Stabilizing Fluid-Fluid Displacements in Porous Media Through Wettability Alteration

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We study experimentally how wettability impacts fluid-fluid-displacement patterns in granular media. We inject a low-viscosity fluid (air) into a thin bed of glass beads initially saturated with a more-viscous fluid (a water-glycerol mixture). Chemical treatment of glass surfaces allows us to control the wetting properties of the medium and modify the contact angle \( \theta \) from 5° (drainage) to 120° (imbibition). We demonstrate that wettability exerts a powerful influence on the invasion morphology of unfavorable mobility displacements: increasing \( \theta \) stabilizes fluid invasion into the granular pack at all capillary numbers. In particular, we report the striking observation of a stable radial displacement at low capillary numbers, whose origin lies on the cooperative nature of fluid invasion at the pore scale.

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I. INTRODUCTION

Two-phase flow in porous media exhibits a rich variety of fluid-displacement patterns [1–3]. Understanding and controlling these displacements is central to many industrial processes and natural phenomena, including enhanced oil recovery [4], shale gas production [5,6], geological CO\(_2\) storage [7,8], operation of low-temperature polymer-electrolyte fuel cells [9], water infiltration in soil [10], and ink spreading on paper [11].

Immiscible fluid-displacement patterns in porous media have been studied in depth in the drainage regime, that is, when the displacing fluid is less wetting to the porous medium than the displaced fluid. The combined effect of viscous forces, capillary forces, and medium disorder result in patterns that range from viscous fingering (VF) to capillary fingering (CF) to stable displacement [1,2,12–15]. From experimental observations in glass micromodels, this fundamental behavior was mapped out by Lenormand et al. [2] on a phase diagram as a function of viscosity contrast \( \Delta \) between the fluids and capillary number \( Ca \), which reflects the relative magnitude of viscous-to-capillary forces.

Extensions to the Lenormand diagram have addressed the effects of gravity [16], pore-scale disorder [17,18], fluid compressibility [3,19], the crossover between regimes including the existence of a Ca-dependent crossover length scale [17,18,20–22], and frictional forces between grains leading to a whole new set of displacement patterns [3,23–27]. Yet, this wealth of observations has been restricted to a drainage process.

Many experimental observations also exist for imbibition in the regime of favorable viscosity contrast—when the invading fluid is more wetting and more viscous than the defending fluid [11]. Much of this work has focused on describing the roughness of the imbibition front in a disordered medium like a porous medium [28–33] or a Hele-Shaw cell with rough surfaces [34–36]. Fundamental observations on pore-scale mechanisms controlling imbibition, such as snap-off and cooperative filling [37] have been incorporated into quasistatic pore-scale models simulating two-phase flow on idealized geometries [38,39] and network representations of porous media [40–43].

In contrast, here we are interested in imbibition in the regime of unfavorable viscosity contrast that favors unstable fluid-fluid displacement: relatively high velocity and high viscosity contrast. Our knowledge and understanding of imbibition in this regime is much less complete, even in simple geometries like a straight capillary tube [44,45] or Hele-Shaw cell [46]. Experiments in transparent porous media cells illustrating the phenomenon of viscous fingering date back to the 1950s [47,48]. Classic experiments have shown a fundamental difference between imbibition and drainage in terms of the length scale of the instability [14], and have pointed to the associated (and still puzzling) dynamic capillary pressure that accompanies these unstable porous media flows [49]. These observations remain largely unexplained, and thus far inaccessible to both pore-scale and continuum models. A reason for this challenge is, in our view, the importance of nonlocal effects at the front [10,50–52].

From the point of view of engineering applications, there is little doubt that wetting properties play a key role in the extraction of oil and gas from hydrocarbon reservoirs [53–56]. Despite the evidence for the potential of wettability alteration as an agent for enhanced oil recovery (including low-salinity water flooding [57], surfactant flooding [58–60], and thermal stimulation [61]), the complex physics of wetting continue to challenge our fundamental understanding of the mechanisms that link surface
chemistry with the fluid dynamics of multiphase flow at the pore and reservoir scales.

