Capillarity-driven flows at the continuum limit†

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We experimentally investigate the dynamics of capillary-driven flows at the nanoscale, using an original platform that combines nanoscale pores (<3 nm in diameter) and microfluidic features. In particular, we show that drying involves a fine coupling between thermodynamics and fluid mechanics that can be used to generate precisely controlled nanoflows driven by extreme stresses – up to 100 MPa of tension. We exploit these tunable flows to provide quantitative tests of continuum theories (e.g. Kelvin–Laplace equation and Poiseuille flow) across an unprecedented range and we isolate the breakdown of continuum as a negative slip length of molecular dimension. Our results show a coherent picture across multiple experiments including drying-induced permeation flows, imbibition and poroelastic transients.

1 Introduction

Fluids confined at the nanoscale play central roles in many areas of science and technology, from geophysics,1,2 plant hydraulics and biomaterials,3,4 to catalysis and filtration.5,6 These contexts have motivated considerable effort to understand both the dynamic7,8 and thermodynamic9,10 behavior of nano-confined liquids, but fundamental points of debate persist. With respect to dynamics, theoretical considerations suggest that continuum fluid mechanics (Navier–Stokes) should govern flows in conduits greater than ~1 nm in lateral dimension8 but significant uncertainty remains with respect to both constitutive properties and boundary conditions. For example: experiments have only constrained the shear viscosity of water to within a factor of three for confinement below 4 nm11 and, while simulations indicate that constrained the shear viscosity of water to within a factor of three and boundary conditions. For example: experiments have only constrained the shear viscosity of water to within a factor of three for confinement below 4 nm11 and, while simulations indicate that constrained the shear viscosity of water to within a factor of three and boundary conditions. For example: experiments have only constrained the shear viscosity of water to within a factor of three for confinement below 4 nm11 and, while simulations indicate that constrained the shear viscosity of water to within a factor of three and boundary conditions. For example: experiments have only constrained the shear viscosity of water to within a factor of three for confinement below 4 nm11 and, while simulations indicate that constrained the shear viscosity of water to within a factor of three and boundary conditions.

† Electronic supplementary information (ESI) available: Details of the platform fabrication, of the experimental procedure, of the analysis methods, and a discussion of alternative hypotheses. Details of the mathematical models presented in the manuscript. See DOI: 10.1039/c6sm00733c

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included to account for molecular adsorption at the pore wall. Our results thus provide an unusually robust experimental test of transport and thermodynamic models at the continuum limit.

2 Methods

Fig. 1a and b presents our sample. Details of the fabrication and of the experimental procedure can be found in the ESI†. Briefly, we used anodization to etch a circular zone in a silicon wafer, leading to a 5.5 μm-thick layer of isotropic, interconnected pores with a distribution of pore sizes in the range, \( r_p = 1.4 \pm 0.4 \) nm and porosity \( \phi = 0.45 \) based on N\(_2\) porosimetry. We used lithography in a glass wafer to form a reservoir accessed by an inlet hole drilled through the glass. The reservoir itself included a serpentine-shaped microchannel connected to a long inlet channel. The latter fed liquid to the porous layer that spanned the distance between the inlet channel and the open edge. Finally, we bonded silicon to glass and opened the pores to the outside at the edge of the sample by dicing (Fig. 1a and b).

We performed drying experiments (Fig. 1c) by filling the pores and reservoir with liquid, and then placing the sample in a vapor of controlled humidity (constant partial vapor pressure \( p_{\text{ext}} \) after sealing the inlet hole. We could evaluate the flow rate through the porous layer due to evaporation from the open edge (right of Fig. 1a and b) by measuring the rate of emptying of the reservoir. To do so, we tracked the position of the air–liquid interface in the serpentine-shaped part of the reservoir (\( X(t) \) in Fig. 1c). The presence of bulk liquid water in the reservoir ensured that the porous area to the left of the inlet channel stayed saturated at all times. As a result, flow in the porous layer occurred only in the zone situated between the inlet channel and the open edge (shaded in orange in Fig. 1c), and the tracking of \( X(t) \) provided an accurate measurement of the flow rate through the nanopores.

