Nonlinear multiphase flow in hydrophobic porous media

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Multiphase flow in porous materials is conventionally described by an empirical extension to Darcy’s law, which assumes that the pressure gradient is proportional to the flow rate. Through a series of two-phase flow experiments, we demonstrate that even when capillary forces are dominant at the pore scale, there is a nonlinear intermittent flow regime with a power-law dependence between pressure gradient and flow rate. Energy balance is used to predict accurately the start of the intermittent regime in hydrophobic porous media. The pore-scale explanation of the behaviour based on the periodic filling of critical flow pathways is confirmed through 3D micron-resolution X-ray imaging.

Key words: multiphase flow

1. Introduction

Multiphase flow in porous media occurs in a wide variety of natural and engineered settings, including carbon geosequestration, geoenery resources recovery, subsurface contaminant control, drug delivery and flow in fuel cells (Berg et al. 2013; Pak et al. 2015; Reynolds & Krevor 2015; Blunt 2017; Zhao et al. 2018; Iglauer et al. 2019; Zhang et al. 2019; Zhao et al. 2019; Gjennestad, Winkler & Hansen 2020; Gao et al. 2021; Zhang et al. 2021). For the last 85 years, multiphase flow has been quantified assuming that each fluid phase has its own pathway and the flow rate has a linear relationship with pressure gradient, governed by an empirical extension of Darcy’s law (Muskat & Meres 1936; Muskat 1938; Blunt 2017),

\[ q_i = -\frac{k_{ri}K}{\mu_i} (\nabla P_i - \rho_i g), \]

where \( q_i \) is the Darcy flux, defined as the volume of phase \( i \) flowing per unit area per unit time, \( K \) is the absolute permeability of the sample, \( k_{ri} \) is the relative permeability, and \( \mu_i \) is the...
viscosity, $\nabla P_i$ is the pressure gradient for phase $i$ and $\rho_i g$ is the contribution of gravity, which is ignored in this study.

The capillary number $Ca$ is defined as $Ca = \frac{\mu q_i}{\sigma}$, where $\mu$ is the average viscosity of the two fluids, $q_i$ is the total Darcy flux of the two phases and $\sigma$ is the interfacial tension. It is well known that $Ca$ has a linear relationship with pressure gradient $\nabla P$ at low flow rate, $\nabla P \sim Ca$ (Blunt 2017; Gao et al. 2020; Zhang et al. 2021).

Recent research has shown that there is nonlinear flow even at low capillary numbers where the capillary force is still dominant at the pore scale (Rassi, Codd & Seymour 2011; Sinha & Hansen 2012; Armstrong & Berg 2013; Rücker et al. 2015; Gao et al. 2020). We observe a so-called intermittent regime with $\nabla P \sim Ca^a$, $1 > a > 0$: the pressure gradient has a power-law relation with flow rate. At the pore scale, some regions of the void space, which provide additional connectivity, are intermittently occupied by both phases, as confirmed through high-resolution X-ray imaging and confocal microscopy (Datta, Dupin & Weitz 2014; Gao et al. 2017; Reynolds et al. 2017; Spurin et al. 2019a, b; Gao et al. 2020). This phenomenon is associated with non-thermal and non-periodic fluctuations in pressure and fluid occupancy representing a nonlinear disordered dynamics (Rücker et al. 2021). Tallakstad et al. (2009) was the first to observe this behaviour and suggested that $a \approx 0.5$ from two-phase flow experiments in a quasi-two-dimensional porous medium. Sinha et al. (2017) also proposed $a = 0.5$ through an analysis of experiments and simulations. Gao et al. (2020) found a threshold capillary number for the onset of intermittency $Ca^t$ of approximately $10^{-5}$ in two-phase steady-state flow tests on a water-wet (hydrophilic) sandstone sample with a water fractional flow (ratio of the volumetric flow rate of water to the total flow rate of oil and water) $f_w = 0.5$, where the exponent $a$ was approximately 0.6. Recently, Zhang et al. (2021) quantified the onset of intermittency as a function of fractional flow for fluids with different viscosity ratio and different rock types. To date, however, only two studies have investigated non-hydrophilic media, which have suggested that there may be more intermittency under these conditions (Zou et al. 2018; Rücker et al. 2019).

