Optimization of capillary flow through open-microchannel and open-micropillar arrays

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Abstract

We report semi-analytical models for capillary flow across surfaces covered by an array of open micropillars or open microchannels that incorporate first-order gravitational effects as well as the reduction of permeability due to meniscus curvature. We experimentally validate our models by measuring the vertical rise of a column of liquid across a series of vertical microstructured surfaces with varying characteristic dimensions, using Newtonian and non-Newtonian liquids. The data show that arrays of open microchannels deliver higher flow rates than comparable arrays of micropillars in most practical configurations. Furthermore, we experimentally demonstrate a flow maximum for open microchannels with respect to channel width that closely agrees with our analytical predictions. In addition, as an application example of the microstructures used in this study, we report electrospray emission from the edge of a chip covered by a microstructured surface that transports the liquid from a reservoir to the emission sites; the supply-limited regime of the current-voltage characteristics of these devices is in agreement with the literature on electrospray droplet emission.

Keywords: electrospray, flow control, non-Newtonian flow, surface tension-driven flow

(Some figures may appear in colour only in the online journal)
permeability can be analytically expressed for steady, laminar flows with constant rectangular cross-section; for flows through pores of varying cross-section, numerical methods are commonly employed. For example, Sangani and Acrivos formulated numerical approximations for sparse, infinitely tall cylindrical micropillar arrays in both square-packed and hexagonally-packed arrangements [9]; also, Xiao et al and Byon et al extended these results by approximating the permeability of finite-height micropillar arrays using Brinkman’s equation [10, 11].

The capillary pressure is governed by the Young-Laplace equation; when it cannot be solved analytically, as is often the case, other methods are used to estimate the driving pressure. For example, Quéré described a variational approach where the capillary pressure is calculated as the change in surface energy per change in volume as the liquid front advances by an infinitesimal amount [12]. In a regular array of microstructures, averaging variations over one period of the array yields an effective capillary pressure. However, many of these methods neglect the effects of meniscus curvature. Xiao et al and Byon et al used Surface Evolver (a software that models the shape of liquid surfaces under de influence of forces and constraints [13]) to determine the meniscus void volume; Xiao et al used the decreased pore volume and the increased liquid-air interface to calculate a more accurate capillary pressure [10], while Byon et al used the void volume to adjust permeability estimates from Brinkman’s equation [11]. However, both of these papers neglect gravitational effects. Moreover, papers by Hale et al include gravity but ignore meniscus effects [14, 15]. Zheng et al considered the effects of using no-slip, partial-stress, and no-stress boundary conditions at the liquid-air interface in open microchannels [16].

In this paper we propose a semi-analytical model that describes the dynamics of capillary flow against gravity in vertical arrays of open microchannels with rectangular cross-section; first-order gravitational effects and the impact of meniscus curvature are considered in predicting both the capillary pressure and the permeability. In addition, previously reported models of capillary flow across arrays of open micropillars are modified by incorporating these new considerations. We also extend our analysis to capture the shear-thinning behavior typical of many non-Newtonian fluids. Our models indicate the existence of multiple flow rate maxima with respect to pore size. One maximum, which occurs only in micropillar arrays and was described by Xiao et al [10], arises from the tradeoff between capillary pressure and viscous resistance. The two other maxima, which occur for both micropillar and microchannel arrays, are related to meniscus and gravitational effects and only appear at low aspect-ratio (i.e. in channels/gaps between adjacent pillars that are about as wide as they are deep) and high Bond number, respectively; these regimes are beyond the scope of most other models. Operating at any of the maxima decreases the sensitivity of flow rate to geometric variation allowing for more robust microfluidic systems. Experimental capillary rise data validate our models by confirming the existence and location of a flow maximum with respect to the width of an open-microchannel. Finally, we report electrospray emission from the edge of a microstructured surface as an example of an application of the porosity geometries we report in this study; the supply-limited regime of the current-voltage characteristics of these devices is in agreement with the literature on electrospray droplet emission.

II. Modeling

II.I. Description of the morphology of the surface microstructures

The morphology of the porous microstructures studied in this work is shown in figure 1. In case (a), open microchannels
with rectangular flow cross-section are arrayed across a flat surface. The channels have a width $w$, a height $h$, and are separated by walls of thickness $d$. The center-to-center spacing of the walls is $s = w + d$. In case (b), micropillars with square cross-section are arrayed across a chip in a square-packed formation. Similarly to the previous case, the micropillars are defined by height $h$, thickness $d$, gap width $w$, and center-to-center spacing $s = w + d$. In practice, the range of combinations of the parameters that describe each kind of microstructure is limited by the specifics of the fabrication process, which includes certain minimum feature size and maximum aspect ratio that can be resolved in a repeatable fashion. (When describing the surface microstructures, *minimum feature size* is the smallest in-plane dimension of the array of micropillars/microchannels; the minimum feature size can be the gap between adjacent micropillars/width of the microchannels, i.e. $w$, the thickness of the wall that separates adjacent microchannels/cross section of the micropillar, i.e. $d$, or both. In the fabrication process flow used in this work (see section III.I), the minimum feature size is limited by the resolution of the lithographic process used to transfer the in-plane features. When describing the surface microstructures, *aspect ratio* is the proportion of the out-of-plane dimension of the micropillar/microchannel, i.e. $h$, to the thickness of the wall that separates adjacent microchannels/cross section of the micropillar, i.e. $d$. From the fabrication point of view, there is a maximum aspect ratio that is achievable by the etch process that carves the features into the substrate. In this work, the etch is conducted with deep reactive-ion etching (see section III.I) and, for a given fixed trench width, the maximum aspect ratio is caused by increasingly slower etch rates as the trench becomes deeper due to the depletion of reactive species within the plasma at the bottom of the trench).