Here we perform a systematic experimental study of the impact of wetting properties on the fluid-fluid invasion morphology in porous media. We effectively extend Lenormand’s diagram to elucidate the impact of wetting properties (as measured by contact angle) on the displacement pattern for highly unfavorable viscosity ratios. We find that, as the invading fluid becomes more wetting, the invasion front becomes more compact and more effectively sweeps the defending fluid at all capillary numbers—both in the viscous-fingering and capillary-fingering regimes. Our main results are a visual phase diagram of the displacement pattern as a function of capillary number and contact angle, and a quantitative analysis of the dependence of the emerging length scale on the wetting properties of the system.

II. EXPERIMENTAL SETUP

We conduct two-phase fluid-displacement experiments in a radial Hele-Shaw cell packed with glass beads. The radial cell consists of a base, a frame, and a lid, all made of soda-lime glass (Fig. 1). The beads are also made of soda-lime glass. The experimental setup is described in detail in Appendix A. The bead matrix is initially fully saturated with a viscous mixture of water and glycerol ($\eta_{liq} = 5.83$ cP), placed by slow injection through the injection port. This initial fluid is displaced by injecting air ($\eta_{air} = 0.018$ cP) at rate $Q$ which is held constant throughout each individual experiment ($Q = 170$, 17.0, 1.70, and 0.170 ml/min). The viscosity contrast between these two fluids is $M \approx \eta_{liq}/\eta_{air} \approx 320$—in the regime of highly unfavorable mobility ratios we are interested in. We study how the invasion morphology changes with the wetting properties by treating the cell and the glass beads using chemical vapor deposition (CVD) of silane-based substances, to achieve specific contact angles $\theta$ to water-glycerol mixtures ranging from almost perfectly hydrophilic to hydrophobic ($\theta \approx 5°, 20°, 60°, 90°, 120°$) (see Appendix A). We ensured reproducibility of the results by repeating each experiment three to five times.

III. EXPERIMENTAL RESULTS

To rationalize the results, we first define an effective capillary number $Ca^*$ that reflects the balance between viscous and capillary forces at the scale of the entire cell as the ratio between a characteristic capillary pressure difference for invasion along the displacement front, $\delta P_c$, and the characteristic viscous pressure loss across the cell in the direction perpendicular to the front, $\delta P_v$ [18,27]. From simple arguments using the classical Laplace pressure and Darcy’s law, we propose the scaling $\delta P_c \sim \gamma / r_{min} - \gamma / r_{max} \sim \gamma / d$, and $\delta P_v \sim (\eta_{liq} Q R) / (\gamma b d^3)$, leading to

$$Ca^* = \frac{\eta_{liq} Q R}{\gamma b d^3}.$$  

This dimensionless number is necessarily a crude representation of the balance between the viscous and capillary forces, because this balance changes over the course of an experiment in a radial system. Also, intentionally, this number does not account for the wetting properties of the system. As we contend below, these effects cannot be subsumed into an effective capillary number.

Our main result is a visual phase diagram of the invasion morphology of air displacing the water-glycerol mixture, as a function of $Ca^*$ and contact angle $\theta$ (Fig. 2). Shown are the displacement patterns at the end of the experiment, when the injected fluid breaks through the perimeter of the cell.

The leftmost column ($\theta = 5°$) corresponds to the well-known drainage regime. At low $Ca^*$, we observe capillary fingering, characterized by intermittent air-water displacements that produce an overall asymmetric pattern. At high $Ca^*$, we observe viscous fingering, characterized by continuous air-water displacements that produce a more radially symmetric pattern. Virtually identical morphologies are observed for slightly less wetting conditions to the liquid ($\theta = 20°$). While the transition between the morphologies is gradual, qualitatively comparing the pattern symmetry and invasion rate (continuous vs intermittent) suggests that the VF-CF transition occurs at an effective capillary number of order one, suggesting that our definition of $Ca^*$ in Eq. (1) is valid.

Wetting properties exert a remarkable control on the fluid displacement at both high and low capillary numbers. At high capillary numbers (bottom two rows, $Ca^* = 50, 5$),...
altering the wetting properties of the substrate towards imbibition (less wetting defending fluid) results in a gradual stabilization of the viscous-fingering displacement. In strict drainage ($\theta = 5, 20^\circ$), VF is a pore-scale instability: the fingers of the invading fluid have a characteristic thickness equal to the pore size of the granular pack (see Video 1 [62]). This characteristic length scale changes as the invading fluid is more wetting ($\theta = 90, 120^\circ$), resulting in fingers whose thickness is clearly larger than the pore scale (see Video 2 [62]). This fundamental observation dates back to linear-displacement experiments in the 1980s [14], where the emphasis was on reporting and understanding the dependence of the emerging length scale on the capillary number [49], rather than the transition from drainage to imbibition.

