Dynamics of fluid mixtures and nano-particles during capillary suction

PROEFSCHRIFT

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Cornelis Johannes Kuijpers

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Voor papa en mama
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Chapter 1: Introduction

1.1 Context

Printing as we now know it, has its roots over five millennia ago, when the Mesopotamians used round cylinder rolls to impress images onto clay tablets. Similar techniques were used by early societies in China and Egypt (Figure 1.1a), were small stamps were used to print on cloth. However, the start of modern printing is generally attributed to the development of the printing press by Gutenberg in 1436 (Figure 1.1b). His printing press consisted of a holder containing the individual letters set in lead. Ink was applied on the letters and a sheet of paper was placed on top of it. Then, a block was placed on top of the paper and a pressure was applied to ensure the ink on the letters was transferred to the page. After each print the paper could be replaced by a new sheet and a duplicate of the page could be printed again. The printing press of Gutenberg allowed much more copies of a book to be created as compared to the preceding technique of manually copying a book by handwriting.

![Figure 1.1: Chinese woodblock printing from the Song dynasty (www.china-mike.com) (a) and a schematic drawing of the Gutenberg printing press (www.sereisumasocarne.blogspot.nl) (b).](image)

Gutenberg’s method is known as offset printing, which is still in use today. It is now used to print books, newspapers or packaging materials, of which large quantities need to be produced. The reason it is mostly used for these types of prints is the high cost, in time and money, to produce the required printing plates. For prints with small quantities of reproduction, this cost is too high and other printing methods, such as laser and inkjet printing are more cost-efficient, since printing plates are no longer required. This is the reason most people at home and at the office have either a laser
or an inkjet printer. In laser printing, the image to be printed is still created before pressing down onto the printing substrate. This is now done by charges, which can be changed from page to page allowing more flexibility. Inkjet printing on the other hand, no longer has contact between the print system and the print substrate. A droplet is forced from a reservoir and falls down onto the printing substrate, which allows for a wider variety in possible print media. The printed image consists of all the printed droplets, which in the past has limited the print quality of this technique. Due to the printing droplets becoming smaller and smaller and the accuracy of deposition gradually increasing, inkjet printing can nowadays challenge the other techniques on both cost as well as print quality.

Inkjet printing has its foundation in the work of Joseph Plateau and Lord Rayleigh with their research on the break up mechanism of a liquid stream in separate droplets in the 1870s [1], [2]. The first inkjet device based on the Plateau-Rayleigh principle was patented by Siemens in 1951 [3]. Since then, a whole range of inkjet devices have been developed using continuous inkjet or drop-on-demand techniques. In the latter, two types of methods are used to generate the droplet. In thermal printheads, the droplet is generated as result of a local heating element generating a gas bubble, which pushes the droplet from the nozzle opening in the printhead. Alternatively, a piezo printhead is based on a material that expands when a voltage is applied over this material. This piezo element then pushes the droplet through the printhead nozzle, creating an inkjet droplet. The release of the droplet from the printhead and the behavior of the droplet before reaching the printing medium has a large influence on the print quality [4]. However, even if you would be able to perfectly control the size of the droplet and the position of the drop on the printing medium, there are still a lot of factors affecting the final print quality. These factors can be the evaporation of the different ink components, the spreading of the droplet on the printing substrate and the absorption of the ink into the substrate. To continuously improve the quality and robustness of inkjet printed images as well as to limit the costs, a thorough understanding of all the relevant processes is necessary.

1.2 Motivation

Apart from the aim of inkjet printer manufacturers to better understand printing inks to improve the print quality and therefore their competitive position, there are also environmental reasons to improve the understanding of ink behavior during printing. In the “Paris Agreement”, written up by the United Nations Framework Convention on Climate Change in 2015, the participating nations came to an agreement to hold the increase in global temperature well below 2 °C as compared to pre-industrial levels, and pursue efforts to limit the temperature increase to below 1.5 °C. Moreover, low
greenhouse gas emissions and climate-resilient development should be prioritized [5]. This obviously impacts the use of fossil fuels for the global energy production, the automotive industry and agriculture, but it will also impact the use of materials, processes and solutions in any industry. Preceding the Paris Agreement, the council of the European Union has already taken steps in 1993 to limit the emission of volatile organic components in a variety of industries, such as vehicle coatings, pharmaceutical products and in printing [6]. This was followed by a more specific directive of the EU council in 2004, specifically focused on limiting the emission of volatile components in paints, varnishes and vehicle refinishing products [7]. As a result the printing industry has moved from inks based on volatile components to water based inks.

In these inks, water is the main constituent and acts as the transporting fluid to move the visible pigment or die, depending on the type of ink, to the printed substrate. These ‘greener’ inks replace the older inks in a process that has been developed and perfected over several decades. These relatively new inks are therefore still under development and the exact behavior of the inks on printing media is not yet fully understood.

Many water-based inks contain pigment particles, which are not volatile, but are hazardous to the environment in their own right. Therefore, the use of these pigments should be minimized. This poses an interesting problem, however, as the pigment is the component resulting in the visible image and is directly responsible for the print quality. The challenge is thus to minimize the use of the pigment particles, while maximizing the print quality. The design of a printing ink should find a balance between the environmental impact and the desired print quality. The optimum lies there where all the used pigment is contributing to the printed image. This sounds trivial, but in reality this design is not straightforward due to the many factors influencing whether or not a pigment particle is contributing to the print quality.

The main contributor is the deposition depth of the pigment particle inside a printed substrate. Most of the common printing substrates are porous media, which means the printing ink, containing the pigment particles, can migrate into the material through openings in the surface. The liquid penetrates up to a certain depth in the porous material and deposits the pigment particle. For certain printing media, such as coated papers, the liquid can penetrate much further than the pigment particles. Depending on the penetration depth of the particle, the pigment particle can (partly) contribute to the printed image and therefore to the print quality or not. When a particle penetrates too deep in the porous medium, intensity loss occurs, meaning the particle is only partly contributing to the printed image [8]–[10]. When the particle is deposited even further, it is no longer visible or even worse, it is visible from the other
side of the printing medium (bleed through). On the other hand, when the particles do not migrate into the porous medium deep enough, the particles can be wiped off. This can be due to people or machines handling the printed medium or just by stacking a new printed product on top of the finished pile. This implies that there is an ideal regime inside the printed medium, where all the pigment should be deposited (Figure 1.2).

![Figure 1.2: Schematic visualisation of an Océ VarioPrint i300, used for high-volume inkjet printing. A printed sheet with thickness $h$, has a pigment distribution inside the paper. There is an ideal regime where all the pigment needs to be deposited to obtain the highest possible print quality and robustness.](image)

Evaporation (of the water as well as other ink components), attachment of the particles to the substrate surface (both inside and at the surface of the porous medium) and spreading of the liquid over the substrate are just a few of the processes affecting the penetration depth of the liquid and the particles. A schematic drawing of some of the processes affecting the liquid penetration depth is given in Figure 1.3.
To develop a printing ink suitable for a specific printing method and to optimize the ink based on the used print surface, a thorough understanding of the contributing processes is necessary. This allows to predict their influences and enables the deposition of the pigment in the perfect regime to minimize the environmental impact while maximizing the print quality and print robustness.

1.3 State of the art

Typically, a water-based printing ink contains at least four components:

(a) the transporting liquid (in this case water)
(b) a co-solvent to control the evaporation rate of the ink mixture
(c) a surfactant to control the spreading of the liquid over the print surface
(d) particles (pigment) that provide the visible image

Many other components are added to control the jetting, spreading and penetration properties of the ink mixture. One of the main contributors determining the pigment penetration depth is the liquid transport of the complex ink mixtures into the paper pores. This liquid penetration occurs due to a process called capillary suction and depends on the pore geometry of the porous material and on the liquid properties. The most commonly used method to describe capillary suction is Darcy’s law, named after Henry Darcy, who studied water uptake in sand beds in the 1850s [11]. A specific case of Darcy’s law for straight capillaries is Lucas-Washburn’s law, which states that
the penetration depth follows a square root of time behavior [12], [13]. Darcy’s law can also be applied to homogeneous liquids penetrating bundles of straight capillaries, homogeneous porous media and column experiments containing glass beads or sand beds [14]–[22]. Over the years, extensions and modifications to Darcy’s law have been developed to predict liquid penetration in swelling porous media [23]–[26], heterogeneous porous media [27]–[30], unsteady flows [31] and non-circular pore shapes [32], [33]. Furthermore, theories have been developed to account for multiphase flow [34] and inertia effects [35]–[37].

When the penetrating liquid is no longer a single component, but becomes a complex mixture, the application of Darcy’s law to predict the penetration dynamics is no longer straightforward. Several studies have verified that the square root of time behavior still holds for liquid mixtures containing water-glycerol [38], water-linear alkanes [39] and water-alcohol mixtures [40]. However, other studies report a deviation from Darcy’s law due to the formation of precursor films [23], [41], [42], dynamic contact angles [43], [44], an increased viscosity [45] and temperature effects [46]. Therefore, the applicability of Darcy’s law to describe a specific penetrating liquid mixture has to be verified, before Darcy’s law can be used to predict the penetration dynamics.

If particles are added to the penetrating liquid mixture, the dynamics become even more complex and Darcy’s law is no longer sufficient to describe and predict the penetration dynamics of all mixture components (liquids and particles). Although the liquid components can in some cases still be described by Darcy’s law, front splitting between the liquid and particle front can occur due to particle attachment to the pore walls. This particle attachment can be described by adhesion models, such as the ones used in filtration theory [47]–[49]. Furthermore, the amount of particles that adhere to the pore surface in comparison to the particles that remain in the liquid as function of time is given by breakthrough curves (BTC). These curves describe the particle concentration in the liquid mixture exiting the porous material over time and are used to determine the filtration or particle retention by the porous material [50]–[52]. The particle retention depends on particle concentration, liquid velocity [53], the attraction or repulsion of the particles to the porous matrix [16]–[18], [54] and on the ratio of the particle diameter to the average pore size [15], [55], [56].

Most of the research describing filtration is focussed on the particle retention by a liquid flowing through a saturated porous medium, due to the applicability of these studies to improve filter efficiency, enhanced oil recovery and pollution prevention [14]–[17], [57]. For applications were capillary suction plays an important role, such as inkjet printing [25], [58]–[62], the prevention of cultural heritage damage [63] and
coating penetration in wood [64], a theory capable of describing particle retention due to capillary suction is necessary [65]–[69].

To verify the applicability of different models to describe both liquid and particle motion in porous media, measurements of the liquid and particles motion during capillary suction is needed. Many different experimental techniques are used for these measurements, all having their own merits. Some are very fast, such as electrical impedance spectroscopy (EIS) [70], high speed camera measurements [43], [56], [61], [71], [72], microscopy [15], infrared spectroscopy [70], [73] and ultrasonic measurements [55]). Others can be applied on a wide variety of liquid – media combinations like automated scanning absorptometer (ASA) [74]–[77] and gravimetric analysis [73], [78], [79]. None of the aforementioned methods, however, directly determines the position of the pigment front. On the other hand, there are experimental techniques that allow to measure the liquid front and particle front position inside a porous material directly, such as nuclear magnetic resonance (NMR) [80]–[86], X-ray imaging [22], [87] and neutron scattering [88]. To measure the liquid and particle dynamics during capillary suction for printing media, an experimental technique needs to fulfil a series of challenging criteria:

- A technique capable of measuring inside a non-transparent porous medium is needed.
- The technique needs to be capable to distinguishing between the particle and liquid components to capture potential front splitting
- The technique needs to be able to operate at very short time and length scales (order of milliseconds and at the micrometer scale) to be applicable to the printing industry.

No single measurement technique is able to address all of these criteria, so a combination of different experimental techniques is needed to validate developed models and to predict liquid and particle transport during capillary suction.

1.4 Objectives and Outline of the thesis

To improve the understanding of inkjet technology, and to decrease the amount of pigment needed for an adequate printing quality, a thorough investigation on the contributing factors, such as evaporation, liquid spreading, agglomeration and capillary suction is necessary. One of the determining factors for print quality is the penetration depth of the pigment particles. This depends on the liquid penetration depth of the different liquid components and on the detachment of the particle front from the liquid front.
The aim of this study is to determine both the particle and the liquid component transport during imbibition in unsaturated porous media experimentally and to provide a mathematical model to predict the dynamics of the different ink components.

Ultimately, this should contribute to a better understanding of the inkjet printing process and the development of ‘greener’ inks that contain less hazardous pigment particles, while keeping the print quality and robustness at an acceptable level. We will use NMR imaging in combination with ASA measurements to non-destructively monitor the liquid and particle front dynamics during capillary suction.

To understand the nanoparticle penetration depth, the thesis starts with an overview of the relevant theory necessary to describe the particle and liquid transport in porous media. Darcy’s law and the Lucas-Washburn equation are described and their applicability to 3 dimensional problems are discussed. Furthermore, a description of particle retention based on filtration theory is discussed to predict the particle front retention in relation to the liquid front. To verify the theory for multi-component liquid – media systems, we use NMR and ASA measurements. These experimental methods are described in Chapter 3 of this thesis.

In the experiments in this study, model porous media with well-defined pore structures are used. Furthermore model liquids are used, containing the most important components of a typical inkjet ink. This model system allows systematic variations of the liquid and media parameters and to investigate their influence on the penetration process. The used liquids (mixtures of water, glycerol and nano-particles) and their properties as well as the porous media (sintered Al₂O₃ and porous filter membranes) used in this study are discussed in Chapter 3 as well.

In Chapter 4 the applicability of Darcy’s law for two component liquids containing water and glycerol is tested by measuring the penetration dynamics of water-glycerol mixtures in porous Al₂O₃ using NMR imaging. Relaxation information is used to investigate the possible de-mixing of the liquid during penetration in the porous material. The transport of the same liquids in a similar porous material at a length and time-scale relevant for inkjet printing is investigated using ASA and is described in Chapter 5. The possibility to extend the results from the NMR measurements to short length and time scales is discussed and measurements on a paper-like filter material are described.

The motion of particles during transport of the liquid mixture in a porous medium is investigated by utilising the strong NMR relaxation dependency on paramagnetic particles. This allows the use of NMR imaging to measure both the liquid and the
particle motion into the porous material at the same time. In Chapter 6 the measured NMR results are presented and compared to the theoretical predictions from Chapter 2. The results are discussed and concluded in Chapter 7 of this thesis. In Chapter 8 ideas for further research are presented, with suggestions to improve the developed theoretical model, as well as, ideas to extend the experimental verification described in this thesis.
Chapter 2: Theory

As explained in the introduction, this thesis describes the development of a mathematical model to describe liquid and particle motion during capillary suction. In this section, Darcy’s law and the Lucas-Washburn equation are introduced to describe liquid penetration in porous media. To describe the particle dynamics during the liquid penetration, an advection model using Langmuir type absorption is used. The derivation of this model is discussed and the application and limitations of the liquid and particle transport models are discussed in this section.

2.1 Liquid absorption

2.1.1 Liquid absorption in porous media
To describe liquid penetration into a porous material, liquid properties, media properties and liquid–media interactions have to be taken into account. To start with a simple description of liquid flow through a straight cylinder we can use the law of Hagen-Poiseuille as given in equation (2.1) [89].

$$Q = -\frac{\pi r^4}{8\eta} \Delta P \quad [\text{m}^3/\text{s}].$$

(2.1)

This gives the volumetric flow rate $Q$ $[\text{m}^3/\text{s}]$ of a liquid with a viscosity $\eta$ $[\text{Pa} \cdot \text{s}]$ due to a pressure difference $\Delta P = P_{\text{out}} - P_{\text{in}}$ $[\text{Pa}]$ over a cylinder with pore radius $r$ $[\text{m}]$ and length $l$ $[\text{m}]$. By using the Hagen-Poiseuille law, we assume laminar flow, meaning low Reynolds numbers. The Reynolds number $Re$ depends on the density $\rho$ $[\text{kg}/\text{m}^2]$, the fluid velocity $v$ $[\text{m}/\text{s}]$, the characteristic length of the system $\delta$ $[\text{m}]$ and the viscosity $\eta$:

$$Re = \frac{\rho v \delta}{\eta} \quad [-].$$

(2.2)

The relevant characteristic length scale in this study is the average pore radius $r$ $[\text{m}]$ of the porous material. The highest Reynolds number encountered in this study occurs when liquid penetration is fastest, i.e. for water sorption in the largest pore size samples ($r = 8.1 \mu \text{m}$) in the beginning of capillary sorption. Using the viscosity and density of water and approximating the liquid velocity as 1 mm/s results in a Reynolds number of the order $10^{-2}$. This ensures laminar flow ($Re << 2300$) and allows the use of
2.1. Liquid absorption

The Hagen-Poiseuille law to describe the liquid penetration dynamics in straight capillaries.

In order to apply the Hagen-Poiseuille law to a porous medium, we need to take into account all liquid pathways and interconnections. To simplify the problem, we assume that the internal structure of the porous material is homogeneous and can be described by an average quantity known as the permeability \( k [m^2] \). This parameter depends on liquid and media parameters and finds its origin in the work of Henri Darcy [11]. The liquid flux \( \vec{q} [m/s] \) through a porous medium due to a pressure difference is then described by Darcy’s law [34]:

\[
\vec{q} = -\frac{k}{\eta} (\nabla P + \rho g \vec{e}_z) \ [m/s],
\]

(2.3)

where \( P [N/m^2] \) is the pressure, \( \eta [Pa \ s] \) the viscosity, \( \rho [kg/m^3] \) the density and \( k [m^2] \) the permeability parameter. Further, \( g [m/s^2] \) is the gravitational acceleration. We assume: a) that the absorbing liquid is incompressible and b) that the porous media can be divided into two zones: dry and fully saturated. Based on these assumptions, it follows from mass conservation that

\[
\nabla \cdot \vec{q} = -\nabla^2 P = 0.
\]

(2.4)

Darcy’s law can be applied to any three-dimensional porous material as long as the investigated medium is larger than the “representative elementary volume” (REV), the porous material does not change during liquid imbibition, and the liquid flow is laminar (i.e. low Reynold numbers). The REV indicates the minimum size of the porous medium, where the media parameters can be considered homogenous.

In this study, we neglect the gravity term in equation (2.3), which is justified for sufficiently small Bond numbers (Bo). The dimensionless Bond number is defined as the gravity force divided by the capillary force:

\[
Bo = \frac{\rho g \delta^2}{\sigma} [-].
\]

(2.5)

The highest Bond numbers in this study occurs for a liquid mixture containing 90 wt% glycerol and 10 wt% water penetrating into the largest pore size samples \( r = 8.1 \mu m \). Using the density and surface tension of this liquid mixture, the Bond number is of the order \( 10^{-5} \), which reflects that capillary forces fully dominate and gravity can, therefore, be neglected. When the liquid uptake can be considered one-dimensional, equation (2.3) can be rewritten to
\[ q = -\frac{k \Delta P}{\eta l} \text{ [m/s].} \] (2.6)

In the special case of a porous medium consisting of parallel capillaries with an average pore diameter \( r \), we can calculate the liquid flux directly by applying the Hagen-Poiseuille law for all capillaries in the porous block and comparing this expression to Darcy’s law to find an expression for the permeability for this special case [90]:

\[ k = \frac{n\pi r^4}{8A} = \frac{\phi r^2}{8} \text{ [m}^2\text{],} \] (2.7)

where the porosity \( \phi \) [-] gives the fraction of the porous material available for liquid flow. To extend the description to anisotropic porous media and to take into account that the pores are not simple straight capillaries, we introduce the tortuosity \( \tau \). The tortuosity factor corrects for the anisotropy of the material and for the change in path length that occurs in a porous medium, as compared to a bundle of straight capillaries. This is schematically visualised in Figure 2.1.

![Figure 2.1](image)

**Figure 2.1:** Schematic visualisation of the front position \( l \) in a bundle of capillaries and the effective path length \( l^* \) in a ‘real’ porous media.

This means that the volumetric flow rate gets modified to include the tortuosity and the penetration depth \( l \) gets corrected with a tortuosity factor \( \tau \) as well. As a result, we find that the permeability of a system of curved pipes \( k_{cp} \) with a narrow pore size distribution can be approximated by equation (5):

\[ k_{cp} = \frac{\phi r^2}{8\tau^2}, \] (2.8)

which is identical to a crude approximation of the Kozeny-Carman equation for cylindrical pores given by Zhang et al. [91]. This approximation allows the permeability
to only depend on measurable parameters and eliminates the Carman parameter $c$, accounting for the shape of the pores, and the specific surface area $S \, [\text{m}^{-2}]$ of the Kozeny-Carman equation as specified in equation (2.9):

$$k_{ck} = \frac{\phi^3}{c(1-\phi^2)S}.$$ \hspace{1cm} (2.9)

A second model for the permeability has been suggested by Katz and Thompson [92], who based their permeability factor on percolation theory. The scaling is identical to the curved pipes case, only the numerical constant differs by a factor 4:

$$k_{kt} = \frac{\phi r^2}{32 \tau^2}.$$ \hspace{1cm} (2.10)

In case of capillary uptake of a liquid into a porous matrix, the pressure difference is a result of the capillary pressure, given by the Laplace pressure $P_c$ [Pa]. The Laplace pressure depends on the surface tension $\sigma$ [N/m] and the radii of curvature $R_1$ and $R_2$ of the curved meniscus. In the case of cylindrical capillaries and negligible gravity, $R_1 = R_2 = r/\cos(\theta)$ and the Laplace pressure becomes [20]:

$$P_c = \sigma \left[\frac{1}{R_1} + \frac{1}{R_2}\right] = \frac{2\sigma \cos(\theta)}{r}.$$ \hspace{1cm} (2.11)

Combining equations (2.6) and (2.11) gives a differential equation, which can be solved by separation of variables:

$$q = \phi \frac{dl}{dt} = -\frac{k}{\eta} \frac{2\sigma \cos(\theta)}{r l}.$$ \hspace{1cm} (2.12)

In order to solve the differential equation we have to define the boundary conditions.

