Scaling Theory for Spontaneous Imbibition in Random Networks of Elongated Pores

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(Received 25 July 2012; published 2 April 2013)

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 nanoporous Vycor glass. Extensive simulations of a pore network model confirm these predictions.

DOI: 10.1103/PhysRevLett.110.144502 PACS numbers: 47.56.+r, 05.40.−a, 68.35.Ct, 68.35.Fx

The dynamics of the imbibition front of an invading fluid in disordered media has attracted substantial scientific attention, from statistical physics [1–3] to material science [4]. Besides the 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 [3,5–7].

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 microstructure and the details of the fluid [8–13], 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].

Whereas the invading front exhibits a common slow-broadening dynamics for a wide range of materials [8–11], the results of recent experiments on nanoporous Vycor glass (NVG) reveal that the roughening dynamics might depend on the microstructure [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 such as 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. Because of 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 smoothes the front. (ii) Elongated pores. Other porous materials such as rock, soil, and porous glasses consist of spongelike 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 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 [3]. 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 on 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 $P_L = -2\sigma/r$,

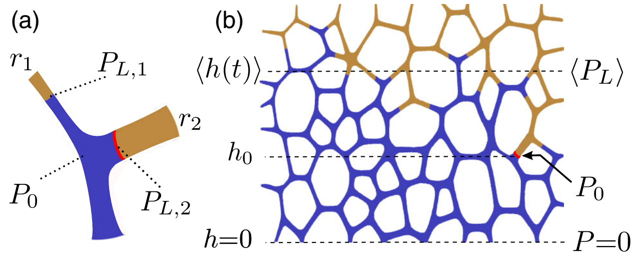

FIG. 1 (color online). Sketch of a junction (a) in a pore network with elongated pores (b). r_i and $P_{L,i}$ denote the radius and Laplace pressure, respectively, in pore i, and P_0 denotes the hydrostatic pressure in the junction. In (b), $\langle h(t)\rangle$ and $\langle P_L\rangle$ denote the average height at time t and the average Laplace pressure.

where σ is the surface tension of the liquid and r is the pore radius. If the pore radii vary between $r_{\rm min}$ and $r_{\rm max}$, the average radius is denoted by $\langle r\rangle$. Then, on large scales, the average height is expected to vary as $d/dt\langle h(t)\rangle = -\langle P_L\rangle/\langle h(t)\rangle$, 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. 1(a)]. One branch has radius r_1, the other $r_2 > r_1$, yielding the Laplace pressures $P_{L,i} = -2\sigma/r_i$. 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 of 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 by

$$P(\langle h(t)\rangle)/P_0 = \langle h(t)\rangle/h_0. \tag{1}$$

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

$$\langle h(t_{\rm resume})\rangle = h_0 r_2\langle 1/r\rangle. \tag{2}$$

This equation has far reaching consequences as follows: (1) The greater the r_2 value, 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 τ for which the meniscus is arrested is proportional to the time $t_{\rm stop}$, when it stopped,

$$\tau \propto t_{\rm stop}. \tag{3}$$

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

$$\tau \propto h^2(t_{\rm stop}) = h_0^2, \tag{4}$$

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

$$p_h(\tau) = h^{-2}\tilde{p}(\tau/h^2). \tag{5}$$

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

$$w(t)/\langle h(t)\rangle = \text{const}, \tag{6}$$

implying $w(t) \propto t^{1/2}$, i.e., a roughening exponent $\beta = 1/2$. The constant in Eq. (6) depends on the pore radius distribution via the ratio of the minimal and maximal pore radius and approaches 1 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 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 Ref. [19].

The scaling theory presented here neglects all geometric and topological details of a pore network. To test its predictions, in particular the strongest in Eqs. (5) and (6), 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 $[r_{\rm av} - \delta, r_{\rm av} + \delta]$. The average aspect ratio $2r_{\rm av}/L$ is set to 5. The pressure at the bottom nodes attached to the liquid reservoir is set to zero, and the pressure at a moving meniscus is the Laplace pressure. Here, we neglect gravity, which is justified as long as capillary forces are much greater than gravitational forces $2\sigma/r \gg \rho N_y L$, where ρ

is the specific weight of the liquid. This is the case, for instance, in experiments with NVG [25].

