Scaling theory for spontaneous imbibition in random networks of elongated pores

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We present a scaling theory for the long time behavior of spontaneous imbibition in porous media consisting of interconnected pores with a large length-to-width ratio. At pore junctions the meniscus propagation in one or more branches can come to a halt when the Laplace pressure of the meniscus exceeds the hydrostatic pressure within the junction. We derive the scaling relations for the emerging arrest time distribution and show that the average front width is proportional to the height, yielding a roughness exponent of exactly $\beta = 1/2$ and explaining recent experimental results for nano-porous Vycor glass (NVG). Extensive simulations of a pore network model confirm these predictions.

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The dynamics of imbibition front of an invading fluid in disordered media has attracted substantial scientific attention, from statistical physics [1–3] to material science [4]. Besides its scientific interest, understanding the mechanisms of imbibition in a porous matrix is of importance in industrial processes such as oil recovery, food processing, impregnation, chromatography, and agriculture [5–7].

During imbibition the liquid-gas interface advances and broadens. The time evolution of the invading front follows simple scaling laws, which are independent of the micro-structure and the details of the fluid [3–5], reminiscent of the universality of critical phenomena. Various physical aspects are involved in the imbibition of a liquid inside a porous matrix, such as viscous drag, capillarity, gravity and volume conservation. The often complex topology of the porous matrix induces local fluctuations in capillary pressures at the interface as well as hydraulic permeabilities in the bulk. Despite these complexities, the average position of the front $\langle h(t) \rangle$ during a purely spontaneous imbibition evolves as $\langle h(t) \rangle \sim t^{1/2}$, known as Lucas-Washburn law [3, 14, 15]. This scaling behavior is valid down to nanoscopic pore scales [16–18].

While the invading front exhibits a common slow-broadening dynamics for a wide range of materials [8–11], the results of recent experiments on nano-porous Vycor glass (NVG) reveal that the roughening dynamics might depend on the micro-structure [19]. The elongation of pores, quantitatively described by their length-to-width radius, appears to play an important role and two extreme limits can be distinguished: (i) short pores with comparable length and diameter. In materials like paper, sand, randomly packed glass beads, etc., where the pore space is highly interconnected [8–11], neighboring menisci coalesce, a continuous imbibition front forms and an effective surface tension emerges. Due to the latter menisci advancement is spatially highly correlated [20], which reduces the height fluctuations of the front by limiting menisci advancement beyond the average front position and drawing forward the menisci lagging behind. This forms a continuous liquid-gas interface and smoothens the front. (ii) elongated pores. Other porous materials like rock, soil, and porous glasses consist of sponge-like topologies with reduced connectivity and elongated pores [5, 21, 22]. For example, NVG is a silica substrate with an interconnected network of long cylindrical pores with characteristic radii of $3–5$ nm. In Ref. [19], an anomalously fast interface roughening has been observed, representing a new universality class for spontaneous imbibition, emerging for large pore aspect ratio. Here, the interface is not able to establish an effective surface tension, leading to strong height fluctuations of the menisci.

In this letter we present a scaling theory for spontaneous imbibition in porous media consisting of a network of interconnected elongated pores (Fig 1). It is based on the observation that at pore junctions the meniscus propagation in the branch with the larger radius can come to a halt when the Laplace pressure of the meniscus exceeds the hydrostatic pressure within the junction. This leads to the emergence of voids behind the invasion front and concomitantly to anomalously fast front broadening as observed experimentally in NVG [19]. It is predicted that the distribution of the meniscus arrest times scales with the square of the height of the meniscus, which implies that the ratio of the average invasion front width and smoothness.

![FIG. 1: Sketch of a junction (a) in a pore network with elongated pores (b). $r_i$ and $P_{L,i}$ denote the radius and Laplace pressure, respectively, in pore $i$, and $p_0$ denotes the hydrostatic pressure in the junction. In (b) $\langle h(t) \rangle$ and $\langle P_L \rangle$ denote the average height at time $t$ and the average Laplace pressure.](image-url)
the average front height is independent of time. This implies that roughening is maximal with an exponent \( \beta = 1/2 \), establishing a universality class different from those known before for spontaneous imbibition \( ^2 \). We then test these predictions in extensive simulations of a pore network model.