In many natural and engineered settings, including soils containing organic material, gas diffusion layers in fuel cells, surgical masks and rock that has been in contact with hydrocarbons, the solid surfaces of the porous material are not uniformly hydrophilic. It is more common to encounter a range of local contact angles, both above and below 90°, representing a mixed-wet state (AlRatrout, Blunt & Bijeljic 2018). However, there have been no quantitative studies of the onset of intermittency under these conditions.

In this paper, we conduct 174 steady-state immiscible two-phase flow experiments through an altered-wettability Bentheimer sandstone sample with different water fractional flows ($f_w = 0.2, 0.4, 0.5, 0.6, 0.7$ and 0.8), where the capillary number varies from $\sim 10^{-7}$ to $\sim 10^{-4}$ during a waterflood displacement. We label the sample ‘hydrophobic’, although the pore surfaces locally have a range of contact angle with both hydrophilic and hydrophobic regions (Lin et al. 2019). We also performed high-resolution pore-scale imaging on a replicate sample for 14 flow rates and fractional flows covering both the linear and intermittent flow regimes. We use energy balance to predict accurately the boundary of the onset of intermittency, which is consistent with our experimental results and in situ pore-scale X-ray images.

2. Materials and methods

We studied two Bentheimer sandstone samples (samples A and B, drilled from the same block). First, the samples were completely saturated with brine. The absolute
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permeability of the samples was measured during single-phase brine flow to be \( K = 1.85 \pm 0.02 \times 10^{-12} \text{ m}^2 \) (Zhang et al. 2021). Then, crude oil from the Middle East was injected and the samples were left in the crude oil for two months at 80°C and 3 MPa pressure. Direct contact of the crude oil with parts of the solid surface altered the wettability from water-wet to a more mixed-wet to oil-wet state, which we will call, for convenience, ‘hydrophobic’ (Lin et al. 2019, 2021). Decane was injected at 3 ml min\(^{-1}\) for 60 min to replace the crude oil. Sample A (5.97 mm diameter and 27.88 mm length) was mounted in a specially designed flooding system (Gao et al. 2017, 2020). The water (brine) phase was 15 wt% KI (potassium iodide) brine, and the oil phase was \( n \)-decane, both injected by high-precision ISCO pumps through a dual injection port (Zhang et al. 2021). The measured viscosity of the brine was 0.821 mPa s, the \( n \)-decane viscosity was 0.838 mPa s (PubChem, Open Chemistry database), while the interfacial tension was measured to be \( \sigma = 47 \text{ mN m}^{-1} \).

During the experiments, a high-precision pressure transducer (Keller PD-33) recorded the pressure difference between the inlet and outlet of the sample. Similar to the experimental protocol in Zhang et al. (2021), we started the two-phase flow experiment from a low water fractional flow and low flow rate: \( f_{w} \) of 0.2 at 0.02 ml min\(^{-1}\) total flow rate (\( Ca = 2.1 \times 10^{-7} \)). The pressure gradient was recorded after 12 h when it stabilized, and then the flow rate increased from low to high and the pressure gradients at steady state were recorded. A total of 29 flow rates were considered for each \( f_{w} \): the highest flow rate was 4.5 ml min\(^{-1}\) (\( Ca = 4.8 \times 10^{-5} \)). Note that the time for the pressure gradient to stabilize depended on the flow rate: it took up to 12 h for the low flow rate (0.02 ml min\(^{-1}\)), while as little as 5 min for the highest rates (greater than 3 ml min\(^{-1}\)). The \( n \)-decane was injected at 3 ml min\(^{-1}\) for 30 min again to return to the initial saturation after each sequence of experiments at the same fractional flow. We repeated this injection sequence for other fractional flows: 0.4, 0.5, 0.6, 0.7, and 0.8; in total 174 flow experiments were conducted.

