis in this chapter has been placed on hard surfaces despite the existence of a large number of soft materials in nature and in applications. It has been shown that droplets behave differently when they are deposited on a viscoelastic material compared to a hard surface [14, 16–19, 44]. For example, the contact angle needs a significant longer amount of time to reach equilibrium on a soft solid compared to a stiff material [19] (see Figure 2.3(a)).

A droplet advancing on a soft surface of polydimethylsiloxane (PDMS) is shown to exhibit a stick-slip motion, in that it repeatedly stops and suddenly continues to flow [44]. This behaviour has been attributed to a deformation, termed as *wetting ridge* of the soft solid at the contact line. The deformation is caused by the vertical component of the surface tension γ_{LG} (see Figure 2.3(b)). Although the phenomenon has been known for a long time, it has recently been the subject of intensive investigations aided by advanced analysing techniques, which experimentally can visualise the deformation [16–18, 45–48]. It has been discussed whether or not the contact angle increases or decreases with decreasing substrate stiffness, which also might be influenced by droplet size and time [45]. The spreading of a droplet on soft surfaces is slowed down as the wetting ridge moves accordingly, thereby causing additional energy dissipation [17, 45]. The height of the wetting ridge is inversely proportional to the stiffness of the substrate [18, 45]. The energy dissipation appears to be dependent on the rheology of the solid. On purely elastic solids, which act like a spring, the work done on the wetting ridge is restored immediately after the passage of the moving liquid front as the solid relaxes, no net work is done and no energy is dissipated [15]. On purely viscous solids, which act like modelling clay, all energy is dissipated. However, since most semi-solids are

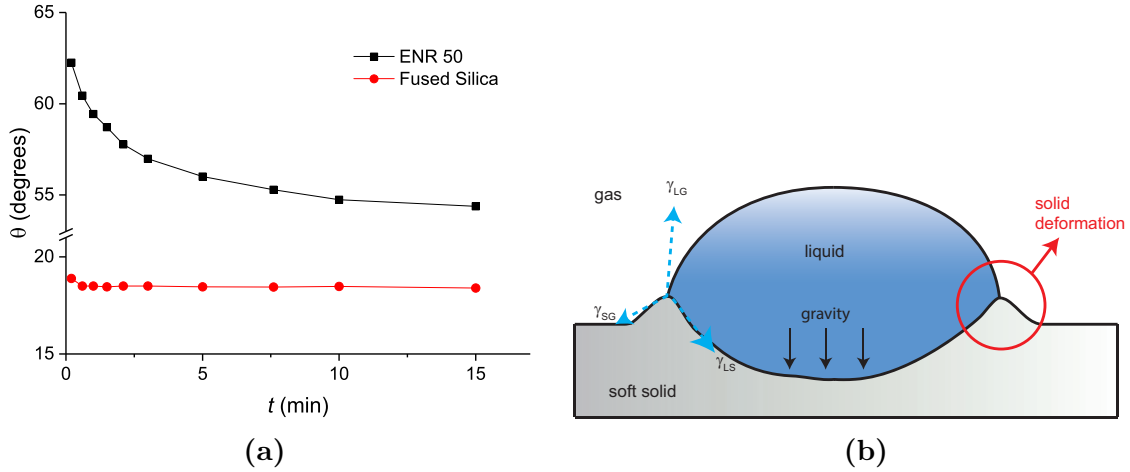


Figure 2.3: (a) Example of the evolution of the dynamic contact angle on a rigid substrate (fused silica, ●) compared to a soft substrate (epoxidised natural rubber, ENR 50, ■) over time. On silica, the equilibrium contact angle was attained after 20 s compared with ENR, which stabilised after 1 h at $\theta = 53^\circ$ (adapted with permission from reference [19]). (b) Schematic of a liquid droplet deforming a soft substrate.

viscoelastic, a fraction of the energy expended, $\dot{E}\Delta$, will be dissipated, as stated in [15]:

$$\dot{E}\Delta \approx \frac{\gamma^2 U \Delta}{2\pi G \sigma}, \quad (2.5)$$

where U is the speed at which the triple line moves, G is the elastic (shear) modulus, and σ is a cutoff length below which the solid no longer behaves in a linearly elastic manner (which is typically in the range of a few nanometres for elastomers [14])[15].

2.2 CAPILLARY FLOW IN SINGLE CAPILLARIES

In this thesis, the term *capillary* usually refers to a tube with a circular cross-section, and the term *channel* refers to a rectangular cross-section. With the term *pores* the voids in porous materials are described, if not stated otherwise.

If a liquid has sufficient adhesive forces with the wall of a capillary, it will enter the capillary and can rise against gravity. The liquid forms a meniscus at the contact line with air and has a concave shape when the liquid wets the walls. The Young-Laplace equation is used to describe the pressure difference created by the shape of the meniscus, the capillary pressure. It is the difference between the pressure in the non-wetting phase and the pressure in the wetting phase:

$$P_c = \frac{2\gamma \cos \theta}{r}. \quad (2.6)$$

As the capillary radius reduces, this pressure difference increases, that is, capillary forces are higher in smaller capillaries. In the case when the contact angle $\theta < 90^\circ$, where $\cos \theta$

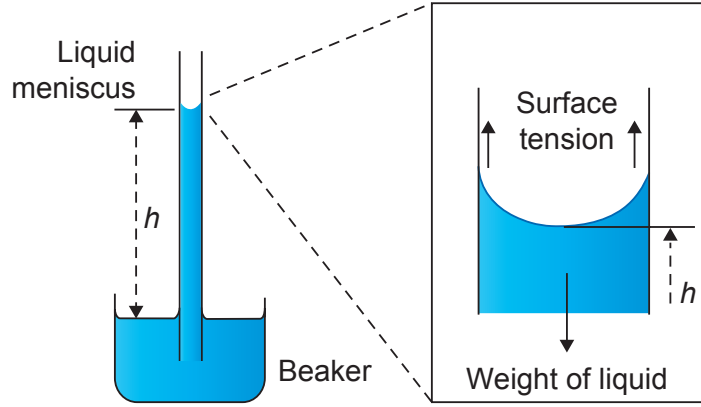


Figure 2.4: Schematic of capillary rise in a single vertical capillary.

is positive, the liquid can spread in the capillary; and when $\theta > 90^\circ$, capillary depression occurs (the meniscus is lower than the outer liquid level). If $\theta = 90^\circ$, then $\cos \theta = 1$ and neither capillary flow nor capillary depression occurs. For a vertical capillary, the rising height is limited by the hydrostatic pressure:

$$P_h = \rho gh, \quad (2.7)$$

where ρ denotes the density of the liquid, g is the gravitational acceleration on earth and h is the rising height, as depicted in Figure 2.4. The beaker is assumed to be infinitely large so that the liquid level is constant. When the process is in equilibrium, the capillary pressure (2.6) is balanced by the hydrostatic pressure (2.7) and we obtain the following equilibrium height or *Jurin's height* [4, 38]:

$$h = \frac{2\gamma \cos \theta}{\Delta \rho g r} \approx \frac{2\gamma \cos \theta}{\rho g r}, \quad (2.8)$$

where the density difference is between the two phases of liquid and gas, and since usually $\rho_{gas} \ll \rho_{liquid}$, only the density of liquid is considered. The equation indicates that the liquid can rise higher in smaller capillaries, with smaller contact angles and higher surface tension between the liquid and the replaced phase, mostly air (γ_{LG} is replaced by γ).

2.2.1 THE LW MODEL

Simply knowing the equilibrium height of a liquid in a capillary does not describe the speed at which the liquid flows into the capillary. If the driving force, the capillary force, F_c , is balanced with the forces from hydrostatic pressure, F_h , from viscosity, F_v , and inertia, F_i , the following equation is obtained [6, 49, 50]:

$$F_c = F_h + F_v + F_i, \quad (2.9)$$

and since $F = P \cdot A$ for a circular cross-section, we obtain

$$2\gamma \cos(\theta) \pi r = \rho g h(t) \pi r^2 + 8\pi \eta h(t) \frac{dh(t)}{dt} + \pi r^2 \rho \frac{d}{dt} \left(h \frac{dh(t)}{dt} \right), \quad (2.10)$$

where η is the dynamic viscosity of the liquid. Inertia is only relevant in the very beginning of the capillary and can be neglected for straight capillaries. When a horizontal capillary is considered (apart from F_i also neglecting F_h), renaming h to l , solving and integration of (2.10) under the assumption of a static contact angle leads to the widely used LW equation, which was developed independently by [Lucas](#) and [Washburn](#):

$$l^2 = \frac{\gamma r \cos \theta}{2\eta} \cdot t, \quad (2.11)$$

where l is the travelled distance [5, 6, 51]. Due to the viscous forces, F_v , described by the Hagen–Poiseuille equation, the liquid decreases its speed over the travelled distance, which is proportional to the square root of time $l \propto \sqrt{t}$ or $l^2 \propto t$. The Hagen–Poiseuille equation implicitly indicates that the flow profile for a Newtonian liquid has the same parabolic shape as in larger pipes if there is no slip on the walls [51]. To know the limitations of these equations, authors often use a variety of numbers to estimate which forces prevail, such as the Reynolds number, Re , the capillary number, Ca , and the capillary length, κ^{-1} . The Reynolds number is an estimation of inertial to viscous forces and given by

$$Re = \frac{\text{inertial forces}}{\text{viscous forces}} = \frac{dl}{dt} \frac{\rho D}{\eta}, \quad (2.12)$$

where D is the hydraulic diameter. Given the large surface-to-volume ratio, which is needed for capillary flow to occur, low Reynolds numbers can be expected where viscous forces dominate over inertial forces [52]. In addition, capillary flow is typically laminar ($Re_{crit} \approx 2300$, [53]). In a horizontal capillary, the capillary pressure is mostly opposed by the viscous drag, and the two forces can be compared with the capillary number [3]:

$$Ca = \frac{dl}{dt} \frac{\eta}{\gamma}, \quad (2.13)$$

To estimate below which size capillary flow can be expected, the capillary length is a good estimation and is given by [3]:

$$\kappa^{-1} = \sqrt{\gamma / \rho g}. \quad (2.14)$$

For pure water at 20°C, the capillary length is 2.7 mm. For example, this shows that when determining the contact angle of water on a surface, the water droplet should be considerably smaller than 2.7 mm so that gravitational forces can be neglected.

2.2.2 MODIFICATIONS OF THE LW MODEL

As mentioned earlier, inertial forces are not accounted for in the classical LW model. Therefore, [Bosanquet](#) developed the equation further, letting

$$\frac{8\eta}{r^2\rho} = a, \quad \frac{P_e r + 2\gamma \cos \theta}{r\rho} = b \quad (2.15)$$

yields the following equation

$$l_2^2 - l_1^2 = \frac{2b}{a} \left\{ t - \frac{1}{a}(1 - e^{-at}) \right\}, \quad (2.16)$$

where $l_2^2 - l_1^2$ denotes the travelled distance and P_e is an externally applied pressure [25, 54, 55]. Initially, when $a \cdot t \ll 1$, no external pressure is applied and l_1 is set to zero, via a Taylor series, Equation (2.16) becomes

$$l^2 = \frac{2\gamma \cos \theta t^2}{r\rho}, \quad (2.17)$$

which describes flow in the inertial regime, where the distance is directly proportional to the time [30]. Subsequently, the dynamics are governed by viscous friction and adopt the form of (2.11).

2.2.3 CAPILLARY FLOW IN OTHER GEOMETRIES

Often the LW model is even used to calculate capillary flow in a porous medium. The porous material is then considered as a bundle of straight-aligned capillaries with an effective radius. However, the success of such calculations will also be determined by the material's characteristics. Many researchers reported that the liquid follows $l \propto \sqrt{t}$ [7, 21] but some found diverging behaviour, partially dependent on the moisture content of the material [56, 57]. Moreover, it has been observed that the liquid penetrates some pores in a porous system while by-passing others and in that manner taking a preferred pathway [27, 29, 30]. Determining the radius and the contact angle can be challenging if a flat surface of the material cannot be produced. Measuring the flow in the material and using (2.11) results in the combination of $r \cdot \cos \theta$. [Marmur and Cohen](#) found a solution to calculate r and $\cos \theta$ independently by determining the capillary rise in vertical experiments [21]. [Hamraoui and Nylander](#) solved the issue by introducing a retardation coefficient, which accounts for principal forces (other than inertia) and other contributions in a porous system [22].

In the field of microfluidics, rectangular cross-sections are usually achieved due to easier fabrication. In such channel geometries, the liquid often fills the corners before it fills the centre of the channels. This behaviour is often termed as *wicking fingers* or as a *precursor* [8, 58, 59]. These precursors can be much faster than the main meniscus, and in vertical capillaries, the presence of precursors can lower the equilibrium height

[58]. For open rectangular channels, the aspect ratio together with the contact angle determines if a liquid enters the channel:

$$\cos \theta > \frac{1}{1 + 2\epsilon}, \quad (2.18)$$

where ϵ is the aspect ratio of the capillary height to width h/w [58]. The lower the walls compared to the thickness of the channel, the smaller its contact angle needs to be in order to enter the channel. The $l \propto \sqrt{t}$ behaviour is also expected for squared channel geometries [10, 11]. Other channel geometries have been studied – for example, [Feng and Rothstein](#) who investigated angled fin-like-structure pairs in PDMS which exhibited capillary flow in one direction but not the other, depending on the surface tension, which was varied by changing the ratio of isopropyl alcohol to water [60]. A similar study was conducted by imitating the surface of the Texas horned lizard as a model for a biomimetic ‘liquid diode’ where the applied liquid spreads more in one direction than the other [61]. Other researchers focused on attempting to optimise the shape of the capillaries for increased flow by a repeated diverging and converging diameter of a capillary [62, 63]. However, these studies are undertaken only in one capillary and do not take interconnectivity into account.