### 2.1.2 Liquid absorption in a partially submerged porous sample

In the nuclear magnetic resonance (NMR) experiments presented in this study, the sample is partly submerged as schematically drawn in Figure 2.2.
Depending on the fraction of the submerged sample we have to take into account 2D effects due to the liquid penetrating from the sides into the porous sample. In this study we neglect these effects, which is allowed only if the outer area of the submerged part is small as compared to the area of the bottom surface of the sample. When the length of the submerged part is given by \( l_0 \) as in Figure 2.2, this ratio is:

\[
\frac{A_{\text{side}}}{A_{\text{bottom}}} = \frac{\pi d_s l_0}{(1/4) \pi d_s^2} = \frac{4l_0}{d_s},
\]

where \( d_s [\text{m}] \) equals the sample diameter. In the NMR experiments in this study, the sample diameter \( d_s = 20 \text{ mm} \), resulting in \( A_{\text{side}}/A_{\text{bottom}} \sim 0.2 \) for samples with 1 mm of the sample submerged. So for small parts of the sample being submerged, the liquid absorption is considered one dimensional.

This means the average amount of liquid absorbed is equal to the penetration length times the porosity \( \phi \). Secondly, since we assume the sample is homogeneous, a flat liquid front is penetrating the porous material once the liquid inside the porous material has reached the water level outside the porous sample. Finally we assume the submerged part of the sample still contributes to the friction of the penetrating liquid column. Under these conditions we can solve equation (11) using integration by parts resulting in the following expression for the penetration length \( l(t) \):

\[
l^2 = \frac{4k \sigma \cos(\theta)}{\eta \phi} t + C,
\]

where \( C \) is the integration constant, which can be determined using the initial conditions for time and the liquid front position. In the NMR experiments in this study, inertia effects are neglected as the transition to a viscous regime occurs at a time \( r^* \) of the order of milliseconds, according to [35]:

Figure 2.2: Definition of the uptake parameters of a sample that is partly submerged in a liquid reservoir.
\[ \tau^* = \frac{\rho r^2}{4\eta} \text{[s]}, \]  

which is much shorter than the timescales relevant for the NMR experiments. We start the experiment at \( t = t_0 \), where the water starts penetrating into the sample resulting in \( l = 0 \). We then find \( C = -\frac{4k \sigma \cos (\theta)}{\eta \phi} r t_0 \), which results in the following expression for \( l \):

\[ l = \frac{4k \sigma \cos (\theta)}{\eta \phi} \frac{1}{r} (t - t_0). \]  

Depending on the porous medium, the permeability from Lucas-Washburn’s equation or from Katz and Thompson can be used to estimate the permeability factor in terms of known quantities.

### 2.1.3 Liquid absorption from a moving reservoir

In the automatic scanning absorptometer method, the liquid is absorbed in porous media via a dye on top of the porous material. Here the conditions to consider the liquid penetration from the dye as a 1D process are discussed. The dye has a length \( L \) [m] and width \( W \) [m] that moves over the surface of the porous sample with a speed \( U \) [m/s]. This situation is schematically given in Figure 2.3. The dye is connected to a liquid reservoir, which keeps the entire absorption area \( A \) [m²], determined by the dye dimensions, filled with liquid at all times.

![Figure 2.3: Illustration of the liquid absorption into a porous material from dye connected to a liquid reservoir.](image)

To validate the use of a one-dimensional model to describe the liquid penetration behavior in this situation we have to compare the contributions of the liquid flow in the three directions to the total absorbed liquid volume. Therefore we take one step
back and compare the pressure contributions in three directions for the pressure gradient. From the pressure field, equation (2.4), we know that

$$\nabla^2 P = \frac{\partial^2 P}{\partial x^2} + \frac{\partial^2 P}{\partial y^2} + \frac{\partial^2 P}{\partial z^2} = 0 \ [\text{Pa}],$$  \ (2.17)

where x and y are the in-plane directions and the z is the depth direction into the porous material. We introduce normalised coordinates using the dye dimensions (width \(W\) and length \(L\)) and the liquid penetration depth \(l \ [\text{m}]\), defined as \(x' \equiv x/W, \ y' \equiv y/L\) and \(z' \equiv z/l\), to obtain:

$$\frac{1}{W^2} \frac{\partial^2 P}{\partial x'^2} + \frac{1}{L^2} \frac{\partial^2 P}{\partial y'^2} + \frac{1}{l^2} \frac{\partial^2 P}{\partial z'^2} = 0 \ [\text{Pa}].$$  \ (2.18)

Since the only significant pressure in the system is the capillary pressure, the second derivative of the pressure in any direction is always of the order \(P_c\) as defined in equation (2.11). We can rewrite equation (2.18) using two conditions defined as \(\zeta \equiv \left(\frac{l}{W}\right)^2\) and \(\psi \equiv \left(\frac{W}{L}\right)^2\):

$$\zeta \frac{\partial^2 P}{\partial x'^2} + \psi \frac{\partial^2 P}{\partial y'^2} + \zeta \frac{\partial^2 P}{\partial z'^2} = 0 \ [\text{Pa}].$$  \ (2.19)

From equation (2.19) it can be seen that the problem is 1D when \(\psi < 1\) and \(\zeta \ll 1\). The first condition depends on the dimensions of the liquid bath only and is fulfilled for rectangular dyes, where \(W < L\). The second condition depends on the liquid and porous media parameters via the penetration depth \(l\) as determined in equation (2.16). In the case of the moving dye on top of the porous medium, no part of the sample is submerged and \(t_0 = 0\). Therefore, the second condition can be rewritten as:

$$\zeta = \frac{4x \sigma \cos(\theta)}{\eta \phi} \frac{W^2}{t} \ll 1 \ [-].$$  \ (2.20)

This indicates that the 1D assumption is valid for relatively slow uptake processes (high viscosity and/or low permeability) for relatively short time scales. This condition is fulfilled in thin porous media as long as the liquid does not penetrated the full thickness of the porous sample.
2.2 Liquid mixture absorption containing particles

2.2.1 Particle adsorption

As discussed in the previous section, a liquid mixture that is brought into contact with a porous medium, starts to penetrate into the material. When this liquid contains nanoparticles, the mixture can penetrate the material as a homogeneous liquid mixture or the components can split into a liquid and a particle front. This depends on the interaction of the mixture components with the porous material. When the particles have an attractive interaction with the porous medium, the particles can stick to the pore surface, delaying the actual motion of the particles and resulting in a separation of the liquid and the particle front. This effect is studied extensively in the field of chromatography [66]–[69].

We consider the particles as equally sized spheres with diameter $d$ [m]. Particles either adsorb to the pore surface with an area $A$ [m$^2$] or stay in the solution with a volume $V$ [m$^3$]. $c_0$ [m$^{-3}$] is the particle density in the solution and $\Gamma$ [m$^{-2}$] the surface coverage of the adsorbed particles. The latter can also be rewritten in terms of the bound particle concentration $c_b$ [m$^{-3}$]:

$$c_b = \Gamma \frac{A}{V} \text{[m}^{-3}\text{]}.$$  \hfill (2.21)

The total particle concentration is equal to $\bar{c} = c_0 + c_b$ [m$^{-3}$]. Assuming that the adsorption is only driven by particle-surface interactions, the maximum absorbed amount equals $\Gamma_m = c_{b,m} \frac{V}{A} \sim d^2$ with $c_{b,m}$ the maximum bound particle concentration. In equilibrium, there is a unique relation between the absorbed amount and the concentration in solution. In case of monolayer absorption, a widely used model is the Langmuir model [93],

$$c_b = c_{b,m} \frac{\kappa c_0}{1 + \kappa c_0},$$  \hfill (2.22)

where $\kappa$ [m$^3$] is the binding constant. When $\kappa c_0 \ll 1$ a linear relation is left: $c_b = c_{b,m} \kappa c_0$. At very high particle concentrations, $\kappa c_0 \gg 1$, $c_b = c_{b,m}$. The Langmuir isotherm is an example of a type I adsorption isotherm, where the number of particles absorbing on the surface is limited by the amount of available absorption sites (Figure 2.4a). In case of multilayer absorption, the model can be extended using the BET isotherm (named after S. Brunauer, P. Emmett, and E. Teller) [94]. In the BET isotherm, the number of particles that can be absorbed is infinite. For low particle concentrations, the particle absorption based on Langmuir and the BET isotherm are equivalent.
2.2.2 Liquid component dynamics

As a first approximation, it is assumed that the imbibition process itself is not influenced by the process of particles absorbing to the porous material surface. In the case of particle retention during imbibition, two domains are present in the pore space. An upstream part without particles and a downstream part containing particles in the solution and attached on the pore walls. This situation is schematically depicted in Figure 2.5.

Figure 2.4: Sorption behavior following the Langmuir and BET sorption isotherms (a) and the corresponding reaction rates (b).

Figure 2.5: Schematic visualisation of the two domains appearing as a result of particle retention during liquid penetration in a pore.
We assume that:

(a) The liquid properties like viscosity, surface tension and contact angle are similar in domains where the liquid contains particles (before the particle front) and in domains that do not contain particles (beyond the particle front).

(b) The permeability of both domains is similar (i.e. pore blocking is similar for both domains).

(c) Osmotic effects counteracting the liquid imbibition due to capillary suction is negligible.

Under these conditions, the liquid velocity can be described by the one dimensional form of Darcy’s law (equation (2.6)) and an explicit relation between the fluid velocity \( v \) [m/s] and time \( t \) [s] can be derived,

\[
v = \frac{kPc}{2\mu\phi} \sqrt{\frac{1}{t}}.
\]  

(2.23)

### 2.2.3 Particle component dynamics

The nanoparticles in the penetrating liquid mixture can have two modes of transport: i.e. they can be advected along with the fluid with a velocity \( v \) or move by diffusion with a diffusion constant \( D \) [m\(^2\)/s] defined by the Stokes-Einstein relation [95],

\[
D = \frac{k_bT}{3\pi\eta d},
\]  

(2.24)

where \( T \) [K] is the temperature and \( k_b \) [J K\(^{-1}\)] Boltzmann’s constant. The importance of diffusion for the particle transport can be estimated with the help of the Peclet number:

\[
Pe = \frac{v d}{D} = \frac{3\pi d k_b P_c}{\phi k_b T} \quad [\text{--}].
\]  

(2.25)

Note that the viscosity drops out of the equation as both the fluid flow and particle diffusion are effected by viscosity in a similar manner. The Peclet numbers encountered in this study for the experiments with liquids containing nanoparticles are in the order of \( 10^5 \) (for the studied porous media with an average pore size \( r = 0.11 \mu m \)) to \( 10^7 \) (average pore size \( r = 8.1 \mu m \)). As \( Pe \gg 1 \), it is concluded that diffusion can be disregarded as a mode for transport and a model based on advection suffices.

Another aspect to judge is the assumption of local equilibrium. This is ensured when the liquid penetration speed is small enough compared to particle migration to the
pore wall. Therefore, we determine the distance the particle travels due to advective transport in the time needed to reach the pore wall due to diffusion ($t_D [s]$). This indicates the particle front width $w_f [m]$. The diffusion time can be calculated from the diffusion length $l_D = \sqrt{6D t_D}$. The front width can then be determined by

$$w_f = vt_D = \frac{vr^2}{6D}.$$  \hfill (2.26)

Using the average speed of the liquid penetrating the studied porous media as an approximation for the local velocity $v$, the largest front width $w_f$ is found for porous samples with the highest average pore size (in this study: $r = 8.1 \, \mu m$). In this case $w_f$ is in the order of 1 mm. For the intermediate pore size ($r = 0.6 \, \mu m$), the front width is in the order of 1 $\mu m$, and for the smallest pore sizes ($r = 0.1 \, \mu m$) it is even smaller. This indicates that the liquid penetration is slow enough to allow the particles to interact with the pore walls for the porous media used in this study.

### 2.2.4 Advection model

Based on the discussions in the previous section, a model that describes particle motion purely based on advection is formulated. Furthermore, we assume that on the time scale of interest there is equilibrium between the particles in solution and the ones attached to the pore wall. The law of mass conservation leads to

$$\frac{\partial \bar{c}}{\partial t} = -\bar{v}(t) \frac{\partial c_0}{\partial x}.$$  \hfill (2.27)

Note that $\nu c_0$ equals the particle flux. Using $\partial_t \bar{c} = (1 + \partial c_b/\partial c_0) \partial_t c_0$, equation (2.27) can be rewritten to

$$\frac{\partial c_0}{\partial t} = -\frac{\nu}{1+\partial c_b/\partial c_0} \frac{\partial c_0}{\partial x}.$$  \hfill (2.28)

Equation (2.28) clearly shows the effect of particle sorption to the pore surface. The effective particle velocity $\nu_p [m/s]$ is decreased with a factor $1 + \partial c_b/\partial c_0$, which increases with increasing binding capacity $R(c_0) \equiv \partial c_b/\partial c_0$ (Figure 2.4b). This binding capacity is determined by the sorption isotherm, and surface to volume ratio of the pore system ($c_b \sim A/V$).

When only monolayer absorption is considered, the Langmuir model (equation (2.22)) can be used, and we find

$$R(c_0) \equiv \frac{\partial c_b}{\partial c_0} = \kappa c_b m \frac{1}{(1+\kappa c_b)^2}.$$  \hfill (2.29)
Combining equation (2.28) and (2.29), the limits of the particle velocity $v_p$ are recovered. At low particle concentrations, $\kappa c_0 \ll 1$, the motion of the particle is retarded the most:

$$v_p \approx v \frac{1}{1 + \kappa c_{b,m}} = v \frac{1}{1 + \left(A/V\right) \kappa t_m}.$$  \hspace{1cm} (2.30)

At very high particle concentration $\kappa c_0 \to \infty$, the binding capacity goes to zero and the particle front coincides with the liquid front:

$$v_p \to v,$$  \hspace{1cm} (2.31)

as the fraction of time a particle resides bound to the surface is low due to the limited binding capacity.

When multilayer absorption is considered, the binding capacity goes to infinity for very high particle concentrations ($\kappa c_0 \to \infty$), as the binding capacity diverges (Figure 2.4b). This results in very high particle retardation near the particle front and therefore a broadening of this particle front. In the experiments in this study, liquids with a low particle concentration are used and sharp particle fronts are observed. Therefore a model based on Langmuir type absorption is used here.

### 2.2.5 The particle front propagation

In the NMR experiments in this study, at $t = 0$, the porous medium is brought in contact with the particle dispersion. The initial particle concentration is homogeneous upon the liquid front located at $x = 0$. The initial particle concentration profile obeys the following relation

$$c(x, 0) = c_0 \left[1 - \Theta(x)\right],$$  \hspace{1cm} (2.32)

where $\Theta(x)$ is the Heaviside function, representing the initial particle front. It follows from equations (2.27) and (2.29) that the effective velocity of the particles at the leading edge of the front is lower than the particle velocity just upstream of the front. As a consequence, the front will propagate through the porous matrix as a discontinuity in the concentration profile: a shockwave. The position of the front is $x = s(t)$ and the concentrations at both sides of the front equal $c_+ \equiv c(s_+, t) = 0$, $\bar{c}_+ \equiv \bar{c}(s_+, t) = 0$, $c_- \equiv c(s_-, t) = c_0$ and $\bar{c}_- \equiv \bar{c}(s_-, t) = c_0 + c_b(c_0)$. The aim of this section is to find an expression for the propagation of the particle front: $ds/dt$.

Given the shockwave nature for the concentration front, we have to rely on mass-conservation arguments and should start with equation (2.27). Here we follow the
Chapter 2: Theory

same line of reasoning as Oliver [96]. The amounts of particles \(N(t)\) and \(N(t + \Delta t)\) in the zone where the front passes between \(t\) and \(t + \Delta t\) can be estimated with

\[
N(t) \approx A_\phi \phi \bar{c}_+(s(t + \Delta t) - s(t)),
\]

and

\[
N(t + \Delta t) \approx A_\phi \phi \bar{c}_-(s(t + \Delta t) - s(t)).
\]

From these equations follows that

\[
\frac{dN}{dt} = A_\phi \phi \frac{\bar{c}_- - \bar{c}_+}{\Delta t} \approx A_\phi \phi \bar{c}_- \frac{ds}{dt},
\]

where \(A_\phi \ [m^2]\) is the cross-sectional area of the sample of interest. \(\frac{dN}{dt}\) can also be directly calculated from integration of \(\bar{c}(x, t)\) for the zone \([s(t), s(t + \Delta t)]\), which gives

\[
\frac{dN}{dt} = \frac{d}{dt} A_\phi \phi \int_{s(t)}^{s(t + \Delta t)} \bar{c}(x, t) dx = A_\phi \phi \int_{s(t)}^{s(t + \Delta t)} \frac{d\bar{c}(x, t)}{dt} dx,
\]

using equation (2.27) and the fact that \(v\) is an explicit function of time (equation (2.23)) we find

\[
\frac{dN}{dt} = -A_\phi \phi \int_{s(t)}^{s(t + \Delta t)} v \frac{dc(x, t)}{dx} dx = -A_\phi \phi v(c_+ - c_-).
\]

By combining equations (2.35) and (2.37) the Rankine-Hugoniot jump condition for the speed of the particle front can be found:

\[
\frac{ds}{dt} = v \frac{c_+ - c_-}{\bar{c}_- - \bar{c}_+}.
\]

With the boundary conditions of interest, equation (2.38) is rewritten as

\[
\frac{ds}{dt} = v \frac{c_0}{c_0 + cb(c_0)} = v \frac{c_0}{c_0 + (A/V)\Gamma(c_0)}.
\]

In case of Langmuir-type of sorption (equation (2.22)), equation (2.39) can be rewritten to

\[
\frac{ds}{dt} = v \frac{1 + \kappa c_0}{1 + \kappa [c_0 + cb, m]} = v \frac{1 + \kappa c_0}{1 + \kappa [c_0 + (A/V)\Gamma_m]}.
\]

The particle front position is then found by integration of this expression
2.2. Liquid mixture absorption containing particles

\[ s(t) = l(t) \frac{1+\kappa c_0}{1+\kappa[c_0+c_{b,m}]} + l_0 = l(t) \frac{1+\kappa c_0}{1+\kappa[c_0+(A/V)\Gamma_m]} + l_0, \]  

(2.41)

where \( l \) is the liquid front position as given in equation (2.16) and \( l_0 \) the initial liquid position. Since the particles are transported by the liquid, the particle front and liquid front are both at the bottom of the sample at \( t = 0 \), which results in \( l_0 = 0 \).

In Figure 2.6, the speed of the particle front \( ds/dt \) is plotted as a function of the particle concentration in the solution \( c_0 \) for different binding capacities, \( (A/V)\Gamma_m \). Figure 2.6 directly shows the limiting cases. For high particle concentrations, \( \kappa c_0 \rightarrow \infty \), the position of the particle and liquid front coincide: \( ds/dt \rightarrow v \) and \( s \rightarrow l \). For low particle concentrations, \( \kappa c_0 \approx 0 \), it can be shown that

\[ \frac{ds}{dt} = v \frac{1}{1+\kappa c_{b,m}}. \]  

(2.42)

This means that at low particle concentrations, the particle retardation only depends on the binding coefficient and the maximum amount of particles that can be attached to the pore walls. This retardation is largest for porous media that can bind large amounts of particles on the pore walls, which occurs for high binding constants and high surface to volume ratios of the pore space.

![Figure 2.6: The ratio between the speed of the particle and liquid front, \( v^{-1} ds/dt \), as a function of \( \kappa c_0 \). Curves are shown for different binding capacities: \( (A/V)\kappa \Gamma_m \).](image)
Chapter 3: Methods and materials

To measure particle and liquid transport during capillary suction in porous media, we use two experimental techniques that complement each other. NMR imaging is used to measure the particle and liquid fronts in the porous media directly. Furthermore, it grants the possibility to investigate de-mixing of the liquid mixture components. To investigate the applicability of the model on thin porous media the ASA method is used, which allows fast measurements of the total liquid absorbed in the porous sample. Apart from these experimental techniques, the liquids and porous media used in this research are described here.