For sample B (6.15 mm diameter and 50.13 mm length), we have followed the same experimental protocol as for sample A but replaced the water phase with 30 wt% KI brine for a better X-ray contrast; the viscosity of the brine was measured as 0.819 mPa s (Gao et al. 2019). The flooding system was placed in a Zeiss XRM-510 X-ray microscope for high-resolution \textit{in situ} imaging (Zhang et al. 2016; Lebedev et al. 2017; Gao et al. 2019; Lin et al. 2019). The scan setting was 3.58 µm voxel size, 0.5 s exposure time, 75 kV X-ray energy and 1601 projections with a flat panel detector. The scan time was around 1 h. We selected and repeated 14 test points: 0.1, 0.2 and 0.8 ml min\(^{-1}\) flow rates for \( f_{w} = 0.2 \); 0.1, 0.2, 0.8 and 1.25 ml min\(^{-1}\) flow rates for \( f_{w} = 0.5 \); 0.1, 0.2, 0.8 and 1.25 ml min\(^{-1}\) flow rates for \( f_{w} = 0.7 \); and 0.1, 0.2 and 0.8 ml min\(^{-1}\) flow rates for \( f_{w} = 0.8 \).

3. Results

The results, for all water fractional flows \( f_{w} \), clearly show a transition from a linear \( a = 1 \) to a nonlinear regime \( a < 1 \) when the capillary number increases (figure 1). We found that the exponent \( a \) and threshold capillary number \( Ca^{d} \) are both functions of the fractional flow (see table 1). The lowest value \( a = 0.50 \pm 0.01 \) occurs when \( f_{w} = 0.4 \), indicating the strongest intermittency, defined as the deviation from a linear Darcy law; \( f_{w} = 0.8 \) had the highest exponent \( a = 0.58 \pm 0.01 \), indicating weaker intermittency. The range of \( a \) is smaller when compared with similar experiments on a water-wet sample, where \( a \) varied
Figure 1. Summary of the measured pressure gradient $\nabla P$ as a function of capillary number $Ca$, for different water fractional flows $f_w$: 0.2, 0.4, 0.5, 0.6, 0.7 and 0.8.

Table 1. Summary of the exponent $a$ for $\nabla P \sim Ca^a$, threshold capillary number $Ca^t$ for the onset of intermittency, and the associated oil-phase capillary number $Ca^1$ and water-phase capillary number $Ca^2$, from figure 1.

<table>
<thead>
<tr>
<th>Fractional flow ($f_w$)</th>
<th>$a (Ca &lt; Ca^t)$</th>
<th>$Ca^t$</th>
<th>$Ca^1$</th>
<th>$Ca^2$</th>
<th>$a (Ca &gt; Ca^t)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1</td>
<td>$\sim 10^{-5.7}$</td>
<td>$\sim 10^{-5.8}$</td>
<td>$\sim 10^{-6.4}$</td>
<td>0.55 $\pm$ 0.01</td>
</tr>
<tr>
<td>0.4</td>
<td>1</td>
<td>$\sim 10^{-5.4}$</td>
<td>$\sim 10^{-5.6}$</td>
<td>$\sim 10^{-5.8}$</td>
<td>0.50 $\pm$ 0.01</td>
</tr>
<tr>
<td>0.5</td>
<td>1</td>
<td>$\sim 10^{-5.3}$</td>
<td>$\sim 10^{-5.6}$</td>
<td>$\sim 10^{-5.6}$</td>
<td>0.51 $\pm$ 0.01</td>
</tr>
<tr>
<td>0.6</td>
<td>1</td>
<td>$\sim 10^{-5.2}$</td>
<td>$\sim 10^{-5.6}$</td>
<td>$\sim 10^{-5.4}$</td>
<td>0.56 $\pm$ 0.01</td>
</tr>
<tr>
<td>0.7</td>
<td>1</td>
<td>$\sim 10^{-5.1}$</td>
<td>$\sim 10^{-5.7}$</td>
<td>$\sim 10^{-5.3}$</td>
<td>0.57 $\pm$ 0.01</td>
</tr>
<tr>
<td>0.8</td>
<td>1</td>
<td>$\sim 10^{-5.1}$</td>
<td>$\sim 10^{-5.8}$</td>
<td>$\sim 10^{-5.2}$</td>
<td>0.58 $\pm$ 0.01</td>
</tr>
</tbody>
</table>

from 0.44 to 0.74 (Zhang et al. 2021). Moreover, the lower fractional flows have smaller threshold capillary numbers $Ca^t$ for the onset of intermittency: $Ca^t$ increased from $10^{-5.7}$ to $10^{-5.1}$ as the water fractional flow $f_w$ increased from 0.2 to 0.8; this is the opposite trend to the water-wet results.