We analyze spontaneous imbibition of a wetting liquid in a porous medium similar to porous glasses, which consists of a network of elongated pores with a length-to-width ratio of the order of 10, i.e. elongated, cylinder-like pores with random radii interconnected at pore junctions as sketched in Fig. 1. The bottom pores are connected to a liquid reservoir with pressure \( p = 0 \). We assume that in each pore a liquid-gas interface forms, denoted as meniscus, that gives rise to a Laplace-pressure \( p_L = -2\sigma/r \), where \( \sigma \) is the surface tension of the liquid and \( r \) the pore radius. If the pore radii vary between \( r_{\text{min}} \) and \( r_{\text{max}} \), the average radius is denoted by \( \langle r \rangle \). Then, on large scales, the average height is expected to vary as \( \langle h(t) \rangle = -(P_L)/\langle h(t) \rangle \), which implies the Lucas-Washburn law \( \langle h(t) \rangle \propto t^{1/2} \).

Consider now a junction at height \( h_0 \), where a pore branches into two (see Fig. 1a). One branch has radius \( r_1 \), the other \( r_2 > r_1 \), yielding the Laplace pressures \( P_{L,1} = -2\sigma/r_1 \). Let \( P_0 \) be the hydrostatic pressure within the junction. As long as \( P_{L,2} > P_0 \) the meniscus in branch 2 is arrested. In the following we will answer the question how long the meniscus in branch 2 will be arrested and we will implicitly assume that it does not get annihilated by the filling of the pore from its other end. This means that we assume the radius \( r_2 \) also to be larger than the radius of the other branch of the junction of the other end. This reduces only the probability of this event by a \( r_2 \)-dependent factor.

\( P_0 = P_0(t) \) is a function of time and depends on how far the front has propagated and can be estimated as follows: Let the average front height be \( \langle h(t) \rangle \). On average one expects the bulk pressure to decrease linearly from bottom to top:

\[
P(\langle h(t) \rangle)/P_0 = \langle h(t) \rangle/h_0
\]

Therefore, with \( P(\langle h(t) \rangle) = (P_L) = -2\sigma\langle 1/r \rangle \) the average Laplace pressure, one obtains \( P_0 = -2\sigma\langle 1/r \rangle \cdot h_0/\langle h(t) \rangle \) and the condition \( P_0 = P_{L,2} \) for the arrested meniscus to resume propagation (at time \( t_{\text{resume}} \)) reads

\[
\langle h(t_{\text{resume}}) \rangle = h_0 r_2/\langle 1/r \rangle.
\]

This equation has far reaching consequences:

1) The larger \( r_2 \) the longer the meniscus is arrested, and the average height that the front has to reach before the meniscus resumes propagation is proportional to the height where it stopped with a proportionality constant larger than one. 2) The time \( \tau \) for which the meniscus is arrested is proportional to the time \( t_{\text{stop}} \), when it stopped

\[
\tau \propto t_{\text{stop}}.
\]

To see this we note that with \( ^2 \) one has \( \langle h(t_{\text{stop}} + \tau) \rangle = h(t_{\text{stop}}) r_2/(1/r) \). With Lucas-Washburn \( \langle h(t_{\text{stop}} + \tau) \rangle \propto (t_{\text{stop}} + \tau)^{1/2} \) and assuming that \( h(t_{\text{stop}}) \propto t_{\text{stop}}^{1/2} \), too, for the relation between the height and the time when the considered meniscus stopped, one obtains \( ^3 \). Consequently from \( ^4 \)

\[
\tau \propto h^2(t_{\text{stop}}) = h_0^2,
\]

which implies that the probability distribution of arrest times for menisci arrested at height \( h \) will scale as

\[
p_h(\tau) = \frac{\tau}{h^2 \langle h(t) \rangle}.
\]

4) The height difference \( w_0(t_{\text{resume}}) = \langle h(t_{\text{resume}}) \rangle - h_0 \) is a measure for the local width of the propagation front (at the lateral coordinates of the position of the arrested meniscus) at time \( t_{\text{resume}} \). The ratio of this local width and the average height is \( w_0(t_{\text{resume}})/\langle h(t_{\text{resume}}) \rangle = 1 - (r_2/\langle r \rangle)^{-1} \), which is independent of the time \( t_{\text{resume}} \). Thus all arrested menisci will contribute a time independent amount to the ratio of the average width \( w(t) \) and average height.

Since the width cannot grow faster than \( h(t) \) this implies

\[
w(t)/\langle h(t) \rangle = \text{const.},
\]

implying \( w(t) \propto t^{1/2} \), i.e. a roughening exponent \( \beta = 1/2 \).