3.1 Nuclear magnetic resonance imaging

3.1.1 NMR principles
NMR (Nuclear Magnetic Resonance) imaging is a non-destructive technique that allows the determination of local moisture content inside a porous material [97]. The NMR measurements in this study were performed using a home built 1D NMR scanner tuned to measure hydrogen profiles similar to Kopinga and Pel [98]. A static magnetic field $B_0$ [T] of 0.7 T is generated by a water-cooled iron cored electromagnet. The sort of nuclei that can be measured depends on the local magnetic field $B$ [T] and the frequency $f$ [Hz] used to excite the nucleus.

$$f = \gamma B,$$  \hspace{1cm} (3.1)

the proportionality factor is the gyromagnetic ratio, that depends on the nucleus to probe (for $^1$H $\gamma = 42.58$ MHz/T). In order to have spatial resolution, the magnetic field is varied in a well-defined manner: i.e. a field with a constant gradient $G$ [T/m] is generated:

$$f = \gamma (B_0 + Gx),$$  \hspace{1cm} (3.2)

where the position of the sample with respect to the centre of the magnet is given by $x$ [m]. When a RF pulse with a frequency matching the frequency in the magnetic field is applied, the hydrogen atoms can be excited and measured using a pick-up coil. The measured signal $S$ is proportional to the number of hydrogen atoms in the measurement volume and decreases over time due to spin-lattice relaxation ($T_1$) and
spin-spin relaxation \( (T_2) \). \( T_2 \) depends on the molecular structure of the probed liquid and on the surroundings of the nuclei (for example pore size). For moisture in porous material \( T_2 \ll T_1 \), the measured signals proportionality is given by

\[
S \sim \rho \left(1 - \exp\left(-\frac{t_r}{T_1}\right)\right) \exp\left(-\frac{t_e}{T_2}\right),
\]

where \( \rho \) [kg/m\(^3\)] is the nuclei density, \( t_r \) [s] (repetition time), the time between subsequent pulse sequences and \( t_e \) [s] is the echo time.

To get the maximum signal, all nuclei need to be excited by an RF pulse that flips the net magnetic moment by exactly 90° with respect to the direction of the applied magnetic field. After such a 90° pulse, the magnetization is located in the so-called transversal plane (Figure 3.1). After the 90° pulse the magnetization follows a precessing motion in the transversal plane. Not all nuclei are in the same local magnetic field due to dipole interaction with the solid matrix of the porous sample. This results in dephasing of the different nuclei with respect to the net magnetic moment -called transversal relaxation- and a decreasing signal in time.

On the other hand, when a nucleus moves during the NMR measurement (due to diffusion), the frequency needed to flip this nucleus by exactly 90° changes. This is a result of the position dependent magnetic field, equation (3.2). The relaxation due to dipole effects as well as the movement of nuclei out of the measurement domain due to diffusion \( T_{2,diffusion} \) results in a decrease of the measured signal in time. This indicates that the transversal relaxation time \( T_2 \) can be split in a dipole part \( T_{2,dipole} \), and a contribution due to diffusion \( T_{2,diffusion} \).
The signal decrease due to static field inhomogeneities in the magnetic field can be reversed when an RF pulse is used to flip the net magnetic moment by 180 degrees. This results in a rephasing of the magnetic moments and an increase of the measured signal until all magnetic moments of the nuclei are realigned and the signal is at its maximum. The dephasing and rephasing due to a 180 degree pulse after the 90 degree pulse is schematically given in Figure 3.2. The magnetic moments are given in the transversal plane and the arrows indicate moments of nuclei in different local magnetic fields. The magnetization is shown in a rotating frame moving along with the average magnetization direction. This rephasing cannot be used to gain a signal from nuclei that have lost their magnetization due to relaxation in the liquid or due to interaction with the pore walls.

There are different pulse sequences available \([97]\) that allow to determine the \(T_1\) and \(T_2\) relaxation time and to determine the contribution of diffusion to \(T_2\) relaxation. In this study, 3 different NMR pulse sequences have been used which are schematically given in Figure 3.3: The Hahn spin echo, a CPMG sequence and the Stimulated echo sequence. Each sequence starts with a 90° pulse with a pulse length \(p_{90}\). After this 90° pulse, a second pulse is applied that is either the same (90°) or a pulse with the same length but an increased power (180°). After the echo time \(t_e\) we measure the signal in a window width \(w_w\). The proportionality of this signal to the number of nuclei and the relaxation parameters is given in equation (3.3).
The Hahn spin echo consists of a $90^\circ$ pulse followed by a $180^\circ$ pulse to obtain an echo. A single Hahn measurement, however, does not give information about the relaxation time behavior and only gives a value for the number of the measured nuclei in the measurement domain [99]. However, repeating this measurement with different repetition times allows the determination of $T_1$ (longitudinal relaxation time). Furthermore, multiple Hahn spin echo measurements with a changing echo time $t_e$ can be used to determine the transversal relaxation time ($T_2$).

This method to determine $T_2$ is, however, very time consuming due to the relatively long repetition time needed in between subsequent measurements (~1 s). A much quicker method to determine the $T_2$ relaxation time is by using a CPMG sequence [100]. A CPMG pulse sequence consists of one $90^\circ$ pulse and a series of $180^\circ$ pulses to refocus the magnetisation repeatedly. When all hydrogen atoms are in similar surroundings, the amplitude of the $n^{th}$ echo in the echo train follows an exponential decay given by
\[ S_n = S_0 \exp \left( -\frac{nt_e}{T_2,\text{dipole}} \right) \text{[a. u.]} \]

(3.5)

where \( S_0 \) [a. u.] is the original signal amplitude [97] and depends on the number of nuclei and the nuclei density (equation (3.3)).

To measure the diffusion of liquid nuclei inside a porous medium one can utilise the signal decay due to the diffusion of excited nuclei out of the measurement domain by using the stimulated echo sequence [101]. In this sequence the magnetization is temporarily stored along the direction of the external magnetic field (z-axis in Figure 3.1), where the signal only decays due to \( T_1 \) relaxation. This allows to preserve the magnetization longer and measure the effects of diffusion. In the stimulated echo sequence, three 90 degree pulses are applied (Figure 3.3). After the second pulse, the ‘primary echo’ is measured and after the third pulse, the ‘stimulated echo’ is recorded. Both the ‘stimulated echo’ and the ‘primary echo’ decay due to diffusion, \( T_2,\text{dipole} \) and \( T_1 \) effects. The diffusion can be determined on the basis of the quotient of the stimulated and primary echo as a function of the time between the second and third pulse \( d_s \) [s]. This results in

\[ \ln \left( \frac{M_{st}}{M_{pr}} \right) = -\left[ \frac{1}{T_1} + (\gamma G)^2 D \tau_e^2 \right] d_s, \]

(3.6)

where \( M_{st} \) and \( M_{pr} \) are the signal from the stimulated and the primary echo respectively. \( \gamma \) is the gyromagnetic ratio of the nucleus, \( G \) the magnetic field gradient, \( \tau_e \) [s] the time between the pulse and the echo and \( d_s \) [s] the difference between \( \tau_2 \) and \( \tau_1 \). After saturating porous samples with demineralised water and measuring the primary and stimulated echo intensity as a function of \( \tau_2 \), \( D \) can be calculated for water in a porous medium.

### 3.1.2 NMR Experimental details

In our setup, we use a static magnetic field of 0.7 T and have a gradient \( G \) of maximum 0.45 T/m. As a result, we can measure the hydrogen concentration as a function of position with a resolution of maximum 0.7 mm. For this study, however, we used a smaller gradient of 0.23 T/m resulting in a resolution of 1.4 mm. As a result, each measurement point is the average of a slice with thickness 1.4 mm. The resulting frequency for hydrogen in our setup is 29.415 MHz. A schematic drawing of the NMR setup and the sample holder is given in Figure 3.4. The combination of the setup and the sample holder allows the measurement of cylindrical samples up to 20 mm in diameter and 70 mm in height.
To measure at different positions, we use a step motor to move the sample through the sensitive area of the NMR equipment. In our case, the step motor can be moved in steps of 0.85 mm. To measure a signal profile, we move the sample holder through the setup in 25 steps of 3.4 mm. This results in a total measurement range of 85 mm including the sample with a length of 50 mm, the liquid bath and the reference compartment. At each position, we conduct a series of measurements and each data point is the average of these measurements. The number of measurements is given by $n_{avg}$. A Hahn pulse sequence is used to measure the water content and a CPMG sequence is used to investigate the relaxation behavior and thereby the liquid mixture configuration at the measured points. A complete signal profile of 25 points takes approximately 10 minutes to measure. Subsequent measurements are conducted until the sample is saturated. The instrument settings for the used pulse sequences can be found in Table 3.1. The used parameters are given for CPMG measurements on liquids with and without nanoparticles.
Table 3.1: Standard input settings for the pulse sequences used in this study to measure liquids with and without nanoparticles.

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<th>CPMG (with particles)</th>
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</tbody>
</table>

We start our experiments by measuring the signal profile of the dry sample in the sample holder before adding the liquid. For a dry sample we measure no signal and we only obtain a signal from the liquid in the reference compartment. This profile is used to ensure a proper positioning of the sample holder as well as a check for residual liquids in the sample.

Next, we feed the liquid to the sample compartment for about 2 minutes and start the measurement. During this time, the empty area below the sample is filled with liquid. Approximately 30 to 60 seconds after the start of the experiment, liquid can be seen to exit from the outflow tube, which means the liquid has reached the outflow tube level and will remain at a constant level from that point onwards. The outflow tube is located at 2-4 millimetres above the bottom of the sample, as shown in Figure 3.4. Therefore, the liquid has reached the bottom of the sample and imbibition starts around the same time the measurement is started.

Then, we measure subsequent profiles until the sample is saturated. An example of a water uptake experiment in 0.2 μm porous Al₂O₃ is given in Figure 3.5. In the experiment each profile point is measured at a specific moment in time by moving the sample through the setup. In order to obtain a profile at a single time, the position and time of each measurement point are stored and a spline interpolation is applied to obtain the signal intensity at every point in time for all the positions. The spline interpolation and the measurement points at 4 positions in the sample are given in Figure 3.5b. As a result of the used time interpolation procedure to approximate the signal intensity at any point, a sharp front passing the position at a certain time will result in a gradual increase of the signal between the two closest measurement points. These points are about 500 seconds apart, which can result in signal being attributed to locations, which are not yet reached by the front in reality. This results in a visibly
more inclined front. Secondly, an interpolation error can occur from the measurement noise if the measured signal intensity is very low. For example, the interpolation error occurs near the end of the Al$_2$O$_3$ sample before the liquid has reached this position, resulting in a negative signal intensity or a signal intensity much higher than expected. This effect is visible at the interpolated time curve for position 70.9 mm in Figure 3.5b.

In Figure 3.5a, a domain at the bottom of the Al$_2$O$_3$ sample, indicated by the red circle, is visible where the measured signal is higher compared to the rest of the sample in the saturated case. This is due to the liquid present in the sample holder next to the submerged part of the sample, as indicated schematically in Figure 3.4. The front position is defined by the position where the liquid level is about 70% of the saturated sample liquid level. The position and time of this point are calculated by interpolation of the nearest measured points.

![Figure 3.5: Water uptake experiment in 0.2 μm porous Al$_2$O$_3$ (a) and the measured signal intensity as a function of time at 4 positions in the Al$_2$O$_3$ sample, including the spline interpolation fit used (b). The front position is measured at about 70% of the saturated signal level. The time between two subsequent profiles is 8.5 minutes.](image)

### 3.1.3 Uptake experiments

The liquids are fed to the sample holder (Figure 3.4) through flexible tubes with an inner diameter of 2.4 mm and a wall thickness of 0.8 mm by two peristaltic pumps (Lead Fluid BQ50s). One pump is used to feed the liquid flow to the sample holder at 5 rpm, whereas the second one pumps liquid back to the reservoir at 30 rpm. Since the connection of the outflow tube is above the connection of the inflow and above the bottom of the sample, this ensures a constant liquid level just above the bottom of the sample. The sample holder allows air to enter from the top to prevent the formation of a vacuum. Using this procedure, we ensure that the liquid available to penetrate the porous samples at all times contains the same components in the same concentrations even though some components might penetrate the sample faster than others.
3.2 Automatic scanning absorptometer

3.2.1 ASA principles
The Automatic Scanning Absorptometer (ASA) is a spiral-scan Bristow device based on the original Bristow wheel. The Bristow wheel method measures the absorption as the length of a liquid track left behind by a given volume of liquid [102]. A liquid container passes over the measured surface at a constant speed resulting in a constant absorption time (i.e. contact time). The absorption time can be varied by altering the speed of rotation of the wheel containing the measurement sample. The ASA method uses a horizontal disk to position the measurement sample under the liquid container following a spiral pattern. Furthermore, the rotational speed of the horizontal disk can be altered during a measurement sequence, which allows several absorption times to be measured in a single experiment.

In this research, an ASA device from Kumagai Riki Kogyo is used (KM 500win). ASA is designed to accurately determine the liquid penetration into porous media on timescales of milliseconds to several seconds. Figure 3.6 shows a photograph and a schematic illustration of the experimental setup.

![Figure 3.6: Photograph (a) and schematic illustration (b) of the Automatic Scanning Absorptometer setup with a schematic representation of the scanning head. The different liquid containing tube sections are numbered 1-4.](image)

The ASA consists of a turntable (sample stage), scanning head (including nozzle), two types of glass capillary (inner diameter 1.04 and 3.03 mm), and a sensor that follows the movement of the meniscus. The scanning head (shown in Figure 3.7), made of stainless steel (SUS 304), has a slit with dimensions $L_{slit} = 4.9$ mm and $W_{slit} = 1.0$ mm. The maximum nozzle dimensions are $L_{max} = 6.2$ mm and $W_{max} = 3.0$ mm. The nozzle rests on top of the porous material placed on a turntable.
The glass capillary is connected with the scanning head via flexible Teflon tubes (with inner diameter ID = 2.0 mm). Liquid flows continuously from the glass capillary to the tip of the scanning head via liquid paths 1 and 2 as shown in Figure 3.6b. At the start of each measurement, the measurement liquid is absorbed into the tubes of the ASA measurement system from a container by pulling up the syringe using liquid paths 3 and 4 as shown in Figure 3.6b. The Teflon cocks can be rotated to control, which liquid paths are accessible. The glass capillary contains water and the absorbing liquid section of the Teflon tubes in liquid path 2 are separated by a short section of empty Teflon. The part of the Teflon tubes containing the liquid under investigation is replaced for each new liquid. An optical sensor detects the movement of the meniscus following liquid transfer to the porous material. The volume of the transferred liquid (TLV) is calculated from the movement of the meniscus.

When a liquid gets in contact with the surface of a porous material, the liquid starts to penetrate this material. During an ASA measurement, liquid will be supplied from a scanning head, which moves along a spiral path as visualised in Figure 3.8. The measurement starts in the centre of the spiral. The rotational speed of the turntable is kept constant over a certain part of the track (grey sections), where after it will accelerate to the next constant value (green dotted sections). There is a small acceleration section after each measurement point. The measurement sections are alternately given in light grey dark grey to clarify the different measurement sections. When the entire measurement is finished the turntable decelerates to a standstill (red striped section). The ASA system only measures the transferred liquid volume (TLV) during the times the rotational speed is constant and records the time that the nozzle has been in contact with the media during such a section, defined as the contact time \( t \) [s]. Note that the width of the measured spiral is equal to the nozzle length \( L \).
ASA setup can measure at time scales from 10 milliseconds up to 10 seconds. Due to the limited volume of the liquid reservoir in our equipment, measurements in this research are limited to a maximum contact time of 2 seconds.

3.2.2 Nozzle dimension considerations

An important parameter for the penetration depth calculations is the contact area \( A \) [m\(^2\)] of the liquid with the porous substrate:

\[
l = \frac{TLV}{\phi} \quad [m],
\]

(3.7)

where \( \phi \) [\(\%\)] is the porosity of the porous material and \( TLV \) [m\(^3\)] the transferred liquid volume. The contact area for each measurement is shown in Figure 3.8 as the grey area, which depends on the length of the nozzle \( L \) and the nozzle trajectory during the spiral movement in that section. In the case that the liquid is non-wetting for the nozzle, one can use the slit length \( L_{slit} \) [m] to determine the area of the porous material through which liquid can be absorbed. However, in the case of a liquid that perfectly wets the nozzle, the liquid will spread over the nozzle surface area much faster than the penetration into the porous material, which results in an area determined by the maximum length of the nozzle \( L_{max} \) [m] indicated in Figure 3.7. For
3.2. Automatic scanning absorptometer

...a partially wetting substrate, the area used to calculate liquid penetration is in between those two limiting cases.

The nozzle dimensions influence the ASA measurement calculations in the determination of the contact time \( t \). The contact time can be calculated using:

\[
t = \frac{W}{2\pi f_{\text{turntable}} r_c} = \frac{W}{2\pi f_{\text{motor}} r_c} \cdot 30 \cdot 10^{-3} \ [s],
\]

where the turntable frequency can be calculated from the motor frequency from \( f_{\text{turntable}} = f_{\text{motor}} / 30 \cdot 10^{-3} \ [Hz] \). The motor frequency \( f_{\text{motor}} [Hz] \) is a constant in each section and a direct output of the ASA software. The average spiral radius for the liquid penetration segment under consideration is given by \( r_c \ [m] \). Depending on the wetting conditions of the liquid on the nozzle, the width \( W \ [m] \) can be equal to the slit width \( W_{\text{slit}} \ [m] \) (for non-wetting liquids), the maximum length of the nozzle area \( W_{\text{max}} \ [m] \) (perfectly wetting liquids) or a value in between.

To determine the nozzle dimensions to be used in this research, we compare two ASA measurements of water absorption on a porous \( \text{Al}_2\text{O}_3 \) disk with two types of nozzles: C and F. One nozzle has dimensions as shown in Figure 3.7 (nozzle C) and a second nozzle has the side areas around the slit reduced to only 0.1 mm in both directions (nozzle F). Results calculated using the slit dimensions are shown in Figure 3.9a and data processes with the maximum nozzle dimensions is plotted in Figure 3.9b.

![Figure 3.9: ASA experiment of water penetration in a porous \( \text{Al}_2\text{O}_3 \) disk using the slit dimensions (a) and the maximum nozzle dimensions (b) to calculate the contact time and contact area for the two nozzles. The lines serve as a guide to the eye and the error bars shown represent the standard deviation in the measurement series with the same liquid – media system.](image-url)
We observe that the uptake dynamics of nozzle F hardly change with a different choice of the nozzle dimensions, i.e. slit dimensions or maximum nozzle dimensions. On the other hand, there is a clear impact for nozzle C due to the non-negligible surface area of the nozzle beyond the slit area. In Figure 3.9a, where we have used the slit dimensions to calculate the contact time and the penetration area, the liquid absorption for nozzle C is higher than for nozzle F for the same contact times. On the other hand, if we use the maximum nozzle dimensions (Figure 3.9b), we observe a lower liquid uptake compared to nozzle F at the same contact time. Since the liquid penetration dynamics should only depend on the liquid and porous media conditions, which are identical in the measurements with both nozzles, the two curves should align in the situation that takes the contributing portion of the edges into account. To determine the area of the edges that contributes to the liquid penetration process via the surface area and the contact time, depending on $L$ and $W$ respectively, we have used the raw data to recalculate $TLV/A$ and $\sqrt{t}$ where we use a fit of the form

$$L = L_{\text{slit}} + x (L_{\text{max}} - L_{\text{slit}}) \text{[m]}, \quad (3.9)$$

$$W = W_{\text{slit}} + x (W_{\text{max}} - W_{\text{slit}}) \text{[m]}, \quad (3.10)$$

where $x$ [-] is a value between 0 and 1 and represents the portion of the side areas that contains liquid and therefore contributes to the liquid uptake. We assume that the portion of the contributing side areas is equal in both directions. We determine the value of $x$ as the value where both nozzles result in the same liquid absorption for the same contact time. This implies that the penetration dynamics are independent of the nozzle used. We find that this alignment occurs for a side contribution of 0.36, so when 36% of the side areas contribute to the absorption surface and the contact time. This results in a nozzle length $L$ of 5.43 mm and a nozzle width $W$ of 1.72 mm. This is determined for water penetration on the porous $\text{Al}_2\text{O}_3$ disks. Since the contact angle of water-glycerol mixtures on $\text{Al}_2\text{O}_3$ is very similar for the used glycerol concentrations [103], we will use these values in the remainder of this study as a first order correction to calculate the surface area and the contact time.

### 3.2.3 Experimental procedure ASA

Media are preconditioned at $T = 23.0 \pm 1.0^\circ \text{C}$ and relative humidity $\text{RH} = 50 \pm 5\%$. In case of the membranes, single samples / sheets are conditioned for at least 20 minutes on a rack located in the climate room. The $\text{Al}_2\text{O}_3$ disks are reused for several measurements. To make sure that all absorbed liquid components are removed, the samples are heated in an oven to 600°C before each measurement. The heating temperature is higher than the auto ignition temperature of the organic components used in this study. After heating, disks are left to cool at room...
temperature for at least 20 minutes, i.e. to equilibrate to the conditions of the climate room.

At the start of a measurement a meniscus is created at the bottom of the nozzle by pressing down the syringe and pushing the liquid out of the Teflon tube into the nozzle. This meniscus is kept as small as possible to keep the initial error in the data acquisition as small as possible, while ensuring a good contact between the nozzle and the porous material.

The measurement is then started and the rotating table starts to rotate resulting in an ASA measurement spiral as visualised in Figure 3.8. The amount of liquid absorbed in each segment, or the transferred liquid volume is recorded by the ASA setup and the exact dimensions of the spiral are known from the experimental settings. The penetration depth can then be calculated for each segment using equation (3.7).

The nozzle follows an Archimedean spiral during the ASA measurement. We calculate the absorption area of each spiral section from the experimental settings, such as the inner and outer radius of the contributing nozzle dimension ($r_{in}$ [m] and $r_{out}$ [m] respectively) and the polar angular coordinate $\theta$ [rad]. This gives an absorption area $A_i$ for each segment $i$ equal to

$$A_i = \frac{1}{2} L (r_{c,i,end} - r_{c,i,begin}) (\theta_{i,end} - \theta_{i,begin}) [m^2],$$

with $r_{c,i,end}$ the average radius of the spiral at the start and $r_{c,i,end}$ the average radius of the spiral at the end of the measurement section. The centre position of the nozzle is calculated from the inner and outer radius of the spiral at that point from

$$r_{c,i} = \frac{r_{ini}+r_{out,i}}{2} [m].$$

The nozzle length $L$ is calculated from equation (3.9).