In the high-resolution images (figure 2), it is evident that large pores are occupied by water, as expected for media that are no longer water-wet (Gao et al. 2020). We used an automated method to calculate contact angles directly on the images at the three-phase (oil–water–solid) contact line (AlRatrout et al. 2017) for $f_w = 0.5, 0.1$ ml min$^{-1}$ injection rate, $Ca = 10^{-6}$. The average contact angle is $103^\circ$, with a standard deviation of $22^\circ$, representing, on average, a hydrophobic medium (mixed-wet or oil-wet) (Lin et al. 2019). However, the sample is not uniformly hydrophobic: locally, there are contact angles both less than $90^\circ$ (hydrophilic) and greater than $90^\circ$ (hydrophobic).

At the pore scale, it has been shown, in uniformly water-wet systems, that the nonlinear flow behaviour is caused by intermittent filling of regions of the pore space alternately by both phases; the oil and water no longer travel through fixed flow pathways and become quasi steady-state (Gao et al. 2020). We use our images to quantify regions of the pore

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Figure 2. Example two-dimensional cross-sections of three-dimensional images showing phase configurations in the same area of the rock sample at the same flow rate (0.2 ml min⁻¹) but different water fractional flows: \( f_w = 0.2 \) (a,b) and 0.8 (c,d). The capillary number is \( 10^{-5.7} \). (a) and (c) are greyscale images, and (b) and (d) are segmented images, where blue is water, red is oil and yellow represents intermittent regions that were periodically occupied by both oil and water during the 1 h scan time.

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As an example, figure 2 shows that there is more intermittency for the lower water fractional flows, consistent with the threshold capillary numbers and exponents listed in table 1. Figure 3 demonstrates how the degree of intermittency increases with flow rate. In the Darcy regime, the volume of any intermittent regions is negligible and the two phases flow through fixed flow pathways. In the intermittent regime, a significant fraction of the pore space is periodically occupied by both phases, facilitating flow; more pathways open up as the capillary number increases, leading to a nonlinear relationship between flow rate and pressure gradient.

4. Quantification of the transition from linear to intermittent flow

We now quantify the onset of intermittency using an energy balance argument. We generalize our previous work Zhang et al. (2021) by identifying oil as the wetting phase...
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\[ \text{Ca} = 10^{-6.0} \]

\[ \text{Water} \]

\[ \text{Oil} \]

\[ \text{Intermittent} \]

\( (a) \) \( (b) \) \( (c) \)

\( 0.385 \text{ mm} \)

\( 0.385 \text{ mm} \)

\( 0.385 \text{ mm} \)

\[ \text{Ca} = 10^{-5.1} \]

\[ \text{Ca} = 10^{-4.9} \]

Figure 3. Three-dimensional views of the segmented phases on a 100 \times 100 \times 400 \text{ voxels} sub-volume of the full image for \( f_w = 0.7 \) and \( \text{Ca} = 10^{-6.0}, 10^{-5.1} \) and \( 10^{-4.9} \). Water is blue, oil is red and intermittent regions are shown in yellow.