2.2.4 CAPILLARY FLOW IN SOFT MATERIALS

Since droplets deform a soft solid at the contact line with the solid, it can be assumed that the capillary flow, which is driven by surface tension, is influenced by a deformation of the capillary walls. [Shanahan and Carré](#) investigated this by modelling and estimated that a wetting ridge is formed if a capillary tube has a Young’s modulus of a few MPa [20]. Accordingly, the wetting ridge moves with the contact line and creates a viscous dissipation within the solid [20, 45]. The force needed to displace the wetting ridge in a soft capillary of circular cross-section depends on the speed U and can be written as

$$F_v = \frac{\gamma^2 r}{G\sigma} \left(\frac{U}{U_0} \right)^n, \quad (2.19)$$

where σ has the same meaning as in Equation (2.5), G is the shear modulus of the soft solid, and n and U_0 are fitting parameters depending on the material characteristics [20]. The softer the material, the higher the viscoelastic braking force. If inertia and hydrostatic pressure are disregarded in Equation (2.10), the balance of forces is now given by

$$2\gamma \cos \theta \pi r = 8\pi \eta l \frac{dl}{dt} + \frac{\gamma^2 r}{G\sigma} \left(\frac{1}{U_0} \frac{dl}{dt} \right)^n. \quad (2.20)$$

The equation can be solved numerically, which is described in Paper I. To the best of the author’s knowledge, before this thesis the equation has not been investigated experimentally. The viscoelastic energy dissipation in the material can prevail over viscous friction F_v and control the spreading rate [20].

CHAPTER 3

POLYSACCHARIDE GELS

A gel is a viscoelastic material with both elastic (solid) and viscous (liquid) properties [64]. Polysaccharide gels are composed of cross-linked polymer chains, which comprise glycosidic-linked monosaccharides. Most polysaccharides are water-soluble and either neutral or anionic, often due to the presence of anionic groups ($-\text{COO}^-$ or $-\text{SO}_3^-$ like in alginates or carrageenans, respectively) [65]. The links between the polymer chains can be either of chemical nature, where covalent bonds are formed, or physical with other interactions, such as ionic interaction, hydrogen bonds or entanglements. For example, thermo-reversible gels can be formed with agarose. Gelation can be induced by multivalent cations in alginates or pectins [64]. The strength of a gel or the shear modulus G , is related to the number of elastically active network chains, which in turn depends on the degree of cross-linking and the network functionality or the potential number of cross-linking points per chain [66].

Since physical gels are used in this work, only physically cross-linked gels are described in the following account. Unlike covalent bonds, the number and position of physical cross-links or junction zones fluctuate with time and temperature [66]. The gel formation can be measured with small deformation rheometry. The storage modulus G' is the stored energy in a system and represents the elastic portion, and the loss modulus G'' represents the viscous portion and measures the energy dissipated as heat [67]. Prior to gel formation, G' is initially lower than G'' , but as the gel is formed both moduli increase. The cross-over where G' becomes greater than G'' , which is occasionally associated with the gelation point [66].

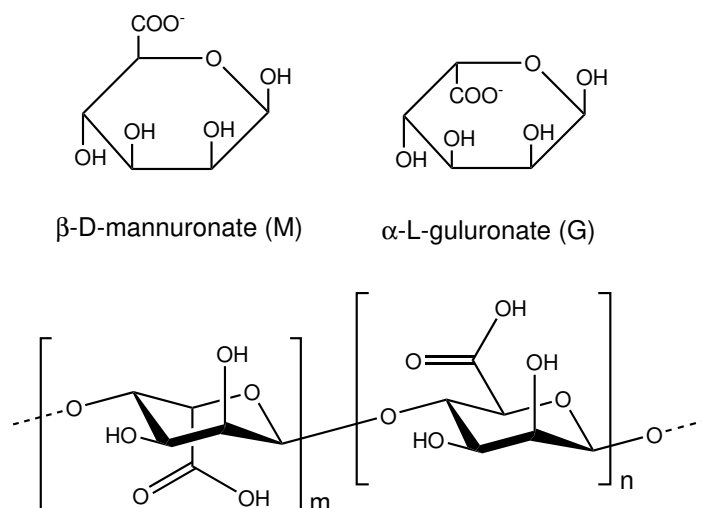


Figure 3.1: Alginate comprising (1 $\rightarrow$ 4) linked β -D-mannuronate (M) and α -L-guluronate (G) monomers which are covalently linked, as shown in the lower part.

Thereafter, G'' occasionally passes through a maximum, then G' and G'' reach a plateau and should be independent for a wider range of frequencies in order for the material to be defined as a strong gel [66].

ALGINATE is a negatively charged polysaccharide derived from marine brown algae and is abundant in nature [68]. Apart from its use as thickening agent in the food industry, calcium alginate gels are highly biocompatible, which makes them suitable for biomedical applications [69], such as tissue engineering [70, 71] and wound dressings for facilitating wound healing [72]. Alginates are linear copolymers of (1 $\rightarrow$ 4) linked β -D-mannuronic acid (M) and α -L-guluronic acid (G) (Figure 3.1) [73]. The ratio between M and G-units varies with organism, season and growth conditions and from which part of the seaweed they have been extracted [73]. A gel is formed through ionic interactions in which multivalent cations, such as calcium, link the G-units of the polymers and form an egg-box model [73, 74]. Therefore, the final strength of the gel is dependent on the content of G-units in the polymer but also on the amount of cross-linking ions. However, it has also been shown that the arrangement of G-units determine the mechanical properties of the final gel, since larger blocks of G-units are needed to form a load-bearing junction [73, 75]. Since gel formation occurs rapidly, simply adding the ions leads to lump formation. There are two common methods to introduce the ions into an alginate solution, referred to as internal gelation and external gelation and these are explained hereafter.

INTERNAL GELATION METHOD Using this method, the cation source is introduced in an inactive form, like an insoluble salt such as calcium carbonate or calcium sulfate. It is solubilised by decreasing the pH, usually using the slowly hydrolyzing glucono-delta-

lactone (GDL) which releases protons solubilising the ion source, which then cross-links the polymer chains [73, 76]. In this manner, a visually homogeneous gel is usually achieved [73].

EXTERNAL GELATION METHOD In this method, the ions are not directly mixed with the polymer solution but diffuse into it and form a gel. This can be done by dripping an alginate solution into a calcium ion solution. The size of the resulting beads can be tailored by the shape of the nozzle and the viscosity of the alginate mixture [73] or by immersing the alginate solution in a dialysis membrane into a calcium chloride bath. Another method for forming externally set alginate gels is to pour the alginate solution into a beaker and then pouring an ion solution on top of it after a membrane is created by spraying the ion solution on the alginate surface. The cross-linking ions will then diffuse into the alginate and form a gel. Straight vertical capillaries are formed using this method, provided that the alginate is anchored to the wall [70, 77, 78]. The cause of this phenomenon is suggested to be either a result of a movement during the cation exchange resembling a Rayleigh–Bénard convection [78, 79] or spinodal decomposition with an anisotropic stress distribution in the gel [80].

CHAPTER 4

EXPERIMENTAL DESIGN AND METHODS

This chapter provides an overview of the experimental design and methods used. A summary is provided above in Figure 1.1 and links to the respective papers. The purpose of this chapter is not to describe everything in detail but to highlight the important methods used in this thesis. Precise descriptions of the methods can be found in the respective papers.

4.1 STRAIGHT CAPILLARIES IN SOFT SOLIDS WITH CIRCULAR CROSS-SECTIONS

Paper I describes how a method has been implemented, which combines the model system of a horizontal straight capillary of circular cross-section with a soft material. It is based on polymeric gels and includes creating a capillary of circular cross-sections of 180, 250, 350 and 630 μm in diameter in the gel. In the transparent gels, it was possible to track the wetting liquid over several centimetres in a single capillary in calcium alginate gels.

To create such a capillary, which is schematically illustrated in Figure 1.1, calcium carbonate (CaCO_3), and glucono delta-lactone (GDL) were added to an alginate solution in a stoichiometric ratio to the G-units of the polymer [76]. The liquid was subsequently siphoned in a 1 ml disposable syringe containing a nylon string, which formed the capillary and was gently removed directly before the measurement. The gel resulted in an alginate concentration of 1.7% (w/w) and was set to form for 24 hours. By changing the thickness of the string, the capillary diameter was tailored. After gelation, the tip of the syringe was cut off while the gel remained inside. Then, the capillary in the gel was horizontally connected to a with methylene blue coloured liquid droplet resting on a surface. The liquids tested were Milli-Q water, a sucrose solution (21.4% w/w) and an hydroxyethyl cellulose (HEC) solution (0.1% w/w). The liquid spontaneously flowed into the air-filled capillary and was recorded with a camera (Casio EX-ZR300, Japan)

with up to 120 fps. Post-processing of the video is described further in section 4.3. To measure the actual diameters, thin cross-sectional slices were cut with a blade and the diameter of the capillary was determined using light microscopy, and the resulting values are used.

4.2 FROM CAD DRAWINGS TO 3D STRUCTURED GELS

A 3D mould was drawn in AutoCAD (Version N.52.0.0 AutoCAD 2017; CAD stands for computer-aided design) and printed by Shapeways (New York, NY, USA) in a material named Fine Detail Plastic (earlier: Frosted Ultra Detail), a UV-cured acrylic polymer that is heat resistant up to 80°C. In a process called material jetting, each layer is deposited with the molten plastic and cured with a UV lamp.¹ Thereafter, a calcium alginate gel was cured in the mould. The concentration of calcium and alginate used and curing time was the same as for the gel used to form the circular capillary. Curing was conducted in a chamber with regulated relative humidity (98%) using a saturated potassium sulfate solution. After gelation and directly before the experiment, the gel was removed from the mould. Since the mould was hydrophobic, the gel released easily. Capillary action was recorded horizontally using a camera, by applying coloured water to the designated reservoirs.

4.3 POST-PROCESSING OF VIDEO DATA

To process the recorded videos, first they were cut into single frames using the software FFmpeg (versions 2013-07-09 git-00b1401, N-54571-g00b1401 and N-87353-g183fd30), which yielded images. The liquid was tracked using a plugin in ImageJ (1.51s) for the straight capillaries with circular cross-sections. After the experiments for Paper I were conducted, the process was further optimised by transferring the images to an image stack, enhancing colour and contrast and converting the image stack to binary images using ImageJ (1.51s). The binary image stack was then imported into Matlab R2015b and R2017a (The MathWorks, Inc., Natick, MA, United States) and tracked². When the slopes of l^2 over t were used, the values were calculated beginning from 50% of the total filling time to exclude inertial effects and ensure a linear relationship.

4.4 CAPILLARY ALGINATE GELS

Creating numerous straight capillaries in an alginate gel can be achieved by external gelation, as illustrated in Figure 4.1. A glass beaker was coated with an alginate solution and dried in an oven, and this process was repeated three times. The alginate solution of

¹Refer to the website <http://www.shapeways.com> for more details on the material.

²An example of the code can be found here: <https://doi.org/10.6084/m9.figshare.6833528>

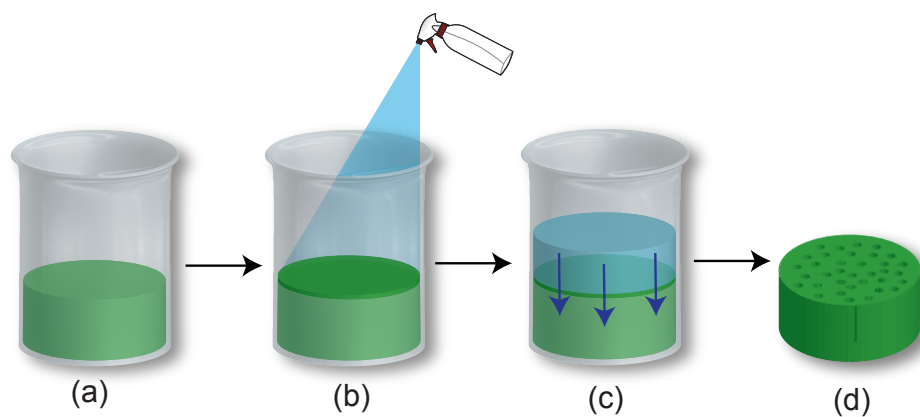


Figure 4.1: Creation of alginate capillary gels using external gelation: (a) Liquid sodium alginate solution in a coated beaker, (b) spraying of a calcium solution on the surface to create a gel membrane, (c) addition of the calcium ion solution on top of the membrane to let the ions diffuse into the sol/gel, (d) alginate capillary gel after cutting off the top membrane.

1.8% (w/w) was poured into the coated beaker and by spraying a 0.5 M CaCl_2 solution on the surface of the alginate solution, a membrane was created. Thereafter, the CaCl_2 solution was gently poured onto the membrane and allowed to diffuse into the polymer solution and was left to stand.

CHAPTER 5

RESEARCH OUTCOME

In this chapter, some of the most important research outcomes of this thesis are described and discussed. Further results and discussion can be found in the respective papers.