In Fig. 2 we report a remarkable finding, which had heretofore remained elusive to direct observation: the complete stabilization of unfavorable mobility-ratio displacements in the regime of low capillary numbers, as a result of wettability alteration (top two rows, Ca* = 0.5, 0.05). Fluid invasion becomes a perfectly stable, radial, outward-growing displacement—which maximizes sweep of the initial fluid—as the invading fluid is more wetting to the substrate.

While this is not visible from the single snapshots in Fig. 2, the growth activity of the displacement front is also heavily mediated by the wetting properties. In particular, the displacement in the drainage CF regime consists of a sequence of avalanches, whose size distribution has been well characterized [63] and whose origin has been assimilated to well-known statistical growth models [15]. This intermittent pattern growth leaves much of the displacement front frozen during invasion (see Video 3 [62]).

In contrast, we find that low-Ca* imbibition leads to a smooth, uniform, simultaneous advancement of the displacement front (see Video 4 [62]). We interpret this feature as the macroscopic consequence of the strong cooperative nature of fluid invasion at the pore scale during imbibition [37–39,64]. In imbibition, due to the shape of the fluid-fluid menisci between grains, invasion past a pore throat often occurs when neighboring menisci touch; this leads to an unstable fluid-fluid interface that advances to adopt a stable configuration. Therefore, loosely speaking, invasion at one pore “pulls” the interface at neighboring pores, in contrast with the prototypical slow-drainage regime—in which invasion can be considered at each pore independently. This nonlocal fluid invasion in imbibition has been illustrated in simple geometries by means of simulations of point injection [39] and experiments of multiphase lock-exchange flows in porous media [64,65]. This strong nonlocal effect along the wetting front has been interpreted in the past as a macroscopic surface tension [49] and, more recently, it has led to the formulation of phase-field models of multiphase flow in porous media [10,66].

IV. QUANTITATIVE ANALYSIS

To gain quantitative insight into the visual trends observed experimentally, we first compute the evolution of the invaded area $A_{\text{inv}}$ as a function of radial distance $r$ using the box-counting method. Taking the final snapshot for each experiment in Fig. 2, we confirm a power-law relation $A_{\text{inv}} \sim r^{D_f}$ over almost a decade of data, where $D_f$ is the fractal dimension [1,2]. The impact of Ca* and $\theta$ on $D_f$ is shown in Fig. 3(a). For strict drainage displacements ($\theta = 5^\circ$), the system displays a transition from $D_f \approx 1.72$ at...
high $C_a^*$ to $D_f \approx 1.8$ at low $C_a^*$, a trend that is consistent with previously reported fractal dimensions for VF and CF in drainage [63], corresponding to classical statistical-physics models: diffusion-limited aggregation [12,67], and invasion percolation [15], respectively. The stabilization of the invasion pattern as a result of wettability alteration is apparent from the increasing trend in $D_f$ as a function of $\theta$ at all capillary numbers. At low $C_a^*$, $D_f \approx 1.9$ for $\theta \geq 60^\circ$, indicative of very compact displacement. At a high capillary number ($C_a^* = 50$), however, the fractal dimension does not capture the stabilization of the displacement with the contact angle evidenced in the experiments (Fig. 2, bottom row). This is because, even though the fingers are wider, the displacement does not involve a “core” of more complete filling of the injected fluid.

A more relevant measure of the stabilizing effect of imbibition in the viscous-fingering regime at high $C_a^*$ is finger width [14,49]. For each displacement experiment, we determine the average finger width $\bar{w}$ at the end of injection as a function of radial distance $r$ [see the inset in Fig. 3(c)]. We report the curves $\bar{w}(r)$ for experimental conditions in the viscous-fingering regime ($C_a^* = 5$), and for all contact angles [Fig. 3(b)]. First, we find a clean trend of $\bar{w}$ as a function of distance: beyond $r = 10$ mm, the average finger width decreases slightly with $r$. We define an effective finger width $\tilde{w}$ for each experiment by further averaging finger width between $r = 10$ and $80$ mm. The effective finger width of the set of fluid-fluid displacements in the viscous-fingering regime exhibits a robust, monotonically increasing trend as a function of contact angle [Fig. 3(c)], illustrating clearly the stabilizing effect of imbibition with respect to drainage.