II.II. Modeling of capillary flow through vertical open-microchannel arrays

The Navier–Stokes equation can be solved exactly for the case of fully developed, laminar, axisymmetric flow of an incompressible fluid through a cylindrical pipe. In this case the volumetric flow rate $Q$ is

$$ Q = \frac{\pi R^4}{8\mu} \nabla p $$

where $R$ is the constant pipe radius, $\mu$ is the viscosity of the liquid, and $\nabla p$ is the pressure gradient. A linear relationship between $Q$ and $\nabla p$ is typical of low-Reynolds number, porous flows, described more generally by Darcy’s law

$$ v_D = \frac{Q}{A} = \frac{k}{\varepsilon \mu} \nabla p $$

where $v_D$ is the Darcy velocity, i.e. the total flow rate per unit area (generally not equal to the actual in-pore velocity of the liquid), $A$ is the constant cross-section of the porous medium in question, $\varepsilon$ is the porosity, and $k$ is the permeability, which is a function of the geometry. For the case of 1D capillary flow against gravity through a cylindrical tube, the Navier–Stokes equation can be integrated over a control volume to describe the height of the rising liquid front [8]. This can be generalized to a broader range of porous media with the substitution $R^2/8 = k\varepsilon a$, which is derived by combining (1) and (2). The resulting 1D equation of fluid motion is

$$ \frac{-d(p_l)}{dr} = \Delta p + \frac{\varepsilon \mu}{k} + \rho g l $$

where $\rho$ is the density of the liquid, $g$ is the gravitational acceleration, $l$ is the height of the rising liquid front, $\Delta p$ is the capillary pressure, and $t$ is the time variable. The left hand side of (3) represents inertial forces, which are negligible in most capillary flows beyond very short time scales. Dropping this term and solving for $l$ yields

$$ l = \frac{k}{\varepsilon \mu} (|\Delta p| - \rho g l) $$

Fries et al derived an explicit function for rise height in terms of time using the W-Lambert function [8]

$$ l = L \left[ 1 + \frac{W(-e^{-1-\frac{\tau}{L}})}{\tau} \right] $$

where $\tau$ is a time constant equal to $\varepsilon \mu \Delta p / (k \rho g)^2$ and $L = \Delta p / \rho g$. Solving for the position of the liquid front amounts to defining the capillary pressure, permeability, and porosity in terms of the geometry of the microstructure.

The capillary pressure can be approximated as the negative change in energy per change in volume for an infinitesimal advance of the liquid front. Conducting this analysis in a single unit cell of the porosity results in

$$ \Delta P = \frac{-1}{\Delta V} \Delta E = \frac{\gamma_{LV}}{F_l h} \left[ \cos \theta \frac{(r - \phi)}{(1 - \phi)} + F_A + \frac{F_C M F Y h l}{\lambda^2} \right] $$

where $\theta = \cos^{-1}[(\gamma_{SV} - \gamma_{SL})/\gamma_{LV}]$ is the contact angle, $\gamma_{SL}$, $\gamma_{SV}$, and $\gamma_{LV}$ are the solid-liquid, solid-vapor, and liquid-vapor interfacial tensions, respectively, $\lambda = [\gamma_{LV} / (\rho g)]^{1/2}$ is the capillary length, $r$ is the roughness, i.e. the total surface area of the microstructure divided by its apparent area, $\phi$ is the solid fraction of the microstructure (as defined in [12]), and $F_A$, $F_Y$, and $F_C$ are correction factors to the liquid surface area, volume, and center-of-mass that account for deviations from an idealized, full-pore flow due to the presence of a meniscus. For open-microchannel arrays, $r = 1 + h/s$ and $\phi = d/s$.

The permeability of an open microchannel of rectangular cross-section is equal to

$$ k_{chan} = \frac{w^2}{12} \left[ 1 - \sum_{n, odd} \frac{1}{n^2 \pi^2} \frac{\tanh(n \pi w / w)}{n \pi w} \right] $$

assuming no-slip boundary conditions on the side and bottom walls and a no-stress boundary condition on the liquid-air interface. For aspect ratios of $h/w > 0.1$ we can approximate (7) with the closed form expression.
where \( \zeta(n) \) is the Riemann zeta function. For an array of open microchannels separated by sidewalls of finite thickness \( d \), the permeability of the array is the product of the single-channel permeability, \( k_{\text{chan}} \), and the void fraction of the microstructures is \((1 - \phi) = w/s\).