The constant in \( ^6 \) depends on the pore radius distribution via the ratio of the minimal and maximal pore radius and approaches one for an unbounded radius distribution (i.e. the front extends over the whole occupied volume).

Note that the invasion front dynamics is now expected to be completely determined by the meniscus arrests, which in turn depend exclusively on the pore radii distribution and the height dependent hydrostatic pressure. Consequently one expects no lateral correlations in the meniscus heights to emerge, as observed in \( ^{10} \).

The scaling theory presented here neglects all geometric and topological details of a pore network. To test its predictions, in particular the strongest \( ^{11} \) and \( ^{12} \), we analyzed the following microscopic model for spontaneous imbibition in a pore network with elongated pores \( ^{19, 23, 24} \): A two-dimensional square lattice of cylindrical capillaries inclined at 45° is considered, which consists of \( N_x \) and \( N_y \) nodes in horizontal and vertical directions, respectively. Capillaries, interconnected at nodes, have the same length \( L \) and random radii uniformly distributed over \( [r_{av} - \delta, r_{av} + \delta] \). The average aspect ratio \( 2r_{av}/L \) is set to 5. The pressure at the bottom nodes attached to the liquid reservoir is set to zero, the pressure at a moving meniscus is the Laplace pressure. Here we neglect gravity, which is justified as long as capillary forces are much larger than gravitational forces \( 2\sigma/r \gg \rho N_g L \), where \( \rho \) the specific weight of the liquid. This is the case for instance in experiments with NVG \( ^{23} \).

The hydrostatic pressures at the nodes of the network drives the dynamical evolution of the menisci configurations. To calculate the temporal change of the filling heights in the partially filled capillaries, one needs to
know the node pressures which themselves depend on the menisci configuration. The node pressures \( P_i \) are determined by the boundary conditions plus the conservation of volume flux at each node: \( \sum_j Q_{i,j} = 0 \), which is equivalent to Kirchhoff’s law. Here, \( Q_{i,j} \) is the volume flux flowing from node \( i \) into the capillary \( j \) attached to it. The sum runs over all of the four capillaries of node \( i \) and is valid for all wet nodes in the system. According to Hagen-Poiseuille’s Law [26], \( Q_{i}^L = -c_i^L \Delta P_i^L / h_i \), with \( c_i^L = \pi (r_i^L)^4 / 8 \eta \) and \( \Delta P_i^L = P_i - P_{L,i}^j \). Here, \( r_i^L \), \( h_i \) and \( P_{L,i}^j \) are the radius, the length and the Laplace pressure of the meniscus in capillary \( j \) of node \( i \), respectively, and \( \eta \) is the viscosity of the liquid. By numerically solving the resulting set of linear equations we compute \( P_i \) and thus \( Q_{i,j} \). These are then inserted into the equation of motion for the heights given by \( Q_{i} = \pi (r_i^L)^2 dh_i / dt \). To integrate these differential equations an implicit Euler scheme with variable time step \( \Delta t \) is employed giving the new positions \( h_i \). When a meniscus reaches the end of a capillary it immediately moves an infinitesimal distance \( \delta \) towards the back node \( i \), and leads asymptotically to correct results.

When it reaches \( \delta \), the meniscus is stuck there until the driving pressure difference is again positive. During this arrest time, the pressure calculation is modified with the corresponding capillary being blocked. We made sure that the simulation results we present in the following are independent of the choice of \( \delta \).

Figure 2 shows three snapshots of the propagating and arrested menisci in the invasion front at three different times. The fraction of arrested menisci grows fast with increasing height and approaches one around \( \langle h \rangle \approx 500 \).

First we checked the essential assumptions underlying our mean field description of the imbibition process, namely that the pressure in a junction can be approximated by the average of the pressure field \( \langle P \rangle = \langle P_L \rangle + \langle h(t) \rangle \). Figure 3(a) shows the probability distribution \( p_n(h,t) \) of the pressure in the junctions at height \( h \) and time \( t \). For a fixed time we have chosen the height such that the ratio \( \langle h(t) \rangle / \langle h \rangle = C \) is constant (\( C=1/4, 1/2, 3/4 \) corresponding to the bottom, middle and upper third of the system). One sees that the distribution of \( P / \langle P_L \rangle \) is centered around \( C \), reflecting that the average pressure indeed is given by \( \langle P \rangle = C \langle P_L \rangle \) (see inset), and that the width systematically shrinks with \( t \). The width, given by the variance of the pressure distribution, \( \sigma_h(t) = (\langle P^2 \rangle - \langle P \rangle^2) / \langle P \rangle \), is analyzed in Fig. 3(b). The inset shows that it scales as

\[
\sigma_h(t) = \delta / \langle h(t) \rangle \rightarrow 0.
\]  

Consequently the pressure distribution becomes increasingly sharp with increasing time, which implies that neglecting pressure fluctuations is a good approximation and leads asymptotically to correct results.