V. DISCUSSION AND CONCLUSIONS

In summary, we report experiments that elucidate the impact of wetting properties on the morphology of fluid-fluid displacement in porous media, in the regime of highly unfavorable viscosity contrast—which when the injected fluid is much less viscous than the initial defending fluid. Our work therefore extends the classical Lenormand diagram [2] to account for the dependence of fluid invasion on wetting properties.

Our experimental investigation focuses on the dependence of the viscous-fingering length scale on wettability—which is made possible by achieving detailed control of the wetting properties of the system (see Appendix A). As such, it complements earlier investigations focused on the dependence of the viscous-fingering length scale on capillary number [14,49]. We demonstrate the stabilizing effect of wettability as the system transitions from drainage to imbibition—that is, as the porous medium is more wetting to the invading fluid. At high capillary numbers, this is best evidenced by the broadening of viscous fingers in imbibition versus drainage [Fig. 2, bottom two rows; Fig. 3(c)].

At low capillary numbers, our experiments provide evidence of the stabilization of fluid invasion during imbibition, even for extremely unfavorable viscosity contrast. In general, the instability is delayed by the effect of wetting, and develops at a higher value of the capillary number. This result bears important implications for enhanced oil recovery and, in particular, for the design of water flooding in heavy oil reservoirs [68].

Our experimental investigation and quantitative analysis of invasion morphologies open up the intriguing possibility of a dynamic scaling analysis, that is, a temporal analysis of the morphology of the displacement front in the spirit of Family-Vicsek models of surface growth [63,69], which has recently been applied to circular geometries [70]. Perhaps more importantly, they also point to the need for the development of a mechanistic model at the pore scale, and a macroscopic model at the continuum scale, that capture the nonlocal effects of wettability on the dynamics of multiphase flow in porous media, including viscous-driven and gravity-driven unstable flows [10,14,49], and capillary fracturing of granular media [27,71].
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APPENDIX A: EXPERIMENTAL SETUP AND WETTABILITY ALTERATION

The experimental apparatus consists of a radial Hele-Shaw cell packed with glass beads. The radial cell consists of a base, a frame, and a lid (Fig. 1). The base is made of a square piece of soda-lime glass. The frame is made of a square piece of 1-cm-thick acrylic with a circular hole of radius $R = 10.65$ cm cut out. The frame is epoxied on top of the base and provides lateral confinement for the glass bead pack that occupies the hole. The circular lid is made of 2-cm-thick soda-lime glass and fits into the hole, providing vertical confinement for the bead pack. The radius of the lid is approximately 10.30 cm, which makes the gap between the lid and the frame large enough to allow fluid to escape freely, but small enough to prevent the outflow of glass beads. The lid has a 1.5-mm hole drilled in the center through which fluids are injected into the cell.

The bead pack is made of nonsintered, soda-lime glass beads. The beads have a mean diameter of $d \approx 490 \mu m$; their size distribution is shown in Fig. 4(a). To compose the pack, we first place a 2-mm-thick, coarse mesh into the cell to provide a reference height for packing. The mesh is a regular square lattice, except at the center where there is a small circular hole [Fig. 4(b)]. We distribute 60 ml of beads uniformly into the mesh, except in the center hole, which we fill with larger beads of diameter $d_c = 1$ mm. When the beads evenly fill all the mesh compartments, we carefully remove the mesh to minimally disturb the pack, and then weakly vibrate the cell laterally by tapping on it. This homogenizes the pack. We then place the glass lid on top of the pack and tap the cell a few more times to ensure the lid fits tightly on top of the beads. The final height of the pack is slightly smaller than the thickness of the mesh since the vibrations slightly reduce the overall pack volume. This packing procedure creates a homogeneous permeability and porosity throughout the bead pack.