For the idealized case of a flat liquid-air interface, the correction factors to the liquid’s surface area, volume, and center of mass are all equal to unity, and the array permeability is given as described thus far. In reality, the liquid-air interface forms a curved meniscus, which results in increased liquid area, decreased liquid volume, and modified capillary pressure relative to a flat interface. The reduction in flow cross-section also causes a reduction in permeability relative to an ideal, rectangular cross-section. Moreover, this reduction in permeability is not proportional to the reduction in cross-section, because the void region caused by the meniscus is where the otherwise fastest flow would have occurred. After subtracting the missing flow from the void region, the true total flow rate \( Q_{\text{true}} = Q_{\text{ideal}} - Q_{\text{void}} \) can be written as

\[
Q_{\text{true}} = v_{\text{avg,full}}A_{\text{full}} - v_{\text{avg,void}}A_{\text{void}}
= \left(1 - \frac{A_{\text{void}}}{A_{\text{full}}}\right)Q_{\text{ideal}} = F_d Q_{\text{ideal}}
\]

where \( A_{\text{full}} \) is the ideal flow area, \( A_{\text{void}} \) is the lost flow area, \( v_{\text{ratio}} \) is the ratio of the average velocity of the lost flow to the average velocity of the total ideal flow, and \( F_d \) is the correction factor accounting for the reduction in flow rate due to a reduction in permeability caused by the meniscus void. Explicit calculation of the correction factors in terms of the liquid properties and microstructure geometry requires a few suppositions. We first assumed that the meniscus forms a perfectly circular arc that meets the top edges of the channel sidewalls at the contact angle \( \theta \), except at the leading edge of the liquid front where we neglect an unknown but unvarying meniscus geometry (analogous to the spherical cap in a cylindrical capillary), resulting in the correction factors

\[
F_A = \frac{\alpha}{\sin \alpha}; \quad F_V = \left[1 - \frac{w}{h}B_s\right]; \quad F_d = \left[1 - \frac{v_{\text{ratio}}}{h}wB_s\right]
\]

where \( \alpha = \frac{\pi}{2} - \theta \) and \( B_s \) is a volume factor whose subscript indicates the relevant geometry, e.g., \( B_s = B_{\text{chan}} = (\alpha - \sin \alpha \cos \alpha)/4 \sin^2 \alpha \) in open microchannels. The contact angle is typically taken as a constant determined by relative surface energies. However, if we assume a uniform contact angle along the entire channel, this implies there is virtually no pressure gradient, since the pressure drop across the meniscus is proportional to the interface curvature and, thus, proportional to \( \cos(\theta) \). Clearly, this cannot be the case because (4) requires a linear pressure gradient between the channel base and the liquid front. In this work, we assume that the cosine of the contact angle varies linearly from 0 at the channel base to 1 near the liquid front, which is equivalent to neglecting the curvature in the axial direction of the channel. In this case, the pressure drop is due to the curvature in the cross-channel direction, which is a reasonable assumption for channels that are much longer than they are wide. A consequence of this assumption is that the previously calculated correction factors vary with location. However, integration over the length of the microchannel allows for the calculation of an average correction factor (indicated by overbars) and equivalent contact angle (i.e., a contact angle that yields the average correction factor when assumed constant across the entire channel). This was done numerically in MATLAB. The velocity ratio \( v_{\text{ratio}} \) is calculated for a range of contact angles and aspect ratios through numerical integration of the velocity profile up to the location of the meniscus. For each aspect ratio, a harmonic mean is taken of the \( F_d \) values along the channel. From this mean, \( F_d \), an equivalent velocity ratio \( v_{\text{ratio}} \) is calculated so as to yield the correct full-channel flow factor when a constant, volume-equivalent contact angle \( \theta_v \) is assumed along the entire channel. Expressions are fitted for \( v_{\text{ratio}} \) and \( F_{\text{CM}} \) in terms of the channel aspect ratio:

\[
\begin{align*}
F_A &= \frac{\alpha_A}{\sin \alpha_A}; \quad F_V = \left[1 - \frac{w}{h}B_s\right]; \quad F_d = \left[1 - \frac{v_{\text{ratio}}}{h}wB_s\right]; \\
F_{\text{CM}} &= \frac{2}{1F_V} \int_0^L zF_d \, dz
\end{align*}
\]

where \( \alpha_A = \frac{\pi}{2} - \theta_h \), \( \alpha_V = \frac{\pi}{2} - \theta_V \), \( \theta_V = 55^\circ \), \( \theta_h = 49^\circ \), and \( B_s = B_{\text{chan}} = (\alpha_V - \sin \alpha_V \cos \alpha_V)/4 \sin^2 \alpha_V \) for open microchannels. Therefore,

\[
F_{\text{CM}} = -0.05688\frac{w}{h} + 1; \quad v_{\text{ratio}} = 0.8083\frac{w}{h} + 1.7957
\]

II.III. Modeling of capillary flow through vertical open-micropillar arrays

The previous analysis can be extended to open-micropillar arrays by recalculating the driving pressure, permeability, porosity, and correction factors in terms of the dimensions of the array; (6) still holds but now \( r = 1 + 4dh/s^2 \) and \( \phi = d^2/s^2 \).