### 3.3 Porous media used in this study

#### 3.3.1 Al2O3 porous cylinders

In this research, we use porous Al$_2$O$_3$ samples with a diameter of 20 mm and a height of 50 mm. We used three different sample batches with an average pore radius of 0.1 μm, 0.6 μm and 8.1 μm. A SEM picture of the used sintered Al$_2$O$_3$ samples is given in Figure 3.10. A thin layer of gold was sputtered on the surface to prevent charge build-up during SEM imaging. The bright white spots in the SEM pictures are most probably an artefact from local charging of the samples during the SEM measurement.
Figure 3.10: SEM pictures of the three types of sintered Al$_2$O$_3$ samples used in this study, the scale bar equals 5 µm on the 0.1 µm average pore radius sample (a), 20 µm on the 0.6 µm pore size sample (b) and 300 µm on the 8.1 µm pore size sample (c).

The pore size distribution of the samples was measured by Mercury Intrusion Porosimetry (MIP) and given in Figure 3.11. Each of the samples has a relatively narrow pore size distribution and a well-defined pore size.

Figure 3.11: MIP measurement of the pore size distribution of the Al$_2$O$_3$ samples.

The samples were produced by Innalox ($r = 0.1$ µm) and Innovacera ($r = 0.6$ µm and 8.1 µm). The porosity of the samples is also extracted from the MIP measurements. We found that the porosity of the smallest pore sized sample is substantially smaller then for the larger ones. The sample properties are given in Table 3.2.

To determine the tortuosity of the samples used in this study, the diffusivity ($D$) of water in saturated porous samples is measured and compared to the diffusivity of bulk water ($D_0$). This diffusivity is measured using the stimulated echo sequence [103]. Inside a porous medium, diffusion is restricted by the pore walls. Consequently, the
Porous media used in this study

diffusivity in the sample is always smaller than the bulk diffusivity. This decrease can be quantified by the tortuosity [104]

$$\frac{D_0}{D} \equiv \tau^2 = \left(\frac{L}{l}\right)^2.$$  \hspace{1cm} (3.13)

Table 3.2: Sample properties of the Al\textsubscript{2}O\textsubscript{3} cylinders used in this study as determined by MIP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Avg. pore radius $r$ [μm]</th>
<th>Porosity $\phi$ [%]</th>
<th>Tortuosity $\tau$ [-]</th>
<th>Pore volume $V_{pore}$ [m$^3$/g]</th>
<th>Pore area $A_{pore}$ [m$^2$/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 μm Al\textsubscript{2}O\textsubscript{3}</td>
<td>0.1</td>
<td>22.8</td>
<td>1.9</td>
<td>0.07·10$^{-6}$</td>
<td>1.2</td>
</tr>
<tr>
<td>1.2 μm Al\textsubscript{2}O\textsubscript{3}</td>
<td>0.6</td>
<td>35.9</td>
<td>1.9</td>
<td>0.17·10$^{-6}$</td>
<td>0.59</td>
</tr>
<tr>
<td>16 μm Al\textsubscript{2}O\textsubscript{3}</td>
<td>8.1</td>
<td>39.5</td>
<td>1.7</td>
<td>0.17·10$^{-6}$</td>
<td>0.043</td>
</tr>
</tbody>
</table>

3.3.2 Al\textsubscript{2}O\textsubscript{3} porous disks

The Al\textsubscript{2}O\textsubscript{3} disks (Figure 3.12a) are 150 mm in diameter and 5 mm in height and manufactured by Innalox B.V., where the porosity and average pore size was determined by Mercury Intrusion Porosimetry (MIP) (AutoPore IV 9500, Micromeritics Instrument Corp.). The pore size distribution (Figure 3.12b) is measured for the 3 disks used in this study on a sample of the top and the bottom side of each disk. Distributions of different samples show small fluctuations, which result in small deviations in the average pore radius ($r$) and the porosity ($\phi$). The average pore radius is determined from the measured total intrusion volume and the pore area ($2V/A$) which assumes the porous medium can be modelled as cylindrical capillaries. An average pore radius of 0.10 ± 0.02 μm and an average porosity of 28 ± 1 % was found. The average pore radius and the porosity of the used samples are given in Table 3.3.

Figure 3.12: Example of an Al\textsubscript{2}O\textsubscript{3} disks used in the ASA experiments (a) and the pore size distribution of the Al\textsubscript{2}O\textsubscript{3} disks determined by MIP measurements (b).
Chapter 3: Methods and materials

After an experiment, we heat the samples to 873 K to remove all water and glycerol by evaporation and thermal, decomposition respectively. We then let the samples cool at room conditions before using them for another experiment. To validate if samples could be used after heating we have measured water uptake, water-glycerol uptake and again water uptake with the same sample using the heating procedure in between. Both water-uptake experiments showed similar results, which indicates that the glycerol is indeed removed from the samples using this heating procedure.

Table 3.3: Physical properties of the porous media used in this study. The errors in the different quantities are the estimated uncertainties of the measurement method.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness $\lambda$ [mm]</th>
<th>Average pore radius $r$ [nm]</th>
<th>Porosity $\phi$ [%]</th>
<th>Tortuosity $\tau$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>5.0 ± 0.1</td>
<td>100 ± 35</td>
<td>28 ± 1</td>
<td>1.7 ± 0.9</td>
</tr>
<tr>
<td>PVDF</td>
<td>0.107 ± 0.01</td>
<td>148 ± 44</td>
<td>61.7 ± 0.2</td>
<td>1.6 ± 0.7</td>
</tr>
<tr>
<td>PVDF</td>
<td>0.108 ± 0.01</td>
<td>218 ± 44</td>
<td>59.9 ± 0.2</td>
<td>1.3 ± 0.7</td>
</tr>
<tr>
<td>MCE</td>
<td>0.107 ± 0.01</td>
<td>71 ± 44</td>
<td>62.2 ± 0.2</td>
<td>1.3 ± 0.7</td>
</tr>
<tr>
<td>MCE</td>
<td>0.155 ± 0.01</td>
<td>194 ± 44</td>
<td>69.9 ± 0.2</td>
<td>1.3 ± 0.7</td>
</tr>
</tbody>
</table>

### 3.3.3 Polymeric filter membranes

The second class of materials studied are polymeric filter membranes, which have a fibrous structure and a thickness comparable to commonly used printing paper. The membranes used in this study are Durapore and MF-Millipore filter membranes produced by Merck Millipore. Both having a well-defined pore size distribution, the first type of membrane is made of hydrophilic polyvinylidene fluoride (PVDF) and the second is made of mixed cellulose esters (MCE). The MCE membranes consist of mixtures of cellulose acetate and cellulose nitrate and contain the surfactant Triton®. SEM images of both membranes are given in Figure 3.13.

![SEM pictures of the two types of membranes used in this study, a PVDF with an average pore radius of 0.15 µm (a) and a MCE membrane with an average pore radius of 0.07 µm (b).](image)

Figure 3.13: SEM pictures of the two types of membranes used in this study, a PVDF with an average pore radius of 0.15 µm (a) and a MCE membrane with an average pore radius of 0.07 µm (b).
For each membrane type we tested two different average pore sizes to investigate the influence of the average pore size on the uptake dynamics. We measured the pore size distribution and the porosity of all four membranes using MIP and measured the tortuosity of the samples using NMR. The average pore size, porosity and tortuosity of the different membrane types are given in Table 3.3.

3.4 Liquid mixtures

Ink is a complex mixture of several different components, each having its own function. The most important components in water-based inks are the co-solvent to control the liquid viscosity, a surfactant to influence the surface tension and pigment particles for colour. In this study, we use a model ink to investigate the influence of the co-solvent, the surfactant and the particles. We use mixtures of UHQ water, glycerol (Cremer, batchnr. 1015/EKL/38636), hexanediol (1,2-Hexanediol, batchnr. STBD8505V) and a 20 wt% Fe₂O₃ dispersion in H₂O (Sigma Aldrich, 720704-100G).

3.4.1 Liquid mixtures without nanoparticles

Glycerol is used to change the viscosity of the absorbing liquid, whereas hexanediol is used to study the effect of surface tension. The properties of the different model inks without nanoparticles are given in Table 3.4. The liquid components in each sample are determined by weight using a lab scale (Mettler Toledo AT261 DeltaRange) with an accuracy of 0.01 mg. The viscosity is measured using a rheometer (Modular Compact Rheometer 301, Anton Paar GmbH) and the surface tension is measured using a bubble pressure tensiometer (SITA science line t60/2, SITA Messtechnik GmbH) with a PEEK capillary. The surface tension of the high viscosity liquids are measured with a Krüss tensiometer (Krüss process tensiometer K12, Krüss GmbH). The density, viscosity and surface tension from literature values are given for comparison [105].

The contact angles are measured on Al₂O₃ disks, which are chemically identical to the porous Al₂O₃ samples used in this study. However, these samples were sintered at a higher temperature to obtain non-porous Al₂O₃. A DSA100 (drop shape analyser) is used to measure the contact angles on the surface of the Al₂O₃. The error estimate for the contact angle measurement equals the standard deviation of the measured contact angle for at least 3 droplets and 3 measurements per droplet.
Table 3.4: Physical properties of the liquids used in this study, the error estimates result from the uncertainties in the measurement methods.

<table>
<thead>
<tr>
<th>Mixture composition [wt%]</th>
<th>Density ρ [g/cm³] literature [104]</th>
<th>Viscosity η [mPa s]</th>
<th>η [mPa s] literature [104]</th>
<th>Surface tension σ [mN/m] Literature [104]</th>
<th>σ [mN/m]</th>
<th>Contact angle θ₀ on Al₂O₃ [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water : Glycerol : Hexanediol</td>
<td>100 : 0 : 0</td>
<td>0.998</td>
<td>0.92 ± 0.01</td>
<td>1.005</td>
<td>72.3 ± 0.1</td>
<td>71.68</td>
</tr>
<tr>
<td>75 : 25 : 0</td>
<td>1.060</td>
<td>1.86 ± 0.01</td>
<td>2.13</td>
<td>70.2 ± 0.1</td>
<td>69.59</td>
<td>80 ± 3</td>
</tr>
<tr>
<td>60 : 40 : 0</td>
<td>1.099</td>
<td>-</td>
<td>3.72</td>
<td>-</td>
<td>69.14</td>
<td>93 ± 1</td>
</tr>
<tr>
<td>50 : 50 : 0</td>
<td>1.126</td>
<td>5.38 ± 0.02</td>
<td>6.00</td>
<td>68.5 ± 0.1</td>
<td>68.39</td>
<td>89 ± 2</td>
</tr>
<tr>
<td>30 : 70 : 0</td>
<td>1.181</td>
<td>20.0 ± 0.1</td>
<td>22.5</td>
<td>66.1 ± 0.2</td>
<td>66.45</td>
<td>86 ± 4</td>
</tr>
<tr>
<td>10 : 90 : 0</td>
<td>1.235</td>
<td>172.4 ± 0.5</td>
<td>219</td>
<td>65.1 ± 0.2</td>
<td>63.76</td>
<td>82 ± 7</td>
</tr>
<tr>
<td>0 : 100 : 0</td>
<td>1.261</td>
<td>-</td>
<td>1410</td>
<td>-</td>
<td>62.28</td>
<td>96 ± 5</td>
</tr>
<tr>
<td>90 : 0 : 10</td>
<td>-</td>
<td>1.32 ± 0.01</td>
<td>-</td>
<td>25.9 ± 0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>50 : 40 : 10</td>
<td>-</td>
<td>5.51 ± 0.01</td>
<td>-</td>
<td>27.6 ± 0.2</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.4.2 Liquid mixtures containing nanoparticles

The liquid mixtures containing nanoparticles are produced by mixing a 20 wt% Fe₂O₃ in H₂O dispersion (Sigma Aldrich) with water and glycerol. The liquid mixtures are prepared by weight similar to the liquid mixtures without nanoparticles. The particle size distribution of the undiluted 20 wt% is measured by dynamic light scattering (Zetasizer Nano ZS, Malvern). The Fe₂O₃ dispersion contains nanoparticles with an average diameter of 62 nm and a distribution as shown in Figure 3.14.

![Figure 3.14: Size distribution of the Fe₂O₃ nanoparticles used in this study as measured by DLS.](image-url)
To stabilise the particles in water, a dispersant (an ethoxylated carboxylic acid) is added by the manufacturer. The liquid properties of the particle containing mixtures used in this study are given in Table 3.5. The addition of the Fe_{2}O_{3} nanoparticles is found to have little effect on the surface tension for the used mixtures. So the surface tension for the liquid mixtures containing nanoparticles can be considered constant with a value of 70 ± 2 mN/m.

Table 3.5: Physical properties of the water – glycerol – Fe_{2}O_{3} nanoparticle mixtures used in this study.

<table>
<thead>
<tr>
<th>Mixture composition [wt%] Water : Glycerol : Fe_{2}O_{3} nanoparticles</th>
<th>Particle concentration (c_{0}) [m^{-3}]</th>
<th>Viscosity (\eta) [mPa\cdot s]</th>
<th>Contact angle on Al_{2}O_{3} (\theta_{0}) [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 : 50 : 0</td>
<td>0</td>
<td>5.1</td>
<td>70 ± 2</td>
</tr>
<tr>
<td>49 : 50 : 1</td>
<td>1.7 \cdot 10^{19}</td>
<td>5.5</td>
<td>71 ± 3</td>
</tr>
<tr>
<td>48 : 50 : 2</td>
<td>3.5 \cdot 10^{19}</td>
<td>5.9</td>
<td>70 ± 2</td>
</tr>
<tr>
<td>45 : 50 : 5</td>
<td>8.9 \cdot 10^{19}</td>
<td>7.6</td>
<td>84 ± 3</td>
</tr>
<tr>
<td>43 : 50 : 7</td>
<td>1.3 \cdot 10^{20}</td>
<td>9.0</td>
<td>77 ± 2</td>
</tr>
<tr>
<td>40 : 50 : 10</td>
<td>1.9 \cdot 10^{20}</td>
<td>12.1</td>
<td>83 ± 2</td>
</tr>
</tbody>
</table>
Chapter 4: Sorption of water-glycerol mixtures in porous Al$_2$O$_3$

To investigate the ability of Darcy’s law to predict liquid penetration of two component liquids, NMR imaging experiments of water-glycerol mixtures penetrating in porous Al$_2$O$_3$ are conducted. The influence of the viscosity is studied over two orders of magnitude by changing the glycerol concentration. Furthermore, the effect of pore size in the micrometer and sub-micrometer regime is investigated. Darcy’s law accurately describes the liquid dynamics for all investigated liquid – media combinations. The permeability in Darcy’s law scales with the pore radius squared as predicted by models of Lucas-Washburn and Katz-Thompson. Furthermore, $T_2$ relaxation analysis shows that the water-glycerol mixtures penetrate the porous Al$_2$O$_3$ samples as a single homogeneous liquid, i.e. no front splitting occurs.

Adapted from Kuijpers et al., Chemical Engineering Science 173: 218-229 (2017)

4.1 Introduction

To describe the liquid penetration process in inkjet printing, the influence of the different liquid and media parameters needs to be understood. Therefore, binary liquid mixtures are used that allow the variation of one or more of the parameters controlling liquid flow. The effect of such binary mixtures on the sorption dynamics and the scaling parameters of Lucas-Washburn’s equation and Darcy’s law have recently been studied with water-ethanol [40]–[43], [106] and water-glycerol mixtures [38], [45].

Water-ethanol has been used to investigate the effect of the liquid surface tension and contact angle in a number of studies [43], [106]. Deviations from the predicted behavior by Darcy’s law and Lucas-Washburn’s equation were found to be a result from prewetting of the porous media by the ethanol phase [41], [42]. On the other hand, a study on water-alcohol mixtures in nanometer sized channels by Oh et al. [40], has shown that although the scaling with viscosity and surface tension holds for different water-alcohol mixtures, the prefactor from Lucas-Washburn’s equation is off by 10-30%. The main reason for deviations from the descriptions by Darcy and Lucas-Washburn in water-ethanol systems is the volatile ethanol phase. This gives a changing
liquid composition during uptake, which opposes the assumption of Darcy and Lucas-Washburn of a homogeneous liquid penetrating into a porous material. It would therefore be interesting to see if Lucas-Washburn’s equation and Darcy’s law do hold in a case where the two components of a binary mixture are not volatile, such as water-glycerol.

Mixtures of water and glycerol have been used to study the effect of channel width in the case of an open microchannel by Yang et al. [38]. They found a good agreement with a modified version of Lucas-Washburn’s equation for the different flow profile in the non-cylindrical channels. On a slightly larger scale, the sorption of water-glycerol is studied in glass capillaries by O’Loughlin et al. [45], who do observe discrepancies between the experimental observations and the theoretical expectations from Lucas-Washburn’s equation, which they attribute to a possible preferential adsorption of the water at the glass walls or a formation of a precursor film. In both studies, the behavior in a channel was studied, but the effect of a more complex interconnected porous material has not been addressed. Furthermore, these studies have been performed in highly idealised porous media, i.e. single channels and capillaries.

In this chapter, NMR imaging experiments of water-glycerol mixtures penetrating in real porous media are used to answer the two main research questions of this chapter. First, the applicability of Darcy’s law and Lucas-Washburn’s equation is investigated for a mixture of two miscible liquids, water and glycerol, in porous Al₂O₃ samples with different pore sizes. Secondly, the occurrence of liquid front splitting of these non-volatile mixtures during imbibition is investigated using T₂ relaxation analysis.

4.2 Water uptake

A set of uptake experiments with water are performed to check the √t behavior predicted by theory and to verify that different samples from the same batch give similar results. The capillary suction of demineralised water into 8 samples of the same batch are measured and the resulting front position as a function of √t – t₀ is given in Figure 4.1.
Figure 4.1: Front position of demineralised water penetrating into 0.1 μm Al₂O₃ versus √(t - t₀).

Figure 4.1 shows that all samples show similar front behavior. Before plotting Figure 4.1, the value of t₀ is determined by a fit through the raw data points to determine the intersection with the y-axis. The saturation level of all samples is also determined (measured near the top of the sample) and found similar for all samples with a moisture content of 18 ± 2 %. This is in line with the measured porosity by MIP (Table 3.2). The fluctuations we find for the saturated sample level are of the same order as the fluctuations of the saturation level within a sample. This is visible in Figure 3.5 by the variation of the signal intensity of the final profile over the length of the sample (excluding the submerged part). This means the samples are indeed reproducible and different samples from the same batch can be used to compare uptake measurements of varying liquids.

The linear dependency of the front position l* on √(t - t₀) (Figure 4.1) suggests that the process can indeed be described by equation (2.16). The slope of the line depends on liquid parameters, the contact angle of the demineralised water on the Al₂O₃ sample and the tortuosity of the Al₂O₃. A linear fit of the data results in a slope of 0.95. With the known liquid and media parameters (Table 3.5), the permeability can be calculated, which in this case is equal to 1.9 ± 0.5 x 10⁻¹⁷ m² or 0.019 ± 0.05 millidarcy (md). From direct calculation of the permeability using the approximations given in equation (2.9) and (2.10) values of 0.08 ± 0.06 md and 0.02 ± 0.01 md are found for the curved pipes and Katz-Thompson approximations respectively. The error approximations are determined using errors estimates in the measured quantities (φ, r, τ and θ) as well as an estimate of the error in the literature values due to temperature fluctuations (η and σ).
4.3 Water – Glycerol mixtures

The previous section shows that the theoretical prediction (equation (16)) can be used to give an estimate for the liquid sorption of a single liquid in a ‘real’ porous material. However, the uptake behavior is faster (higher permeability) than predicted by the theory. To check the predicted scaling, the sorption behavior of a mixture of demineralised water with glycerol is investigated. The liquid uptake profiles for glycerol concentrations of 25 wt%, 40 wt% and 50 wt% penetrating into Al₂O₃ samples with an average pore radius of 0.1 μm are given in Figure 4.2. From these profiles, the front position is determined as a function of time. The addition of glycerol changes the surface tension and, more pronounced, the viscosity of the imbibing solution (Table 3.5).

![Figure 4.2: Liquid uptake of water – glycerol mixtures in 0.1 μm porous Al₂O₃ containing 25 wt% (a), 40 wt% (b) and 50 wt% (c) glycerol.](image)

By rescaling with the viscosity and the surface tension, the theory predicts a single curve for all glycerol concentrations (since the contact angle does not change significantly (Table 3.5). The front position as a function of the rescaled time is given in Figure 4.3. The saturation levels for all liquids are found to be the same within the measurement accuracy. The spread in the data points results from an uncertainty in determining the time t₀ at which the liquid has reached the bottom of the sample and imbibition has started. Finally, there is an uncertainty in determining the front position due to the measurement points being 3.4 mm apart and each measurement point being the average of a measurement slice with a thickness of 1.4 mm.
Figure 4.3: Measured front position versus rescaled time of water-glycerol mixtures in 0.1 μm Al₂O₃. The colours indicate which liquid mixture is used and the symbols represent which sample of the batch is used.