(which we label phase 1) and water as non-wetting (which we label phase 2). We hypothesize that intermittency first occurs when the work done due to fluid injection over a characteristic pore scale \( l \) is sufficient to create a fluid meniscus. Note that this is not the same as equating the pressure drop across a pore to the capillary pressure, which occurs at higher flow rates. We define \( l \) as a characteristic distance between pores. The average pore volume associated with a pore is thus \( \phi l^3 \), where \( \phi \) is the porosity. The change in pressure \( P \) over a distance \( l \) is equal to \( -l \nabla P \), where \( \nabla P \) is the pressure gradient. The mechanical work of fluid injection, \( P \nabla V \), can be written as \( -\phi l^4 \nabla P \). The energy to create an interface in a pore of typical radius \( r \) is \( \sigma r^2 \), which, at the onset of intermittency, we assume is equal to \( -\phi l^4 \nabla P \). We ignore the change in surface energy due to changes in the fluid–solid interfacial areas.
To estimate the pressure gradient, we assume Darcy-like flow on average with a total flow rate $q_i$ and a limiting mobility $f_w/\mu_1$, which represents flow of the wetting phase (1, oil) into and out of regions of the pore space filled with the non-wetting phase (2, water) with an effective relative permeability, at least in the viscous-flow limit of $f_w$. Hence from (1.1) we estimate $\nabla P \approx -\mu_1 q_i^t/\kappa f_w$. We then expect the onset of intermittency when

$$\sigma r^2 = \frac{\mu_1 q_i^t \phi l}{\kappa f_w}. \quad (4.1)$$
This can be rearranged to write the threshold water (non-wetting) phase capillary number \( C_d^2 = \mu_2 f_w q_i^t / \sigma \) and oil (wetting) phase capillary number \( C_d^1 = \mu_1 (1 - f_w) q_i^t / \sigma \) as

\[
C_d^2 = Y^i (f_w)^2
\]

and

\[
C_d^1 = Y^i f_w (1 - f_w) \frac{\mu_1}{\mu_2},
\]

and the dimensionless number \( Y^i \) is defined by

\[
Y^i = \frac{\mu_2 Kr^2}{\mu_1 \phi l^4}.
\]

For Bentheimer sandstone, the mean pore radius \( r \) is 24 \( \mu \)m (Blunt 2017) and \( l \) has a value of approximately 150 \( \mu \)m (Gao et al. 2020), which is the mean pore-to-pore distance obtained from pore-network analysis (Raeini, Bijeljic & Blunt 2017). Then we calculate \( Y^i \) to be \( \approx 10^{-5} \).

In figure 4, our results for sample A (table 1) are plotted on a phase diagram as a function of \( C_d^1 \) and \( C_d^2 \) (Datta et al. 2014). Equations (4.2) and (4.3) accurately predict the onset of intermittency for all fractional flows.

Furthermore, we quantify the fraction of the pore space that is intermittently occupied based on the pore-scale images for sample B (figure 5). In the Darcy regime, it has zero intermittent phase or a small amount of intermittent occupancy that is insufficient to perturb the linear Darcy law (Gao et al. 2020). Once nonlinear behaviour emerges, the fraction of the pore space periodically occupied by both phases increases up to 28% in the cases studied. In figure 5, we also show a good agreement between our theory and previously published work for mixed-wet Bentheimer sandstone from Zou et al. (2018), with a different viscosity ratio (the oil–water viscosity ratio was 1.46), where the three experiments are all in the predicted intermittent regime or near the threshold line. It should be noted that in previous work we showed that the energy balance theory also accurately predicted the onset of intermittency for a wide range of data in the literature on water-wet samples for different rock types and viscosity ratios (Zhang et al. 2021).

5. Conclusions

We have measured the pressure gradient and imaged the nonlinear pore-scale dynamics as a function of capillary number for different water fractional flows on hydrophobic porous media with a wide range of local contact angle during steady-state immiscible two-phase displacement. The Darcy flow regime and the transition to intermittent flow regime have been observed. Using energy balance, we have proposed the threshold line for the onset of intermittent flow, (4.2) and (4.3), which accurately matches the experimental results and is consistent with the pore-scale images. The work provides a quantification of nonlinear flow that is likely to be encountered in many processes, including carbon dioxide storage, subsurface gas production, in porous fibrous layers within fuel cells, microfluidics devices used in drug delivery, and catalysis, which involve multiphase fluid flow in porous materials.

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REFERENCES


MUSKAT, M. 1938 The flow of homogeneous fluids through porous media. Soil Sci. 46 (2), 169.