By counting the number of menisci arrested at height \( h \) for a time \( \tau \) we obtained the arrest time distribution

FIG. 2: (a,b) The mechanisms of menisci advancement in the pore-network model (a) after reaching a node, and (b) during backward motion and arrest of a meniscus due to negative pressure difference. (c) Snapshots of the arrested (blue circles) and advancing (red circles) menisci in the invasion front at three different times. Broken (full) lines represent empty (full) pores, \( H \) is the average height at the corresponding time.

FIG. 3: (a) Probability distribution \( p(P) = p_n(h,t) \) of the pressure at junctions at height \( h \) and time \( t \). Heights are chosen such that for a given time \( C := h / \langle h(t) \rangle \) is constant, data are shown for \( C = 1/4, 1/2, \) and \( 3/4 \) and different times. Inset: Average pressure in junctions at height \( h \) at different times. (b) Variance of the pressure distribution for different times as a function of \( h \). Inset: Scaling plot, \( \sigma_h = \sigma_h(t) / \langle h(t) \rangle \) vs. \( h \). For all data \( N_x = 16 \).
The invasion front thus involves a finite fraction of the occupied volume and comprises connected clusters of empty pores whose size distribution gets broader with increasing time. Based on the conditions for meniscus arrests presented above one can derive a scaling form for the distribution of cluster sizes as follows. Consider an empty cluster that contains $S$ pores at time $t$ (i.e. with width $w(t)$). Its lateral size scales as $L \sim S^{1/d_f}$ and its surface area as $F \sim S^{d_s/d_f}$, where $d_f$ and $d_s$ are the bulk and surface fractal dimension of the empty clusters ($d_f = d$ and $d_s = d - 1$ in the case of compact clusters). Almost all pores in the boundary $F$ of the cluster have arrested menisci, and for a meniscus to be arrested the radius of its pore has to be larger than the radius of an adjacent pore, which is an event that occurs with some probability $q < 1$. Assuming that the conditions for meniscus arrest in all boundary pores are independent from one another and the boundary consists of the order of $S^{d_s/d_f}$ pores, the probability for collective meniscus arrests in boundary pores is proportional to $\exp(-\alpha \cdot S^{d_s/d_f})$, where the constant $\alpha$ involves $\ln q$ and a geometric factor. Since the lateral dimension $S^{1/d_f}$ of the cluster must not exceed the width $w(t)$, one obtains for the probability of an arbitrary empty pore in the front region to belong to a connected cluster with $S$ empty pores:

$$q_S = \mathcal{N}^{-1} S \exp(-\alpha \cdot S^{d_s/d_f}) \cdot \tilde{g}(S^{1/d_f}/w(t)),$$

where $\mathcal{N}$ is a normalization factor and $\tilde{g}(x)$ is a scaling function that is 1 for $x \ll 1$ and 0 for $x \rightarrow 1$. A cluster analysis of our simulation of the 2$d$ pore network model confirms the stretched exponential behavior of $q_S$ at large times $(w(t) \gg S^{1/d_f})$ with $d_s/d_f$ close to $0.5 = (d-1)/d$.

In conclusion we have presented a scaling theory for the inhibition of an arbitrary wetting liquid through any porous medium consisting of random networks of elongated pores. We tested the predictions in extensive simulations of a pore network model. Meniscus arrest times at pore junctions are shown to scale with the age of the invasion front whose width is therefore proportional to its average height. This establishes a universality class for invasion front broadening that is realized in nano-porous Vycor glass [19] and is expected to determine roughening dynamics in similar porous media. Since meniscus arrest is solely determined by the relation of radii of the pores emanating from one junction, it should be possible to relate dynamical quantities accessible via light or neutron scattering to characteristics of the pore radius distribution of the porous medium.

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