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Nano-particle dynamics during capillary suction

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Abstract
Due to the increased use of nanoparticles in everyday applications, there is a need for theoretical descriptions of particle transport and attachment in porous media. It should be possible to develop a one dimensional model to describe nanoparticle retention during capillary transport of liquid mixtures in porous media.

Water-glycerol-nanoparticle mixtures were prepared and the penetration process in porous Al₂O₃ samples of varying pore size is measured using NMR imaging. The liquid and particle front can be measured by utilizing $T_2$ relaxation effects from the paramagnetic nanoparticles.

A good agreement between experimental data and the predicted particle retention by the developed theory is found. Using the model, the binding constant for Fe₂O₃ nanoparticles on sintered Al₂O₃ samples and the maximum surface coverage are determined. Furthermore, we show that the penetrating liquid front follows a square root of time behaviour as predicted by Darcy’s law. However, scaling with the liquid parameters is no longer sufficient to map different liquid mixtures onto a single master curve. The Darcy model should be extended to address the two formed domains (with and without particles) and their interaction, to give an accurate prediction for the penetrating liquid front.

Keywords
Porous media, sintered Al₂O₃, Darcy’s law, Fe₂O₃ nanoparticles, particle adsorption, NMR imaging

1. Introduction
With the increasing number of engineered nanoparticles used in everyday applications ranging from inkjet printing (pigment particles), contrast agents in medical applications (Nuclear Magnetic Resonance imaging) and removal of contaminants in the subsurface [1], [2], there is an increasing demand to understand and predict particle transport in porous media. Whether the porous medium is the paper used in printing, different soil layers in the subsurface or the human body, the transport, and more specifically, the retention of particles in such media are of utmost importance. 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 [3]–[6]. A review on the flow of dispersed particles
through porous media is given by Zamani and Maini [7]. 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. [8], 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 [9]. Most of the experimental data available consist of breakthrough curves (BTC), where the outflow concentration of particles is measured over time using techniques like light extinction [10], X-ray fluorescence [11], turbidimeter [12] and atomic absorption spectrometer [13]. The advantage of these measurements is the high time resolution that can be obtained as well as the possibility to measure on any porous material. The main drawback of these methods, however, 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. For example 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 [14].

A secondary method that is often used to monitor particle retention in porous media is microscopy to measure particle transport in micromodels or columns filled with glass beads [15]–[17]. Similarly to the BTC methods, these yield high time resolutions, but the method can only be applied to transparent media. A technique that allows local measurements in non-transparent porous media is NMR imaging [18]–[21]. Paramagnetic particles for contrast enhancement offer new opportunities to study particle motion in porous media [22].

Nanoparticle penetration during capillary suction in porous media has been the topic of far fewer studies [23], [24]. 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 [25]. The experimental techniques allowing to study liquid penetration in unsaturated porous media consist of microscopy for transparent porous media, ultrasonic measurements [26], and NMR.

In the field of inkjet printing, but also in the penetration of spills containing particles on porous media, the particle transport and retention in such unsaturated porous media is important. More precisely, the particle penetration and retention during capillary penetration of the liquid mixture determines the penetration depth of the particles. NMR can be used to study these kind of particle transport processes, where both the liquid penetration as well as the particle retention can be visualised using T2 relaxation effects similarly to the ones used in medical applications for T2 weighing [10]. This method allows a time and position resolved method to quantify the penetration depth of particles and liquid during the capillary suction process. Models describing these effects, where particles can move along with the liquid front or attach to a surface are developed in the field of chromatography [27]–[30].

The aim of this study is first of all to measure both the particle and the liquid components during imbibition in porous media. Secondly, we aim to develop a model that quantitatively describes the particle retention occurring during capillary suction of a complex liquid mixture containing particles.
This model is derived in chapter 2 and the theoretically predicted limiting cases are addressed. In section 3 we discuss the used liquid mixtures, the porous medium and the experimental method. To measure the penetration of liquids containing paramagnetic nanoparticles, we use 1D NMR imaging, which is explained in detail in section 3 as well. In section 4, the main results of this study are presented. The liquid and particle fronts as a function of time are visualised and the binding constant and the maximum surface coverage for the used Fe₂O₃ nanoparticles on the Al₂O₃ surface are determined. Furthermore, the limiting cases predicted by the developed model are verified using sintered Al₂O₃ samples with an average pore radius differing over two orders of magnitude in the micrometer and submicrometer regime.

2. Theory
When a liquid mixture containing nanoparticles is brought into contact with a porous medium, the mixture imbibes into the material. Depending on the interaction of the liquid with the porous material, the mixture can penetrate the material as a homogeneous liquid or the components can split into a liquid and a particle front. Several models exist for the penetration of liquids into porous media, most of them being based on Darcy’s law [31]. 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 [27]–[30].