The hydrostatic pressures at the nodes of the network drive 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 and 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 the Hagen-Poiseuille law [26], $Q_i^j = -c_i^j \Delta P_i^j / h_i^j$, with $c_i^j = \pi (r_i^j)^4 / 8\eta$ and $\Delta P_i^j = P_i - P_{L,i}^j$. Here, r_i^j, h_i^j, 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 η 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 $Q_i^j = \pi (r_i^j)^2 dh_i^j / dt$. To integrate these differential equations, an implicit Euler scheme with variable time step Δt is employed giving the new positions h_i^j. When a meniscus reaches the end of a capillary, it immediately moves an infinitesimal distance $\delta \simeq 0.01L$ into the adjacent capillaries, creating new menisci, as shown in Fig. 2(a). This avoids the microscopic treatment of the filling of the junction [27] and is valid as long as the filling time of the node is negligible. The filling time was estimated in Ref. [27] and is indeed orders of magnitude smaller than the meniscus arrest times as long as capillary forces are much greater than gravitational forces. When two menisci meet, they vanish; thus, the capillary is entirely filled. If, because of a negative pressure difference, a meniscus retracts, it proceeds backward as long as its distance from the back node is larger than δ [see Fig. 2(b)]. When it reaches δ, 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 δ.

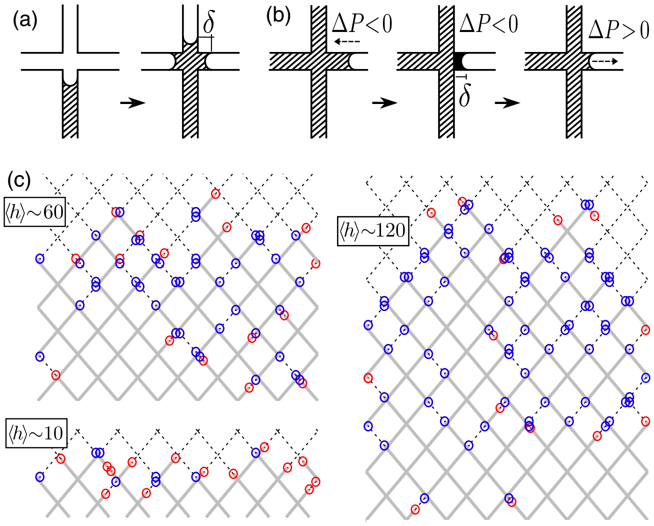

FIG. 2 (color online). [(a) and (b)] The mechanisms of menisci advancement in the pore-network model (a) after reaching a node and (b) during backward motion and arrest of a meniscus due to negative pressure difference. (c) Snapshots of the arrested (blue circles; dark circles) and advancing (red circles;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

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 $P \approx \langle P_L \rangle h / \langle h(t) \rangle$. Figure 3(a) shows the probability distribution $p_{h,t}(\langle P \rangle / \langle P_L \rangle)$ 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 $h/\langle h(t) \rangle =: C$ 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 $\sigma_h(t) = (\langle P^2 \rangle_{h,t} - \langle P \rangle_{h,t}^2)$, is analyzed in Fig. 3(b). The inset shows that it scales as

$$\sigma_h(t) = \tilde{\sigma}_h / \langle h(t) \rangle \xrightarrow{t\to\infty} 0. \tag{7}$$

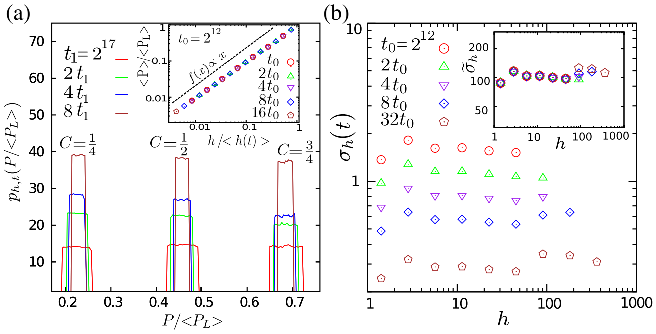

FIG. 3 (color online). (a) Probability distribution $p(P) = p_{h,t}(P)$ of the pressure at junctions at height h and time t. Heights are chosen such that for a given time $C := h/\langle h(t) \rangle$ is constant; data are shown for $C = 1/4$, $1/2$, and $3/4$ and different times. Inset: Average pressure 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, $\tilde{\sigma}_h = \sigma_h(t)/\langle h(t) \rangle$ vs h. For all data, $N_x = 16$.