We also performed independent imbibition experiments on the same sample, by submersion in liquid after evacuation (Fig. 1d). We monitored the advancing wetting front (\( Y(t) \) in Fig. 1d) by time-lapse photography, taking advantage of the change of color of the porous silicon layer as a function of its filling state (see micrograph in Fig. 1d).

In order to describe the thermodynamic states of liquid and vapor in a unified way, we use liquid potential,

\[
\Psi = \frac{(\mu - \mu_0)/v_m}{C^{\text{liq}}} \quad \text{for the liquid}
\]

\[
\Psi = \frac{RT}{v_m} \ln \left( \frac{p}{p_{\text{sat}}} \right) \quad \text{for the vapor}
\]

where \( P \) and \( p \) represent respectively the liquid and the partial vapor pressures, \( p_{\text{sat}}(T,P_0) \) is the saturated vapor pressure and \( RT \) is the thermal energy.
3 Results and discussion

We first recorded drying dynamics at a variety of imposed relative humidities $p_{\text{ext}}/p_{\text{sat}}$. The measured emptying dynamics of the reservoir is shown as $X(t)$ in Fig. 2a. The results show the establishment of a steady-state after a transient of a few minutes (Fig. 2b). From the speed, we used the geometry of the porous layer to calculate the steady-state volumetric flux in the porous medium (Darcy velocity), $J$ [m s$^{-1}$]. Data as in Fig. 2c revealed two regimes.

We begin by considering the linear regime (1 in Fig. 2c) with the physical picture of the pore-scale depicted in Fig. 2d. Here, we assume that the nano-menisci remained pinned at the open edge of the porous layer and that local equilibrium was established between the pore liquid behind the nano-menisci and the bulk vapor (partial pressure $p_{\text{ext}}$); we expect this equilibrium to hold to good approximation due to the large transport resistance in the porous medium relative to that in the vapor (see ESI†).

To evaluate this equilibrium, we suppose that, despite the strong confinement imposed by the pores, the properties of the liquid are unperturbed relative to that of a bulk phase. In other words, the pore liquid responds to the lowering of the vapor pressure with a reduction of its hydrostatic pressure, as predicted by the well-known Kelvin equation ($\Psi_{\text{liq}} = \Psi_{\text{vap}}$ from eqn (1)).

$$P_{\text{edge}} - P_0 = \Psi_{\text{ext}} = \frac{RT}{v_m} \ln \left( \frac{P_{\text{ext}}}{p_{\text{sat}}} \right).$$

(2)

Eqn (2) provides an expression for the pressure difference that drives flow through the nanoporous layer between the inlet channel ($P = P_0 > 0$) and the open edge ($P = P_{\text{edge}} < 0$). This liquid stress has its dynamic origin in capillarity, due to the curvature $r^{-1}$ of the liquid–air interface; compatibility with the phase equilibrium (eqn (2)) is ensured through the Kelvin–Laplace relation

$$\Psi_{\text{ext}} = -2\sigma r^{-1}.$$  

(3)

Here, we neglect both the pressure drop along the serpentine microchannel and the capillary pressure associated with the macroscopic air–liquid interface in the reservoir, such that the pressure of liquid entering the porous layer is approximately atmospheric (see ESI†). Assuming Darcy flow\textsuperscript{28} through the porous medium, we thus predict linear response of the permeation rate with respect to $\Psi_{\text{ext}}$:

$$J = -\kappa (P_{\text{edge}} - P_0)/L = -\kappa \Psi_{\text{ext}}/L.$$  

(4)