2.1 Particle adsorption
We consider the particles as equally sized spheres with diameter \( d \) [m]. Particles either adsorb to the pore surface with an area \( A \) [m²] or stay in the solution with a volume \( V \) [m³]. \( c \) [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]:

\[
c_b = \Gamma \frac{A}{V} [m^{-3}].
\] (1)

The total particle concentration is equal to \( \bar{c} = c + c_b \) [m⁻³]. Assuming that the sorption 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 [32],

\[
c_b = c_{b,m} \frac{k_c}{1+k_c c},
\] (2)

where \( k_\text{c} \) [m³] is the binding constant. When \( k_c \ll 1 \) a linear relation is left: \( c_b = c_{b,m} k_c \). At very high particle concentrations, \( k_c \gg 1 \), \( c_b = c_{b,m} \).

2.2 Liquid motion
As a first approximation, it is assumed that the imbibition process itself is not influenced by the particle sticking process. 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 drawn in Figure 1.
Figure 1: Schematic visualisation of the two domains appearing as a result of particle retention during liquid penetration in a pore.

For low particle concentrations, the liquid properties, such as the viscosity, surface tension and contact angle are similar for domains, where the liquid contains particles (before the particle front) and domains that do not contain particles (beyond the particle front), and the permeability of both domains is similar (i.e. pore blocking is similar for both domains). Furthermore we assume osmotic effects counteracting the liquid imbibition due to capillary suction are negligible. Under these conditions, the liquid velocity can be described by Darcy’s law. From Darcy’s law the liquid front \( l \) [m] is given by

\[
l = \sqrt{\frac{2kp_c}{\mu \phi}} \sqrt{t},
\]

(3)

where \( \mu \) [Pa \cdot s] is the liquid viscosity, \( p_c \) [Pa] the capillary pressure, \( k \) [m\(^2\)] the permeability and \( \phi \) [\( - \)] the porosity. In this case, the explicit relation between the fluid velocity \( U \) [m/s] and time \( t \) [s] is:

\[
U = \sqrt{\frac{kp_c}{2\mu \phi}} \frac{1}{\sqrt{t}}.
\]

(4)

For high particle concentrations and a sharp front between the domains with and without particles, a more extensive model is necessary. Although the contact angle and surface tension of those domains remains similar for the particle concentrations used in this study, the viscosity changes significantly for high particle concentrations (> 5 wt%). Therefore, an accurate model for the higher particle concentrations needs to describe the motion of the two domains separately, taking into account the different viscosities. Furthermore, the interaction between the particle rich and particle depleted domain needs to be described.

2.3 Particle motion

The nanoparticles in the penetrating liquid mixture can have two modes of transport. They can be advected along with the fluid with a velocity \( U \) or move by diffusion with a diffusion constant \( D \) [m\(^2\)/s] defined by the Stokes-Einstein relation [33],

\[
D = \frac{kBT}{6\pi\mu d},
\]

(5)
where $T$ [K] is the temperature, $d$ the particle diameter and $k_b$ [J K$^{-1}$] Boltzmann’s constant. The importance of diffusion for the particle transport can now be estimated with the help of the Peclet number:

$$Pe = \frac{U l}{D} = \frac{3\pi d k_p c}{6 k_b T} [-].$$

(6)

Note that the viscosity drops out of the equation as both the fluid flow and particle diffusion are affected by viscosity in a similar manner. The Peclet numbers encountered in this study are of the order $10^5$ (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 can be concluded that diffusion can be disregarded as a mode for particle transport and a model based on advection suffices.

A second issue concerns the assumption of local equilibrium of particle attachment. 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 same period of time it takes a particle to reach the pore wall due to diffusion ($t_D$ [s]). This gives us an indication of 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

$$w_f = U t_D = \frac{Ur^2}{6D}.$$

(7)

Using the average speed of the liquid penetrating the studied porous media as an approximation for the maximum local velocity $U$ [m/s], the largest front width $w_f$ is found for Al$_2$O$_3$ with the highest average pore size ($r = 8.1 \mu m$), which is of the order of 1 mm. In the intermediate pore size, the front width is of the order 1 $\mu m$, and for the smallest pore sizes 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 studied in this research.