5.1 LIQUID TRAVELS SLOWER IN SOFT SOLIDS COMPARED TO STIFF MATERIALS

The widely used LW equation describes the spreading rate of a wetting liquid in a capillary with circular cross-section without interconnections. What is not included is how the wetting is influenced by the modulus of the material, as described in 2.1.4. The same model system as described by Lucas and Washburn is investigated in Paper I, but with soft walls instead of stiff ones. A transparent calcium alginate gel was used as a soft solid, which contained 98% water. The walls are very hydrophilic, with a low contact angle of below 10° . The gel was not removed from the syringe, only the string was removed from the gel after the top was cut off. Then, the capillary was connected horizontally to a coloured water droplet and the water penetrated the capillary immediately. The dynamics were recorded and the position per recorded frame was extracted with a tracking plugin of ImageJ. In Figure 5.1(a), the squared travelled distance l^2 of the tracked meniscus is plotted versus time. Four different diameters, 180, 250, 410 and 630 μm of capillaries in an alginate gel, were investigated. The shaded areas represent the standard deviation of each time point ($n \geq 5$). The dashed lines are the respective curves calculated using Equation (2.11). The results show that capillary flow is fast initially and decreases its velocity over the travelled distance. The experimental values form a straight line following the relationship of $l^2 \propto t$, which can be referred to as Washburn behaviour. This relationship is commonly found in various kinds of porous materials as well as in single capillaries [1, 7, 10, 12]. The larger diameters indicate faster spreading rates, as the largest capillary with a diameter of 630 μm was already filled after 0.75 s, while it took in average 2.56 s for the capillary of 180 μm to be filled. That the spreading is faster in larger capillaries can seem contradictory since the driving force is higher in smaller capillaries according to Equation (2.6). However,

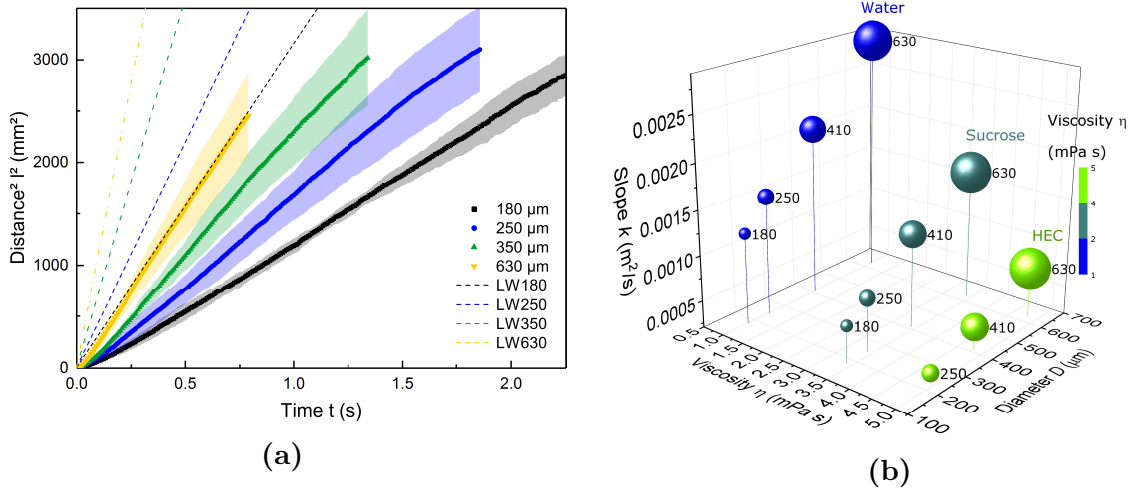


Figure 5.1: (a) Squared position of water l^2 versus time t in a capillary of an alginate gel in different sizes, demonstrating the relationship $l^2 \propto t$ in soft solids. The dashed lines indicate LW behaviour in rigid materials, calculated by using Equation (2.11). (b) shows the slopes on the z-axis resulting from (a) for water, sucrose solution and HEC solution over the viscosity on the x-axis and diameter of the capillary on the y-axis; the size of the balls indicates the capillary diameter, and their colour is scaled according to their viscosity (reproduced from [81], Paper I).

the opposing force, the pressure drop due to viscous friction, (F_v in Equation (2.10)) is larger in smaller capillaries, which make the liquid slow down more than in capillaries with larger diameters. To compare various results of different liquids and diameters, the linear fits are calculated and compared in Figure 5.1(b). The graph shows the slopes in m^2/s on the y-axis for the three liquids, which are pure water, sucrose solution and HEC solution. The slopes are plotted in relation to the measured viscosity of the liquid and the capillary diameter. The latter is also stated next to the balls in μm as well as indicated by the scaled size of the balls. Out of the tested wetting liquids and diameters, the capillaries with a diameter of 630 μm had the highest spreading rate and were filled fastest with water, as the highest ball indicates. Further, HEC had the highest viscosity out of the tested liquids, due to its low concentration it behaves as a Newtonian liquid. The dynamics of the HEC solution resulted in the lowest slopes, specifically the smallest capillary of 250 μm diameter, which had the lowest determined slope. The sucrose solution had a viscosity between HEC and water and the spreading rate is predicted to be between these two liquids according Equation (2.11). The results are in agreement with the prediction and it can be confirmed that larger capillary diameters and lower viscosities of the wetting liquid result in faster capillary flow.

Interestingly, if the slopes of the experiments are compared with the predictions based on the LW model, using the same properties of the liquids and diameters as in the experiments, large discrepancies are found, as illustrated by the dashed lines in Figure 5.1(a). The liquid spreading in the experiments was remarkably slower than that

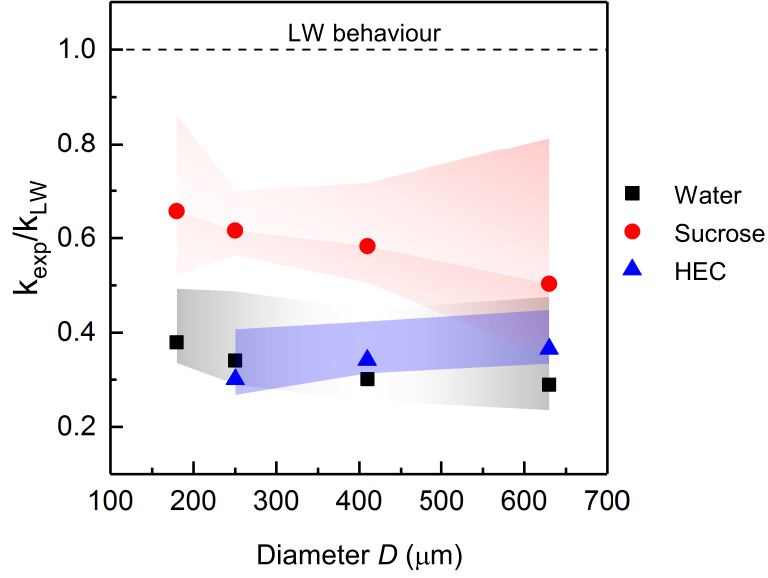


Figure 5.2: Ratio of the slopes of experimentally determined values to Equation (2.11) over the diameter D in alginate gels with the wetting liquids water (■), sucrose solution (●) and HEC solution (▲). The shaded areas represent the standard deviation and the dashed line LW behaviour, (reproduced with slight changes of style from [81], Paper I).

predicted by the LW model. Figure 5.2 illustrates how much the experiments deviate from the predictions. The ratio of the experimentally determined slopes, k_{exp} , to the predicted slopes of Equation (2.11), k_{LW} , is plotted versus the capillary diameter D with the wetting liquids, as indicated in the graph. The dashed line at $k_{\text{exp}}/k_{\text{LW}}$ at 1 represents LW behaviour. As evident from the graph, water and HEC solution were only approximately 30% to 40% as fast as the predicted values by LW. This was the case for all tested diameters, and a trend of the influence of diameters cannot clearly be identified, partially due to high standard deviations, which are indicated by the shaded areas. The HEC solution and pure water deviated more from the predicted values of Equation (2.11) than the sucrose solution did. An osmotic effect can be anticipated to cause that difference. This, and other possible effects, will be discussed in the section below.

5.1.1 POTENTIAL CAUSES FOR THE DEVIATION OF EXPERIMENT AND LW

INERTIAL EFFECTS are usually predominant in flow processes with high spreading rates and liquids with high densities. Bosanquet and Ridgway et al. included inertia in capillary flow, which is dominant before viscous forces prevail, as described in Equation (2.16) [30, 54]. The inertial regime is described in Equation (2.17), which is valid for $a \cdot t \ll 1$ (term a see (2.15)). In Figure 5.3, the cross-over time and distance is plotted for the different regimes with water in a capillary of $D = 630 \mu\text{m}$ and $\theta = 0^\circ$

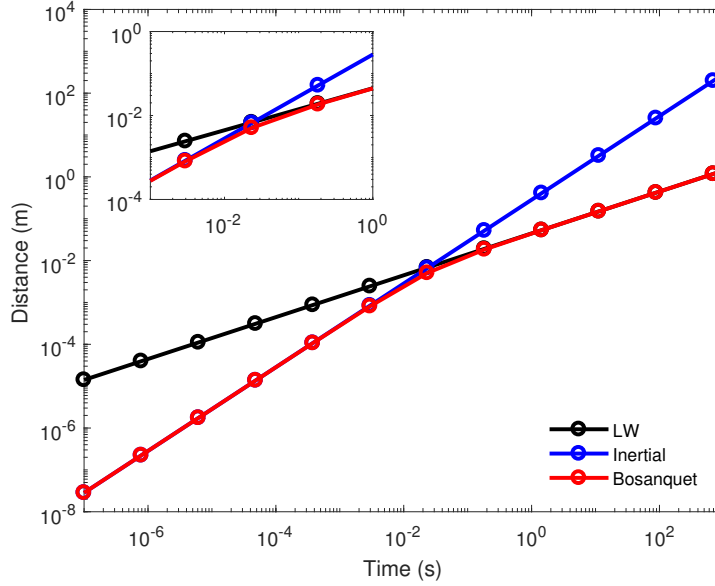


Figure 5.3: Cross-over time and distance when inertial goes over to viscous flow behaviour for water in a capillary of $D = 630 \mu\text{m}$ and $\theta = 0^\circ$, according to LW (2.11) ($\circ$), Bosanquet (2.16) ($\circ$) and inertial flow (2.17) ($\circ$); insert shows a magnification.

according to Equations (2.11), (2.16) and (2.17). The graph shows that the liquid in the inertial regime is faster initially (where $l \propto t$), while the later behaviour is dominated by viscous forces (exhibiting $l^2 \propto t$ relationship), as described by the Bosanquet equation (2.16). The cross-over occurs at $t \approx 0.025 \text{ s}$, below that inertia is predominant for the largest capillaries tested here and water as spreading liquid. Small capillaries, low densities and low viscosity lead to a decrease in the cross-over time, that is, the value of 0.025 s is the highest value that can be achieved out of the conditions used in this study. When $t = 0.025 \text{ s}$, the travelled distance is 17 mm according to LW (2.11) or 13 mm according to Bosanquet (2.16); however, in the experiments, this time equals a distance of $l \approx 4.4 \text{ mm}$ away from the entrance. At this initial time, three or four video frames are recorded, whereas the great majority of frames is taken after that. It should also be noted that the calculated slopes are based on times beginning from 50% of the entire spreading time, which begins at 0.39 s for water in $630 \mu\text{m}$, equivalent to a travelled distance of 35 mm from the entrance. Smaller diameters and higher liquid densities (as in the case of sucrose) will still not change the threshold time to later times than the time already mentioned. Therefore, it is concluded that inertial effects are not the reason for the deviation from our experiments to the LW equation.

DYNAMIC CONTACT ANGLE is another common reason for addressing deviations to Equation (2.11) [82]. The equation assumes a static contact angle, but it has been shown that the contact angle changes over time [83]. Therefore, the contact angle was determined directly in the capillary during the penetration process by analysing video

frames taken with an optical microscope in 140 fps. For water in alginate capillaries, contact angles of $\sim 25^\circ$ were determined at a distance of approximately 20 mm from the entrance. If the fitted slopes from the experiments are used to recalculate θ_{LW} with Equation (2.11), contact angles close to 90° are obtained, as Figure 5.4 illustrates. The calculated contact angles are plotted as a function of the capillary diameter with different liquids, as indicated in the graph. The values are far higher compared to both contact angles measured statically as well as dynamically in the capillary. Therefore, it is concluded that the dynamic contact angle is not, or not solely, the cause for the large deviation to the LW equation.

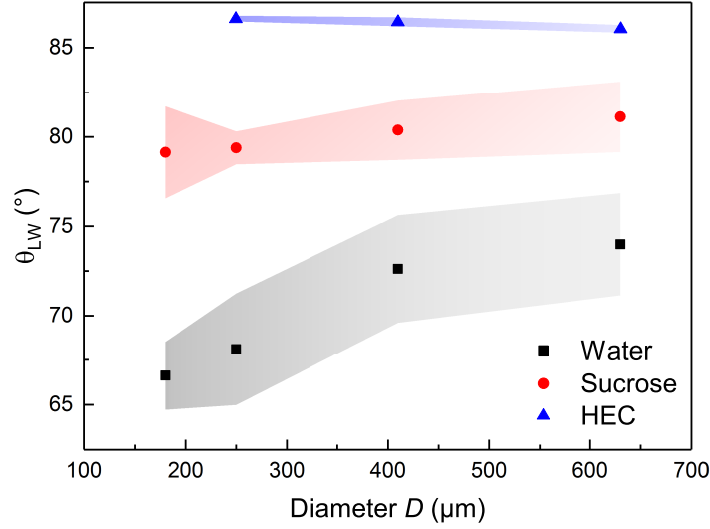


Figure 5.4: Calculated contact angles from the experimentally determined slopes, k_{exp} and Equation (2.11) with the wetting liquids water (■), sucrose solution (●) and HEC solution (▲).