Factors \( F_A \) and \( B_s = B_{\text{pill}} \) are determined using numerically computed correlations from [10]. The expression for \( v_{\text{ratio}} \) is modified with respect to the microchannel case by introducing multiplying factors based on the ratio of the void volume in channels to that in pillars. All other correction factor definitions for microchannels are carried over for micropillars. The resulting expressions are

\[
F_A = 0.43 + \cos \theta_h \left[0.73 + 4.66\left(\frac{d}{s}\right)^2 - 5.53\frac{d}{s} - 0.046 \cos \theta_h - 0.124 \cos^2 \theta_h \right] + \frac{d}{s} \left[3.76 + 1.77 \cos^2 \theta_h - 4.05\left(\frac{d}{s}\right)^2\right]
\]
\[ B_{\text{pil}l} = -0.175 + \cos \theta_V \left[ -0.345 - 5.83 \frac{d}{s} + 0.924 \cos \theta_V \right] + 2.71 \left( \frac{d}{s} \right)^2 - 0.439 \cos^2 \theta_V \]
\[ + \frac{d}{s} \left[ 4.07 + 2.41 \cos^2 \theta_V - 2.80 \left( \frac{d}{s} \right) \right] \]  
\[ \sqrt{\text{ratio}} = \frac{B_{\text{chan}}}{B_{\text{pil}l} \left( \frac{s + w}{2w} \right)} \left( \frac{0.8083 \frac{w}{h} + 1.7957}{2} \right) \]  

The permeability of the open-micropillar arrays is calculated using Brinkman’s equation as explained in Xiao et al [10]. The numerically derived permeability for square-packed arrays of infinitely tall cylindrical pillars [9] is adapted to our square cross-section pillars by replacing \( c = \phi = \frac{2 \pi}{(1/2)} \) with \( c = \phi = \frac{2 \pi}{(1/2)} \) and the factor \( 4 \pi \) with 16 in (17); this is a reasonable substitution at high porosity. Finally,

\[ k_{\text{pil}l} = (1 - \phi) \lambda F \frac{s^2}{h^2} \left[ 1 - \frac{\tanh(D)}{D} \right] \]

\[ k_{\text{Num}} = \frac{1}{16} \left[ \ln \left( \frac{h^2}{\lambda} \right) - 0.738 + \phi - 0.887 \phi^2 + 2.038 \phi^3 \right] + O(\phi^5) \ldots \]

\[ D = \frac{h}{s} \sqrt{\frac{1 - \phi}{k_{\text{Num}}}} \]

II.IV. Geometric flow maxima in open-microchannel and open-micropillar arrays

Equation (4) can be rendered dimensionless via multiplication by the factor \( \mu \lambda / \gamma \), yielding an equation for the Capillary number \( Ca = \mu \lambda / \gamma \). Maximizing \( Ca \) will not necessarily maximize flow rate over a given width of wicking chip surface, since flow rate depends on porosity in addition to pore velocity. Multiplying \( Ca \) by the porosity \( \epsilon = (1 - \phi) \lambda F \) and the dimensionless feature height \( h^* = h/\lambda \) gives the dimensionless flow rate per unit length \( q^* \). For open-microchannel arrays (Model 1) and open-micropillar arrays (Model 2), \( q^* \) is given by, respectively,

\[ q_{\text{chan}}^* = \frac{F_{\text{chan}} w^2}{F_{\text{chan}} s} \left[ \frac{31 \zeta(5)}{30 \zeta(4)} \frac{w}{\pi h} \left( \frac{\pi h}{w} \right) \right] \times \left( \frac{1 + \frac{2 \zeta(5)}{30 \zeta(4)} \frac{w}{h}}{h^*} \right) \frac{\cos \theta - F_{A_{\text{chan}}} - F_{V_{\text{chan}}}}{h^*} \]

\[ q_{\text{pil}l}^* = \frac{F_{\text{pil}l}}{F_{\text{pil}l} s} k_{\text{Num}} \left[ \frac{1 - \tanh(D)}{D} \right] \times \left( \frac{1 + \frac{2 \zeta(5)}{30 \zeta(4)} \frac{w}{h}}{h^*} \right) \frac{\cos \theta - F_{A_{\text{pil}l}} - F_{V_{\text{pil}l}}}{h^*} \]