where $\kappa$ is the Darcy permeability of the porous layer and $L$ is the geometrical length of the permeation path (Fig. 1). The blue line and inset in Fig. 2c clearly illustrate the robustness of this linear regime down to $\Psi_{\text{ext}} \approx -50$ MPa. We extract the permeability from the best-fit slope: $\kappa = (1.87 \pm 0.08) \times 10^{-17}$ m$^2$ (Pa s)$^{-1}$, a value that is in the lower range of permeability of rocks considered impervious such as granite.\textsuperscript{28} We compare this result to Carman–Kozeny theory

$$\kappa = \frac{\eta r_{\text{eff}}^2}{8\pi\tau}$$  

(5)

where $\eta$ is the viscosity of the liquid and $r_{\text{eff}}$ is an effective pore size.\textsuperscript{29} The tortuosity $\tau$ is expected to take physically reasonable values close to, $\tau = 3$ which would correspond to an ideal isotropic architecture of cylindrical pores.\textsuperscript{29} Using the value of $\kappa$ experimentally determined above and $\tau = 3$, we find a preliminary estimate of $r_{\text{eff}} = 1.0$ nm, which lies in the lower range of the pore sizes estimated from N$_2$ porosimetry.

Independently of the pore geometry, we also use the transient responses (Fig. 2b) to perform a second check of the value of permeability extracted from the steady-state drying experiments. Poroelastic theory predicts that pressure diffuses through a porous medium with a diffusivity $C = \kappa/(\phi \chi)$ where $\chi$ is the effective compressibility of the fluid-filled solid. To generate the black curve in Fig. 2b, we used $\kappa$ estimated above and took for $\chi$ the bulk compressibility of liquid water (4.5 $\times$ 10$^{-10}$ Pa$^{-1}$) (see ESI†); the agreement with experiments indicates that we have measured a coherent value of the permeability and that confinement has not strongly perturbed the thermodynamic properties of the pore liquid.

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Fig. 2  Drying dynamics with water. (a) Position of the air–water interface in the serpentine-shaped reservoir, $X(t)$, reflecting the loss of water by evaporation at the open edge (Fig. 1c). (b) Early transients: data in (a) normalized by the steady-state speed $v$. The dashed, black curve shows the prediction from the theory of poroelasticity (see ESI†). (c) Volumetric flux as a function of the imposed relative humidity $p_{\text{ext}}/p_{\text{sat}}$ (top axis) calculated with eqn (2) from the imposed relative humidity $p_{\text{ext}}/p_{\text{sat}}$ (top axis). The lines represent the two predicted regimes from eqn (4) and (7). (d and e) Schematic diagrams of our model for these two regimes, with sketches of the spatial profiles of the liquid potential.
We now consider the plateau regime of the flow at larger driving forces (2 in Fig. 2c) with the physical picture depicted in Fig. 2e. Once the pressure difference required for equilibrium (Kelvin equation, eqn (2)) exceeds the capillary pressure that can be maintained by the pores through the variable curvature of the liquid–air nano-menisci at the open edge of the porous layer, we suppose that the nano-menisci recede from the edge and that the flow within the porous medium becomes multiphase – liquid between \( y = 0 \) and \( L - \varepsilon \) [with corresponding linear mass conductance \( g_{\text{liq}} \) and hydraulic resistance \( R_{\text{liq}} = (L - \varepsilon)g_{\text{liq}} \) [m s\(^{-1}\)], see ESI†], and vapor between \( y = L - \varepsilon \) and the open edge at \( y = L \) (linear conductance \( g_{\text{vap}} \) and resistance \( R_{\text{vap}} = \varepsilon g_{\text{vap}} \)). Using the Laplace equation for the capillary pressure (eqn (3)) and considering that the maximum meniscus curvature allowed in a pore of radius \( r_p \) with equilibrium contact angle \( \theta \) is \( r^{-1} = \cos \theta / r_p \), this retreat of the nano-menisci occurs when \( \Psi_{\text{ext}} < \Psi_c \) where

\[
\Psi_c = -2\pi \cos \theta / r_p.
\]

(6)