DIFFERENCES IN CHEMICAL POTENTIAL between water as the spreading liquid and the surrounding gel should be considered when concentration differences occur. However, when the same experiments were conducted but with a calcium solution as the wetting liquid with the same concentration as in the calcium alginate gel, no difference in spreading rate was measured. The sucrose solution in Figure 5.2 shows slightly lower deviations to the LW equation, and one could assume that an osmotic effect is the reason. However, this would result in the opposite effect. Water from the alginate gel would most likely flow into the sucrose solution. In turn, a thinning effect of the sucrose solution would occur, and the viscosity would decrease. However, if lower η is inserted into Equation (2.11), it would lead to higher k_{LW} , and lower slope ratio; therefore, bringing it closer to water and the HEC solution in the graph. Thus, if the viscosity is lower than expected due to osmotic effects, the prediction would deviate even more from the experiment. Therefore, it is concluded that the difference in chemical potential did not cause the deviation to the LW equation.

INTERSTITIAL FLOW has been shown to occur on both agarose gels [84] and alginate gels [85] when water is moved by external pressure. It refers to the movement of liquid not only in the designated capillary but which extends into the gel boundary layer of the flowing water and causes an energy reduction. As investigated by co-author Tobias Gebäck in Paper I, the total volumetric flow in the capillary can be calculated and a correction term can be inserted into the LW equation to account for the permeability of the gel. However, with an expected permeability of the alginate gel [86], this effect of the loss of kinetic energy is too small to cause such a large deviation in the spreading rate as compared to the predictions.

DEFORMATION will occur at the three-phase contact line when a droplet is deposited on a soft surface, as described in section 2.1. Moreover, it has been proposed that the deformation also has consequences on the spreading rate of a meniscus in a circular capillary [20]. Accordingly, it is not only viscous braking of the liquid that has to be taken into account but also braking due to the viscoelasticity of the material, as shown in Equation (2.20). The softer the material, the higher is the emerging wetting ridge at the contact line and the slower the spreading. Shanahan and Carré reported a height of a wetting ridge of 60 nm with a silicone rubber that had a Young's modulus of 1.9 MPa [20]. The gels used here were determined to have a Young's modulus of ca. 11 kPa. This agrees well with values in existing literature, where an alginate gel of 2% had a Young's modulus of approximately 14 to 16 kPa [87]. The value is much lower than the silicone rubber used by the authors in reference [20]. It follows that an even higher wetting ridge could have been formed in the alginate gels used here. This indicates that a wetting ridge in front of the moving meniscus in the alginate gels slowed down the meniscus due to the viscoelasticity of the gel, which can be predicted by Equation (2.20), as illustrated in Paper I.

COMPLEMENTARY STUDIES It has been shown that the wetting liquid is considerably slower than expected in the alginate capillaries, and numerous anticipated reasons were eliminated to identify that the braking force due to viscous dissipation inside the gel was the limiting factor. A wetting ridge has been experimentally shown for droplets spreading on a surface [45] but never for capillary flow. However, the wetting ridge associated with the decreased spreading rate has not been directly detected in this study. Therefore, complementary studies are needed in order to confirm the hypothesis. There is only a small difference in the refractive index between the gel comprising mainly water and the spreading water itself. Optically differentiating between the deformed gel and spreading water is therefore a challenge. In Figure 4 of Paper I, micrographs of the meniscus in the gels are presented. An examination of the images revealed that there is no deformation, which can either be due to that the size of the wetting ridge is smaller than the resolution of the image or that the mentioned refractive index is expected to be almost the same. Thereafter, studies were conducted with alginate gels by limiting the amount of calcium ions to limit the amount of junctions with the aim of reducing the modulus of the gel [73]. However, no significant difference in the spreading rate

could be detected. This might partially be due to the fact that the variation in elastic modulus was too small to measure a significant difference; on the other hand, it might be due to the high variation between repetitions in general. Most studies, visualizing the existence of a wetting ridge upon droplet deposition were conducted on PDMS. Its modulus can easily be modified by at least one order of magnitude difference by the ratio of the cross-linker to the pre-polymer [88]. In the system used in the current study, the PDMS was interacting with the nylon string used to form the capillaries, which made it difficult to remove. The hypothesis could be tested using another type of string.

A more direct method to measure the wetting ridge could be Laser Speckle Imaging (LSI) [89, 90]. It is a technique based on an interference pattern produced when coherent light scatters from a turbid medium. Photons travel on different diffusion path lengths through the medium, creating a speckle pattern which is in principle a ‘static snapshot of the structure’ [89]. Any motion in the sample changes the speckle pattern and a series of speckle patterns can then be related to each other and visualise the motion of, for example, drying paints [89]. When scattering particles are added to the alginate gel, the deformation upon passing of the meniscus should be possible to detect using LSI.

5.1.2 POTENTIAL LIMITATIONS

The method used to form a capillary in an alginate gel, described in section 4.1, has numerous advantages, such as ease of preparation. However, there are certain limitations related to this method, which are addressed below.

SWELLING Swelling could influence capillary flow in that the radius would decrease over time and that part of the wetting liquid is used for swelling. However, investigations using microscopy on open channels did not reveal swelling. If it occurred, the gel would rise and the capillary would become out of focus, which was not observed. Moreover, the time scales of when capillary flow occurred is only a few seconds in this study and swelling of alginate during that time is not expected, as it has been shown to swell in time scales of minutes or hours [91].

INFLUENCE OF THE DYE Methylene blue is used as a dye for the wetting liquid in order to increase the visibility in the videos. This dye was selected because very small amounts are needed (0.03 wt% were used) in comparison to other dyes, such as safranin, and since the surface tension of this dye was closer to water than that of another solution coloured with safranin. Methylene blue has a positive charge in water [92]. It can be expected that it interacts with the alginate chains. Alginate has a negative charge in solution, and forms a gel by ionic interactions with calcium ions. As this reaction happens very fast and a uniform distribution of ions may be difficult to achieve, an insoluble calcium source was added (CaCO_3), followed by a slowly hydrolyzing acid (GDL). Over time, the protons from GDL are released and have a solubilizing effect on the CaCO_3 , which leads to the cross-linking of the alginate units [76, 93]. Since GDL and CaCO_3 were added in a stoichiometric ratio to the binding G-units of the alginate,

the pH is believed to remain the same [76, 94]. It is estimated that the calcium ions will occupy the majority of the carboxylic acid groups. Diffusion of dye into the gel may take place, but is of slower nature, which explains slight residues of blue colour after rinsing the gel with pure water. Further, the effect is the same in all experiments and should therefore not influence the comparison between the different experiments.

5.2 DYNAMICS OF WATER PENETRATING BRANCHED CHANNEL SYSTEMS

Thus far, straight capillaries without interconnections have been investigated in this thesis. However, most 3D porous materials usually do not consist of straight-aligned capillaries, but have complex networks of interconnected channels. Often, they also greatly vary in terms of pore size within a single system. Therefore, capillary flow in geometries was investigated, which were closer to geometries in real 3D materials but designed so that they allowed for tracking of menisci without microscopy, which restricts the field of view. A simple method was developed to produce defined open channels in gels, where the 2D geometry can easily and quickly be modified. This is done in open channels of rectangular cross-section in an alginate gel, as described in section 4.2. The geometry can easily and quickly be drawn digitally and printed as a mould without the more expensive and tedious route of lithography and clean-room fabrication methods. The mould can be used and cleaned many times. Cleanliness and purity are also assured by making gels fresh for each use and discarding them afterwards.

Some of the geometrical designs, which were investigated in this thesis are illustrated in Figure 5.5. Each of the reservoirs, where the water was applied, can hold a volume larger than the entire channel. Further details with the exact sizes can be found in the respective papers (Paper I for (a) and (b) and Paper II for geometry (c) and (d)). For increased understanding, a [video](#)¹ of such wicking tests has been uploaded.

First, it was investigated how the flow in a main channel was influenced when side channels are added on either one or both sides. Further, it was studied if and how the tilting angle of the side channels influences the spreading rate in the main channel (Fig. 5.5(a)). The results are described and discussed in section 5.2.1. Second, it was investigated if the width of the side channels, w_s , had an effect on the spreading rate in the main channel. The side channels in Figure 5.5(a) had a width of 0.6 mm, and in the geometries in 5.5(b), w_s was varied with at 0.3 and 0.4 mm. As illustrated in Fig 5.5(c) and (d) the tilting angle of the side channels was kept constant at 90°, but the number of side channels, their width and length were varied. Even w_s in one channel geometry in (c) was increased to compare the results from Figures 5.5(a) and (b). Apart from the spreading rate of the meniscus in the main channel, the volume flow including the side channels has been investigated and is described in section 5.2.2. In this manner, the geometry resulting in the largest volume flow could be identified, which did not appear

¹Available at <https://doi.org/10.6084/m9.figshare.6833459.v1>

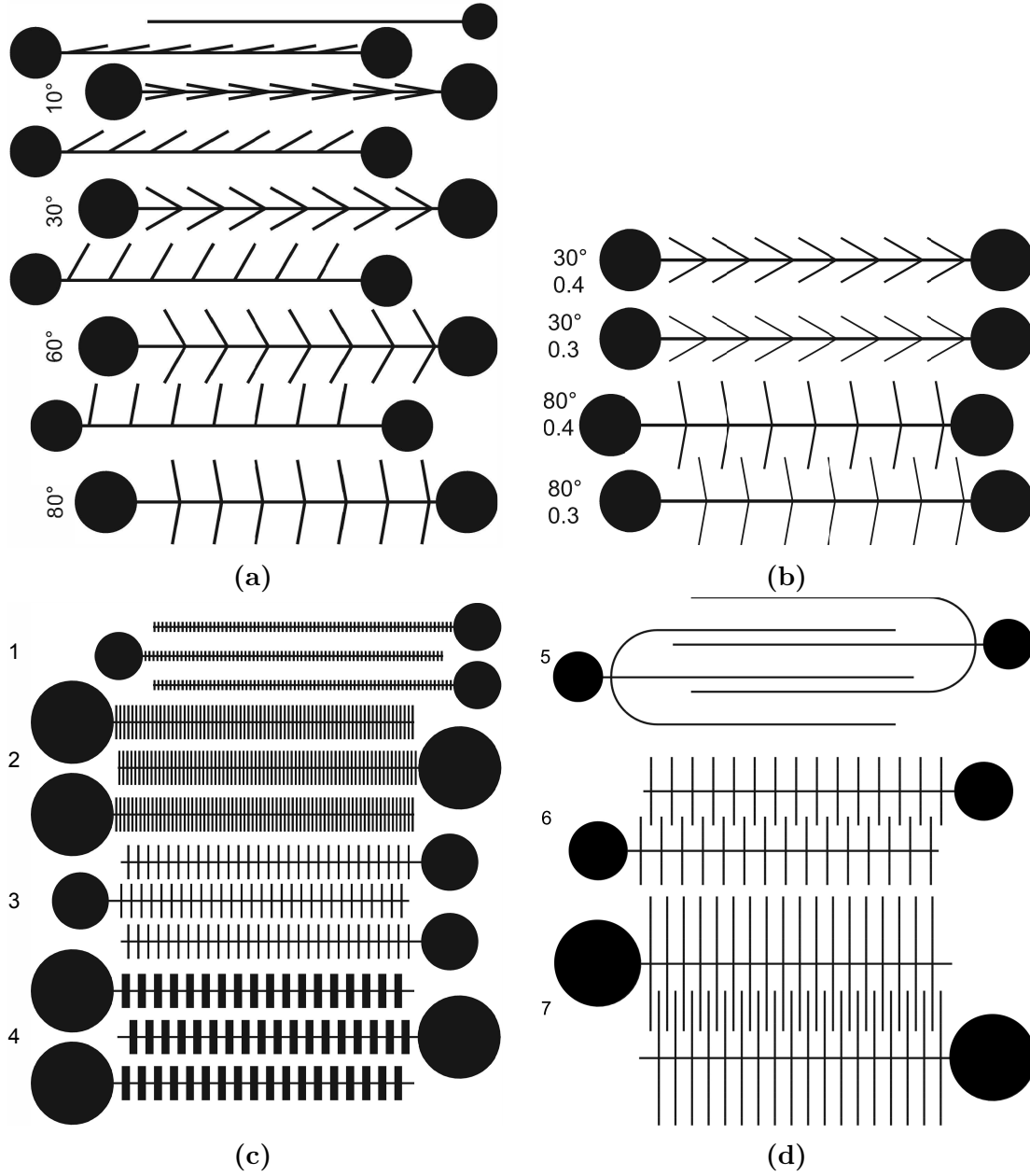


Figure 5.5: Geometrical design. (a) variation of the tilting angle from 10° to 170° (application from both sides), all channels had $w = h = 0.6$ mm; (b) variation of the width of the side channels $w_s = 0.3$ and 0.4 mm with four different tilting angles (in both flow directions), and channel height $h = 0.6$ mm; (c) and (d) variation of the number, l_s and w_s of the side channels, for all channels $h = 0.4$ mm and in the main channels $w = 0.4$ mm.