An asterisk accompanying a length variable indicates division by \( \lambda \), thereby producing a dimensionless quantity. contour plots of \( q^* \) against dimensionless feature spacing \( s^* \) and the ratio of feature size-to-spacing \( d/s \) are shown in figure 2 for several values of \( h^* \) and \( l^* \). The left column (figures 2(a), (c), (e)) displays the results for open-microchannel arrays and the right column (figures 2(b), (d), (f)) displays the results for open-micropillar arrays (for \( d/s < 0.5 \), where \( k_{\text{Num}} \) is valid). Perhaps the most striking difference between the microchannel plots and the micropillar plots is the location of the global flow rate maximum. For microchannels, this maximum always occurs in the limit \( d/s \to 0 \), whereas, for micropillars, it falls somewhere in the range \( 0.2 < d/s < 0.5 \). This makes sense if one considers how flow rate depends on the microfeature density, \( d/s \), in either model. In Model 1, the flow within an individual microchannel does not depend on how near or far any adjacent channels lie, because each microchannel is entirely closed-off from its neighbors. Packing density only enters the calculation when considering the flow from a series of channels averaged over their spatial extent. In Model 2, packing density is far more significant. The capillary pressure and permeability depend strongly on packing density, and the flow between two adjacent columns of pillars is coupled to the flow through the neighboring columns. For very low packing densities, capillary pressure falls off precipitously.

Two distinct flow regimes can be identified in microchannel arrays. When \( h^* l^* \ll 1 \) (i.e. low Bond number), meniscus effects dominate and maximum flow occurs when \( w \) is on the order of \( h \) (figure 2(a)). For increasing channel widths, the decreasing aspect ratio means the meniscus void becomes a growing portion of the flow cross-section until it eventually intersects the bottom surface. When \( h^* l^* \gg 1 \) (i.e. high Bond number), gravitational effects dominate and maximum flow occurs when \( w \) is on the order of \( l^* \) (figure 2(e)). When \( h^* l^* \sim 1 \), both gravitational and meniscus effects are significant (figure 2(c)). The same regimes exist for the corresponding micropillar arrays, except viscous effects are also present, which further alters the shape and location of the flow maximum (figures 2(b), (d), (f)). For the same values of \( h^* \) and \( l^* \), the magnitude of the global flow maximum in microchannel arrays is always greater than in micropillar arrays, indicating the superiority of microchannels as liquid wicks.

III. Experimental

III.1. Fabrication of microstructured surfaces

The microstructured surfaces used in this work were fabricated using standard CMOS manufacturing and the process
flow is shown in figure 3. A 6-inch, 500 μm-thick, single side-polished, single-crystal silicon wafer with the top side coated with a 0.5 μm-thick thermal silicon dioxide film was used as starting substrate. First, contact photolithography was used to transfer the front views of the porosities described in figure 1 into a spun-coated, 1 μm-thick, positive tone OCG825 photoresist that covers the top of the substrate; however, the areas that eventually serve as flow paths are patterned with a uniform forest of sacrificial micropillars with square cross-section 5 μm wide. Subsequently, the features are etched into the oxide film underneath the resist using a CHF₃ reactive-ion etching (RIE) step. The same features are then transferred into the silicon using deep reactive-ion etching (DRIE), which is the cycling of isotropic SF₆ plasma etching steps alternated by C₄F₈ plasma passivation steps that results in anisotropic etching of single-crystal silicon [17], making possible the creation very high aspect ratio structures [18]. When the desired etch depth is reached (the etch is time controlled), the sacrificial micropillars are undercut using an isotropic SF₆ RIE step, leaving behind only the device geometry (figure 4). Including dummy features to fill-in the space between device features mitigates aspect-ratio dependent etching (ARDE) effects.

Figure 2. Contour plots of dimensionless flow rate per unit length $q^*$ against dimensionless feature spacing $s^*$ and the ratio of feature size-to-spacing $d_s^r$ for several values of $h^*$ and $l^*$.
that typically appear when designs containing different feature spacing are transferred to the same substrate [19]. The remaining photoresist film is removed using oxygen plasma, and the oxide is stripped with HF acid. Table 1 summarizes the dimensions of the different samples made.

### III.II. Wicking characterization of microstructured surfaces

Polyethylene oxide (PEO, molecular weight \( M = 6 \times 10^5 \)) purchased from Sigma Aldrich was used to prepare solutions in ethanol/water mixtures. Due to its lower solubility in ethanol, PEO was first dissolved in deionized water alone at concentrations as high as 6% w/v. The solutions were heated to 50 °C on a temperature-controlled hot plate and kept at this temperature for several days. Vigorous shaking was applied intermittently until the solutions appeared uniform in consistency. At this point, solutions were diluted to lower concentrations using various amounts of water and ethanol to achieve desired solvent ratios. After dilution they were, again, shaken vigorously and allowed to sit overnight.