After rescaling, the curves for different glycerol concentrations collapse on a single master curve. Since the other scaling parameters (apart from the contact angle) are media quantities and do not depend on the liquid used, this indicates the predicted dependency on surface tension and viscosity is correct.

The contact angle is relatively constant, but is very close to 90 degrees (Table 3.5). Therefore, when the permeability is directly calculated from the slopes in Figure 4.3, very large fluctuations and errors would be introduced due to the multiplication with \( \cos(\theta) \). Therefore, the value for the pre-factor containing the permeability as well as the contact angle is calculated to verify that this value is constant with different imbibing liquids. For each liquid several measurements were conducted on different samples of the same batch. The pre-factor is found to be 0.07 ± 0.02 mD for all studied glycerol concentrations. As expected, this factor does not change with glycerol concentration, since the permeability only depends on the medium and the contact angle was found to be relatively constant for the measured water-glycerol mixtures on Al₂O₃ (Table 3.5). The jump in liquid penetration speed for water sorption in very small capillaries (<0.3 μm) as reported by Fisher et al. [107] was not observed in this research where the scaling as predicted by Darcy’s law still holds for an average pore radius of 0.1 μm.
4.4 Effect of average pore size

The effect of the average pore size on the imbibition of water – glycerol mixtures is studied with 2 more batches of Al₂O₃ with an average pore radius of 0.6 µm and 8.1 µm. The uptake dynamics of water – glycerol mixtures in each sample is measured and the front position is plotted as function of rescaled time. The bigger pore sizes allows measurements with higher glycerol concentrations, as bigger pore sizes speed up the process, as shown by equations (2.6) and (2.7). Furthermore, it allows to verify the applicability of Darcy’s law in micrometer sized pores. The results of measurements with higher glycerol concentrations in the 0.6 µm and 8.1 µm porous Al₂O₃ samples are shown in Figure 4.4.

Figure 4.4a shows the adjusted pre-factor, i.e. \( k \cos(\theta) / \phi r^2 \), as calculated from uptake experiments, as a function of different glycerol concentration in samples with three different average pore sizes. The adjustment of the permeability with the contact angle is to decrease fluctuations and errors occurring from the contact angle being very close to 90 degrees. The second adjustment, i.e. dividing the permeability by the porosity times the pore radius squared, allows a comparison of the different pore sizes in one graph as the permeability in both Lucas-Washburn and Katz-Thompson scales with \( \phi r^2 \) (equations (2.8) and (2.10) respectively).

After correcting for the pore radius, the pre-factor of the different sample batches is found to be very similar, within the accuracy of the measurement technique. This is also predicted by the permeability models of Lucas-Washburn and Katz-Thompson. The other dependent quantity (tortuosity) is relatively constant for all samples, whereas the pore radius changes over 2 orders of magnitude.
In Figure 4.4b, the saturation liquid levels $S$ for the same sample – liquid combinations are given after correction with the reference level $S_{\text{ref}}$ and the porosity. The saturation level is not unity in all cases, indicating air entrapment for some media liquid combinations. The error bars indicate the standard deviation of the measured signal between several measurements of the same liquid media system.

Since all liquid and media systems in this study can be scaled to an approximately constant value for the adjusted pre-factor $(k \cos(\theta)/\phi r^2)$, the uptake behavior of water-glycerol mixtures in porous Al$_2$O$_3$ can indeed be described by Darcy’s law and that the permeability scales with $\phi r^2$. However, due to very large contact angles and the fluctuations in the measurements as a result of the used measurement techniques, the exact value for the permeability and the best applicable theoretical model could not be verified.

O’Loughlin et al. [45] have reported discrepancies between the theoretical expectations and the experimental results for water-glycerol mixtures penetrating in a vertical glass capillary. This discrepancy was found to increase with increasing water content of the solution. In this chapter, it is shown that the liquid sorption behavior can be scaled with liquid and media parameters and the scaling behavior as predicted by Darcy’s law holds for all studied water-glycerol mixtures. No trend related to the increase of the water content in the mixture other than the trends predicted by Darcy’s law were observed.

### 4.5 $T_2$ relaxation analysis

The previous results show that the uptake dynamics of water-glycerol mixtures in the considered porous Al$_2$O$_3$ samples can be described with Darcy’s law. As this law applies to homogeneous liquids only, we may assume the water-glycerol mixtures can be considered as such. This implies there is no splitting of the front during uptake. This opposes the front-splitting behavior of water-ethanol mixtures which were observed by Cao et al. [43], where the ethanol phase could evaporate and form a pre-wetting layer in the porous material due to the lower boiling temperature of ethanol.

To verify the absence of front-splitting during uptake, the $T_2$ relaxation times halfway in the sample are measured as a function of time. If there would be a significant splitting of the water and glycerol fronts, this can be observed in the $T_2$ relaxation analysis, since the relaxation time of a water-glycerol mixtures in a porous medium is dependent on the glycerol concentration (Figure 4.5a). Here the $T_2$ relaxation distribution is shown for 0.1 µm porous Al$_2$O$_3$ saturated with water-glycerol concentrations ranging from pure water to pure glycerol. Figure 4.5a shows that the relaxation time decreases with increasing glycerol concentration and shows that the
signal decay is mono-exponential as shown by the single peak in the relaxation distribution. The same mono-exponential behavior is found in larger pore sizes (Figure 4.5b) and the relaxation time increases with increasing pore size. This is expected, since the surface to volume ratio is smaller in larger pore sizes resulting in a less restricted movement of the nuclei and thus larger relaxation times. The inverse of the $T_2$ relaxation time, calculated from the mono-exponential decay of the signal intensity, is given in Figure 4.5c. The inverse relaxation time is plotted as a function of the glycerol concentration in the imbibing mixture for all three pore sizes used. The differences in relaxation time are significant and can be measured with the used measurement equipment. This indicates that a splitting of the front is detectable based on the differences in $T_2$ relaxation times.
Chapter 4: Sorption of water-glycerol mixtures in porous Al2O3

Figure 4.5: $T_2$ relaxation time distribution of water-glycerol mixtures in 0.2 µm Al2O3 (a), the pore size dependency of the $T_2$ relaxation time distribution (b) and the $T_2$ relaxation time dependency on pore size and glycerol concentration.

The $T_2$ relaxation time behavior during uptake of water-glycerol mixtures ranging from pure water to 50wt% glycerol in water is studied in 0.1 µm porous Al2O3. In all cases, a mono-exponential decay is observed, from the moment the liquid enters the measurement domain roughly halfway the measured sample. The measured relaxation times during uptake are shown in Figure 4.6. The time it takes the liquid to reach the measurement domain, $t_{front}$, is subtracted from the measurement time and the time is rescaled with the viscosity and surface tension to compare the behavior of the passing liquid fronts for different water-glycerol concentrations.
The relaxation time increases as the pores are filled by the passing liquid (the highlighted area in Figure 4.6), after which it stabilizes to the final relaxation time of the saturated sample. As already observed in Figure 4.5c, the final relaxation time of the saturated sample depends on the glycerol concentration in the mixture. In the event of front splitting (i.e. water moves quicker than glycerol) a jump in the relaxation time as the 2nd liquid phase passes the measurement domain would be expected. The dotted line in Figure 4.6 serves as a guide for the eye.

Such a jump or additional plateau that could indicate a splitting of the front is not observed and the change of the $T_2$ relaxation time is similar for all water-glycerol mixtures (after rescaling the measurement time with liquid parameters). Therefore, there is no indication of a splitting of the liquid front, further supporting the use of Darcy’s law for this liquid – media system.

### 4.6 Conclusion

In this chapter, it is shown that NMR can be used to study the penetration dynamics of water-glycerol mixtures and allows the investigation of front splitting in non-transparent media. Relaxation time analysis have shown that the mixtures used in this study penetrate into the porous media as one homogeneous liquid without a splitting of the liquid fronts. The uptake dynamics of liquids ranging from 0 up to 90wt% glycerol in water in porous Al$_2$O$_3$ with an average pore radius of 0.1 µm, 0.6 µm and 8.1 µm are studied.
The liquid front behavior can be rescaled with liquid and media parameters to obtain one master curve. The main conclusion is that the uptake behavior of water-glycerol mixtures in porous Al₂O₃ can indeed be described by Darcy's law. The scaling with liquid and media parameters holds over several orders of magnitude for both viscosity and pore size in the micrometer and sub-micrometer domain. Furthermore, it is shown that the permeability scales with the pore radius squared, which is also predicted by the permeability models of Lucas-Washburn and Katz-Thompson. These results agree with the findings of Huber et al. [39].

The pre-factor, which is incorporated in the permeability, could not be verified due to the large fluctuations and errors arising from the contact angle measurements at very high contact angles (near 90 degrees). In order to accurately describe the pre-factor the dynamic contact angle should be taken into account rather than the stable one as measured in this research [43], however this information is not available for the non-transparent porous media used in this research.
Chapter 5:
Capillary absorption of liquid mixtures in thin porous media

To further address the applicability of Darcy’s law to inkjet printing processes, quantitative measurements of the penetration depth of water-glycerol-hexanediol mixtures in thin porous media are studied with an Automatic Scanning Absorptometer (ASA). The penetration depth scales with liquid (viscosity and surface tension) and media parameters (average pore radius) as predicted by Darcy’s law. The penetration dynamics in PVDF and MCE filter membranes deviates from Darcy’s law, indicating specific liquid–media interaction with at least one of the liquid components. Furthermore, a linear time regime is observed in the early stages of liquid penetration. This can on the one hand indicate that either the liquid does not move into the fibrous samples as a homogenous liquid or that the porous material deforms during the liquid imbibition process. On the other hand, it could be an effect resulting from the complexity of the porous structure itself and an indication of surface film flow formation.

Adapted from Kuijpers et al., Chemical Engineering Science 178: 70-81 (2018)

5.1 Introduction

Over the years, extensions to Darcy’s law are made for deforming porous media [26], unsteady flows [31], gravitational flows and multiphase liquid penetration [34]. Furthermore, the application of Darcy’s law in different liquid–media combinations has been addressed [20], [43], [45], [108]. In order to test and validate Darcy’s law and to verify which extensions need to be taken into account for a specific liquid–media system, there is a need for experimental methods to accurately quantify the liquid transport in porous media in a time and space resolved manner.

This is especially true in the area of inkjet printing, where experimental data is limited due to the complex nature of the porous medium (paper) and the complexity of the used printing inks [24]. An important aspect of liquid absorption after jetting is that it occurs on short time and length scales, which limits the amount of experimental methods capable of monitoring the liquid absorption in real-time. These short length
and time scales originate from the fact that many printing media are thin, i.e. paper, and the printing ink is designed to stay in the top layer of a printing substrate.

A drawback of most of the fast experimental methods available is the limited combinations of liquids and porous substrates that can be studied. For high speed camera experiments, a transparent porous medium is required [61], [71]. Electrical impedance spectroscopy (EIS) relies on a non-conducting porous medium and a conducting fluid to measure liquid penetration. Furthermore, as EIS is probing conductivities and capacitances, a direct translation into liquid penetration involves a number of non-trivial assumptions. On the other hand, ASA can be applied on any porous substrate using any liquid capable of penetrating in the porous material. ASA monitors the liquid volume that penetrates into the porous medium in a given time [75]. However, as a result, ASA needs a model to extract the penetration depth from the measured transferred liquid volumes, involving assumptions about both the liquid distribution and the penetration directions relevant for the studied problem. In the reported studies in literature, a 1D flow problem is assumed, but not justified [75]–[77].

In this chapter, ASA is used to quantify the penetration depth of liquids in thin porous media during capillary suction and the ASA results are interpreted to explain penetration behavior. Firstly, to study the influence of the length and timescale on the capillary absorption, the penetration dynamics measured by ASA on well-defined Al₂O₃ samples with a thickness in the order of millimeters are compared to results obtained with 1D NMR imaging on similar liquid – media systems on centimeter sized samples (Chapter 4, [103]). Secondly, the possibility to extend the results to fibrous porous media, such as printing paper, using polymeric filter membranes with a fibrous structure and a well-defined pore size distribution is investigated. The membranes are reasonably homogenous, which should allow the use of Darcy’s law to predict the liquid penetration dynamics.

5.2 Quantitative results using ASA

To verify the possibility to use ASA to measure liquid penetration in thin porous media accurately, the accessible time and length scales and the reproducibility of the ASA method are investigated. In Figure 5.1, results for three different media are shown. An uncoated printing paper, a porous Al₂O₃ disk and non-porous Teflon. As expected, there is no absorption measured on the Teflon plate. The printing paper and the Al₂O₃ plates do show liquid absorption. The absorption in the Al₂O₃ plate is much faster, which is apparent from Figure 5.1 considering the higher liquid absorption for the same contact time as compared to Teflon and printing paper. Figure 5.1 shows the
possibility to access contact times from 15 milliseconds up to 1.5 seconds using the ASA setup. In this time, the average water penetration into the different porous media can be calculated using equation (3.7) and ranges from 50 µm to 4.3 mm.

![Figure 5.1](image)

*Figure 5.1: Typical time scales accessible in an ASA experiment and the liquid volume transferred to different media for the standard liquid reservoir in the case of paper and Teflon ($D_{in}$=1.04 mm) and the larger reservoir for the Al$_2$O$_3$ measurement ($D_{in}$=3.03 mm).*

The reproducibility of the method is tested by measuring the absorption of water-glycerol mixtures into the Al$_2$O$_3$ plates. The absorption of 25 wt% and 50 wt% glycerol in water is measured three times on the same Al$_2$O$_3$ plate and the results are presented in Figure 5.2. The bars in Figure 5.2 indicate the standard deviation in the measurement series. The spread in the results equals 10%, which indicates a good reproducibility.
5.3 Validation of 1D Darcy model for ASA measurements

Firstly, to validate the 1D Darcy model to calculate the penetration depth from the transferred liquid volume, the square root of time scaling and the scaling with liquid \((\sigma, \eta)\) and media \((r)\) parameters predicted by Darcy’s law (equation (2.16)) are verified. Secondly, the ASA results are compared to the NMR measurements presented in Chapter 4 on a chemically identical material at larger length and time scales. The only difference between the two types of samples apart from the length scale is the porosity which equals 28 % in the samples used in this study as compared to 23% for the samples used for the NMR measurements.

The uptake dynamics of mixtures containing water, glycerol and hexanediol into Al\(_2\)O\(_3\) disks with an average pore radius of 0.1 \(\mu\)m are investigated to study the scaling with the viscosity \(\eta\) and the surface tension \(\sigma\). The addition of glycerol to the liquid mixtures increases the viscosity, which can be changed over two orders of magnitude. By adding hexanediol the surface tension of the penetrating liquid can be substantially decreased, i.e. in the order of 60% reduction. The viscosity and surface tension of the used liquid mixtures are described in Table 3.4. Figure 5.3 shows the ASA measurements of the water-glycerol-hexanediol mixtures. As expected from Darcy’s law, the penetration depth \((l = TLV/A\phi)\) at a specific contact time decreases with increasing glycerol concentration and the resulting increase in viscosity. A decrease in
penetration depth is also observed as a result of the addition of hexanediol and the corresponding decrease in surface tension.

![Figure 5.3: Penetration depth as a function of the contact time for several liquid mixtures penetrating in a porous Al₂O₃ disk with an average pore radius of 0.1 µm.](image)

As described in section 2.1.3, the penetration depth calculated from the liquid transferred volume is only accurate, while the liquid penetration can be regarded as a 1D process. This can be validated with the criteria given in equation (2.20). For the water-glycerol-hexanediol mixtures in Figure 5.3, we are well below the limit described for $\zeta \equiv l^2/W^2$, for which the highest value is of the order $10^{-2}$, found for the uptake of pure water. Therefore the liquid penetration may be described by a one-dimensional model, such as Darcy’s law.

To validate the scaling with viscosity and surface tension predicted by Darcy’s law and to test the expected $\sqrt{t}$ behavior the predicted penetration depth $l$ is plotted on a rescaled x-axis $(\sqrt{\sigma/\eta} \sqrt{t})$ in Figure 5.4. At least three measurements were conducted for each liquid - media combination.
5.3. Validation of 1D Darcy model for ASA measurements

Figure 5.4: Liquid penetration depth against rescaled time for water-glycerol-hexanediol mixtures in porous Al₂O₃ disks.

After rescaling with liquid parameters \((\sigma, \eta)\) and \(\sqrt{\ell}\), all absorption measurements collapse on a single master curve. This shows the liquid penetration of water-glycerol-hexanediol mixtures in thin porous Al₂O₃ disks can indeed be described by Darcy’s law and we can use Darcy’s law to predict the penetration depth of such liquids in the considered thin porous media.

A similar parameter scaling on centimetre sized samples was found with NMR imaging measurements in Chapter 4. Figure 5.5 shows a comparison of the ASA results on thin Al₂O₃ plates with these NMR results. The results are presented on a log-log scale due to the large difference of accessible time and length scales of the two methods. The penetration depth \((l = TLV/\phi A)\) in the ASA method is equivalent to the liquid front position, as determined for the NMR measurements. Figure 5.5 shows that the results of both methods align on the same master curve, which implies that the same physical processes occur at both time scales. Furthermore it indicates that the parameter scaling with the viscosity and the surface tension holds, as predicted by Darcy’s law (equation (2.16)) on both length scales.
Figure 5.5: Comparison of ASA measurement with the NMR measurements of Chapter 4 on water-glycerol mixtures penetration in porous Al₂O₃ samples. Several measurements for each liquid mixture are plotted in the same graph.

A more quantitative comparison of the ASA and NMR data is done as follows: A linear fit is made through the data points of each liquid separately, for both techniques. Equation (2.16) is rewritten to obtain an expression for the slope of these fits:

$$
\frac{l}{\sqrt{\frac{\sigma}{\eta} \sqrt{t}}} = \frac{4 \kappa \cos(\theta)}{\phi r} \text{[m].}
$$

(5.1)

For the NMR data, the time $t$ contains the correction for the experiment start time $t_0$. While the porosity $\phi$ and average pore radius $r$ of the materials are known parameters, the permeability and contact angle are the unknowns. To quantitatively compare the results of the ASA method with the NMR results, the factors $\kappa \cos(\theta)$ are calculated for the ASA measurements and compared to the NMR results of Chapter 4. The values of $\kappa \cos(\theta)$ for each liquid mixture are given in Figure 5.6.
5.3. Validation of 1D Darcy model for ASA measurements

The permeability factor ($k \cos(\theta)$) deduced from both measurement techniques is found to be similar within the spread of the measurements, although the ASA results seem to show higher values. The two methods are expected to produce similar results, since the Al$_2$O$_3$ samples are produced by the same manufacturer following the same procedure, which should result in the same permeability. The only difference is the size of the samples and the porosity. The porosity of the ASA samples is slightly higher (28%) than of the samples for the NMR measurements (23%) and the permeability is proportional to the porosity. However the difference is small and does not fully explain the difference. On the other hand, the difference between the two methods is similar to the spread in the measurement results. Since the contact angle for water – glycerol mixtures on Al$_2$O$_3$ is very similar (Table 3.4) the values for the permeability factor are expected to be constant for different glycerol concentrations.

Since the penetration depth calculated from the ASA measurements shows a quantitative alignment with the direct measurement of the penetration depth using NMR, the measurement procedure can be used to calculate the penetration depth of water-glycerol mixtures penetrating in Al$_2$O$_3$. To investigate a wider applicability to more complex porous media, such as inkjet printing media, liquid penetration in porous filter membranes is investigated.
5.4 Model applicability to fibrous porous media

To investigate ASA application for penetration depth measurements of liquids in fibrous porous media, ASA measurements are conducted on polymeric filter membranes. These membranes have a well-defined pore size distribution, a well-known porosity and tortuosity and a fibrous structure similar to printing paper (Figure 3.13). These membranes are homogeneous and do not contain filler materials or local fibre treatments, such as typically found in paper. Therefore, the membranes can be used to study the application of Darcy’s law to fibrous materials on length scales relevant for printing processes. Once again, water-glycerol-hexanediol mixtures are used to test the scaling with liquid parameters. We used two batches of membranes, PVDF and MCE membranes to investigate the dependency on liquid – media interaction.

5.4.1 PVDF membranes

The uptake dynamics of water-glycerol and water-hexanediol mixtures in two types of PVDF membranes, with an average pore radius of 0.15 and 0.22 µm, are presented as a function of time in Figure 5.7. Firstly, Figure 5.7 shows slower uptake dynamics with an increasing glycerol concentration, as expected from the increasing viscosity. Secondly, the same liquids penetrate faster in the bigger pore size. This is consistent with the predicted penetration depth (equation (2.16)), as the permeability scales with \( r^2 \) (equation (2.8) and (2.10)).

![Figure 5.7: ASA measurement of the uptake dynamics of water-glycerol and water-hexanediol mixtures in PVDF membranes with an average pore radius of 0.15 and 0.20 µm.](image-url)
5.4. Model applicability to fibrous porous media

It is stressed that the PVDF membranes used in this study have a thickness of 0.11 mm, which means that any penetration beyond this point is a result of lateral liquid penetration into the porous material. Interpretation of the data in terms of a 1D penetration model cannot be done above this value. The penetration dynamics up to this point are compared with the prediction by Darcy’s law using a scaling with the liquid and media parameters ($\sigma rt/\eta$) in Figure 5.8a. The expected square root of time behavior is checked in Figure 5.8b.