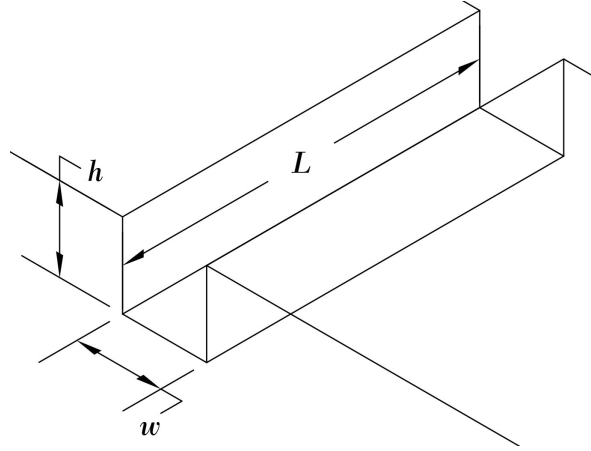
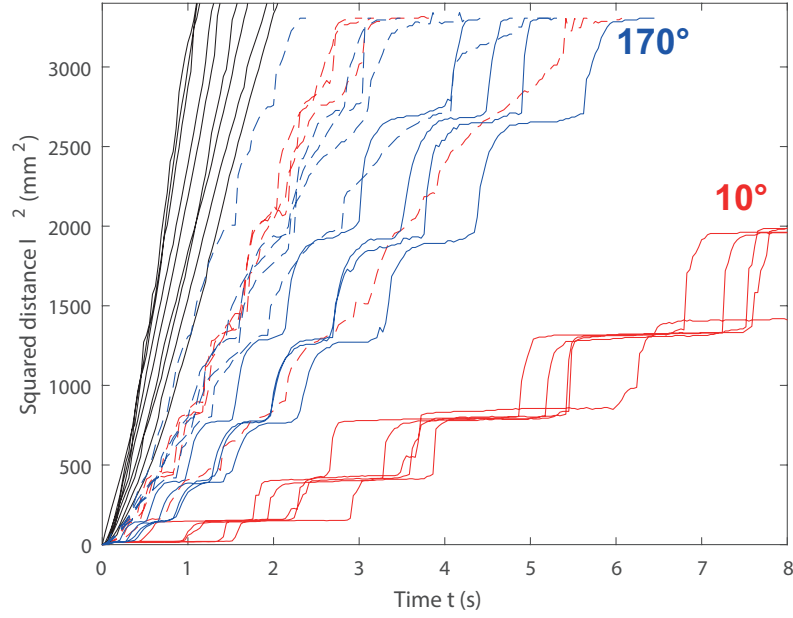


Figure 5.6: Explanation of channel denotations

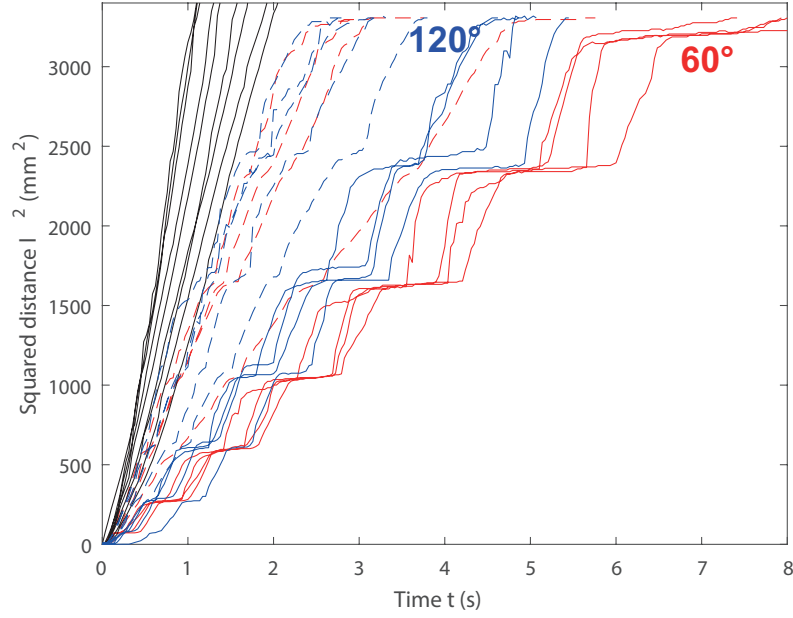
to be equal to the one with the fastest spreading rate.

5.2.1 INFLUENCE OF THE SIDES CHANNEL'S TILTING ANGLES

In open rectangular channels of $w = h = 0.6$ mm, the spreading rate of the meniscus in the main channel was measured (see channel denotations in Figure 5.6). In Figure 5.5(a), the geometrical design of the 3D printed device is illustrated. A channel without any side channels was compared with a geometry with side channels on one or two sides. The branches were designed to have tilting angles from 10° to 80° and if the liquid is applied from the other direction tilting angles of 100° to 170° were realised. Figure 5.7 illustrates the spreading rate, l^2 , plotted versus the time in the main channel for each repetition for the cases of 10° and 170° in (a) and 60° and 120° in (b), with channels on one and both sides compared to a channel without any side channels. Note that the y-axis is squared. Due to the spreading of the data, at least four experiments were conducted for each geometry. However, plotting the average of the data would average out the stops. Therefore, all repetitions were plotted. Spreading in the straight channel appears linear in the graph, that is, LW behaviour is obtained (Equation (2.11) where $l^2 \propto t$). This is confirmed by numerous other studies and various geometries [1, 7–13, 49] and in Paper I. It is evident from the graph that irrespective of the tested geometry, the meniscus in the straight channel was always fastest. Introducing side channels slowed down the spreading rate in the main channel. The decrease was moderate for the case with side channels on one side and more pronounced for channels with side channels on both sides. The spreading was slowest, with tilting angles of 10° on two sides. It is worthwhile to indicate that the geometries of 10° and 170° were exactly the same, but the liquid was applied on the other side. Again, one geometry can result in very different dynamics depending on the flow direction. Further, it is evident that the meniscus stops at the junctions, fills the side channels and subsequently continues to flow, which is also described as stick-slip motion or pinning of the meniscus. The stopping of the meniscus



(a)



(b)

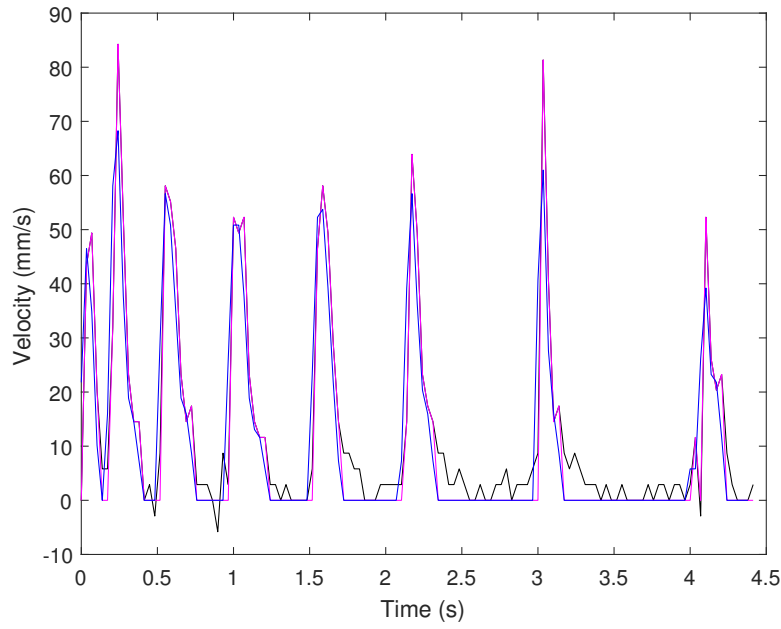
Figure 5.7: Dynamics of the meniscus in l^2 over time showing each repetition in straight channels without side channels (—) in both graphs. (a) with side channels on one side of 170° (---) and 10° (---), and with side channels on two sides tilting 170° (—) and 10° (—); (b) with side channels on one side of 120° (---) and 60° (---), and with side channels on two sides tilting 120° (—) and 60° (—).

can be attributed to a missing driving force to fill the main channel at the junction points by the capillary pressure. This pressure difference is missing as soon as the meniscus encounters a junction. Close-up videos revealed that the liquid stopped exactly at that point, where the walls are missing, which is described in detail in Paper II. The lowest spreading rate was measured for a tilting angle of 10° with side channels on both sides. The geometries of 60° to 170° resulted in similar spreading rates, while 30° also exhibited slower rates than the higher tilting angles. The small angles or sharp edges appear to take the longest time for the liquid to get around. The resolution of the shapes of the gel are of importance and therefore the resolution of the printed mould will be discussed in section 5.2.3.

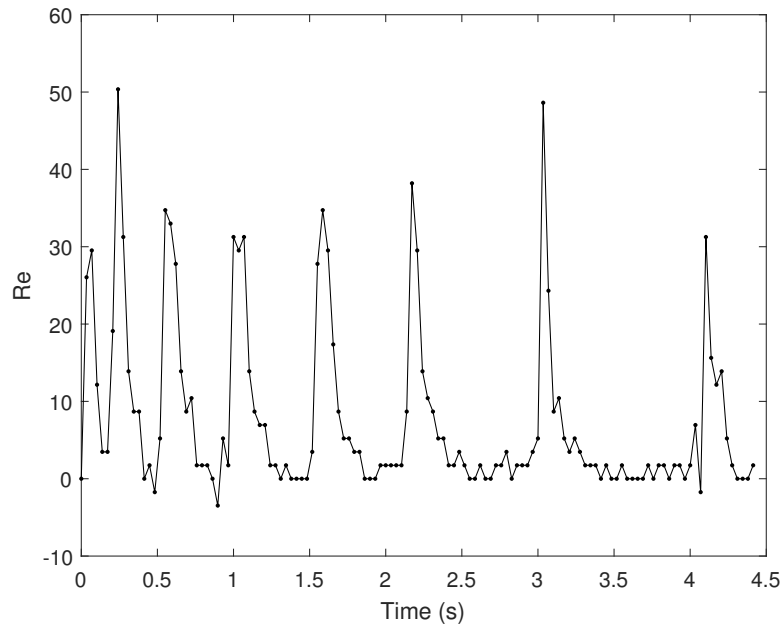
STOP DURATIONS AND THE MATLAB CODE To better understand the liquid stops, the duration for which the liquid stopped were analysed. For this the velocity was calculated as $\Delta l / \Delta t$ using MATLAB². The time difference Δt was determined when the velocity was zero or close to zero. A velocity threshold was set to differentiate between recording noise and real flow. The number of stops, calculated where the velocity was zero, should then be equal to the number of junctions, as seen in the video recordings. However, this was not always the case, as Figure 5.8(a) illustrates. The velocity forms peaks and valleys, where the liquid flows and stops. The original data obtained when the velocity is calculated directly from the differences in distances and times is plotted in black and the modified velocity where low values are set to zero is plotted in magenta. The last peak around 4 s has one point where the velocity is zero but is actually part of a peak where there was no junction. Therefore, the threshold value was adjusted for each single experiment. Moreover, a smoothing factor has been applied to the velocity with a window of maximum two frames, as the blue line illustrates, which includes the modification. This single time point after 4 s is averaged away by the smoothing function. Using this method, it was possible to calculate the stop duration. Since the method includes some estimations of when exactly the velocity was zero and when the meniscus began flowing again, the results should be interpreted as an estimation of the stop durations rather than precise values.

As also visible in the graph, the valleys get longer with increasing t , that is, the stop duration was longer towards the end of the channel (all stop durations are plotted in Figure 5 in Paper II). For certain geometries, the first velocity peak could not be differentiated from the second peak, that is, when the meniscus did not stop in the measured time windows (fps) but rather slowed down and accelerated. Since the liquid flow becomes slower the longer it has travelled in a channel, the stop durations at junctions also become longer. Inertia is expected to play a role here, since it is important every time the liquid changes its state of motion, that is, when the liquid stops and begins to flow. The Reynolds number (Equation (2.12)) sets the inertial versus viscous forces in relation and is plotted in Figure 5.8(b) for one experiment in the 170° geometry.

²An example of the code to calculate the stop duration is uploaded on the following link: <https://doi.org/10.6084/m9.figshare.6833537>



(a)



(b)

Figure 5.8: (a) Calculated velocity directly from the distances versus the times (—), where the velocity below a threshold of 10 mm/s is set to zero (—) and modified and smoothed with a window of 2 values (—) with an example of a channel with side channels on both sides of 170° ; (b) resulting Reynolds number versus time with the unmodified velocity.

The values used for this calculation are: $\rho = 998.2 \text{ kg/m}^3$, $\eta = 1.002 \cdot 10^{-3} \text{ Pa s}$ and $D = 0.6 \cdot 10^{-3} \text{ m}$. The graph illustrates that there is a high variation in Re with values from 0 until up to 50 and therefore also an alteration in the dominating forces.