### 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

$$\frac{\partial c}{\partial t} = -U(t) \frac{\partial c_0}{\partial x}.$$  

(8)

Note that $U \cdot c$ equals the particle flux. Using $\partial_t \vec{c} = (1 + \partial c_b/\partial c_0) \partial_t c_0$, equation (8) can be rewritten to

$$\frac{\partial c_0}{\partial t} = -\frac{U}{1+\partial c_b/\partial c_0} \frac{\partial c_0}{\partial x}.$$  

(9)

Equation (9) clearly shows the effect of particle sorption to the pore surface. The effective particle velocity $U_p$ [m/s] is decreased with a factor $1 + \partial c_b/\partial c_0$, which increases with increasing binding capacity $R(c) \equiv \partial c_p/\partial c_b$. This binding capacity is determined by the sorption isotherm, and surface to volume ratio of the pore system ($c_p \sim A/V$). Following equation (2) we find
\[ R(c) \equiv \frac{\partial c_b}{\partial c_0} = \kappa c_{p,m} \frac{1}{(1+\kappa c_0)^2}. \]  

Combining equation (9) and (10), the limits of the particle velocity \( U_p \) are found. At low particle concentrations, i.e. \( \kappa c_0 \ll 1 \), the motion of the particle is retarded the most:

\[ U_p \approx U \frac{1}{1+\kappa c_{b,m}} = U \frac{1}{1+(A/V)kT_m}. \]  

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:

\[ U_p \to U, \]  

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

### 2.5 Equations for the particle front

The aim of this section is to find an expression for the propagation of the particle front: \( ds/dt \). 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

\[ c(x,0) = c_0[1 - \Theta(x)], \]  

where \( \Theta(x) \) is the Heaviside function, representing the initial particle front. Equations (8) and (10) show 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 \( c_+ \equiv c(s_+,t) = 0, \quad \bar{c}_+ \equiv \bar{c}(s_+,t) = 0, \) \( c_- \equiv c(s_-,t) = c_0 \) and \( \bar{c}_- \equiv \bar{c}(s_-,t) = c_0 + c_b(c_0) \).

Given the shockwave nature for the concentration front, we have to rely on mass-conservation arguments and should start with equation (8). Here we follow the same line of reasoning as Olver [34]. 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

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

and

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

From these equations it follows that

\[ \frac{dN}{dt} \approx \frac{N(t+\Delta t) - N(t)}{\Delta t} = A \phi \frac{\bar{c}_- - \bar{c}_+}{\Delta t} \approx A \phi \frac{s(t+\Delta t) - s(t)}{\Delta t} \approx A \phi \frac{\bar{c}_- - \bar{c}_+}{ds/dt}, \]  

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

(17)

using equation (8) and the fact that \( U \) is an explicit function of time (equation (4)) we find

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

(18)

By combining equations (16) and (18) the Rankine-Hugoniot jump condition for the speed of the particle front can be found:

\[
\frac{ds}{dt} = U \frac{c_+ - c_0}{c_+ - c_-}.
\]

(19)

With the boundary conditions of interest, equation (19) can be rewritten as

\[
\frac{ds}{dt} = U \frac{c_0}{c_0 + c_p(c_0)} = U \frac{c_0}{c_0 + (A/V) \Gamma_m(c_0)}.
\]

(20)

In case monolayer absorption (equation (2)), equation (20) can be rewritten to

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

(21)

The particle front position can then be found by integration of this expression

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

(22)

where \( l \) is the liquid front as given in equation (3) 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, 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, \( (A/V) \Gamma_m \). The limiting cases are immediately apparent from Figure 2. For high particle concentrations, \( \kappa c_0 \to \infty \), the position of the particle and liquid front coincide: \( ds/dt \to U \) and \( s \to l \). For low particle concentrations, \( \kappa c_0 \approx 0 \), it can be shown that

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

(23)

This implies 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: The ratio between the speeds of the particle and liquid fronts, $U^{-1} \frac{ds}{dt}$, as a function of the particle concentration in solution $\kappa c_0$. Curves are shown for different binding capacities: $(A/V)\kappa \Gamma_m$.

3. Materials and methods

3.1 NMR imaging

3.1.1 Principles of NMR

NMR (Nuclear Magnetic Resonance) imaging is a non-destructive technique that allows the determination of local moisture content inside a porous material [35]. The NMR measurements in this study were performed using a home built 1D NMR scanner tuned to measure hydrogen profiles [36]. A static magnetic field $B_0 [T]$ of 0.7 T is generated by a water-cooled iron cored electromagnet. In order to create a spatial resolved measurement technique, a position dependent modification to the static magnetic field is applied using a gradient $G [T/m]$:

$$f = \gamma (B_0 + Gx) [Hz], \quad (24)$$

where the position of the sample with respect to the centre of the magnet is given by $x [m]$ and the proportionality factor is the gyromagnetic ratio $\gamma$, which equals 42.59 [MHz/T] for $^1H$. The hydrogen atoms can be excited using a RF pulse with a frequency matching the frequency in the magnetic field and measured using a pick-up coil. The measured signal $S$ [a.u.] is proportional to the number of hydrogen atoms in the measurement volume and decreases over time due to spin-lattice relaxation ($T_1 [s]$) and spin-spin relaxation ($T_2 [s]$). $T_2$ depends on the molecular structure of the probed liquid and on the surroundings of the nuclei. This makes $T_2$ dependent on the particle concentration and the local pore size of the porous material. For moisture in porous material $T_2 << T_1$, the measured signals proportionality is given by

$$S \sim \rho \left(1 - \exp\left(-\frac{t_r}{T_1}\right)\exp\left(-\frac{t_e}{T_2}\right)\right) \text{[a.u.]} \quad (25)$$

where $\rho [kg/m^3]$ is the nuclei density, $t_r [s]$ the repetition time, which is the time between subsequent pulse sequences and $t_e [s]$ is the echo time. The transversal relaxation time $T_2$ can be split in a volume $T_{2,v}$ and a surface part $T_{2,s}$:
\[ T_{2}^{-1} = T_{Z,v}^{-1} + T_{Z,s}^{-1}. \] (26)

The volume term can be approximated by
\[ T_{Z,v}^{-1} = T_{Z,0}^{-1} + R_{2}c, \] (27)

as observed by Rhee and Kim [37] for iron-ferrite (\( \text{Fe}_3\text{O}_4 \)) nanoparticles, with \( R_{2} \) \([\text{m}^3/\text{s}]\) the relaxivity of the nanoparticles. They found the reverse of the relaxation time to be directly dependent on the particle concentration. For small surface to volume ratios (i.e. large pores), in absence of nanoparticles, the transversal relaxation is equal to \( T_{Z,0} \).

Inside a porous material, the surface relaxation term of equation (26) consists of a term for relaxation at the pore surface and a contribution for the relaxation due to bound particles on the pore wall. However, when both the particles in solution and the particles on the pore space contribute to the relaxation dynamics, the concentrations of the bound and surface particles cannot be separately computed from the MRI signal [10].

There are different pulse sequences available that allow the determination of the \( T_{2} \) relaxation time. A detailed description of the basics of NMR and possible pulse sequences can be found in dedicated text books [35]. In this study, we use a CPMG pulse sequence to measure \( T_{2} \) [38], which consists of one 90° pulse and a series of 180° pulses (same pulse length but increased power as compared to a 90° pulse) 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
\[ S_n = S_0 \exp \left( -\frac{nT_{2}}{\text{a. u.}} \right), \] (28)

where \( S_0 \) \([\text{a. u.}]\) is the original signal amplitude [35].

### 2.1.2 Experimental details

In our setup, we use a static magnetic field of 0.7 T and have a gradient \( G \) of 0.23 T/m resulting in a spatial resolution of 1.4 mm. As a result, each measurement point is the average of a slice with thickness 1.4 mm. 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. Besides the sample that is measured, the sample holder also contains a reference compartment and the liquid bath of the penetrating liquid. The sample holder is schematically drawn in Figure 3. The combination of the setup and the sample holder allows the measurement of cylindrical samples up to 20 mm in diameter and a maximum of 70 mm in height.

The liquids are fed to the sample holder through flexible tubes, where the connection of the outflow tube is located above the connection of the inflow tube, as well as 2-4 millimeter above the bottom of the sample (Figure 3). Furthermore the liquid is removed from the sample holder faster than it is fed through the inflow tube, which ensures a constant liquid level just above the bottom (i.e. lowest surface) of the sample. This ensures the sample is in contact with the liquid during the experiment. The sample holder allows air to enter from the top to prevent the formation of a vacuum. More details of the setup can be found in Kuijpers et al. [36].
Each liquid profile consists of 25 data points, each 3.4 mm apart, resulting in a total measurement domain of 85 mm. This includes the sample with a length of 50 mm, the liquid bath and the reference compartment. To obtain one data point, a series of measurements is conducted and the results at this point are averaged. The number of measurements is given by $n_{avg}$. We use a CPMG pulse sequence to measure the water content and to investigate the relaxation behaviour. Each liquid profile of 25 points takes 10 minutes to measure. Subsequent measurements are conducted until the samples are saturated. The instrument settings for the CPMG pulse sequence are: $t_e = 0.7 \text{ ms}$, $w = 0.5 \text{ ms}$, $p_{90} = 30 \mu s$, $t_r = 1.5 \text{ s}$, $n_{avg} = 4$ and $n_{cpmg} = 512$.