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 τ, we obtained the arrest time distribution $p_h(\tau)$, which is shown in Fig. 4(a). Three regimes can be identified: A short time regime, where $p_h(\tau)$ is nearly constant, an intermediate time regime extending over ~ 1.5 decades for all heights h with a slope close to -1 in the log-log plot, and a large time regime, extending over ~ 1 decade in τ with a slope close to $-1/2$. Finally, the distribution is cut off at a time proportional to h^2. A closer look at the arrest events shows that the main contribution for the intermediate regime comes from pores with a *single* (arrested) meniscus in a pore [see inset of Fig. 4(a)]. Pores that have (arrested) menisci at both ends cause the large time regime of $p_h(\tau)$, which decays much slower but has a smaller amplitude. These pores have statistically a larger radius than pores with only one arrested meniscus; consequently, their probability is lower but arrest times are longer.

The intermediate and large time regime of the distribution, including the cut off, scale nicely with h^2 as predicted by Eq. (5), as shown in Fig. 4(b). The intermediate and large arrest times dominate the mean, which is therefore proportional to h^2, as expected from Eq. (4); see inset of Fig. 4(b). Events with a brief arrest time, which make for the short time regime that does not scale with h^2 [see Fig. 4(b)], are caused by secondary arrests of menisci and by small radii differences in adjacent pores and dynamic fluctuations in the node pressures due to the propagation and release of nearby menisci.

We also computed the average height $\langle h(t)\rangle$ and width $w(t) = (\langle h^2(t)\rangle - \langle h(t)\rangle^2)^{1/2}$ of the imbibition front and found that the ratio $w(t)/\langle h(t)\rangle$ approaches a constant value for large times, which confirms the prediction (6). Since $\langle h(t)\rangle \propto t^{1/2}$, the width also increases as $w(t) \propto t^{1/2}$, implying a roughness exponent of $\beta = 1/2$. The initial decrease of $w(t)/\langle h(t)\rangle$ indicates a preasymptotic increase of $w(t)$ with an exponent slightly smaller than $1/2$, as reported in Ref. [19].

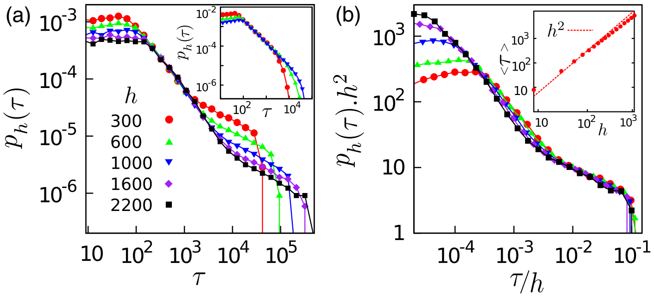

FIG. 4 (color online). (a) The probability distribution $p_h(\tau)$ of the arrest times τ of menisci arrested at fixed height h in log-log scale. Inset: arrest time distribution of single meniscus in a pore. (b) Scaling plot according to Eq. (5). Inset: Average arrest time $\langle\tau\rangle$ at a given height h, with the dashed line proportional to h^2; see Eq. (4). Parameter for all data are $\delta_r/r = 0.1$, $N_x = 8$, 100 disorder realization.

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. On the basis of 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 $\mathcal{L} \sim S^{1/d_f}$, and its surface area scales as $\mathcal{F} \sim S^{d_s/d_f}$, 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 $\mathcal{F}$ of the cluster have arrested menisci, and for a meniscus to be arrested the radius of its pore has to be greater 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 $\exp(-\alpha S^{d_s/d_f})$, where the constant α 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 the probability of an arbitrary empty pore in the front region to belong to a connected cluster with S empty pores

$$q_S = \mathcal{N}^{-1} S \exp(-\alpha S^{d_s/d_f})\, \tilde{g}(S^{1/d_f}/w(t)), \tag{8}$$

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 $x \to 1$. A cluster analysis of our simulation of the $2d$ 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 imbibition 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 nanoporous 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.

We thank P. Huber and D.-S. Lee for stimulating discussions.

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