Feng and Rothstein investigated similar but smaller geometries in PDMS [60]. The authors varied the surface tension γ by adjusting the ratio of isopropyl alcohol to water. At a specific value of γ , the liquid penetrated the channel in one direction, but not the other one. Compared to the system studied here, the wetting liquid, water, has a higher surface tension (72 mN/m for water compared to 22 mN/m for isopropyl alcohol) and has stronger adhesive forces to the gel as the contact angle of water is very low on the gel (described in section 5.1). A Reynolds number of 0.4 for the maximum velocity is stated in reference [60]. Compared to the experiments in this thesis, this is rather low and suggests, again, that inertial forces are of greater importance in the geometries described here. A combination of increased inertial forces and the small contact angle of water on the alginate gel is suggested to be the reason for why a complete stop was not observed in the system studied here. Other factors that could influence the stop duration are the deformation of the gel as well as the resolution of the printed device and, therefore, the gel (discussed below in section 5.2.3)

INFLUENCE OF THE SIDE CHANNEL'S WIDTH All side channels in Figure 5.5(a) had a width of 0.6 mm. In order to investigate how the size of the side channels influences the flow, experiments using geometries with side channels of 0.3 mm and 0.4 mm were conducted in addition to the ones already done (Figure 5.5(b)). Angles from 30° to 150° were investigated. As described in Paper II (Figure 8), the greater the width of the side channels, the longer was the stop duration. This difference was specifically pronounced with tilting angles of 30° , where the stop duration was significantly longer compared to the other geometries and widths. As described above, the stop duration was dependent on the junction number, as the liquid decreases its velocity with increased travelled distance and, thus, inertial forces become less important. Similarly, the longer stop durations for larger side channels can be explained. At the entrance of a channel, the driving force P_c is important and less is viscous flow. Since P_c is larger in smaller capillaries, the liquid is more likely to enter the thinner channel first. This is in line with the assumptions that smaller pores fill first in a porous medium [25, 29, 30]. The liquid stopped at junctions in the system studied here and, similarly, the liquid is expected to stop at junctions in a porous material of equal or larger size with an interconnected structure. Other adjacent channels are filled first before the liquid finally continues to flow in one specific channel. This underlines the observation of others, who stated selective pathways in porous materials [26, 27, 30].

5.2.2 INFLUENCE OF THE LENGTH, WIDTH AND NUMBER OF SIDE CHANNELS

In the previous section, the effect of adding side channels to a main channel on the spreading rate and how their tilting angle and width influenced the flow was investigated.

5.2. DYNAMICS OF WATER PENETRATING BRANCHED CHANNEL SYSTEMS

Table 5.1: Length l_s and width w_s of side channels, number of junctions and the total volume, including side channels V_{tot} , which the channel can fit of the geometrical designs from Figures 5.5(c) and (d); the length of the main channel was kept at 60 mm.

Channel	Paper III	l_s (mm)	w_s (mm)	V_{tot} (mm ³)	# Junctions
1	A	0.8	0.4	28.8	75
2	G	$3.2 = 4 \cdot l_{s1}$	0.4	86.4	75
3	C	$3.2 = 4 \cdot l_{s1}$	0.4	39.3	29
4	E	$3.2 = 4 \cdot l_{s1}$	$1.6 = 4 \cdot w_{s1}$	83.3	18
5	B	$60.0 = 75 \cdot l_{s1}$	0.4	$28.8 = V_1$	1
6	D	$6.4 = 8 \cdot l_{s1}$	0.4	$40.3 \approx V_3$	15
7	F	$12.8 = 16 \cdot l_{s1}$	0.4	$83.3 = V_4$	18
Straight	Straight	-	-	9.6	0

With the geometrical design presented in Figure 5.5(c) and (d), the following research questions were addressed concerning if and how the flow is influenced by

- (i) the number of side channels,
- (ii) the length of the side channels, and
- (iii) how very wide side channels influence the flow dynamics.

Further, the total volume flow including the side channels was investigated and compared to the spreading rate in the main channel. For the geometries used, the tilting angle was kept constant at 90°, but the length and number of the side channels was varied. Certain channel geometries were designed in a manner that would ensure that they have the same volume when filled (that were geometries 1 and 5, 3 and 6, and 4 and 7). The main channels had a width and height of 0.4 mm and a length of 60 mm. Table 5.1 lists the length l_s and width w_s of the side channels, the total volume V_{tot} of the channel including side channels (excluding the reservoir) and the number of junctions. The objective of the different side channel designs was to determine the influence of the length, width and number of side channels on the filling dynamics in the main channel and the liquid volume flow rate. The channels are given numbers, as depicted in Figure 5.5(c) and (d), and their respective names in Paper III are stated. Note that, apart from l_s , the number of junctions was also varied. The width of the side channels was always the same except in geometry 4. Geometries 1 and 5 had the same total volume but a great difference in junctions (75 versus 1). Geometry 6 was designed to have half as many junctions as geometry 3, but twice as long side channels. As the number of junctions was odd in geometry 3, the total volume differed slightly, with 39.3 mm³ in geometry 3 versus 40.3 mm³ in 6. Geometry 7 was designed to have the same total volume as geometry 4 but with longer side channels. The results were compared to a straight channel without any side channels, which had the same length, height and width as the main channel in the other geometries.

In Figure 5.9(a), the squared travelled distance is plotted versus the time in the main channel. For reasons of clarity, the mean values are plotted instead of each repetition.

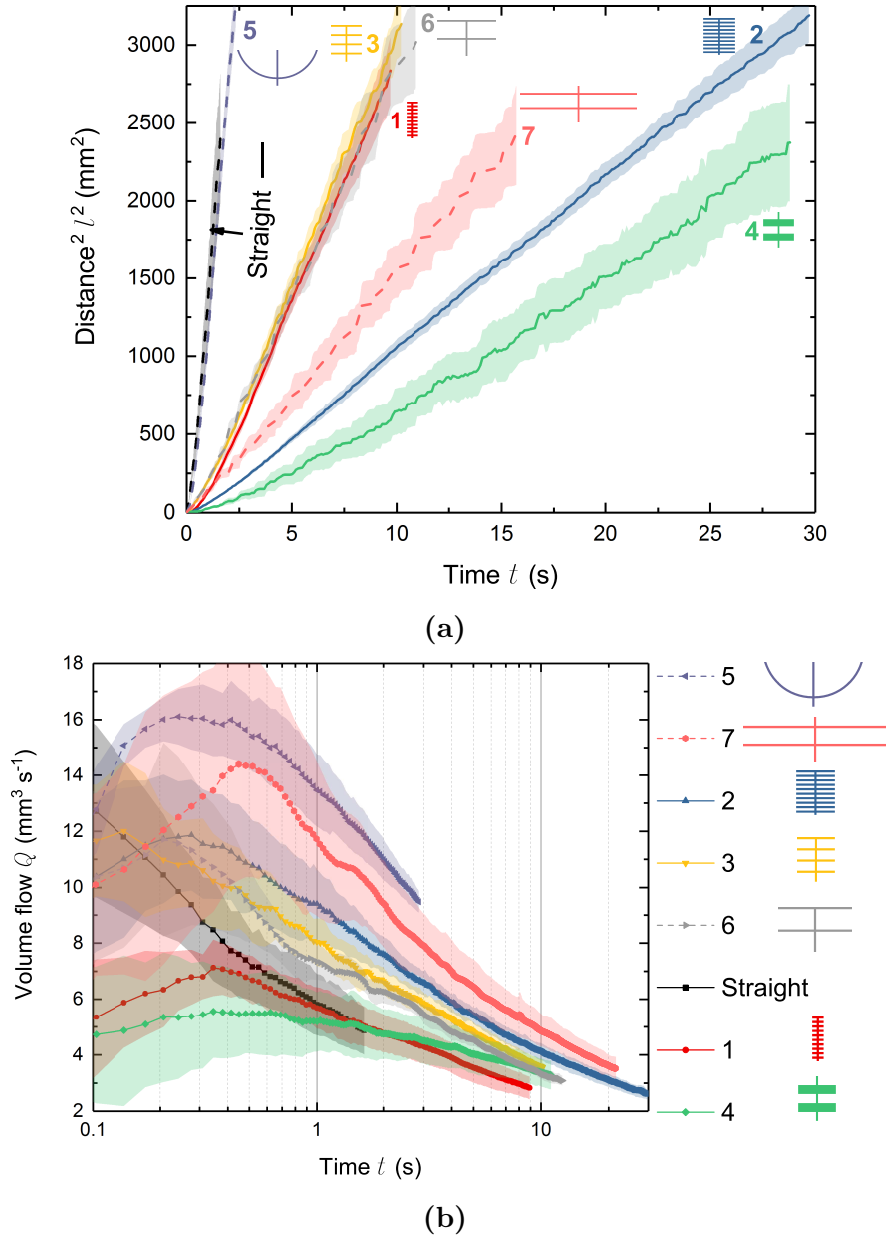


Figure 5.9: (a) Averaged squared travelled distance over time in the main channel; (b) volume flow, including all side channels, versus the log-spaced time; both graphs are based on the geometries illustrated in Figures 5.5(c) and (d) as well as a straight channel without side channels ('Straight'). The geometries are indicated in the graphs; colours are equal in (a) and (b), and the shaded areas represent the standard deviations.

The shaded areas visualise the standard deviations. Similar to the results presented in Figure 5.7, the liquid exhibited a stick-slip motion, resulting in steps in the plot, but the stops are averaged out by calculating the mean values (see Figure 1 in Paper III where each repetition is plotted). The steps in the graph could be related to the length of the side channels so that geometry 1 had small steps compared to 6 and 7 (termed A versus D and F in Paper III). The stop duration has been investigated in the geometries with the longest side channels, which were geometries 6 and 7, where 7 had double as long l_s as geometry 6. At the first junction, the liquid did not stop and the junction was disregarded. The mean values of the stop duration were 0.74 s for geometry 6 and 1.19 s for geometry 7 (see the supporting information of Paper III). This indicates that the stop durations increase with an increase in the length of the side channels. The anticipated reason is that the liquid meniscus stops until the whole side channel is filled and that it takes longer for longer side channels to be filled than for shorter side channels.

In all tested geometries, the exhibited spreading rates follow LW dynamics, $l^2 \propto t$, as is expected. It is evident from Figure 5.7(a) that geometry 4 resulted in the slowest transport, while the dynamics of the straight channel and geometry 5 were equally fast. It is important to point out that the liquid did not stop at the junction in geometry 5. It is hypothesised that this is related to the (only existing) junction that was situated only 1.4 mm away from the entrance. In geometries 6 and 7, the first junctions were 2.3 mm and 1.6 mm away from the entrance, respectively, and the liquid did not stop noticeably in these geometries either. Since the liquid has a high spreading rate in the beginning, inertial forces are high and the liquid passes the junction without stopping. The spreading rate in the main channel of geometry 5 was almost the same as in the straight channel. Geometry 1 had the same total volume as geometry 5, but exhibited approximately 60% slower spreading. It was equal as fast as geometries 3 and 6, followed by geometry 7, geometry 2 and finally geometry 4 had the lowest spreading rate. Interestingly, geometries 4 and 7 have the same volume, but resulted in very different spreading rates, where geometry 7 with much smaller w_s had approximately 50% faster flow than the flow in geometry 4. Further, geometries 3 and 6 were equally fast with the same V_{tot} but geometry 3 had double as many side channels as geometry 6.

It is worth commenting that the liquid filled the corners in the side channels of geometry 4 before it filled the centre of the channels. These wicking fingers or precursors are schematically illustrated in Figure 5.10(a). This has been observed and investigated by other researchers on channels of rectangular cross-sections [8, 58, 59]. The precursors in such geometries are much faster than the main meniscus and rise higher than the equilibrium height in a vertical channel [58, 59]. They are based on the fact that capillary forces are created not only between two parallel walls but also between walls perpendicular to each other. In the other geometries tested here, no wicking fingers were observed as the side channels were narrower. It has been reported that the aspect ratio of the channel $\epsilon = h/w$ together with the contact angle determines if the liquid penetrates the open microchannel (lower ϵ requires lower θ), as described by Equation (2.18) [58]. For the side channels of geometry 4, the aspect ratio was 0.25, while for all other

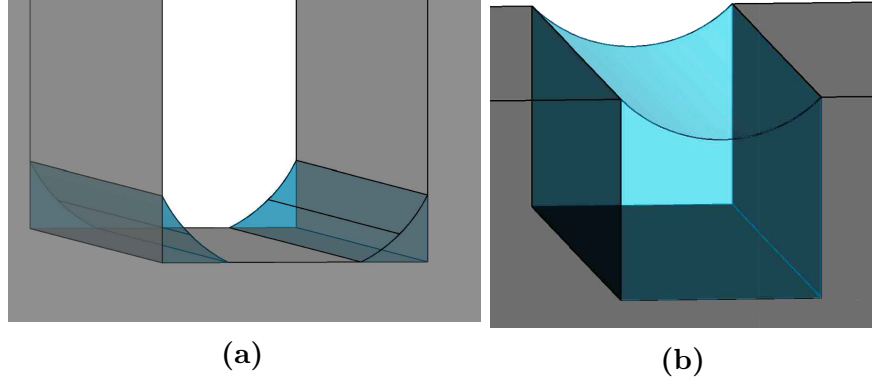


Figure 5.10: Schematic drawing of (a) precursors or wicking fingers in the corners in blue ahead of the main meniscus in a rectangular channel, and (b) the shape of water when it fills an open rectangular channel, thereby illustrating that it does not adopt a straight shape.

geometries $\epsilon = 1$. According to Equation (2.18), the contact angle needs to be less than 48° to penetrate the side channel of geometry 4, which was fulfilled. However, with $w_s = 1.6$ mm, the side channels are close to the capillary length of water $\kappa^{-1} = 2.7$ mm [3]. Hence, the channels are filled by capillary forces, but since the width is close to κ^{-1} , gravity becomes increasingly important in those channels compared to all other studied geometries, which explains the low spreading rate and different flow mechanism.