### 3.2 Samples and liquids

#### 3.2.1 Al$_2$O$_3$ porous cylinders

In this research, we use the same kind of porous Al$_2$O$_3$ samples as used by Kuijpers et al. [36]. The samples have a diameter of 20 mm and a height of 50 mm. We use three different sample batches with an average pore diameter of 0.21 μm, 1.17 μm and 16,2 μm. The samples were produced by Innalox (0.21 μm) and Innovacera (1.17 μm and 16.2 μm). The average pore diameter, porosity, pore volume and pore area of the samples are measured using MIP. The sample properties are given in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Avg. pore radius ($r$) [μm]</th>
<th>Porosity ($\phi$) [%]</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$_2$O$_3$</td>
<td>0.1</td>
<td>22.8</td>
<td>$0.07 \cdot 10^{-6}$</td>
<td>1.2</td>
</tr>
<tr>
<td>1.2 μm Al$_2$O$_3$</td>
<td>0.6</td>
<td>35.9</td>
<td>$0.17 \cdot 10^{-6}$</td>
<td>0.59</td>
</tr>
<tr>
<td>16 μm Al$_2$O$_3$</td>
<td>8.1</td>
<td>39.5</td>
<td>$0.17 \cdot 10^{-6}$</td>
<td>0.043</td>
</tr>
</tbody>
</table>

#### 3.2.2 Penetrating liquids

The liquids used in this research are obtained by mixing glycerol (>99.0% pure), demineralised water and a 20 wt% Fe$_2$O$_3$ dispersion in H$_2$O (Sigma Aldrich, 720704-100G). The Fe$_2$O$_3$ dispersion contains nanoparticles with an average diameter of 62 nm and the particle distribution has its maximum at a particle diameter of 38 nm. The particle size distribution of the undiluted 20 wt% Fe$_2$O$_3$ in H$_2$O dispersion is measured by dynamic light scattering (Zetasizer Nano ZS, Malvern). To stabilise the
particles in water a dispersant (an ethoxylated carboxylic acid) is added by the manufacturer. The liquids are found to be stable up to particle concentrations of 20 wt%. The liquid mixtures are prepared by weight using a lab scale (Mettler Toledo PG2002-S) with an accuracy of 0.01 g. Mixing of the components was done by a vortex mixer (444-1372, VWR) for at least one minute.

The liquid properties are given in Table 2. The viscosity measurements are done using a rheometer (Modular Compact Rheometer 301, Anton Paar). The contact angles are measured on a substrate, which is chemically identical to the porous cylinders, but were sintered at a higher temperature to obtain non-porous Al₂O₃. This gives a first approximation for the contact angle in the pore space and provides a measure for the particle concentration dependency of the contact angle. A drop shape analyser (DSA100, Krüss) is used to measure the contact angles on the surface of the Al₂O₃ samples. The contact angle is measured after the liquid has been in contact with the surface of the Al₂O₃ samples for 6 seconds. The error estimate for the contact angle measurement is the standard deviation of the measured contact angle for at least 5 droplets. The addition of the Fe₃O₃ nanoparticles is found to have little effect on the surface tension for the used mixtures. So the surface tension can be considered constant with a value of 70 ± 2 mN/m.

<table>
<thead>
<tr>
<th>Mixture composition [wt%] Water : Glycerol : Fe₂O₃ nanoparticles</th>
<th>Particle concentration ((c_0)) [m⁻³]</th>
<th>Viscosity ((\eta)) [mPa·s]</th>
<th>Contact angle on Al₂O₃ ((\theta_0)) [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 : 50 : 0</td>
<td>0</td>
<td>5.1 ± 0.1</td>
<td>70 ± 2</td>
</tr>
<tr>
<td>49 : 50 : 1</td>
<td>((1.7 \pm 0.1) \cdot 10^{19})</td>
<td>5.5 ± 0.1</td>
<td>71 ± 3</td>
</tr>
<tr>
<td>48 : 50 : 2</td>
<td>((3.5 \pm 0.1) \cdot 10^{19})</td>
<td>5.9 ± 0.1</td>
<td>70 ± 2</td>
</tr>
<tr>
<td>45 : 50 : 5</td>
<td>((8.9 \pm 0.1) \cdot 10^{19})</td>
<td>7.6 ± 0.1</td>
<td>84 ± 3</td>
</tr>
<tr>
<td>43 : 50 : 7</td>
<td>((1.3 \pm 0.1) \cdot 10^{20})</td>
<td>9.0 ± 0.1</td>
<td>77 ± 2</td>
</tr>
<tr>
<td>40 : 50 : 10</td>
<td>((1.9 \pm 0.1) \cdot 10^{20})</td>
<td>12.1 ± 0.1</td>
<td>83 ± 2</td>
</tr>
<tr>
<td>25 : 70 : 5</td>
<td>((9.4 \pm 0.1) \cdot 10^{19})</td>
<td>33.5 ± 0.2</td>
<td></td>
</tr>
</tbody>
</table>