The bead matrix is initially fully saturated with a viscous mixture of water and glycerol, placed by slow injection through the injection port. We always confirm uniformity of the packing by observing a circular invasion of this viscous liquid. To displace the initial fluid, we inject air at rate $Q$, which is held constant throughout each individual experiment. The viscosity contrast between these two fluids is $M = \eta_{\text{air}}/\eta_{\text{liq}} = 320$. To allow a clear view on the transparent porous matrix, pictures are taken from the bottom of the Hele-Shaw cell with a digital single-lens reflex (SLR) camera (Canon EOS 1D) as well as with a Complementary Metal Oxide Silicon (CMOS) monochrome Universal Serial Bus (USB) camera (maximum frame rate of 30 fps). We use the high-resolution pictures obtained with the SLR camera for image processing of the final pattern before breakthrough of the invading fluid through the edges of the cell. Light-emitting-diode light panels illuminate the setup from all sides to ensure picture quality.

As our interest focuses specifically on the impact of wetting properties on the invasion morphology, the Hele-Shaw cell and the glass beads are chosen to be made out of the exact same material: soda-lime glass. The wetting properties of soda-lime glass are modified to either become almost perfectly hydrophilic (contact angle of the water-glycerol mixture in the presence of air $\theta$ is approximately $5^\circ$) or hydrophobic ($\theta \approx 120^\circ$). To ensure cleanliness of the substrate before altering wettability, we use a liquid-chemical acid mixture to attack and remove any impurities on the glass surfaces. Rinsing with highly purified water, the substrate is

\[ \begin{align*}
\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 & : 75 \% : 25 \% \quad \text{Vacuum oven} \\
& \quad 100 \ ^\circ\!\!\circ \text{C} \\
\text{Highly purified H}_2\text{O} & \quad \text{Flow} \\
150 \ ^\circ\!\!\circ \text{C} & \\
\end{align*} \]

FIG. 5. Wettability alteration on soda-lime glass using chemical vapor deposition (CVD). The silanization procedure is tuned to achieve the desired wetting properties for five different contact angles with respect to the viscous water-glycerol mixture and air: (1) $\theta = 5^\circ \pm 1.2^\circ$, O$_2$ plasma ash; (2) $\theta = 20^\circ \pm 0.8^\circ$, no CVD treatment; (3) $\theta = 62^\circ \pm 1.8^\circ$, dichlorodimethylsilan, 5% in a vacuum oven at 150$^\circ$C; (4) $\theta = 89 \pm 0.8^\circ$, dichlorodimethylsilan, 5%; (5) $\theta = 121 \pm 2.3^\circ$, (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane.
let dry in an vacuum oven at 60°C by flushing the vacuum chamber with gaseous N₂. An O₂ plasma ash is applied on the dry substrate (glass beads) as well as on the Hele-Shaw cell to obtain hydrophilic conditions where in case of an hydrophobic surface treatment, silane-based substances are applied using CVD to homogeneously modify wettabillity of the experimental solid framework (Fig. 5).

APPENDIX B: INVASION DYNAMICS

The dynamics of the fluid-fluid displacement in the different invasion regimes are demonstrated by videos from sequences of images taken during air injection. Each image is obtained by subtracting the initial image prior to air invasion. Air shows as white, and water and beads show as black (see Supplemental Material [62]).

Video 1: Viscous fingering in drainage.—Experimental conditions: \( Q = 170 \text{ ml/min}, \theta = 5° \). The length scale of the instability is the pore scale. The video is in real time.

Video 2: Viscous fingering in imbibition.—Experimental conditions: \( Q = 170 \text{ ml/min}, \theta = 120° \). The change in wetting properties leads to thicker fingers compared to those of Video 1. The video is in real time.

Video 3: Capillary fingering in drainage.—Experimental conditions: \( Q = 0.170 \text{ ml/min}, \theta = 5° \). Intermittent propagation of the air-liquid interface, advancing at alternating locations. The final pattern is asymmetric, with thick, dense fingers. Video speedup of 60.

Video 4: Stable displacement in imbibition.—Experimental conditions: \( Q = 0.170 \text{ ml/min}, \theta = 120° \). Smooth, uniform, simultaneous advancement of the displacement front, as a macroscopic consequence of the strong cooperative nature of fluid invasion at the pore scale. Video speedup of 230.