Figure 5.8: Water-glycerol-hexanediol penetration in porous PVDF membranes plotted on a linear time scale (a) and on a square root of time scale (b). The straight lines in the plots serve as a guide for the eye.

Figure 5.8a shows the predicted time scaling with pore size, surface tension and viscosity holds for water-glycerol mixtures, as the results align on a single curve for both membrane types (0.15 and 0.22 µm average pore radius). Furthermore, we observe a much higher liquid penetration speed for the water-hexanediol mixtures. Since we did not observe this specific behavior for the water-glycerol-hexanediol mixtures penetrating in porous Al₂O₃ (Figure 5.4), this indicates a specific interaction between hexanediol and the PVDF membrane.

Two regimes are visible for the uptake dynamics of water-glycerol in the PVDF membranes. In the early stages of penetration ($\sigma rt/\eta < 0.5$), (indicated by the light blue area in Figure 5.8a) linear uptake dynamics are visible whereas at later times we observe square root of time behavior (Figure 5.8b). If we assume that the porous medium is filled behind the wetting front, this effect cannot be fully addressed to inertia, as the transition to a viscous regime occurs at a time $\tau^*$ of the order of milliseconds, according to [35]:

$$\tau^* = \frac{\rho r^2}{4\eta} \text{ [s].} \quad (5.2)$$
Ben Jazia et al. observed a similar effect for the absorption of water-ethanol microdroplets in polystyrene microbeads assemblies [41]. They attributed the linear time regime to a precursor film formation by the evaporated ethanol, accelerating the spreading of the imbibition front. Although water and glycerol are not as volatile as ethanol and are not expected to evaporate as easily, it is possible that a thin liquid film is formed on the fibers of the PVDF membrane resulting in a similar effect. This film can behave as plug flow on the pore surface which extends the inertial time scale far beyond the time predicted by equation (5.2). A second possibility might be that the PVDF membrane swells, which can also alter the penetration dynamics and cause the liquid behavior to deviate from Darcy’s law. Thirdly, the extended linear regime could be a result from the complexity of the porous material itself as suggested by Liu et al. [109] and Schoelkopf et al. [110]. A closer investigation on the interaction between water, glycerol and hexanediol with the PVDF membrane is necessary to verify these hypotheses.

### 5.4.2 MCE membranes

A similar study is done using the same water-glycerol mixtures on MCE membranes. The penetration depth of two membranes (0.07 µm and 0.19 µm average pore radius) is plotted as a function of rescaled times $\left( \frac{\sigma r t}{\eta} \right)$ and $\sqrt{\frac{\sigma r}{\eta}} \sqrt{t}$. Once again, the 1D penetration model can only be applied as long as the penetration depth is smaller than the membrane thickness (0.11 and 0.16 mm respectively for the two membrane types). The results are plotted in Figure 5.9, where data points showing a penetration depth larger than the membrane thickness are omitted.

The scaling with the pore size also holds for this class of membranes. However, we observe an increase of the penetration speed with increasing glycerol concentration that cannot be attributed to the effects of viscosity and surface tension alone. This indicates that either the contact angle of water-glycerol mixtures on MCE membranes decreases with increasing glycerol concentration, or that glycerol has a very specific interaction with the MCE membranes. It is possible that glycerol acts as a plasticiser for this class of membranes.
Furthermore, Figure 5.9a shows a linear regime for the early stages of absorption although not as pronounced as observed for the PVDF membranes (Figure 5.8). This linear regime is also visible in Figure 5.9b as the visible offset in time of a straight line through the data points. This effect could also indicate a formation of a thin wetting film via evaporation at the advancing menisci, or a swelling behavior of the porous material, resulting in liquid uptake that can no longer be described by Darcy’s law. The swelling behavior could be caused by one of the liquid components plasticizing the membrane, which can result in a linear absorption if the liquid penetration is no longer limited by the viscous drag. A more detailed study on the interaction of water-glycerol mixtures with MCE membranes is necessary to address these discrepancies with Darcy’s law.

5.5 Conclusion

In this chapter, the applicability of ASA to quantitatively measure the penetration depth of water-glycerol-hexanediol mixtures in thin porous media is shown. The penetration depth obtained with ASA measurements on thin Al₂O₃ samples are compared to NMR measurements on centimetre sized samples of Chapter 4 and show a relatively good agreement with respect to the spread in the measurements. The scaling with liquid (η, σ) and media parameters (r) is found to agree with the predictions of Darcy’s law.

When ASA is used to measure the penetration depth of water-glycerol-hexanediol mixtures in porous filter membranes, a deviation of scaling from the surface energy viscosity ratio suggests that the flow mechanism is other than equilibrium capillary
flow. This deviation occurs for the PVDF membranes when liquids containing hexanediol are used and for water-glycerol mixtures on MCE membranes.

Furthermore, we observe a linear liquid penetration regime at the early stages of penetration that is too long to result from inertia effects. This could indicate the formation of a precursor film in the fibrous porous media as suggested by Ben Jazia et al. or could be related to a swelling of the porous material during liquid uptake given that one of the ingredients is able to plasticise the membrane. However, a detailed study on the interaction of these membranes with water-glycerol-hexanediol mixtures is necessary to understand this behavior more profoundly.
Chapter 6: Nano-particle dynamics during capillary suction

To understand and predict the pigment penetration, not only the liquid but also the particle dynamics during uptake have to be addressed. The penetration of complex mixtures containing Fe$_2$O$_3$ nanoparticles, as a model for a pigment particles, in porous Al$_2$O$_3$ samples is discussed in this chapter. The accuracy and applicability of a 1D model for nanoparticle penetration during capillary suction, is investigated using NMR imaging experiments. The binding constant for Fe$_2$O$_3$ nanoparticles on sintered Al$_2$O$_3$ samples and the maximum surface coverage are determined using different particle concentrations. These are then used to predict the particle retardation as compared to the liquid front for pore sizes ranging two orders of magnitude in the micrometer and sub-micrometer regime.

A good agreement between the experimentally determined particle front and the predicted particle retention is found. Furthermore, the liquid front penetrates with a square root of time as predicted by Darcy’s law. However, the scaling with the viscosity and surface tension no longer holds. The Darcy model should be extended to describe the two domains (with and without particles) separately, to give an accurate prediction for the penetrating liquid front.

Adapted from Kuijpers et al., Journal of Colloid and Interface Science 521: 69-80 (2018)

6.1 Introduction

In the case of inkjet printing, the attachment of particles in the paper porous system during capillary flow determines the penetration depth of the particles, which in turn affects the print quality and print robustness [9]. Therefore, experimental methods capable of measuring the particle and liquid dynamics in unsaturated porous media during capillary suction are necessary.

Particle transport in saturated porous media has been the topic of many studies in the last couple of decades, and theories to predict the particle retention based on colloid filtration theory (CFT) are developed for many liquid – media systems [17], [47], [48], [111]. A review on the flow of dispersed particles through porous media is given by
Zamani and Maini [49]. The retention of nanoparticles depends on both liquid and media properties, including the interaction between the liquid and the porous material. An analysis on the importance of the different liquid, media and interaction parameters defining nanoparticle transport in porous media is given by Babakhani et al. [14], who reanalysed data from published column experiments to determine the five key continuum model parameters to predict nanoparticle transport.

Validating the developed theoretical models and, in most cases, finding the attachment efficiency of a liquid – media system, requires experimental data [16]. Most of the experimental data available comes from breakthrough curves (BTC), where the outflow concentration of particles is measured over time using techniques like light extinction [82], X-ray fluorescence [18], turbidity [50] and atomic absorption [112]. The advantage of BT measurements is the high time resolution as well as the possibility to measure on any porous material. However, the main drawback of the BT method, is the use of a sample average for the particle retention measurement. Furthermore, BTC’s is often used for saturated sample measurements, which is not necessarily mimicking a real life application. Last but not least, the BTC approach is not suitable for measuring particle motion during capillary suction, as particles do not leave the porous material during the capillary suction.

Nanoparticle penetration during capillary suction in porous media has been the topic of far fewer studies [113], [114]. A review of particle retention and detachment in unsaturated porous media, especially at the air-water interface (for example at the liquid penetration front during capillary suction) is given by Flury and Aramrak [115]. Experimental techniques allowing to study liquid and particle penetration in unsaturated porous media consist of microscopy for transparent porous media, ultrasonic measurements [55], and NMR imaging [80], [81], [116], [117].

NMR can be used to study the particle transport processes during capillary suction, as the particle retention can be visualised using $T_2$ relaxation effects similarly to the ones used in medical applications for $T_2$ weighing [82], [118]. This method allows to quantify in a time and position resolved manner the penetration depth of particles and liquid during capillary suction.
In this chapter, the liquid and particle fronts as a function of time are visualised using NMR imaging experiments. From these measurements, the binding constant and the maximum surface coverage for the used Fe$_2$O$_3$ nanoparticles on the Al$_2$O$_3$ surface are determined. Furthermore, the limiting cases predicted by the particle retention model of section 0 are verified using sintered Al$_2$O$_3$ samples with an average pore radius differing over two orders of magnitude from the micrometer down to the submicrometer regime.

6.2 Visualising particle penetration in non-transparent media

In order to couple signal and particle motion, the particle distribution at the end of a capillary suction experiment is investigated. Al$_2$O$_3$ samples with an average pore radius of 0.6 µm are brought in contact with liquid mixtures containing Fe$_2$O$_3$ nanoparticles. All the liquid mixtures contain 50 wt% glycerol, $x$ wt% Fe$_2$O$_3$ nanoparticles and $(50 - x)$ wt% water, where nanoparticle concentrations $x = 0, 1, 2, 5, 7$ or 10 wt% are used. The signal profiles for the saturated Fe$_2$O$_3$ samples are given in Figure 6.1. The liquid profiles shown in Figure 6.1 consist of the signal intensity of the first echo of a CPMG sequence at each position. This echo is measured after an echo time of 0.7 ms.

Each signal profile contains three domains, the reference compartment, the liquid bath and the Al$_2$O$_3$ sample. The first domain is the signal from the reference compartment containing a 1 M CuSO$_4$ solution. This reference is used to normalise the signal; e.g. the proton density can be calculated by correcting for the reference volume and the porosity of the porous material. The second domain is the signal from the liquid bath and the third contains the signal in the porous Al$_2$O$_3$ sample. Note that there is an overlap between the liquid bath and sample domain, as a small part of the sample is submerged in the liquid bath introducing an initially multidimensional inflow.
6.2. Visualising particle penetration in non-transparent media

In the sample, two regions can be distinguished. At the bottom of the sample (the left side in Figure 6.1), a low signal is observed due to the presence of particles. At the second region (near the end of the sample) the signal is more or less constant for all studied particle concentrations. A sharp transition between the two layers is observed for high initial particle concentrations (7 and 10 wt%) and a more diffuse transition is found for low initial particle concentrations (≤ 5 wt%). The position of the interface also depends on the initial particle concentration as predicted by equation (2.41). To investigate this change in the front behavior, a cross section of the samples in the length direction is made (Figure 6.2), which shows the particle front inside the samples.
The particle front is locally sharp for all particle concentrations, but at low Fe$_2$O$_3$ concentrations, very small particle uptake is seen near the sample corners. This underlines that an NMR measurement at low particle concentrations in the initial liquid contains a contribution from a part of the sample with and a part without particles. This results in a more diffuse or gradual, smooth front as found in Figure 6.1. The question why the particles penetrate faster at the sides and centre, rather than the corners for low particle concentrations cannot be answered yet and needs further investigation.

### 6.3 Quantifying particle penetration in non-transparent media

As theoretically described in equation (3.5), a measured signal intensity is lower for liquids that have a shorter $T_2$ relaxation time (i.e. faster CPMG decay), since the signal decays further during the echo time $t_e$. The $T_2$ relaxation time depends on the particle concentration, as observed by Rhee and Kim for iron-ferrite (Fe$_3$O$_4$) nanoparticles [119]. They found the reverse of the relaxation time to be directly dependent on the particle concentration. This indicates that the liquid and particle behavior inside the porous medium can be studied in more detail by investigating the CPMG decays.

The CPMG decays in the liquid bath, the start of the sample and at the end of the sample are given in Figure 6.3a, b and c respectively for each of the studied liquids. From the CPMG decays in the liquid bath (Figure 6.3a) a faster decay is observed, i.e. a shorter $T_2$ relaxation time, for higher Fe$_2$O$_3$ concentrations as expected.
At the end of the sample the CMPG decays are similar for all particle concentrations except for the highest concentration Fe$_2$O$_3$ nanoparticles. The relaxation behavior is also the same for the liquid penetration case without particles. This indicates that, apart from the liquid containing 10 wt% Fe$_2$O$_3$, very few particles, if any, reach the end of the sample during the liquid penetration process.

At the start of the sample (Figure 6.3b), the CPMG decays for high particle concentrations ($\geq 5$ wt%) are similar to the decays found in the liquid bath, except that the relaxation is faster i.e. a shorter $T_2$ relaxation time, due to the confinement in the porous material. The CPMG decays are fitted with an exponential fit, using either a mono-exponential or dual-exponential fit to capture the relaxation times. The dual exponential decays occur for particle concentrations of 1 and 2 wt% at the start of the sample (Figure 6.3b), and at a concentration of 10 wt% Fe$_2$O$_3$ nanoparticles at the end of the sample (Figure 6.3c). The original signal amplitude $a_0$ (corrected for the decay during the echo time) is given in Figure 6.4a and the inverse $T_2$ relaxation times are given in Figure 6.4b.
Figure 6.4: The initial signal amplitude $a_0$ (a) and the inverse $T_2$ relaxation time (b), of the exponential decay fits at three positions (liquid bath, start sample and end sample). The open symbols show the shortest relaxation time, in case of dual exponential decays, the second relaxation times are given by the closed symbols. The lines serve as a guide for the eye.

The original signal amplitude $a_0$ in the liquid bath doesn’t vary as a function of particle concentration. This indicates that the signal decrease at the liquid bath observed in Figure 6.1a is purely an effect from the change in the $T_2$ relaxation time and the signal decay during the echo time $t_e = 0.7$ ms. The same effect is found for the two positions inside the porous material, although the original signal intensity of the liquid without nanoparticles is somewhat higher than found for the particle containing liquids. This effect is probably due to the changing liquid configuration that affects the saturation of the porous material as also observed in Chapter 4 for different water-glycerol mixtures.

Secondly, the initial signal amplitude $a_0$ in the liquid bath is much higher than inside the porous material. This is to be expected due to the larger liquid volume in the measurement domain. The liquid bath has a diameter of 22 mm as opposed to the 20 mm sized samples. Secondly, the porous medium can only contain liquid in the pore space, so the signal amplitude should be corrected by the porosity. These two effects result in a conversion factor of about 3.4 which is similar to the difference found in Figure 6.4a. The difference between the signal intensity at the start and at the end of the sample can be explained by local pore blocking and only part of the pore space being filled with water, which reduces the available liquid in the measurement volume.

The inverse $T_2$ relaxation time (Figure 6.4b) in the liquid bath scales linearly with the particle concentration as expected from Rhee and Kim [119]. This linear concentration dependency also holds for the inverse relaxation time at the start of the sample. The slope and offset are higher, which indicates that the relaxation time of the liquid is lower in the sample than in the liquid bath. The larger offset is expected due to the
6.4  Dynamics of particle and liquid motion during capillary suction

As shown in the previous section, the liquid and particle front can be distinguished using NMR imaging for a saturated sample. However, NMR imaging also allows to study the dynamics of particle and liquid motion during uptake. In this section, the particle and liquid front as a function of time in the 0.6 μm average pore radius Al₂O₃ samples is studied. The used liquid contains 7 wt% Fe₂O₃ nanoparticles and 50 wt% glycerol. The rest of the liquid mixture is made up of water. The uptake of the liquid mixture in the porous Al₂O₃ sample is given in Figure 6.5a.

![Figure 6.5](image-url)

Figure 6.5: 7wt% Fe₂O₃ and 50wt% glycerol in water uptake in 0.6 μm average pore radius Al₂O₃ (a). The time between two subsequent profiles equals 10 minutes. The extracted particle front at a signal height of 0.5 a.u. is plotted as a function of the liquid front position determined at the same height (b). The line serves as a guide for the eye.
The particle front clearly lags behind the liquid front. This indicates that a portion of the particles in solution become bound to the pore surface and the penetrating mixture splits in a particle rich and particle depleted domain. The theory predicts a linear relation between the positions of the liquid and the particle fronts (equation (2.41)). To verify this prediction, the particle front is plotted as function of the liquid front in Figure 6.5b.

The particle front indeed shows a linear dependency on the liquid front as predicted by the theory in equation (2.41). Furthermore, the shape of the liquid profile in the porous material seems similar for all times until the liquid has reached the end of the sample. To investigate this self-similarity, the profiles until the liquid front has reached the end of the sample are plotted, where the x-axis of Figure 6.5a is rescaled with the liquid front position \( l \), to obtain a single master curve. The rescaled graph is given in Figure 6.6, where the position is rescaled as \( x' = x/l \), where \( x' \) is the new position and \( x \) corresponds to the position from the beginning of the sample. Only the first profile deviates from the others, due to the small number of data points available for the profile. This shows that the uptake dynamics for the 7 wt% Fe₂O₃ nanoparticles is self-similar until the end of the sample is reached. Similar self-similar behavior is found for the 5 and 10wt% nanoparticle concentrations.
6.5 Influence of Fe$_2$O$_3$ nanoparticle concentration on uptake dynamics

The slope of a fit through the data points of Figure 6.5b is equal to 0.52. This means that the particle front lacks behind the liquid front by 48%. Assuming that the particles from the liquid beyond the particle front are attached to the pore wall, the amount of particles that attach on the pore walls can be estimated and the resulting fill factor of the pore surface determined. Using the Fe$_2$O$_3$ particle density $\rho_{Fe_2O_3} = 5.25$ g/cm$^3$ [120], the pore area and pore volume of Table 3.2 and assuming spherical particles with an average diameter of 62 nm, a surface coverage $\Gamma = 3.4 \cdot 10^{13}$ m$^{-2}$ and a bound particle concentration $c_b = (A/V)\Gamma$ of $1.2 \cdot 10^{20}$ m$^{-3}$ is found. Note that the bound particle concentration in this case is very close to the initial particle concentration for 7 wt% Fe$_2$O$_3$ nanoparticles ($c_0 = 1.3 \cdot 10^{20}$).

This surface coverage relates to 10.4 % of the available pore surface being filled with particles and the average distance between two particles being approximately 2.6 times the particle diameter. Theoretically, the close-packed density of randomly packed hard spheres equals 64% [121]. The surface coverage found in this case is lower as the particles repel one another to stabilise them in the liquid.

6.5 Influence of Fe$_2$O$_3$ nanoparticle concentration on uptake dynamics

To investigate the applicability of the particle retention model derived in section 0, capillary suction measurements have been performed with particle concentrations of 1, 2, 5 and 10 wt%. Signal profiles were measured as a function of time and the particle and liquid fronts were extracted from the data. The particle front position is then plotted as a function of the liquid front position in Figure 6.7 to test the linear relationship predicted in equation (2.41). For high particle concentrations (7 and 10 wt% nanoparticles) a linear relationship through zero is found as predicted. At the lowest particle concentrations (1 and 2 wt% nanoparticles) a different behavior is observed due to the 3D effects found for these low concentrations (Figure 6.2). At the intermediate particle concentration of 5 wt% Fe$_2$O$_3$ nanoparticles in the liquid mixture, a linear behavior is observed for the higher front positions (i.e. later times in the uptake dynamics), but a deviation from this linear relation occurs for the early stages of penetration. This may indicate that the 1D sharp front assumption is only applicable at later times for this specific particle concentration. What causes this deviation at low time scales is unknown and further investigation is needed to explain this non-linear behavior.
Chapter 6: Nano-particle dynamics during capillary suction

Figure 6.7: Particle and liquid front behavior during imbibition of water-glycerol mixtures containing 1, 2, 5, 7 and 10 wt% Fe$_2$O$_3$ nanoparticles. The line serves as a guide for the eye.

The particle concentration has a small influence on the slope in Figure 6.7 for the higher particle concentration’s (≥ 5 wt%). The dependency of $s/l$ can be predicted using equation (2.41). The relative front position $s/l$ as function of the initial particle concentration $c_0$ is given in Figure 6.8. Using a fitting procedure, an approximation for the maximum bound particle concentration $c_b$ and the binding constant $\kappa$ can be determined.

Figure 6.8: The relative front position as function of the initial particle concentration. The data points (5, 7 and 10 wt% Fe$_2$O$_3$) are fitted using a fit of the shape $\frac{s}{l} = \frac{1 + \kappa c_0}{1 + \kappa [c_0 + c_{b,m}]}$. 
Combinations of the max bound particle concentration $c_{b,m}$ and the binding constant $\kappa$ fitting the three data points in Figure 6.8 are given in Table 6.1. The square of the difference between the measurement points and the predicted points using the fit parameters is given in the third column of Table 6.1. This shows that the fit accuracy is sensitive to the choice of the binding constant and the max bound particle concentration and the available data points can only be used to get a first approximation of these parameters for this liquid – media system. The parameters that give the best fit in Figure 6.8 results in a binding constant $\kappa$ of $2.06 \cdot 10^{-21} \text{[m}^3\text{]}$ and a maximum bound particle concentration $c_{b,m}$ of $5.78 \cdot 10^{20} \text{[m}^{-3}\text{]}$. This gives a maximum surface coverage $\Gamma_m$ of $1.7 \cdot 10^{14} \text{[m}^{-2}\text{]}$, which is about 51% of the available pore surface. This is slightly below the theoretical maximum for randomly packed hard spheres of 64%, as expected on the basis of the repulsive interaction of the nanoparticles to stabilize them in the liquid. This indicates that Langmuir absorption can be used to predict the particle retardation of the Fe$_2$O$_3$ nanoparticles in porous Al$_2$O$_3$.