### 3.3 Experimental procedure

First, a moisture profile of the dry sample, before adding the liquid, is used to ensure a proper positioning of the sample holder as well as a check for residual liquids in the sample. Next, the liquid is fed to the sample compartment for about 2 minutes and the measurement is started. During this time, the empty area below the sample is filled with liquid. Approximately 30 seconds to one minute after the start of the experiment, liquid can be seen to exit from the outflow tube, indicating that the liquid will remain at a constant level from that point onwards. Liquid profiles are then measured until the sample is saturated. A time interpolation is applied to construct the liquid profile at 10 minute intervals from the separate NMR measurements. More details on the experimental procedure can be found in Kuijpers et al. [36].

### 4. Results

#### 4.1 Visualising particle penetration in non-transparent media

In order to couple signal and particle motion, we first investigated the particle distribution at the end of the capillary suction process. Al₂O₃ samples with an average pore radius of 0.6 µm where brought in contact with liquid mixtures containing Fe₂O₃ nanoparticles. All the liquid mixtures contain 50 wt% glycerol, \(x\) wt% Fe₂O₃ nanoparticles and \((50 - x)\) wt% water, where we have used \(x = 0, 1, 2, 5, 7\) or
10 wt% nanoparticles. The signal profiles for the saturated Fe₂O₃ samples are given in Figure 4. The liquid profile shown in Figure 4a consists 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 Al₂O₃ sample. The first domain is the signal from the reference compartment containing a 1 M CuSO₄ 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 Al₂O₃ 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.

![Figure 4: Liquid profiles of the saturated Al₂O₃ samples (r = 0.6 μm) with an initial nanoparticle concentration of 0, 1, 2, 5, 7 or 10 wt%.

In the sample, two regions can be distinguished. At the bottom of the sample (the left side in Figure 4), we observe a low signal due to the presence of particles. At the second region (near the end of the sample) we find that 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 (22). To investigate this change in the front behaviour, a cross section of the samples in the length direction is made (Figure 5), which shows the particle front inside the samples.
Figure 5: Saturated Al₂O₃ samples cut in the length direction, from left to right the original liquid mixture contains 1, 2, 5, 7 and 10 wt% Fe₂O₃ nanoparticles.

The particle front is locally sharp for all particle concentrations, but at low Fe₂O₃ 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 4. 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.

4.2 Quantifying particle penetration in non-transparent media

As theoretically described with equation (28), the measured signal intensity is lower for liquids that have a shorter $T₂$ relaxation time (i.e. faster CPMG decay), since the signal decays further during the echo time $t_e$. This relaxation time depends on the particle concentration (equation (27)), so we can investigate the liquid and particle behavior inside the porous medium 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 can be found in Appendix A: Supplementary material (Figure SM11).

The CPMG decays are fitted with an exponential fit, using either a mono-exponential or dual-exponential fit to capture the decay. The dual exponential decays occur for particle concentrations of 1 and 2 wt% at the start of the sample, and at a concentration of 10 wt% Fe₂O₃ nanoparticles at the end of the sample. The original signal amplitude $a₀$ (corrected for the decay during the echo time) is given in Figure 6a and the inverse $T₂$ relaxation times are given in Figure 6b. We observe a faster decay, i.e. a shorter $T₂$ relaxation time, for higher Fe₂O₃ concentrations as expected from equation (27).
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 4a 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 by Kuijpers at al. for different water-glycerol mixtures [36].

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 effect result in a conversion factor of about 3.4 which is similar to the difference found in Figure 6a. The difference between the signal intensity at the start and at the end of the sample can be explained by local pore blocking and part of the pore space being filled with water, which reduces the available liquid volume.

The inverse $T_2$ relaxation time (Figure 6b) in the liquid bath scales linearly with the particle concentration as expected (equation (27)). We also observe a linear concentration dependency 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 confinement of the liquid in the pore space, which results in faster relaxation. The higher dependency on concentration is a result of the interaction of the liquid with bound particles on the pore walls, which change the relaxation dynamics at the liquid – solid interface.

At the end of the sample, we see no dependence on concentration apart from the 10 wt% Fe$_2$O$_3$ nanoparticles case. The relaxation behaviour 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. We observe a dual exponential decay for the 1 and 2 wt% nanoparticles case at the start of the sample, the long relaxation time is similar to that found for the measurement without particles and the short relaxation time falls in the linear dependency shown by the lines in Figure 6b. This indicates that in the measurement slice, two domains are present. A part of the domain contains particles whereas the other contains only liquid, which is consistent with the visual observation of two domains in the cross section images in Figure 5.