### Table 1. Final dimensions of fabricated wicking samples. C\# indicates an open-microchannel geometry and P\# indicates an open-micropillar geometry.

| Sample | s [\( \mu \text{m} \)] | d [\( \mu \text{m} \)] | w [\( \mu \text{m} \)] | h [\( \mu \text{m} \)] |
|--------|----------------|----------------|----------------|----------------|
| C1     | 125            | 26             | 99             | 128            |
| C2     | 125            | 55             | 70             | 116            |
| C3     | 250            | 47             | 203            | 127            |
| C4     | 250            | 73             | 177            | 132            |
| C5     | 250            | 101            | 149            | 139            |
| C6     | 500            | 289            | 211            | 141            |
| P1     | 125            | 45             | 80             | 121            |
| P2     | 250            | 93             | 157            | 140            |
| P3     | 500            | 289            | 211            | 143            |

Figure 3. Schematic of the process flow used to manufacture the microstructured surfaces used in this study. When the sacrificial pillars are removed, the pieces film stack on top of such features fall to the bottom of the trench.

Figure 4. Left: an array of micropillars with dummy micropillar structures patterned with DRIE; the top surface of all the features is capped by a photoresist/silicon dioxide film stack. Right: an array of micropillars with a thin silicon dioxide film on top of each structure after the dummy micropillar structures and the photoresist film are removed.
During the experiments, an open Pyrex dish on a hotplate was filled-in with the desired solution, which was maintained at 30 °C via a thermometer feedback loop to ensure consistent viscosity. The test sample was exposed to oxygen plasma for three minutes no more than 15 min before testing; this procedure removes any organic contamination on the silicon chip, as well as generates a conformal thin layer of silicon oxide on the surface of the chip. After this, each sample was loaded.
with double-sided tape onto a plastic holder at the end of a stainless steel post. The post hung from a larger support structure and had the freedom to rotate so that it would rest vertically under the influence of gravity. The support structure was mounted on an adjustable stage, which allowed for it to be lowered until the hanging sample came into contact with the free-surface of the test liquid. The rise of liquid through the microstructured surface of the silicon chip was recorded at frame rates between 40 and 50 fps using a Moticam 3.0 camera. Automated analysis of the videos to extract liquid rise height as a function of time proved difficult due to a number of factors, including the presence of multiple moving liquid fronts, low contrast of the liquid and sample, and reflections of lighting sources on the sample. Instead, videos were analyzed manually, measuring position of the predominant liquid front using a ruler fixed to a screen on which the videos were stepped in known frame intervals at 9X magnification. The uncertainty of approximately 0.5 mm in the ruler measurements corresponds to an uncertainty of 56 μm of the actual liquid position, which is 0.28% of the 2 cm sample length and adequate to resolve the movement of the liquid across the surface. A schematic of the apparatus used to characterize the wicking of the silicon chips is shown in figure 5.

IV. Results and discussion

The predictions of Model 1 were compared to the data collected using a series of chips that span a range of microchannel geometries (figure 6). The working liquid used in these experiments was 1% PEO in 40/60 ethanol/water, which causes flow dynamics that are slow enough to collect well-resolved data points but fast enough to limit the effects of solvent evaporation. Viscosity and surface tension values were taken directly or extrapolated from literature as 0.03 Pa.s and 0.04 N m⁻¹, respectively. Since all samples were treated with oxygen plasma shortly before testing, in principle, the contact angle should approach 0° (i.e. the surfaces are rendered completely wetting). However, a contact angle of 0° results in overestimation of the wicking rates. This issue has been addressed in other published work with a higher ‘effective’ viscosity resulting from dynamic contact phenomena [20] or by assuming partial stress at the free-surface of the liquid [16].

Using a contact angle of 30° in our model yields fairly good agreement with data across several different samples and liquids. The use of a 30° contact angle is also in agreement with dynamic contact angle predictions reported by other investigators for flow velocities typical in the earlier stages of capillary rise [21]. From figure 6 it can also be seen that the predictions of a modified Model 1 that does not take into account gravitational and meniscus effects are significantly less accurate.

The data collected and Model 1 show good agreement for all samples in which \( w/h < 2 \). Beyond this limit, Model 1 is not expected to accurately describe the data because the meniscus will contact the channel bottom and capillary rise will occur primarily in the channel corners. Meniscus height versus time data from samples within the limit \( w/h < 2 \) were fitted to (5) using the `nlinfit` function in MATLAB. The two extracted parameters, \( L \) and \( \tau \), were plugged into the derivative of (5) to estimate the rise velocity, and this value was multiplied by the microfeature height to give the volumetric flow rate per unit length \( q \). The experimentally derived values of \( q \) are plotted against theoretical predictions in figure 7. The microchannel height varied among the samples between 116 and 139 μm because the etch that created the microstructured surfaces was time-controlled and suffered from wafer-to-wafer and across-wafer variation. Therefore, theoretical predictions are plotted in two ways: the predictions of \( q \) using the exact, measured channel heights are plotted as points (red triangles) against the exact channel widths, much like the experimental data; we also plotted a curve (solid red line) calculated using the average channel height of 128 μm, to convey the trend with varying channel width. These predicted rise rates slightly overestimate the actual rise rates, but both theory and data suggest a flow maximum for a channel width around 125 μm, which is about the height of the channels fabricated.