It is challenging to draw definite conclusions from the results depicted in Figure 5.9(a). Therefore, a method has been developed and used to investigate the volume flow using the same videos which were analysed previously. The resulting image frames were optimised and converted to a binary image stack (with the liquid representing black pixels). The number of black pixels for the filled channel was set equal to the liquid volume which the channel could, in principle, fit, and the black pixels were then counted in each image and related to the volume using Matlab. In this manner, it was possible to account for the total flow, including the filling of the side channels, and not only that in the main channel. This method does have a few errors due to certain surface effects, such as the fact that the liquid does not fill the channel top in an exactly flat shape but in a concave shape (as illustrated in Figure 5.10(b)). Additionally, it assumes that the channels have exactly the same shape in the gel as in the CAD drawing (discussed more in detail in section 5.2.3). However, it has been used as a method to estimate the volume flow and to compare the dynamics in the tested geometries by taking the entire channel into account.

The results are plotted in Figure 5.9(b), which shows the volume flow rate, Q , versus the log spaced time, t , for the straight channel and geometries 1 to 7. The shaded areas illustrate the standard deviations. As evident, after it passed a maximum, Q decreased with increasing time, as it was expected. Moreover, graphs of each repetition also revealed that Q was continuous and did not stop or become zero at the junctions in contrast to the filling of the main channel, as discussed earlier.

Comparing Q to the spreading rate in the main channel, it is evident that they did

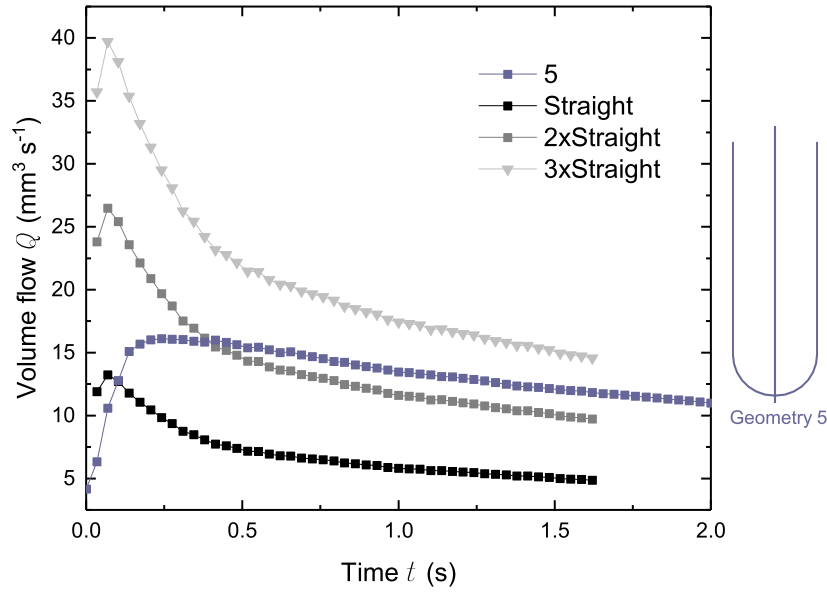


Figure 5.11: Volume flow of geometry 5 in comparison to a straight channel without side channels, original data and multiplied by 2 and 3. Geometry 5 is indicated next to the graph.

not exhibit the same behaviour for different geometries. The largest volume flow rate was measured in geometry 5, with only one junction and two long side channels. In Figure 5.9(a), the spreading rate of geometry 5 was also the fastest, but had the same spreading rate as the straight channel. However, the volume flow rate was much lower in the straight channel compared to the spreading rate in only the main channel in geometry 5. This can be explained by the mechanism that once the liquid had passed the junction in geometry 5, there were three menisci drawing the liquid and the driving force should therefore have been three times larger than in the straight channel. However, Q_5 is still lower than $3 \cdot Q_{Straight}$, as plotted in Figure 5.11, but still larger than $2 \cdot Q_{Straight}$ for times > 0.5 s. It is also worth to note that the dynamics of geometry 5 plotted in Figure 5.11 exhibit a much smoother curve than the straight channel, particularly in the beginning when $t < 0.5$ s, but also after that; this was not an averaging effect but visible for the individual curves. This suggests that the existence of the side channels in geometry 5 prevent high peaks in volume flow and enables a more stable flow rate.

In Paper III, the Darcy permeability was computed by co-author Tobias Gebäck using the lattice Boltzmann method for geometries 1 to 7 (except of geometry 5 since it had no repeating sections and the permeability is therefore not defined) and for a straight channel. The permeability describes the ease with which a liquid can flow through the channel and decreases with an increasing Reynolds number. Figure 5.12 illustrates the results, where the permeability is plotted in bars. The straight channel was least permeable, thereby indicating that the liquid had the highest flow resistance, followed by geometries 6, 7 and 3. The highest permeability was recorded for geometry 4. The different flow mechanism of geometry 4 has been taken into account, and is

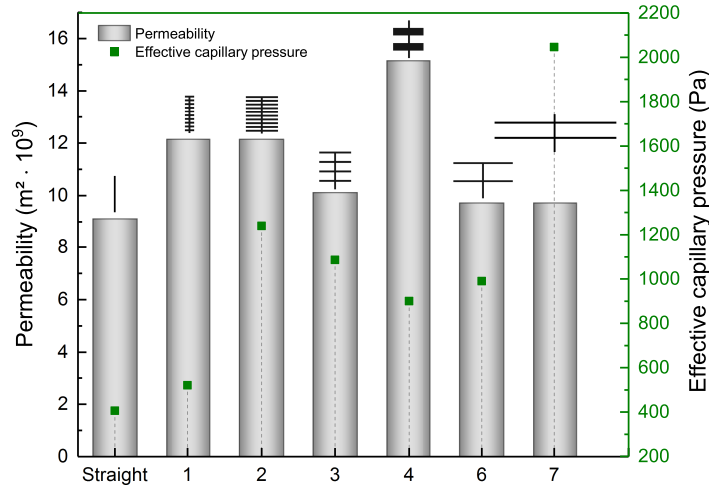


Figure 5.12: Computed Darcy permeability using the lattice Boltzmann method plotted as bars and the calculated effective capillary pressure (■) on the second y-axis for the straight channel and geometries 1 to 7 (except of 5). The geometries are indicated in the graph.

not discussed further here. As the length of the side channel has very little influence on the permeability, it could be related to the respective length of the main channel which the side channels occupy, that is, the width of the side channels multiplied by the number of junctions (see also Figure 6 in Paper III). However, geometry 4 deviates from this relationship due to its different flow mechanism in the wide side channels. Using the volume flow rate, Q , plotted in Figure 5.9(b) after the individual peak, the effective capillary pressure was calculated and indicated in Figure 5.12 on a second y-axis as green squares. It is evident that the straight channel had the lowest driving capillary pressure and the lowest permeability. All other geometries had side channels, where more than one meniscus can actively draw the liquid column, which explains that the effective capillary pressure was higher in all other geometries than in the straight channel. In longer side channels, the menisci can draw the liquid for a longer time, for example in geometry 7, which had the longest side channels and exhibits the highest effective capillary pressure, but had the same permeability as geometry 6, which had only half as long side channels as geometry 7. Further, with its open geometry due to wide side channels, geometry 4 had a high permeability but a low effective capillary pressure, which indicates that the driving force was low but so was the flow resistance once the meniscus has passed. This could explain why the volume flow in geometry 4 decreases least with time, as Figure 5.9(b) shows.

The results indicate that it is not only the total volume which the channel can fit that is of importance for the volume flow, but also the length and width of the side channels and the number of junctions, which can be related to the connectivity of a porous material.

5.2.3 POTENTIAL LIMITATIONS OF THE EMPLOYED METHOD

The method employed to fabricate the microchannels, as described in section 4.2, is fast, cost-efficient and simple. However, there are certain limitations, which must be considered when interpreting the results.

DEFORMATION In section 5.1, it was reported and discussed how the modulus of the substrate influences the flow. As the same gels are used, it is expected that deformation also occurs in the same manner. This can be considered as a disadvantage, in that the results are not valid for hard materials, or as an advantage, as many real porous materials are actually soft solids. However, it is estimated that the dynamics in the more complex structures used here follow similar mechanisms as the dynamics in hard materials. As stated in Paper I, the spreading rate of liquids may be slower than that in hard materials with the same hydrophilic character, but as the focus in Papers II and III, lies on the comparison between the dynamics of the different geometries, absolute values can be disregarded.

ROUGHNESS OF THE 3D PRINTED DEVICE Like all 3D printed materials, the moulds used to produce the gels contain a certain roughness, which is caused by the printing process. This roughness will also be imprinted in the gels, where the experiments were conducted and, as described in Chapter 2, wetting is influenced by the roughness. As the roughness is slightly visible in the moulds, tests have been conducted with the printing direction in line with the flow and perpendicular to the flow. No difference was found with regard to the spreading rate of the meniscus when the two experiments were compared.

3D PRINTING RESOLUTION Apart from the roughness of the printed device, the resolution can be an important factor when it comes to, for example, the stop durations. As it has been reported in section 5.2.1, specifically sharp angles of tilted side channels exhibit large stop durations. It indicates that the exact shape of the edges does influence the flow. The resolution of the printed device has not been investigated in this thesis. The producer recommends a minimum surface detail of 0.1 mm.³ Thus, height and width of the channels were designed to have a minimum size of 0.3 mm. Moreover, all devices are printed by the same producer and the same material. The resolution should therefore be the same for the used devices and it is expected that the results are comparable within this thesis. Further, the resolution of the printed device does not necessarily have to be equal to the resolution of the resultant gel. The gel could be removed easily and no residues were left on the mould. Air bubbles at the edges of the channels were carefully removed with a small brush immediately after the alginate sol was cast into the mould. However, no measurements have been conducted to investigate how precisely the resulting gel was shaped.

³<https://www.shapeways.com/materials/fine-detail-plastic>

FROM 2D TO 3D As the channels are in one plane, they are only two-dimensional and, moreover, they are open on the top. If the channels also had the top wall for capillary forces to act, it is expected that (i) the flow would have been faster and (ii) that the stop durations at the junctions would have been shorter. The added side channels were situated mostly on both sides opposite each other (not after each other) and so the walls, where capillary forces can act, were removed. Since capillary forces also act between adjacent walls, the existence of a top wall would have led to a decrease in stop duration or even prevented stopping. In particular, for the channels with larger width, it is expected that a top wall would have increased the spreading rate substantially and might even have changed the flow pattern in some of the channels.

5.3 DEVELOPMENT OF A POROUS ALGINATE GEL WITH ENHANCED VOLUME FLOW

The previous sections describe how the flow in porous materials can be tailored by the geometrical design, where model materials were used. It was concluded that the interconnection of pores slows down imbibing liquids compared to straight channels. To increase capillary transport, materials can be designed containing straight-aligned capillaries without interconnection. Alginate gels can be produced in such a manner that they spontaneously form straight capillaries of circular cross-section, without interconnections, only by adjusting the manner in which the cross-linking ions are introduced. Unlike the geometries discussed in 5.1 and 5.2, this gel contains many capillaries arranged in a three-dimensional order. The method of introducing the cross-linking ions to the alginate solution differs from the one used for the other experiments discussed above, in that a calcium ion solution is added on top of the gel and slowly diffuses into the solution, as described under 4.4. Two micrographs are shown in Figure 5.13(a) and (b) of an externally set capillary alginate gel of which (a) shows a fresh gel and (b) shows a freeze-dried gel, both cut with the capillary direction. As evident from (a), the gel had straight vertical capillaries, which were homogeneously distributed. One way of tailoring the capillary diameter is by adjusting the concentration of the calcium solution on top of the gel [95, 96], where higher concentrations of cross-linking ions led to smaller capillaries. In our experiments, the size varied from 60 to 110 μm . It is not only the diameter that decreased but also the density of capillaries that increased consistently with the increase in the volume of the ion solution, which in turn led to an increase in the number of calcium ions on top of the gel. By introducing other multivalent ions, such as lead, copper, strontium or barium, the capillary diameter can be further tailored in a range from 5 to 300 μm [77, 95, 96]. An excess of calcium ions is necessary to form capillaries [96], which is why no capillaries were formed using cross-linking ratios of < 2 of calcium ions to G-units. This indicates that capillary formation only occurs upon excess of calcium ions above the saturation of G-units. Increasing amounts of calcium ions also initially reduced the capillary diameter; upon adding more ions, the size was less dependent on the number of calcium ions. However,

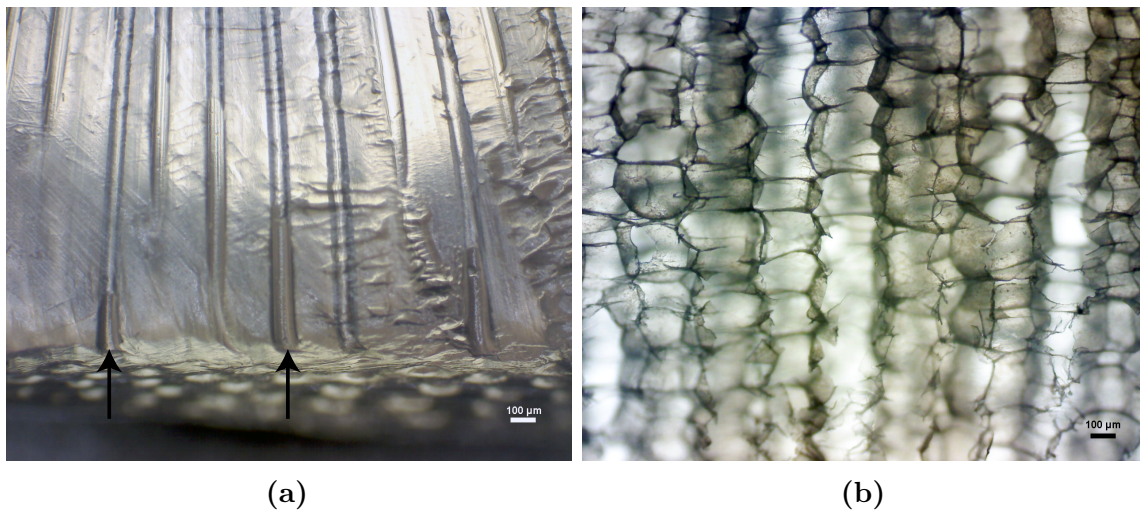


Figure 5.13: Capillary alginate gels prepared using external gelation, where (a) shows a micrograph of a calcium alginate gel containing circular capillaries of micrometre size; two capillaries are indicated by the black arrows in capillary direction; the scale bar is 100 µm. (b) shows a micrograph of the freeze-dried gel in a section cut in capillary direction; the scale bars are 100 µm in (a) and (b).

the capillary density consistently increased with increasing concentration of calcium ions.