4.3 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, we study the particle and liquid front as a function of time in the 0.6 µm average pore radius Al$_2$O$_3$ samples. We use a liquid containing 7 wt% Fe$_2$O$_3$ 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 Al$_2$O$_3$ sample is given in Figure 7a.

![Figure 7: 7wt% Fe$_2$O$_3$ and 50wt% glycerol in water uptake in 0.6 µm average pore radius Al$_2$O$_3$](image)

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 (22)). To verify this prediction, the particle front is plotted as function of the liquid front in Figure 7b.

The particle front indeed shows a linear dependency on the liquid front as predicted by the theory in equation (22). 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. This self-similarity can be shown in detail by plotting the profiles until the liquid front has reached the end of the sample, where the x-axis of Figure 7a is rescaled with the liquid front position $l$, to obtain a single master curve. The rescaled graph is given in Appendix A: Supplementary information (Figure SM12). Similar self-similar behaviour is found for the 5 and 10wt% nanoparticle concentrations.
The slope of a fit through the data points of Figure 7b is equal to 0.52. This means that the particle front lacks behind the liquid front by 48%. If we assume that the particles from the liquid beyond the particle front are attached to the pore wall, we can estimate the amount of particles that attach on the pore walls and the resulting fill factor of the pore surface. Using the Fe$_2$O$_3$ particle density $\rho_{\text{Fe}_2\text{O}_3} = 5.25 \text{ g/cm}^3$ [39], the pore area and pore volume of Table 1 and assume spherical particles with an average diameter of 62 nm, we find a surface coverage $\Gamma = 3.4 \cdot 10^{13} \text{ m}^{-2}$ and a bound particle concentration $c_b = (A/V)\Gamma$ of $1.2 \cdot 10^{20} \text{ m}^{-3}$. 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% [40]. The surface coverage found in this case is lower as the particles repel one another to stabilise them in the liquid.

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

To investigate the applicability of the model, 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 8 to test the linear relationship predicted in equation (22). For high particle concentrations (7 and 10 wt% nanoparticles) we observe a linear relationship through zero as predicted. At the lowest particle concentrations (1 and 2 wt% nanoparticles) we observe different behaviour due to the 3D effects observed for these low concentrations (Figure 5). At the intermediate particle concentration of 5 wt% Fe$_2$O$_3$ in the liquid mixture we observe a linear behavior 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.
The particle concentration has a small influence on the slope in Figure 8 for the higher particle concentration’s (≥ 5wt%). The dependency of $s/l$ can be predicted using equation (22). The relative front position $s/l$ as function of the initial particle concentration $c_0$ hardly changes for concentrations between $5.0 \cdot 10^{19}$ and $2.0 \cdot 10^{20}$ m$^{-3}$. Therefore, we can obtain an approximation for the maximum bound particle concentration $c_b$ and the binding constant $\kappa$.

Different combinations of the max bound particle concentration $c_{b,m}$ and the binding constant $\kappa$ are possible and the three data points available can be used to obtain a first approximation of these parameters for this liquid – media system. This results in a binding constant $\kappa$ of $2.06 \cdot 10^{-21}$ [m$^3$] and a maximum bound particle concentration $c_{b,m}$ of $5.78 \cdot 10^{20}$ [m$^{-3}$]. This gives a maximum surface coverage $\Gamma_m$ of $1.7 \cdot 10^{14}$ [m$^{-2}$], which is about 51% of the available pore surface. This is slightly below the theoretical maximum for randomly packed hard spheres of 64% [41], 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$_3$.

4.5 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 (22). Therefore we use 3 types of Al$_2$O$_3$ samples with an average pore radius of 0.1, 0.6 and 8.1 μm. 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. We have studied the imbibition of a liquid containing 5 wt% Fe$_2$O$_3$ nanoparticles and the resulting liquid profiles are given in Figure 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 $\text{Al}_2\text{O}_3$, the signal is multiplied by the sample porosity $\phi$ to directly compare the signal intensities (Table 1).

For the smallest pore size sample, with an average pore radius of 0.1 $\mu$m, a decrease in signal at the start of the sample is visible (Figure 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 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 a lower part, 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 particles. For the intermediate pore size (Figure 9b, e), the particle front penetrates to roughly half the sample length, as extensively discussed in section 4.4. For the highest average pore radius of 8.1 $\mu$m, a lower signal throughout the sample and much shorter $T_2$ relaxation times are observed (Figure 9c, f). We can, therefore, conclude that the particle front moves along with the liquid front during capillary uptake of the liquid containing 7 wt% $\text{Fe}_2\text{O}_3$ 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 4.4, we can predict the retardation of the particle front using equation (22). Results are given in Table 3. The predicted front retardation is similar to the measured front domains in Figure 9, where we observe a particle front speed of roughly 10-20% for the 0.1 $\mu$m average pore radius sample, 45-60% for the 0.6 $\mu$m case and no retardation for the largest pore radius sample (8.1 $\mu$m). The retardation of the front should be visible for the highest pore radius as well, however, we have seen that the particle front width is of the same order as the predicted particle retardation, which explains why this retardation is not visible in Figure 9c.
Table 3: Calculated retardation of the particle front for the liquid – medium combinations of Figure 9.