Table 6.1: Possible combinations of binding constant and max bound particle concentration to fit the data in Figure 6.8.

<table>
<thead>
<tr>
<th>Binding constant $\kappa$ $[10^{-21} \text{m}^3]$</th>
<th>Max bound particle concentration $c_{b,m}$ $[10^{20} \text{m}^{-3}]$</th>
<th>R-square value $10^{-5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>5.5</td>
<td>1.3</td>
</tr>
<tr>
<td>2.06</td>
<td>5.78</td>
<td>1.1</td>
</tr>
<tr>
<td>2.0</td>
<td>5.9</td>
<td>1.1</td>
</tr>
<tr>
<td>1.8</td>
<td>6.3</td>
<td>8.9</td>
</tr>
<tr>
<td>1.6</td>
<td>7.1</td>
<td>4.7</td>
</tr>
<tr>
<td>1.0</td>
<td>10.5</td>
<td>19</td>
</tr>
</tbody>
</table>

6.6 Influence of pore size on uptake dynamics

A second method to validate the derived model is by changing the contribution of the $\kappa(A/V)\Gamma_m$ term in equation (2.41). Therefore 3 types of Al$_2$O$_3$ samples with an average pore radius of 0.1, 0.6 and 8.1 $\mu$m are used. Since the material chemistry is the same in all cases, the binding capacity and the maximum surface coverage are expected to be the same. Therefore, the contribution of the $\kappa(A/V)\Gamma_m$ term is changed by 2 orders of magnitude over the three sample types. The imbibition of a liquid containing 5 wt% Fe$_2$O$_3$ nanoparticles is measured and the resulting liquid profiles are given in Figure 6.9a, b and c.
In the case of 0.1 and 0.6 µm average pore radius, the mixture contains 50 wt% glycerol. For the largest pore size (average pore radius of 8.1 µm), 70 wt% glycerol is used to ensure the liquid transport is slow enough to measure several liquid profiles during the liquid uptake. To compare the different types of Al₂O₃, the signal is multiplied by the sample porosity $\phi$ to directly compare the signal intensities (Table 3.2).

![Image](image.png)

**Figure 6.9:** Uptake of mixtures containing 5 wt% Fe₂O₃ and 50 wt% glycerol (a, b) or 70 wt% glycerol (c), into porous Al₂O₃ with an average pore radius of 0.1 µm (left), 0.6 µm (middle) and 8.1 µm (right). The liquid profiles are shown above (a, b, c) and the CPMG decays at three positions in the sample are shown below (d, e, f). The time between two subsequent profiles is 10 minutes.

For the smallest pore size sample, with an average pore radius of 0.1 µm, a decrease in signal at the start of the sample is visible (Figure 6.9a). This indicates that the particles only penetrate into the very beginning of the sample. This is also visible in the measured CPMG decay of the signal at the start of the sample (Figure 6.9d), which shows a faster decay as compared to a liquid without particles. In this case, the decay is dual exponential, probably due to the measurement domain at this point containing one domain where the particles have not penetrated yet and a second domain that has been reached by the particle front. The CPMG decay at the centre and end of the sample are the same and do not contain particle effects.
For the intermediate pore size (Figure 6.9b, e), the particle front penetrates to roughly half the sample length, as extensively discussed in section 6.5. For the highest average pore radius of 8.1 µm, a lower signal throughout the sample and much shorter $T_2$ relaxation times are observed (Figure 6.9c, f). It can, therefore, be concluded that the particle front moves along with the liquid front during capillary uptake of the liquid containing 7 wt% Fe$_2$O$_3$ nanoparticles and 70 wt% glycerol.

Using the maximum surface coverage $\Gamma_m = 1.7 \cdot 10^{14}$ [m$^{-2}$] and the binding constant $\kappa = 2.1 \cdot 10^{-21}$ [m$^3$]) as determined in section 6.5, the retardation of the particle front can be predicted using equation (2.41). Results are given in Table 6.2. The predicted front retardation is similar to the measured front domains in Figure 6.9, where a particle front speed of roughly 10-20% is observed for the 0.1 µm average pore radius sample, 45-60% for the 0.6 µm case and no retardation for the largest pore radius sample (8.1 µm). The retardation of the front should be visible for the highest pore radius as well, however, the particle front width is of the same order as the predicted particle retardation, which explains why this retardation is not visible in Figure 6.9c.

<table>
<thead>
<tr>
<th>Avg. pore diameter (2$r$) [µm]</th>
<th>$c_0$ [m$^{-3}$]</th>
<th>$A/V$ [m$^{-1}$]</th>
<th>$\frac{1 + \kappa c_0}{1 + \kappa [c_0 + (A/V)\Gamma_m]}$</th>
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<td>$1.9 \cdot 10^{7}$</td>
<td>0.15</td>
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<td>$8.9 \cdot 10^{19}$</td>
<td>$3.4 \cdot 10^{6}$</td>
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</tr>
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<td>16.2</td>
<td>$9.4 \cdot 10^{19}$</td>
<td>$0.25 \cdot 10^{6}$</td>
<td>0.93</td>
</tr>
</tbody>
</table>

6.7 Coupling of particle and liquid front dynamics

To quantitatively describe the particle front position rather than a retardation compared to the liquid front, the liquid front position needs to be accurately predicted. To describe this liquid front position with Darcy’s law it is assumed that:

Firstly, the particles binding on the pore wall does not influence the liquid penetration speed. Secondly, that the liquid can be described by an average viscosity and surface tension and that the liquid – medium interaction is the same in the particle rich and particle depleted domains.
To verify these assumptions, the liquid penetration speeds of liquids containing different Fe$_2$O$_3$ particle concentrations in 1.17 µm porous Al$_2$O$_3$ are compared. All of the liquids contain 50 wt% glycerol and the viscosity of the penetrating liquids is given in Table 3.5. The liquid penetration speed is plotted as a function of time in Figure 6.10a. Similarly to Chapter 4, the time is corrected with an offset time $t_0$.

A higher particle concentration results in slower liquid uptake, which is expected due to the higher viscosity of liquids containing higher nanoparticle concentrations. To correct for the viscosity effect and to validate that the liquid transport follows the square root of time behavior predicted by Darcy’s law (equation (2.16)), the liquid front versus the square root of time divided by the liquid viscosity is plotted in Figure 6.10b. The contact angle and surface tension of the used liquid mixtures is found to change very little for the used liquid mixtures (Table 3.5).

From Figure 6.10, a dependency of the liquid front speed on the nanoparticle concentration is observed that cannot be fully explained by the changed liquid parameters (i.e. viscosity and surface tension). This indicates that Darcy’s law is not sufficient to predict the liquid penetration speed in this case. One of the assumptions was that liquid parameters and liquid – media interaction are the same throughout the liquid, which is not the case for situations where a retarding particle front occurs. A different model describing the liquid front should be developed to quantitatively predict the liquid and particle front during penetration. Darcy’s law should therefore be extended to describe both the particle rich and the particle depleted domain of the liquid and their interaction to accurately predict the particle and liquid front position as function of time.
6.8 Conclusion

Most experimental research to validate particle retention and filtration models of nanoparticles involves saturated porous media [49], [122], [123]. However, to describe particle motion during capillary suction as relevant for inkjet printing processes, experimental data in unsaturated porous media is needed. NMR imaging is used to measure nanoparticle motion during capillary transport in situ. These experiments are used to validate the 1D model developed in section 0, that qualitatively and quantitatively describes particle transport with respect to liquid transport in porous media during capillary suction. This model avoids the use of a filtration coefficient, commonly used in filtration models [49], allowing a simple description for the particle retention. As the fluid velocity is high during capillary uptake, advective transport is the dominating transport mode of the particles. The retardation of the particle front as compared to the liquid front increases with the binding constant $\kappa$, the surface to volume ratio of the porous medium $A/V$, and the maximum surface coverage $\Gamma_m$. The particle front is less retarded when the initial particle concentration $c_0$ is higher.

The particle concentration of the penetrating liquid between $1.7$ and $9.4 \cdot 10^{19}$ particles per cubic meter is investigated in this chapter. The concentration dependency allows us to determine the binding constant and the maximum surface coverage of the particles on the pore surface. The binding constant $\kappa$ of the Fe$_2$O$_3$ nanoparticles is found to be equal to $2.06 \cdot 10^{-21}$ [m$^3$] and the maximum surface coverage $\Gamma_m$ equals 51% of the Al$_2$O$_3$ pore surface. This value is close to the theoretical maximum of 74% for a perfectly packed monolayer of spherical particles and a surface coverage of 64 % for randomly packed hard spheres [124]. The retardation of the particle front could be predicted using the developed model within the measurement accuracy. To validate the concentration dependency predicted by equation (2.41), and to conclusively determine the combination of binding constant $\kappa$ and max bound particle concentration $c_{b,m}$, a wider range of initial concentrations should be investigated.

For small particle concentrations (1 and 2 wt% Fe$_2$O$_3$ nanoparticles), the particle front penetrates fast from the bottom and sides of the sample, but does not penetrate through the corners. We do not observe these 3D effects for the liquid components of the mixture. In order to explain this behavior, further investigation on the early stages of liquid and particle penetration is necessary. Special attention should be paid to the stability of the particle front. Conducting a series of experiments with the same liquid – porous media combination, containing a low particle concentration (1 ,2 wt% Fe$_2$O$_3$) and making cross sections at different times during uptake, could give valuable insights on the particle penetration dynamics and the resulting 3D effects.
For the larger particle concentrations, a self-similarity of the liquid profiles during liquid penetration is found. This indicates that the particle retardation also holds for different time and length scales, i.e. for thin porous media. The liquid penetration speed follows the square root of time behavior predicted by Darcy’s law as previously seen for water-glycerol mixtures penetrating into porous Al₂O₃ [103]. However, the scaling with the average liquid viscosity is no longer sufficient. An extension of Darcy’s law governing both the particle rich and the particle depleted domain of the liquid and their interaction should be developed to accurately predict the particle and liquid front position as function of time.
Chapter 7: Conclusions

The aim of this study was to determine and model both the particle and the liquid component transport during imbibition of water based inks in unsaturated porous media. We used a combination of NMR imaging and ASA measurements during capillary uptake experiments. NMR imaging is used to measure the dynamics of the mixture components inside the porous material in a spatial resolved manner. ASA only gives the total transferred liquid volume from the liquid bath into the porous material, but it allows to measure on time and length scales typically found in the inkjet printing industry. The main conclusions of this work are summarized here.

To describe the penetration depth of absorbed pigment particles, first the liquid penetration has to be accurately described. Darcy’s law can be used to describe the capillary absorption of single liquids. However, an inkjet ink is more complex and the applicability of Darcy’s law has to be addressed for complex liquid mixtures. In Chapter 4 and Chapter 5, the application of Darcy’s law to liquid mixtures is studied in porous Al₂O₃ samples. In this study, we show that Darcy’s law describes capillary suction of water-glycerol-hexanediol mixtures in porous Al₂O₃.

The predicted square root of time behavior is verified as well as the scaling with liquid (viscosity \( \eta \), surface tension \( \sigma \)) and media parameters (average pore radius \( r \)). Data of imbibition measurements with varying glycerol and hexanediol concentrations using NMR imaging and ASA collapse on one master curve for time and length scales spanning 3 orders of magnitude. The decomposition of the water-glycerol mixtures during absorption in Al₂O₃ is studied using \( T_2 \) relaxation analysis. The water-glycerol mixture behaves as a homogenous mixture during imbibition.

When similar liquid mixtures are penetrating polymeric filter membranes (PVDF and MCE membranes), the predicted scaling with liquid components (\( \eta, \sigma \)) no longer holds. This effect might occur due to swelling of the porous material if the membranes are plasticised, but could also be a result of the formation of a precursor film. Darcy’s law is no longer sufficient to predict the penetration dynamics in polymeric filter membranes.

We have shown that the liquid and particle front can be measured separately using NMR imaging (Chapter 6). The Fe₂O₃ nanoparticles used in this study are paramagnetic
and reduce the $T_2$ relaxation times locally. This results in a lower measured signal at positions where the particle concentration is high. Using this effect, the liquid and particle front can be measured simultaneously.

Using NMR imaging to measure the particle penetration front, a self-similarity of the liquid profiles during liquid penetration is found for large particle concentrations (>5 wt%). This indicates that the particle retardation also holds for different time and length scales, i.e. for thin porous media. This means the particle retention is relevant on the typical length scales for inkjet printing processes. For low particle concentrations (1 and 2 wt% Fe$_2$O$_3$ nanoparticles), 3D effects are observed, which are not visible in liquid absorption experiments without particles. The particle front penetrates fast from the bottom and sides of the sample, but does not penetrate through the corners. These effects are not observed for the liquid components of the mixture in our NMR experiments.

The liquid penetration speed for particle-containing mixtures (water-glycerol with Fe$_2$O$_3$ nanoparticles) follows the same square root of time behavior predicted by Darcy’s law, which was also observed for the liquid mixtures in Chapter 4 and Chapter 5. However, the scaling with the average liquid viscosity is no longer sufficient. This is a result of the front splitting occurring, where the particle front lacks behind the liquid front. Darcy’s law no longer holds when front splitting occurs, i.e. in the case of liquid mixtures containing nano-particles.

The particle retention model developed in Chapter 2 accurately predicts the particle front following the liquid front for the largest pore radius samples (8.1 μm). Furthermore, by varying the input concentration $c_0$, the binding constant $\kappa$ and the maximum surface coverage $\Gamma_m$ are determined. For the Fe$_3$O$_4$ nanoparticles used in this study, the maximum surface coverage on the Al$_2$O$_3$ samples (pore radius $r = 0.6$ μm) is found to be 51% of the available pore surface.
The overall conclusion of this study is that a theoretical description based on advective transport and assuming monolayer absorption (Langmuir type absorption) can predict the particle retention of water-glycerol mixtures containing Fe$_2$O$_3$ nanoparticles during capillary suction in the used model material (Al$_2$O$_3$).

Although this model is not fully capable of predicting the pigment penetration depth of a water-based inkjet ink, it provides a simple, yet accurate, description for the particle retention of nanoparticles in homogenous porous media during capillary suction.

This provides a stepping stone to a more complete model incorporating the interactions between the liquid and the printing substrate as well as an extension of Darcy’s law to accommodate for front splitting. Ideas for further research and to extend the developed model are given in Chapter 8.
Chapter 8: Outlook

In this chapter, preliminary results on CaCO$_3$ samples are shown, which illustrate the applicability of the Al$_2$O$_3$ results to the coating layer of a printing paper. It is shown that CaCO$_3$ samples without the addition of extra filler material behave similar to the Al$_2$O$_3$ samples used in this study. However, when latex particles are added to the CaCO$_3$ substrate, the penetration speed decreases significantly. This effect is also important for printing media as most printing substrates (incl. their coating layer) contain filler material to optimize their properties, to obtain the highest print quality and robustness possible. Suggestions are made to investigate liquid–media interactions, which could explain the discrepancy with the predicted behavior by Darcy’s law for filter membranes and for the latex containing coating sample. Furthermore, an extension of the current model for swelling porous media is suggested, which is required for paper-like printing substrates. Finally, a suggestion is made to extend the model to accommodate for front splitting, as occurring for the imbibition of liquid mixtures containing nanoparticles. A first ansatz to such a model is defined and compared to the experimental results in Chapter 6. This shows that taking into account only the viscosity change in the particle rich and particle depleted domain is not sufficient to predict the liquid front position as function of time when front splitting occurs.

8.1 Liquid penetration in paper coating materials

The work presented in this thesis forms an important step towards understanding and predicting the pigment penetration dynamics during the imbibition of water-based inkjet inks in a porous medium. However, many open items still remain. In this section, preliminary results of water-glycerol absorption in porous coating materials are described to investigate the applicability of the developed measurement techniques to printing substrates.

Printing substrates, such as paper, generally contain a coating layer to improve the properties of the printing material. The coating layer ensures a homogeneous substrate, which makes sure the ink penetration into, and spreading over the print substrate is the same over the sample substrate. Furthermore, the coating layer makes the print substrate appear whiter. This increases the visibility of the ink and therefore the print quality. The main constituent of this coating layer is often CaCO$_3$. 

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To investigate the possibility to use the liquid and particle transport models developed in this study, the liquid uptake of water-glycerol mixtures in CaCO₃ samples is measured using NMR and compared to the Al₂O₃ results of Chapter 4.

Cylindrical CaCO₃ samples produced by Omya AG (Hydrocarb 60, with and without Acronel S728 Latex particles (BASF GmbH)) are used. The samples have a diameter of 20 mm and a height of 30 mm. The pure CaCO₃ sample has a slightly larger average pore radius of 0.07 μm as opposed to 0.06 μm for the sample containing latex. The sample that contains latex contains a binder in the form of n-butyl acrylate styrene latex (Acronal S728) making up 12 wt% of the sample. The main difference between the two sample types is the porosity, which is 29.9% for the sample without latex and 18.8% for the sample with latex added during the sample preparation. Both samples have a narrow pore size distribution and are monodisperse, similar to the samples used by Gane et al.[125].

The uptake of 50wt% water and 50wt% glycerol in a Hydrocarb 60 ME sample is measured and the resulting liquid profiles are given in Figure 8.1a. The same measurement procedure as described in section 3.1.2 is used. The signal profiles after time interpolation are shown where the time between two subsequent profiles is 10 minutes.

Figure 8.1: Uptake experiment of 50 wt% water and 50 wt% glycerol in a Hydrocarb 60 ME CaCO₃ sample (a) and the determined front position as function of rescaled time (b) for 50 wt% water-glycerol imbibition in Hydrocarb 60 ME CaCO₃ and porous Al₂O₃.

Figure 8.1a shows a liquid front penetrating into the CaCO₃ sample. It takes the liquid approximately 70 minutes to saturate the sample. The liquid front position is determined and plotted as a function of rescaled time ($\sqrt{2\sigma r/\eta}t - t_0$) in Figure 8.1b. To compare the uptake dynamics in the CaCO₃ sample with the results of this study, the liquid front position for 50 wt% water and 50 wt% glycerol uptake experiments in
0.1 μm Al₂O₃ is given in Figure 8.1b as well. Note that although the average pore radius of the Al₂O₃ samples (0.1 μm) is different from the CaCO₃ sample, this will not influence the comparison due to the rescaling with the average pore size. This indicates that the behavior of the liquids is very similar in both porous materials. To determine if the behavior is really identical, further information on the contact angle and the permeability of the CaCO₃ sample is necessary.

**As the liquid uptake of water-glycerol mixtures in CaCO₃ and Al₂O₃ samples show very similar uptake dynamics, Al₂O₃ can be used as a model material for one of the main coating constituents in printing applications.**

The uptake of water into the latex containing CaCO₃ sample (12 wt% Acronel S728 latex particles) is measured and the resulting time profiles are given in Figure 8.2a. The liquid uptake is significantly slower than for the sample without the addition of latex.

Following the same analysis as before, the front position as a function of the rescaled time is determined (Figure 8.2b). The measurement point for the first profile is omitted as part of the sample is submerged in the penetrating liquid, which results in a negative time for \( t - t_0 \) for this point. The penetration of water in this latex containing sample can still be described by Darcy’s law, however the liquid penetration rate is about a factor of 10 lower than found in the sample without latex.

This is remarkable as the liquid penetration is found to be faster with decreasing glycerol concentration for the Al₂O₃ samples in Chapter 4. This effect could in part be due to a change in the permeability resulting from the addition of latex. However, the biggest contribution is probably from the internal contact angle that gets closer to 90°.
degrees. Knowledge on the permeability and the contact angle of water on these samples is necessary to fully explain the differences with the Hydrocarb 60 ME results.

These preliminary experiments show that the uptake dynamics of water-glycerol mixtures in CaCO₃ with and without latex of type S728 can be measured with NMR and described by Darcy’s law. The uptake speed of the CaCO₃ sample without latex is approximately the same as found for the Al₂O₃ samples used in this study after correcting for the average pore size. However, when latex is added the process becomes roughly ten times slower. This can be a result of the liquid mixture used, the contact angle or a change of the permeability.

As the results on CaCO₃ samples in this section are the result of only a few samples, more research on the uptake dynamics in these media is necessary to translate the results from this study to predictions of pigment penetration depths in printing media.

8.2 Interactions of liquid components with the porous material

One of the important factors determining the uptake dynamics of liquids in porous media are liquid-media interactions. These are physical interactions in the form of the contact angle, which determines whether or not the liquid penetrates into the sample at all. Furthermore, the uptake speed can be heavily influenced by the contact angle.

In this study, we have seen that the contact angle determined for a non-porous sample is not necessarily representative for the contact angle in the pore space. Several studies have also suggested that the dynamic contact angle needs to be taken into account to quantify the liquid penetration dynamics [44]–[46]. To accurately predict the liquid penetration dynamics during capillary suction, the contact angle inside a porous material should be quantified. As the contact angle cannot be measured directly in these type of materials, a systematic study on the penetration dynamics for different contact angles should be conducted. A method to change the contact angle in the uptake experiments could be to apply a surface treatment to the pore surface of the porous material, i.e. by deposition of a monolayer of organic material [84], [126]. A second method to change the contact angle systematically is to change the liquid mixture composition by adding surfactants.