5.3.1 INTERNAL OR EXTERNAL GELATION DETERMINES MECHANICAL PROPERTIES

Two set of gels were compared, the capillary alginate gel, which was made by an external introduction of ions, and another set of gels were produced by external introduction of ions. The same stoichiometric ratio and an alginate concentration of 2% (w/w) was used. Uniaxial compression tests were conducted that measure the shear stress needed to maintain the gel at various deformations and the results are plotted in Figure 5.14 for 5% (a) and for 10% (b) strain. As the figure indicates, the stress decreases exponentially with time, which is characteristic for physically cross-linked polymer gels and an example for viscoelastic behaviour. The externally set gel levelled off to a value near zero, whereas the internally set gel remained at a higher, almost constant, non-zero value. Figure 5.14(c) illustrates the moduli of the gels ($G = \text{stress/strain}$) with 5% (solid line) and 10% (dashed line) strain versus time for internally and externally set gels. The externally set gels exhibited a more plastic behaviour as they tended to recover less to their initial height compared to the internal gels (see Table 1 in Paper IV). A clear difference of internally set gels with considerably higher moduli was observed. The large difference in stress relaxation at equal electrolyte concentrations suggests that the gelation method introduces differences in the microstructure of the gels, which determine their rheological behaviour. This difference cannot be accounted for only by the existence of capillaries

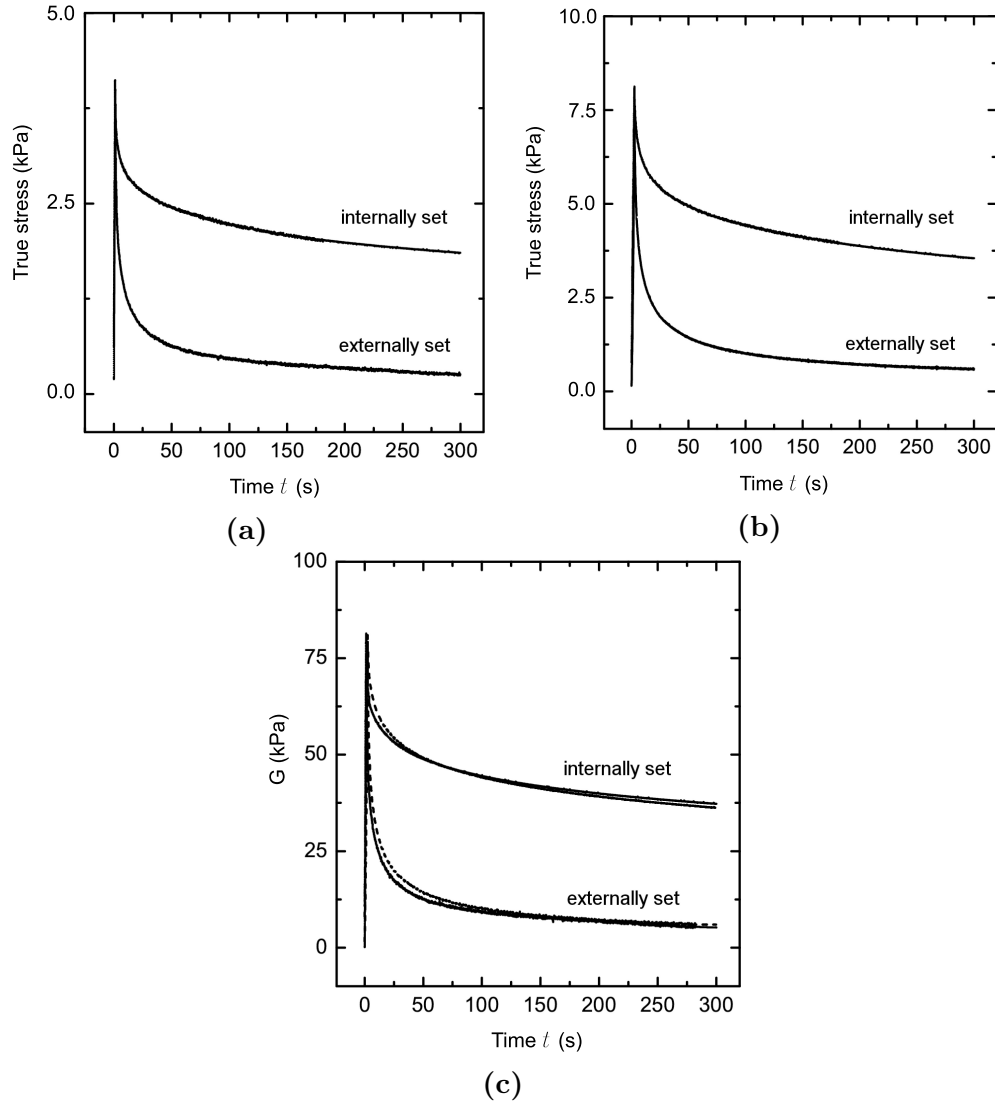


Figure 5.14: Stress relaxation curves at (a) 5% strain and (b) 10% strain and (c) modulus G for 5% strain (solid line) and 10% strain (dashed line) for internal and external gelation (reproduced from [97], Paper IV).

in the externally set gel, but suggests a difference in microstructure induced by the method used to introduce cross-linking ions to the polymer solution.

The microstructure was investigated by analysing the voids using TEM images (see Figure 7 in Paper IV). For both types of gels, voids starting at approximately 50 nm could be observed, which are similar to pore sizes of carrageenan and pectin [98, 99]. As physical gels have rather inhomogeneous structures, the pore sizes varied largely, with the largest pores being approximately 200 nm, but also dense networks and clusters were visible. The TEM images taken in the bulk of the two gel types, far away from the capillaries in the external set gel, revealed no clear difference.

Generally, alginate capillary gels could be used to take up liquids spontaneously without the need of applying external pressure or lithography techniques to result in channels [100]. Alginate gels with spontaneously formed capillaries have been shown to be suitable for cell seeding, such as muscle cells [101]; however, the results regarding equal spatial distribution are insufficient using external pumps [102]. Instead of pumping, surface tension-driven flow could be used to achieve a better spatial distribution of cells in alginate capillary gels. Garg et al. made use of capillary flow in dried capillary alginate gels for cell seeding, and found the method superior to other tested methods in terms of cell seeding efficiency, cell dispersion and cell viability than previously described seeding approaches of injection, centrifugal and orbital cultures in a dried capillary alginate gel [103]. As anticipated, investigating the dynamics of a wetting liquid was a challenge due to the dense packing of capillaries, where it is difficult to follow just one or few menisci and which makes the gel less transparent and optical access is limited.

CHAPTER 6

CONCLUDING REMARKS AND FUTURE WORK

The objective of this thesis was to deepen the understanding of the mechanism with which a liquid spreads in a soft porous material only driven by surface tension. It has been shown that the dynamics of a liquid in a soft channel of circular cross-section follow the LW law of $l^2 \propto t$, but at a remarkably slower rate than expected. The deviation is suggested to be due to a viscoelastic energy dissipation caused by the low modulus of the capillary walls. A soft solid will deform at the three-phase contact line of gas, liquid and solid. Consequently, the spreading rate increases with increasing stiffness of the walls at the same hydrophilicity. As the accompanied deformation could not be observed directly, this remains a hypothesis and has to be confirmed in further studies.

The typical LW behaviour is also exhibited by water in open-branched channel structures in a soft hydrophilic material. Comparing the spreading rate of liquid in the main channel in branched channel systems to a channel without any side channels indicated that the liquid spreads fastest in an unbranched channel. This is observed regardless of the side channels being situated on only one or two sides of the main channel. The spreading rate is lower for side channels on two sides than on only one side. Spreading is also influenced by the tilting angle, which side channels have in respect to the main channel in that angles of 30° and lower caused slower spreading rates. The liquid meniscus stops when it encounters a junction of two side channels, also referred to as pinning, as the side channels are filled. The stop durations are increased by

- longer travelled distances in the main channel,
- low tilting angles, particularly 30° or lower,
- larger or wider side channels, and
- longer side channels.

If this is related to a porous 3D material, our findings suggest, that the stop duration highly depends on the geometry of the system and could cause a selective pathway of a

spreading liquid. The stop time increases for larger or wider capillaries, which in turn suggests that smaller pores are filled first in an interconnected porous system.

Side channels close to the entrance of the capillary do not result in stops of the meniscus in the main channel, as the liquid velocity there is very fast. However, the spreading rate of the meniscus in the main channel does not account for liquid taken up by the side channels. Therefore, the flow was analysed, including the side channels, and the volumetric flow rate was determined. It revealed that the volume flow rate is highest in channels with few but long side channels.

This suggests, that an increased interconnectivity of a porous material could result in lower volume flows. Instead, low interconnectivity and long channels are suggested for fast liquid volume transport. An example of a material with low interconnectivity and long straight capillaries of circular cross-section is a calcium alginate gel produced using an external gelation. The mechanical properties of the gel were investigated and related to the microstructure. The gel could be used to efficiently take up liquids without the need of pumps. These liquids could include solutions for cell seeding to improve the spatial distribution of cells, as external pressure-driven flow currently causes inhomogeneous cell distribution.

FUTURE INVESTIGATIONS As suggested above, the deformation which caused the meniscus to decrease the spreading rate could not be observed directly and should therefore be studied further to confirm the results. One suggested method to directly investigate this is Laser Speckle Imaging (LSI) [89, 90], where the sample is illuminated with an expanded coherent light beam and speckle patterns can be recorded at any given time. Relating different speckle patterns of the times when the meniscus passes through enables a visualisation of the deformation in the gel.

A more indirect method is to determine the dependence of the spreading rate on the modulus of the gel by producing channels of the same material but highly varying shear modulus, preferably in the order of magnitudes, and investigate the spreading rate of a liquid. The modulus of the material could, for example, be tailored by the cross-linking ratio, as has been done with PDMS [104]. Due to the deformation of the material, it is expected that the liquid spreads slower as the modulus decreases.

With regard to the stiffness, it is estimated that the modulus of the material strongly influences the liquid motion particularly at junctions in open channels, which could be investigated by changing the modulus of the material. Another interesting study would be how the spreading rate in the main channel changes in the same geometries but with closed channels. If the same material, calcium alginate, would be used, an increased spreading rate is expected since one more wall is present where the driving capillary pressure can act. It could also be investigated if and how long the liquid stops in comparison to an open channel. An investigation of exactly how the alginate gel wall looks would also be beneficial to assess the spreading rate and put it into a wider perspective.

ACKNOWLEDGEMENTS

I would like to express my deepest appreciation to Anette Larsson, my main supervisor. You have helped me whenever I needed it, regardless of what the situation was like. I hope you remain as positive and caring as you are. It has been a real pleasure to work with you and I am sure our paths will cross again. I also owe a very important debt to Anna Ström, my co-supervisor, who was always happy to answer my questions. It was fun discussing work-related matters and other subjects with you. I am happy to have had you and Anette as my supervisors, as you are both great scientists and your different views in certain things made me understand the diversity of science and the scientific world once more. I would also like to express gratitude to Sven Engström for being a great examiner.

Special thanks goes to the financial support from SuMo Biomaterials, which made this project possible. With that, I also want to thank everybody in my SuMo project group, who I met regularly during the time of my PhD and who always gave valuable comments, tips and suggestions for my project.

I also want to thank all my co-authors for the support and input, particularly Tobias Gebäck, and apologise that I had to mess up your working hours in the end. Further, I appreciate the feedback offered by my other co-supervisors Mats Stading and Karin Hedsten. Romain Bordes is acknowledged for fruitful discussions and so is Gavin Jeffries for help with the dynamic contact angle measurements. A big appreciation goes to everybody who had read and corrected my thesis.

I am also very happy to have been in our small group of Pharmaceutical Technology. A big thanks goes to everybody, even former members, for interesting discussions, keeping up my motivation and lending an ear during frustrating periods.

It has also been a pleasure to be part of the Diamond division with all people involved — former and current — and I appreciate working together with all of you and will remember the enjoyable *fikas* we had.

Last but not least, I want to thank my family, my wonderful and loving husband Daniel and our adorable daughters Lotta and Tilda. Thank you for showing so much patience and giving me the time I needed. You are the colours of my life and I am very lucky and happy to have you by my side.

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