<table>
<thead>
<tr>
<th>Avg. pore diameter $(2r)$ [µm]</th>
<th>$c_0$ [m$^{-3}$]</th>
<th>$A/V$ [m$^{-1}$]</th>
<th>$\frac{1 + \kappa c_0}{1 + \kappa [c_0 + (A/V) g_m]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.21</td>
<td>$8.9 \cdot 10^{19}$</td>
<td>$1.9 \cdot 10^7$</td>
<td>0.15</td>
</tr>
<tr>
<td>1.17</td>
<td>$8.9 \cdot 10^{19}$</td>
<td>$3.4 \cdot 10^6$</td>
<td>0.49</td>
</tr>
<tr>
<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>

### 4.6 Coupling of particle and liquid front dynamics

To quantitatively describe the particle front position rather than a retardation compared to the liquid front, we need to accurately predict the liquid front position. 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 2. The liquid penetration speed is plotted as a function of time in Figure 10a. Similarly to Kuijpers et al. [36], 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 behaviour predicted by Darcy’s law (equation (3)), the liquid front versus the square root of time divided by the liquid viscosity is plotted in Figure 10b. The contact angle and surface tension of the used liquid mixtures is found to change very little for the used liquid mixtures (Table 2).

![Figure 10](image_url)  

**Figure 10:** Liquid front as a function of time (a) and as function of the square root of time rescaled with the liquid viscosity (b) for different Fe$_2$O$_3$ nanoparticle concentrations.

From Figure 10, we still observe a dependency of the liquid front speed on the nanoparticle concentration that cannot be fully explained by the changed liquid parameters such (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 we made is 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.

**Conclusion**

Most experimental research to validate particle retention and filtration models of nanoparticles involves saturated porous media [7], [42], [43]. However, to describe particle motion during capillary suction, experimental data in unsaturated porous media is needed. To the best of the authors knowledge, NMR imaging is used for the first time to measure nanoparticle motion during capillary transport in situ. These experiments are used to validate a 1D model 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 [7], 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.

We have investigated the particle concentration of the penetrating liquid between 1.7 and 9.4 \( \cdot 10^{19} \) particles per cubic meter. 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 \( \text{Fe}_2\text{O}_3 \) nanoparticles is found to be equal to 2.06 \( \cdot 10^{-21} \) \( [\text{m}^3] \) and the maximum surface coverage \( \Gamma_m \) equals 51\% of the \( \text{Al}_2\text{O}_3 \) 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 [41]. We were able to predict the retardation of the particle front using the developed model within the measurement accuracy. To validate the concentration dependency predicted by equation (22), 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\% \( \text{Fe}_2\text{O}_3 \) nanoparticles), we observed that 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 behaviour, 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\% \( \text{Fe}_2\text{O}_3 \) 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, we have found a self-similarity of the liquid profiles during liquid penetration. This indicates that the particle retardation also holds for different time and length scales, i.e. for thin porous media. The liquid penetration speeds follows the square root of time behavior predicted by Darcy’s law as previously seen for water-glycerol mixtures penetrating into porous Al₂O₃ [36]. 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.

**Acknowledgement**
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Appendix A: Supplementary material

Figure SM11: The CPMG decays for $\text{Al}_2\text{O}_3$ samples (average pore radius 0.6 $\mu$m) saturated with liquid mixtures containing 0, 1, 2, 5, 7 and 10 wt% nanoparticles, measured at a position in the liquid bath (a), at the bottom of the sample (b) and at the top of the sample (c).

Figure SM12: Self-similarity of 7wt% $\text{Fe}_2\text{O}_3$ and 50wt% glycerol in water uptake in 1.2 $\mu$m porous $\text{Al}_2\text{O}_3$. The time between profiles equals 10 minutes. The position is rescaled as $x' = x/l$, where $x'$ is the new position, $x$ corresponds to the position from the beginning of the sample and $l$ to the position of the liquid front. The first profile deviates from the others due to the limited amount of measurement points.
References


C. A. Poulain and B. A. Finlayson, “A comparison of numerical methods applied to