Liquid–media interactions can also cause a change in the porous material itself. This is especially true for printing media as they tend to swell when brought into contact with water. For water-based inks these swelling effects can change the liquid penetration
dynamics and thereby also affect the pigment penetration depth. Furthermore, we have seen in Chapter 5 that water-glycerol-hexanediol mixtures no longer follow Darcy’s law when penetrating fibrous filter membranes. To address the consequences of a changing porous material during imbibition a more extensive study on the effects of a swelling porous material is advised. The liquid penetration model used here needs to be extended to incorporate the swelling porous material, like for example the one developed by Kvick et al. [127]. Furthermore, experimental verification of the model could be done by using ASA measurements of water-glycerol mixtures penetrating the fibrous filter membranes. Cross-sections of the filter membranes can be made for different contact times and studied by microscopy. This method is very time-consuming but provides a direct measure of the liquid penetration depth which is normally lacking. A second challenge is to find a dye that visualises the liquid front but does not alter the imbibition dynamics.

For particle containing liquid mixtures another factor contributes to the liquid – media interaction in the form of the binding constant $\kappa$ (equation (2.22)). The effect of the binding constant should be investigated by modifying the interaction of the pore wall with the nanoparticles. On the one hand, this can be influenced by modifying the pore space applying a surface treatment. On the other hand, the way the particles are stabilized in the liquid could be adapted. In this research the Fe$_2$O$_3$ nanoparticles are stabilized in the liquid with a dispersant. By choosing a different dispersant the binding constant can be changed. This would allow the particle penetration depth to be tuned which provides methods to control the pigment penetration depth in inkjet inks and optimize the print quality and robustness.

8.3 Quantifying nanoparticle concentrations locally

In order to accurately predict the pigment penetration depth of water-based inkjet inks, the particle concentration needs to be quantified locally. Therefore, a calibration curve for the $T_2$ relaxation times for liquids containing different nanoparticle concentrations inside a porous material, should be constructed. This requires a systematic study on the different contributions to the $T_2$ relaxation time. The $T_2$ relaxation time is influences by:

- the liquid being enclosed in the pore space
- the particles immersed in the penetrating liquid
- the particles absorbed on the pore surface.
Firstly, the contribution of the liquid confinement in the pore space can be investigated by a study of liquids without nanoparticles in samples with different average pores sizes. This changes the surface to volume ratio and therefore the contribution of the relaxation on the pore walls. This effect is also shown in Figure 4.5.

Secondly, the contribution from the nanoparticle concentration in the liquid mixture can be studied for different particle concentrations outside the porous material for the bulk liquid. Finally, the contribution of particles bound to the pore surface can be investigated systematically for a series of different initial nanoparticle concentrations penetrating into a range of porous samples with different average pore sizes. Using this information a measured relaxation time can be linked to the local particle concentration.

A second aspect of quantifying the local particle concentration is to understand the 3D effects occurring for low particle concentrations as observed in Figure 6.2. The NMR samples should be cut in the length direction after being brought in contact with the nanoparticle mixtures for different times. The cross sections allow to study the development of the 3D effect in time for all particle concentrations, which gives valuable insights to understand this unexpected behavior. For high particle concentrations, these cross sections show whether a similar effect occurs at the early stages of liquid penetration or that this effect is limited to liquid mixtures containing low particle concentrations (≤ 5 wt%).

8.4 Extension to Darcy’s law for separating liquid mixtures

An extension of Darcy’s law governing both the particle rich and the particle depleted domain of the liquid and their interaction should be developed to accurately predict the particle and liquid front position as function of time. This two different domains need to be described independently with their own liquid and media properties, such as the viscosity, surface tension, contact angle, average pore radius, porosity and permeability. As a first order approximation, most of these parameters can be considered to remain constant for the particle rich and particle depleted domain, except for the viscosity as this is found to change significantly more than the other parameters (section 3.4.2). An ansatz for such a model based on two domains (Figure 2.5), one with and one without particles is given in this section.
As both liquid domains remain connected, the liquid flux in the particle rich domain $q_1$, is equal to the liquid flux in the particle depleted domain $q_2$ and defined by the liquid front speed times the porosity:

$$q_1 = q_2 = q = \phi \frac{dl}{dt} [\text{m/s}].$$  \hspace{1cm} (8.1)

Assuming both liquid domains can be described using Darcy’s law (Equation (2.6)) results in

$$q_1 = - \frac{k_1 \Delta P_1}{\mu_1 s},$$  \hspace{1cm} (8.2)

$$q_2 = - \frac{k_2 \Delta P_2}{\mu_2 (1 - s)},$$  \hspace{1cm} (8.3)

where the interface position between the particle depleted and particle containing liquid domain is given by the particle front position $s$. As the permeability is assumed constant for both domains ($k_1 = k_2 = k$) and the pressure differences of the two domains amount to the capillary pressure ($\Delta P_1 + \Delta P_2 = P_c$), the capillary pressure can be described as

$$P_c = - \frac{q_1 \mu_1 s}{k} - \frac{q_2 \mu_2 (1 - s)}{k}.$$  \hspace{1cm} (8.4)

After rearranging equation (8.4) in the same form as equation (2.6), we find

$$q = - \frac{k}{[\mu_1 s + \mu_2 (1 - s)]} \frac{P_c}{l}.$$  \hspace{1cm} (8.5)

Equation (8.5) shows that a modification of the liquid flux and therefore the liquid penetration speed is necessary to accurately describe the liquid front position $l$ as a function of time. This modification depends on the viscosity of the two domains (with and without particles) and the particle front retardation ($s/l$). This can be obtained from the particle retention model described in Chapter 2.

To verify this ansatz, the liquid front positions of the 5, 7 and 10 wt% nanoparticle concentrations penetrating in 0.6 μm porous Al₂O₃, as shown in Figure 6.10, are replotted where the viscosity is rescaled with $[\mu_1 s + \mu_2 (1 - s)]$ instead of only the viscosity of the particle containing liquid ($\mu_2$). The resulting liquid front positions are given in Figure 8.3.
8.4 Extension to Darcy’s law for separating liquid mixtures

Figure 8.3: The liquid front position of liquid containing 5, 7 and 10 wt% nanoparticles and 50 wt% glycerol where the time is rescaled with a weighed viscosity (equation (8.5)).

The liquid front positions for different initial particle concentrations in Figure 8.3 do not align on a single master curve. This indicates that the extended Darcy model, where only the viscosity is considered different in both domains, is not sufficient to describe the effect of the retarding particle front on the liquid front speed. This indicates that other parameters such as the permeability or porosity might be different for the two domains. These might change due to the particles attaching to the pore walls and reducing the effective pore radius. Further research is needed to address the influence of the particle sticking effect on these parameters. This information can then be used to extend the developed model for the capillary suction of liquid mixtures where front splitting occurs.
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Summary

Dynamics of fluid mixtures and nanoparticles during capillary suction

In the current society, sustainable development and the reduction of the impact of products and processes on the environment, becomes more and more important. This is driven by the demands of customers as well as legislation from the European Union and the United Nations. In the field of inkjet printing, this has led to the development of water-based inks as a ‘greener’ substitute to the solvent based inks used before. These water-based inks generally contain water as a solvent, a co-solvent to control the evaporation rate, a surfactant to control the spreading over the printing substrate and pigment particles, which result in the printed image. However, these nanoparticles are the most expensive part of the ink and are hazardous to the environment in their own right. Therefore, their use should be minimized. This poses an interesting problem as the nanoparticles are needed to form the printed image and therefore directly affect the print quality and print robustness.

In the current inkjet inks, not all pigment particles are optimally used. On the one hand, there is a number of particles penetrating too far into the printing substrate (e.g. paper), resulting in intensity loss. On the other hand, pigment particles that are left close to the surface of the printing material, can stain or move to unwanted locations. Therefore, the inks should be optimized to have all the pigment particles penetrate to an optimal penetration depth, where the contribution to the print quality and print robustness is maximized. To do this, a more thorough understanding of the liquid penetration process in printing porous media and the factors affecting the pigment penetration depth is necessary.

In this thesis, a mathematical model is developed that describes liquid and particle motion during uptake in a porous material. The model is based on Darcy’s law combined with an advection model using Langmuir type absorption to describe particle retention effects. To validate the predictions of this model, two complimentary experimental techniques are used. On the one hand, Nuclear Magnetic Resonance (NMR) imaging is used to measure particle and liquid transport in the porous media directly. Furthermore, it grants the possibility to investigate de-mixing of the liquid mixture components by utilizing $T_2$ relaxation effects. On the other hand, Automated Scanning Absorptometer (ASA) measurements are used to investigate liquid penetration in thin porous media, which allows fast measurements of the total liquid
absorbed in the porous sample on time and length scales relevant for inkjet printing. Both experimental techniques are described in Chapter 3.

Chapter 4 discusses the ability of Darcy’s law to predict liquid penetration of two component liquids in a model porous media (Al₂O₃). Therefore, NMR imaging experiments of water-glycerol mixtures penetrating in porous Al₂O₃ are conducted. The influence of the viscosity is studied over two orders of magnitude by changing the glycerol concentration. Furthermore, the effect of pore size is investigated. Darcy’s law accurately describes the liquid dynamics for the investigated liquid – media combinations. The permeability in Darcy’s law scales with the pore radius squared as predicted by models of Lucas-Washburn and Katz-Thompson. Furthermore, $T_2$ relaxation analysis shows that the water-glycerol mixtures penetrate the porous Al₂O₃ samples as a single homogeneous liquid, i.e. no front splitting occurs.

To further address the applicability of Darcy’s law to inkjet printing processes, quantitative measurements of the penetration depth of water-glycerol-hexanediol mixtures in thin porous media are studied in Chapter 5. The penetration depth measured with ASA scales with liquid (viscosity and surface tension) and media parameters (average pore radius) as predicted by Darcy’s law. However, the penetration dynamics in PVDF and MCE filter membranes deviates from Darcy’s law, indicating specific liquid – media interaction with at least one of the liquid components. Furthermore, a linear time regime is observed in the early stages of liquid penetration. On the one hand, this can indicate that either the liquid does not move into the fibrous samples as a homogenous liquid or that the porous material deforms during the liquid imbibition process. On the other hand, it could be an effect resulting from the complexity of the porous structure itself and an indication of surface film flow formation.

To understand and predict the pigment penetration, not only the liquid but also the particle dynamics during uptake have to be addressed. The penetration of complex mixtures containing Fe₂O₃ nanoparticles, as a model for pigment particles, in porous Al₂O₃ samples is discussed in Chapter 6. The accuracy and applicability of the 1D model, presented in Chapter 2, is investigated using NMR imaging experiments. The binding constant for Fe₂O₃ nanoparticles on sintered Al₂O₃ samples and the maximum surface coverage are determined using different initial particle concentrations. These are then used to predict the particle retardation as compared to the liquid front for pore sizes ranging two orders of magnitude in the micrometer and sub-micrometer regime.
The overall conclusion of the work is that the developed model can predict the particle retention of water-glycerol mixtures containing Fe$_2$O$_3$ nanoparticles during capillary suction in the used model material (Al$_2$O$_3$). Although this model is not fully capable of predicting the liquid penetration depth of liquid mixtures containing nanoparticles, it provides a simple, yet accurate, description for the particle retention of nanoparticles in homogenous porous media during capillary suction.

To illustrate the potential to apply the current model to porous media relevant in the printing industry, preliminary results of NMR experiments on CaCO$_3$ samples are shown in Chapter 8. CaCO$_3$ is one of the main constituents of coating layers typically used on printing paper to enhance print quality and robustness. These results show liquid uptake dynamics that is very similar to the Al$_2$O$_3$ samples used in this study as the model material. This shows that the results of this study are promising and could lead to a better understanding and prediction of pigment penetration depths of water-based inkjet inks.
Samenvatting

Dynamica van vloeistof mengsels en nanodeeltjes tijdens capillaire opname

In de huidige maatschappij wordt duurzame ontwikkeling en verminderen van de impact van producten en processen op het milieu steeds belangrijker. Deze ontwikkeling wordt gedreven door de eisen van consumenten en door wetgeving vanuit de Europese Unie en de Verenigde Naties. In het domein van inkjet printen heeft dit geleid tot de ontwikkeling van water gebaseerde inkten, als een ‘groener’ alternatief voor inkten met vluchtige componenten die voorheen gebruikt werden. Deze water gebaseerde inkten bevatten water als het oplosmiddel, een tweede oplosmiddel om de verdampingssnelheid te controleren, een component om de spreiding over het print oppervlak te beïnvloeden en pigment deeltjes. Deze pigment deeltjes zorgen voor de zichtbare tekst of afbeelding. De nanodeeltjes zijn echter het duurste onderdeel van de inkt en zijn bovendien schadelijk voor het milieu. Om deze redenen moet het gebruik van deze nanodeeltjes tot een minimum beperkt worden. Dit geeft een interessante tweestrijd aangezien deze nanodeeltjes nodig zijn voor het vormen van de geprinte afbeelding en daardoor direct bijdragen aan de print kwaliteit en zorgen voor een robuust print resultaat.

In de huidige inkjet inkten worden niet alle pigment deeltjes optimaal gebruikt. Aan de ene kant zijn er deeltjes die te ver in het print materiaal (zoals papier) trekken, met als gevolg verlies van intensiteit. Aan de andere kant zijn er deeltjes die te dicht bij het oppervlak achter blijven. Dit kan resulteren in vlekken of het verplaatsen van de pigment deeltjes naar plaatsen waar geen inkt zou moeten komen. Vandaar dat de inkten geoptimaliseerd moeten worden. Alle pigment deeltjes moeten doordringen tot een ideale diepte in het materiaal, waar de bijdrage van de pigment deeltjes aan de print kwaliteit en een robuust print resultaat maximaal is. Om dit te bereiken is een beter begrip van de opname van vloeistoffen in print materialen enerzijds en, de invloed van de factoren die de indring diepte van de pigment deeltjes bepalen anderzijds, noodzakelijk.

In deze thesis is een wiskundig model ontwikkeld dat de vloeistof en deeltjes bewegingen tijdens opname in een poreus materiaal beschrijft. Het model is gebaseerd op de wet van Darcy gecombineerd met een advectie model. In het advectie model wordt absorptie van het Langmuir type gebruikt, om het achterblijven van het deeltjes front ten opzichte van het vloeistof front te beschrijven. Om de voorspellingen
van dit model te toetsen worden twee, elkaar aanvullende, experimentele methoden gebruikt. Aan de ene kant wordt kernspinresonantie (NMR) gebruikt om het deeltjes en het vloeistof front direct te kunnen meten. Bovendien geeft NMR de mogelijkheid om het ontmengen van de vloeistof mengsels tijden opname te onderzoeken door gebruik te maken van $T_2$ relaxatie effecten. Aan de andere kant wordt een automatisch scannende absorptometer (ASA) gebruikt om vloeistof opname in dunne poreuze materialen te meten. Dit maakt snelle metingen van de totale hoeveelheid geabsorbeerde vloeistof mogelijk op tijd en lengte schalen die relevant zijn voor het inkjet print proces. Beide technieken worden beschreven in Hoofdstuk 3.

In Hoofdstuk 4 wordt de mogelijkheid onderzocht om de wet van Darcy te gebruiken om de indringdiepte van vloeistof mengsels, bestaande uit twee componenten, te beschrijven in een model materiaal ($\text{Al}_2\text{O}_3$). Om dit te onderzoeken zijn NMR experimenten van de opname van water-glycerol mengsels in $\text{Al}_2\text{O}_3$ uitgevoerd. De invloed van de viscositeit is over 2 ordes van grootte gevarieerd door de glycerol concentratie in de vloeistof mengsels te veranderen. Bovendien is het effect van de poriegrootte van het poreuze materiaal onderzocht. Het is mogelijk om de wet van Darcy te gebruiken om de vloeistof dynamica te beschrijven voor de onderzochte combinaties van vloeistof en poreus materiaal. De permeabiliteit in de wet van Darcy schaalt met de porie straal in het kwadraat, zoals ook voorspeld door de modellen van Lucas-Washburn en Katz-Thompson. Bovendien laat $T_2$ relaxatie analyse zien dat de water-glycerol mengsels in de poreuze $\text{Al}_2\text{O}_3$ monsters trekken als een homogene vloeistof. Dat wil zeggen dat er geen ontmenging optreedt tijdens de opnamen.

Om de toepassing van de wet van Darcy voor inkjet print processen verder te onderzoeken zijn kwantitatieve metingen van de indringdiepte van water-glycerol-hexanediol mengsels in dunne poreuze materialen bestudeerd in hoofdstuk 5. De indringdiepte, zoals gemeten met ASA, schaalt met de eigenschappen van de vloeistof (viscositeit en oppervlakte spanning) en het poreus materiaal (gemiddelde porie grootte) zoals voorspeld door de wet van Darcy. De vloeistof dynamica tijdens opname in PVDF en MCE filter membranen wijkt echter af van het door de wet van Darcy voorspelde gedrag. Dit geeft aan dat er een specifieke interactie optreedt met het poreuze materiaal voor ten minste een van de componenten in het vloeistof mengsel. Bovendien is een lineair regime gevonden in de vroege stadia van vloeistof absorptie. Dit kan aan de ene kant een gevolg zijn van ontmenging van het vloeistof mengsel tijdens de opname in het poreuze materiaal, of het poreuze materiaal vervormd tijdens de opname. Aan de andere kant kan dit een gevolg zijn van de complexiteit van het poreuze materiaal zelf en een indicatie voor het ontstaan van vloeistoffilms op het oppervlak van de poriën.
Om het indringen van de pigment deeltjes beter de beschrijven en te voorspellen, moet niet alleen de vloeistof maar ook de deeltjes dynamica tijdens opname onderzocht worden. De absorptie van complexe mengsels die Fe$_2$O$_3$ nanodeeltjes (als model voor de pigment deeltjes) bevatten in poreus Al$_2$O$_3$ wordt beschreven in Hoofdstuk 6. De mogelijkheid om het 1D model, zoals beschreven in Hoofdstuk 2, toe te passen en de nauwkeurigheid hiervan is onderzocht met NMR experimenten. De bindingsconstanten voor Fe$_2$O$_3$ nanodeeltjes op gesinterd Al$_2$O$_3$ en de maximale bedekking van het oppervlak zijn bepaald met behulp van verschillende deeltjes concentraties in het originele vloeistof mengsel. Deze waarden zijn gebruikt om het achterblijven van de deeltjes front, ten opzichte van het vloeistof front, te voorspellen voor poriegroottes variërend over twee ordes van grootte in het micrometer en sub-micrometer regime.

De algemene conclusie van dit werk is dat het ontwikkelde model het achterblijven van het deeltjes front voor water-glycerol mengsels met Fe$_2$O$_3$ nanodeeltjes kan beschrijven tijdens opname in het gebruikte model materiaal (Al$_2$O$_3$). Ondanks dat dit model nog niet volledig in staat is de indringdiepte van de vloeistof mengsels met nanodeeltjes te beschrijven, geeft het een simpele maar nauwkeurige beschrijving van het achterblijvende deeltjes front in homogene poreuze materialen tijdens capillaire opname.

Om de mogelijkheid om het huidige model te gebruiken voor poreuze materialen, die relevant zijn in de print industrie, te illustreren, zijn voorlopige resultaten van NMR experimenten op CaCO$_3$ monsters beschreven in Hoofdstuk 8. CaCO$_3$ is een van de belangrijkste componenten van coatinglagen zoals typisch gebruikt in printpapier, om de print kwaliteit te verhogen en een robuuste print te garanderen. Deze resultaten laten zien dat de vloeistofopname in dit materiaal zich zeer vergelijkbaar gedraagt aan de Al$_2$O$_3$ monsters zoals gebruikt in deze studie als model materiaal. Dit toont aan dat de resultaten van deze studie veelbelovend zijn en kunnen leiden tot een beter begrip en betere voorspellingen van de indringdiepte van pigment deeltjes in water gebaseerde inkjet inkt.
List of publications

Related to this dissertation


Other publications


Dankwoord

Het heeft met bijna vijf en een half jaar een stuk langer geduurd dan ik in eerste instantie verwacht en gepland had, maar nu is het eindelijk zover. Het laatste ontbrekende stuk van mijn proefschrift is een feit. Allereerst wil ik mijn begeleiders op de TU/e bedanken. Henk en Olaf, heel erg bedankt voor jullie begeleiding tijdens mijn promotie, zowel in de periode dat ik fysiek aanwezig was op de TU/e, als de laatste perioden waarin onze communicatie vooral via mail ging.

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Kees Kuijpers was born on the 22nd of September 1989 in Eindhoven together with his twin brother Paul Kuijpers. After receiving his VWO-diploma in 2007 at Scholengemeenschap Were Di in Valkenswaard, he studied Applied Physics at the Eindhoven University of Technology. In 2013 he graduated within the Mesoscopic Transport Phenomena (MTP) group with a specialization on Physics of Transport in Fluids.

From 2013 he started a PhD project at the Eindhoven University of Technology (TU/e) in the group Transport in Permeable Media (TPM) under the supervision of Prof.dr.ir. Olaf Adan and Dr.ir. Henk Huinink. The project is financed within the Material Innovations Institute (M2i) framework in close collaboration with Océ Technologies BV. The results of this research are presented in this dissertation. Since 2017 he is employed at ASML via Bright Society as a productivity engineer.