The receding of the nano-menisci stops at a distance \( \varepsilon \) from the edge at which phase equilibrium can be satisfied again, i.e. at a location where the liquid potential is equal to \( \Psi_c \), given the imposed boundary conditions \( \Psi(0) = 0 \) at the reservoir level and \( \Psi(L) = \Psi_{\text{ext}} \) at the open edge. This new steady-state position \( \varepsilon / (\Psi_{\text{ext}}) \) is thus found by satisfying \( \Psi(L - \varepsilon) = \Psi_c \) given the resistors-in-series configuration of Fig. 2e. Based on Darcy’s law for the liquid phase and Knudsen diffusion for the vapor phase, we estimate \( g_{\text{vap}}/g_{\text{liq}} = 10^{-4} \) which implies \( \varepsilon / L \approx g_{\text{vap}}/g_{\text{liq}} < 1 \) (see ESI††). It follows that the vapor–liquid interface stays close to the edge, resulting in a pressure gradient in the liquid phase equal to \( \Psi_c/(L - \varepsilon) \approx \Psi_c/L \), leading to

\[
J_c = -\kappa \Psi_c / L
\]

(7)
to excellent approximation. The flow predicted by eqn (7) is independent of the imposed external condition (vapor pressure \( p_{\text{ext}} \)); this independence explains the plateauing of the drying flux observed experimentally at low values of relative humidity, \( p_{\text{ext}}/p_{\text{sat}} \) (Fig. 2c). In this regime the driving force for the flow is set by the intrinsic capillary pressure of the pores \( \Psi_c \) instead of Kelvin pressure \( \Psi_{\text{ext}} \).

Comparing eqn (4) and (7), we remark that \( \Psi_c \) corresponds to the intersection point between the two regimes 1 and 2 and thus provides an independent measure of the intrinsic pore capillary pressure \( \Psi_c = -76 \pm 5 \) MPa. Using Laplace law (eqn (6)) with \( \theta = 25 \pm 5^\circ \) (see ESI††) then yields a new pore size estimate \( r_{p,\text{c}} = 1.7 \pm 0.2 \) nm. This value agrees well with the range estimated from \( N_2 \) porosimetry, but there is an apparent inconsistency with the pore radius \( r_{\text{eff}} = 1.0 \) nm deduced from Carman–Kozeny eqn (5).

In order to resolve this conflict and check the validity of our interpretation of the drying regimes, we measured imbibition dynamics in the same sample (Fig. 1d). During imbibition of a dry sample, the liquid front position is expected to follow

\[
y(t) = \sqrt{4w t}
\]

(8)

known as the Lucas–Washburn (LW) law.30 Interestingly, the two important parameters governing imbibition dynamics are precisely the permeability \( \kappa \) and the intrinsic capillary pressure \( \Psi_c \) estimated from the drying analysis above. Fig. 3a shows that imbibition in our system followed the LW \( \sqrt{t} \) scaling and quantitatively agreed with eqn (8), using the values of \( \kappa \) and \( \Psi_c \) estimated from drying (Fig. 3b). This result confirms the appropriateness of our interpretation and analysis of the drying regimes. This analysis allows the independent extraction of both viscous (\( \kappa \)) and capillary (\( \Psi_c \)) contributions, a feature not accessible with imbibition experiments that only access the product \( \kappa \times \Psi_c \) (see eqn (8)).

To resolve the apparent contradiction in the pore size estimates, we could adjust the tortuosity to a larger value (\( \tau \approx 10 \)) to reconcile eqn (5) with \( r_{\text{eff}} = 1.7 \) nm, but such a value of \( \tau \) seems unphysically high29 (see ESI†). Alternatively, we note that eqn (5) is based on the assumption of a developed Poiseuille flow in the pores with a zero-velocity (no-slip) condition at the pore wall. However, large deviations to the no-slip boundary conditions have been reported at the nanoscale27,28 and described with the concept of slip length \( \delta \) which accounts for slippage (\( \delta > 0 \)) or sticking (\( \delta < 0 \)) of the fluid at the wall. The hydrodynamic radius across which the Poiseuille flow profile is established is then

\[
r_{\text{h}} = r_p + \delta \quad \text{and the effective radius in Carman–Kozeny eqn (5) becomes}\n\]

\[
r_{\text{eff}} = r_p + \delta = \left( 1 + \frac{\delta}{r_p} \right)^2.
\]