The predictions of Model 2 were compared to the data collected using a series of chips that span a range of micropillar geometries. The working liquid used in these experiments was again 1% PEO in 40/60 ethanol/water. Similar to the analysis of the liquid rise through open-microchannel arrays, Model 2 shows good agreement with the data from the wicking characterization of open-micropillar arrays, although the model slightly overestimates liquid rise rates (figure 8). However, the model proposed by Xiao et al [10] (dashed, green line) is significantly less accurate because it does not account for gravity or the decreased permeability associated with the meniscus cutting into the otherwise fastest portions of the velocity profile.
After experimentally confirming the validity of Model 1 and 2 for a variety of geometries, we sought to directly compare the wicking merits of microchannels to micropillars. Unfortunately, non-idealities in the fabrication of the silicon chips resulted in a shift of the intended microfeature dimensions such that there were no microchannels with a sidewall thickness equal to the side length of one of the micropillars. Therefore, we decided to compare a particular micropillar sample (P2) to two different microchannel samples: one with $d$ slightly larger than the pillars (C5) and the other with $d$ slightly smaller (C4). If both microchannel samples performed better than the micropillars, it would suggest their superiority for wicking at equivalent sizes. This is, in fact, what was observed (figure 9). It should be noted that the plotted data indicates height of the moving liquid front as a function of time, not flow rate per unit length. A sample with slower height rise than another can actually deliver higher flow rates if it is significantly more porous than its competitor. The data was fitted and flow rate per unit length $q$ was calculated from the fitted rise velocity. At a height of 5 mm, the volumetric flow rates per unit length were as follows: P2: $q = 8.45 \times 10^{-8}$ m$^2$ s$^{-1}$, C4: $q = 1.68 \times 10^{-7}$ m$^2$ s$^{-1}$, C5: $q = 1.66 \times 10^{-7}$ m$^2$ s$^{-1}$. Therefore, both open-microchannel array samples deliver about twice as much liquid per unit length of surface than the open-micropillar array sample of roughly equivalent dimensions.

We also examined the wicking capability of one particular microstructure for several different liquids of varying viscosity. Microchannel sample C5 was tested in water, 1% PEO in 40/60 ethanol/water, and 4% PEO in 40/60 ethanol/water. The results are shown in figure 10, left. Model 1 fits the experimental data for water and 1% PEO quite well. However, the 4% PEO data does not match Model 1 as well; at early times liquid rise is faster than predicted while at later times liquid rise is much slower than predicted. This is a result of non-Newtonian liquid behavior in the 4% PEO that is not accounted for in Model 1. Fully describing the behavior of such a liquid requires accounting for polymer relaxation times, non-zero normal stresses, and viscosity that varies with strain rate. A relatively simple way to describe the last of these factors, non-constant viscosity, is to model it with a power law, i.e. the shear stress is $\tau = \eta_0 (du/dy)^n$ instead of $\tau = \mu (du/dy)$, where $\mu$ is the liquid velocity, $y$ is the direction perpendicular to the velocity across which the variation in velocity occurs, $\eta_0$ is the flow consistency index, and the effective viscosity $\mu_{eff}$ is equal to $\eta_0(du/dy)^n$. Using $\eta_0 = 1.3 \times 10^7$ Pa.s$^n$ and $n = 0.4$ in a modified Model 1, called Model 1*, provides a much better fit of the liquid’s shear thinning behavior (figure 10, right).
Finally, we characterized the liquid transport properties of the microstructured surface in the context of electro-hydrodynamic jetting [22]. Microfabricated arrays of externally-fed electrospray emitters using wicking nanostructures such as black silicon [23, 24] and plasma-enhanced chemical vapor deposited (PECVD) carbon nanotube forests [25] have been shown to operate uniformly while emitting pure ions because of the flow regulation of the wicking structure, enabling high-throughput production of ions from ionic liquids. With a suitable working liquid, the microstructured surfaces studied in this work could be used to extend the kinds of particles produced by microfabricated, externally-fed electrospray sources, e.g. droplets and nanofibers [26], because the structure of these surfaces has characteristic dimensions two orders of magnitude larger than the characteristic dimensions of the nanostructured surfaces previously mentioned. In these experiments, a chip with open microchannels was supported vertically in a bath of liquid and its position was adjusted so that the liquid would rise all the way to the top edge of the sample. High voltage was applied in step increments, and the current response was recorded using a PC. With water as the working liquid, electrospray initiates at some threshold voltage and the measured current increases quickly just beyond this voltage; further increases in bias voltage result in a more slowly increasing current that varies linearly with voltage in the high-voltage regime. For bias voltages close to the onset voltage, the emission process is barrier-limited, i.e. the ionization conditions determine the volumetric flow rate $Q$, which grows at an increasing rate with growing electric field strength. For larger bias voltages the emission becomes supply-limited, i.e. controlled by the wicking microstructure. The growing flow rate results in growing viscous losses, which limits the delivery of more liquid. This concept is analogous to the steady-state motion of a skydiver who has reached terminal velocity. Previous work has shown that electrospray current for viscous liquids varies as the square root of the flow rate [27] when the emission is composed of droplets; Ganan-Calvo et al confirm this relationship by independently adjusting the flow rate with a pump. However, in the electrospray emission from the silicon chips, the flow rate is a dependent variable controlled by the parameters of the experiment, e.g. properties of the liquid and electric field acting on the liquid surface. Although we could not directly measure the flow rate, we suspect that our results are consistent with the previously studied scaling based on the following argument. Flow through the designed wicking structures can be described with Darcy’s law, which states that the flow rate is proportional to the pressure gradient $\nabla p$. In our experiments, surface tension will wick the liquid to the edge of the microstructured surface, but it is the electric field that provides the driving pressure behind the spray. Electrostatic pressure at a conducting surface scales as the square of the normal electric field $E$, and, for a fixed set of conditions in the apparatus, the electric field at a particular location is proportional to the voltage $V$. Therefore, the flow rate should scale as the square of the applied voltage $Q \propto \nabla p \propto E^2 \propto V^2$. Combined with the experimental observation that the emitted current varies linearly with voltage in the high-voltage regime, this implies that $I \propto Q^{1/2}$, in agreement with the work of Ganan-Calvo et al.