(9)

The value \( r_{\text{eff}} = 1.0 \) nm estimated previously is compatible with a pore size of \( r_p = 1.7 \) nm if a negative slip length of \( \delta = r_p - r_h = -0.4 \) nm is used. Interestingly, this value is close to the typical thickness of a monolayer of water molecules, as can be estimated from \( d_w = (v_{\text{m}}/V_a)^{1/3} = 0.31 \) nm, where \( V_a \) is Avogadro’s number. This correspondence suggests that a monolayer of water molecules could be immobilized at the pore wall (Fig. 4a), as has been proposed for nanoporous glasses.29,31

To investigate these hypotheses further and isolate the contributions of boundary conditions from those of the geometrical tortuosity, we measured both \( J_c \) (plateau-drying) and \( w \) (imbibition) for 3 additional liquids (acetone, ethanol, and isopropanol) of larger size (\( d = 0.46–0.50 \) nm) and a variety of surface tensions and viscosities (Table S1 in ESI††). From eqn (5)–(9), both rates
should vary in proportion to the following grouping of liquid-dependent properties: \( (\sigma \cos \theta \eta) \times (1 + \delta r_p)^3 \) with \( \delta = -d \). The plot in Fig. 4b shows that the rates collapse onto straight lines across the series of four liquids when the macroscopic values of \( r, \theta, \) and \( \eta \) and \( \delta = -(\nu_M/A) \approx 1.7 \pm 0.2 \) nm are used, and with \( r_p = r_{p,c} \approx 1.7 \pm 0.2 \) nm. This collapse, independent of the choice of tortuosity, confirms that sticking of a mono-molecular layer can explain the observed dynamics. Further, the best-fit slope of each line provides a consistent value of \( \tau = 4.5 \) (via eqn (S20) and (S21) in ESIF) for both imbibition and drying, a value that is physically reasonable for non-ideal pore architectures.

We note that other scenarios involving fine tuning of the liquid parameters (e.g. \( \eta, \sigma, \) see Section V in ESIF) could be invoked to accommodate our observations. However, we favor the hypothesis of an immobile monolayer of liquid, which allows us to reproduce all of our experiments across methods and liquids with the bulk liquids’ properties and no adjustable parameters. We also remark that our model can be extended in a completely coherent manner to a distribution of pore sizes (see ESIF).

### 4 Conclusions

In conclusion, we have demonstrated for the first time the use of drying to precisely and independently measure viscous and capillary effects at the nanoscale. We found an unusual coherency which contrasts the large deviations from theory reported for nanoscale flows even in much larger conduits.\(^8,19\) We also demonstrated that the thermodynamic stress implied by Kelvin equation expresses itself as a mechanical pressure in the liquid even in pores that measure just 6–10 molecules in diameter. While this mechanical equivalence of the Kelvin stress has been shown to hold in static situations,\(^17,32,33\) our results provide the first demonstration in a dynamic context (permeation flows) and across an unprecedented range of stresses (down to \( -100 \) MPa).

In technological contexts, the two regimes of passive evaporation-driven flow elucidated here have direct implications for the precise control of fluid flow in micro and nanosystems\(^8\) and membrane science.\(^4\) Our results also show that nanoporous solids can be a promising alternative to hydrogels for the development of biomimetic systems that use liquids under large negative pressures similarly to plants.\(^3,4\) Finally, in geophysical contexts, our experimental platform provides a new basis for evaluating the role of capillary phenomena in controlling the mobility of fluids within reservoirs exploited in, for example, hydraulic fracturing\(^2\) and sequestration of carbon dioxide.\(^1\)

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