Electrospinning, i.e. the generation of nanofibers using high electric fields, was attempted by repeating the previous experiment using 3% PEO in 50/50 ethanol/water. Following
the same procedure we used for the electrical atomization of water, we observed electrospray, not electrospinning, of the PEO solution. The current versus voltage characteristics are plotted in figures 11(c) and (d). The characteristic of the current versus voltage plot is not as overtly linear as it was for electrospraying water. We attribute this behavior to the shear-thinning properties of the PEO solution, which, as we pointed out before, can be modeled as a power-law fluid, i.e. \( \tau = \eta (du/dy)^n \) and i.e. \( \mu_{\text{eff}} = \eta (du/dy)^{n-1} \). For a given porous geometry, the strain rate is proportional to the flow rate, and the value of \( n \) will be less than one for a shear-thinning fluid. We previously modeled a similar PEO solution as a power-law fluid with \( n \approx 0.5 \), suggesting that for this case \( \mu_{\text{eff}} \propto (du/dy)^{-1/2} \approx Q^{-1/2} \). Darcy’s law states that the flow rate is proportional to pressure gradient and inversely proportional to the viscosity. If pressure still scales as \( V^2 \), then we have \( Q \propto \nabla p / \mu_{\text{eff}} \propto V^2 / Q^{1/2} \), which implies \( Q^{1/2} \propto V^2 \). If we assume that current still scales with the square root of the flow rate, as it should for viscous droplets, then the emitted current should vary as the square of the applied bias voltage. Our observations validate this scaling.

Inspection of the collector electrode following electrospray of the polymer solution revealed two primary deposition areas above either corner of the wicking sample. This suggests that liquid is wicking through the open microchannels to the top edge of the sample where it then travels along the edge to the corner. Electrospray occurs from these sharp corners, not from the open end of each microchannel. However, the experimental results suggest that the microstructured surface is responsible for transporting the liquid from the reservoir to the emission sites at the edge of the chip, allowing continuous atomization of the liquid. Therefore, it might be possible to leverage the work reported in this study into arrays of externally-fed electrohydrodynamic jetting emitters that can operate continuously while producing particles such as droplets or nanofibers.

V. Conclusions

We derived semi-analytical models that describe the dynamics of capillary flow against gravity in vertical arrays of open micropillars and open microchannels with

Figure 11. Average current versus voltage for electrohydrodynamic jetting of water from the edge of a microstructured surface: full voltage range (a), and supply-limited range (b). A linear relationship between the average current and the bias voltage is observed \( R^2 = 0.9812 \). Average current versus voltage for electrohydrodynamic jetting of 3% PEO in 50/50 ethanol/water from the edge of a microstructured surface: full voltage range (c), and supply-limited range (d). A quadratic relationship between the average current and the bias voltage is observed, \( R^2 = 0.9864 \).
rectangular cross-section. Incorporating first-order gravitational effects and the impact of meniscus curvature improved flow rate predictions relative to models that neglect these factors. Our models indicate the existence of multiple flow rate maxima with respect to pore size. One maximum, which occurs only in micropillar arrays and was previously described in the literature, arises from the tradeoff between capillary pressure and viscous resistance. The two other maxima, which occur for both micropillar and microchannel arrays, are related to meniscus and gravitational effects and only appear at low aspect ratio and high Bond number, respectively; these regimes are beyond the scope of most other models. Operating at any of the maxima decreases the sensitivity of flow rate to geometric variation allowing for more robust microfluidic systems. Experimental capillary rise data validate our models and confirm the existence and location of a flow maximum with respect to the width of an open-microchannel. Finally, we reported electrospray emission from the edge of a microstructured surface as an example of an application of the porosity geometries we report in this study; the supply-limited regime of the current-voltage characteristics of these devices are in agreement with the literature on electrospray droplet emission, opening the possibility to implement arrays of externally-fed electrohydrodynamic jetting emitters that can operate continuously while producing droplets or nanofibers while using suitable working liquids.

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