Wetting considerations in capillary rise and imbibition in closed square tubes and open rectangular cross-section channels

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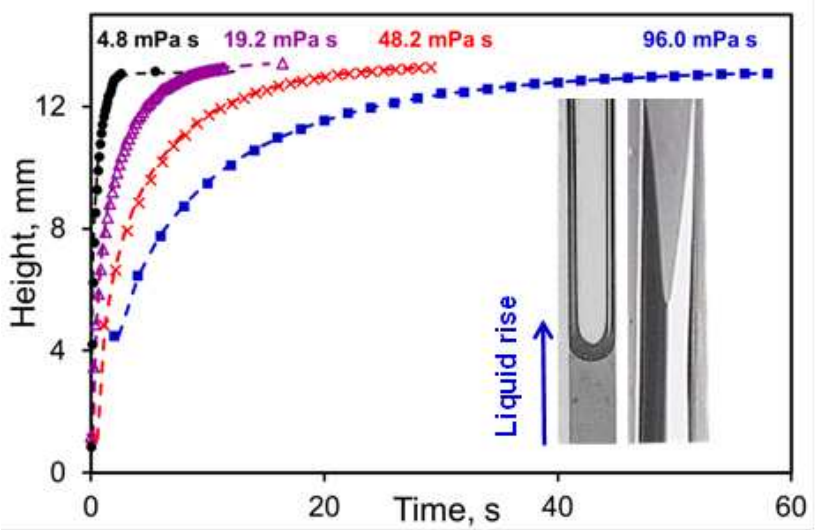

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Abstract

The spontaneous capillary-driven filling of microchannels is important for a wide range of applications. These channels are often rectangular in cross-section, can be closed or open, and horizontal or vertically orientated. In this work, we develop the theory for capillary imbibition and rise in channels of rectangular cross-section, taking into account rigidified and non-rigidified boundary conditions for the liquid-air interfaces and the effects of surface topography assuming Wenzel or Cassie-Baxter states. We provide simple interpolation formulae for the viscous friction associated with flow through rectangular cross-section channels as a function of aspect ratio. We derive a dimensionless cross-over time, T_c, below which the exact numerical solution can be approximated by the Bousanquet solution and above which by the visco-gravitational solution. For capillary rise heights significantly below the equilibrium height, this cross-over time is $T_c \approx (3X_e/2)^{2/3}$ and has an associated dimensionless crossover rise height $X_c \approx (3X_e/2)^{1/3}$, where $X_e=1/G$ is the dimensionless equilibrium rise height and G is a dimensionless form of the acceleration due to gravity. We also show from wetting considerations that for rectangular channels, fingers of a wetting liquid can be expected to imbibe in advance of the main meniscus along the corners of the channel walls. We test the theory via capillary rise experiments using polydimethylsiloxane oils of viscosity 96.0, 48.0, 19.2 and 4.8 mPa s within a range of closed square tubes and open rectangular cross-section channels with SU-8 walls. We show that the capillary rise heights can be fitted using the exact numerical solution and that these are similar to fits using the analytical visco-gravitational solution. The viscous friction contribution was found to be slightly higher than predicted by theory assuming a non-rigidified liquid-air boundary, but far below that for a rigidified boundary, which was recently reported for imbibition into horizontally mounted open microchannels. In these experiments we also observed fingers of liquid spreading along the internal edges of the channels in advance of the main body of liquid consistent with wetting expectations. We briefly discuss the implications of these observations for the design of microfluidic systems.

Keywords: Lucas-Washburn, capillary rise, microfluidic channel.

1. Introduction

The capillary-driven imbibition of liquids into tubes, channels and porous media is fundamental to a diverse range of applications, such as printing (Schoelkopf J et al., 2002), lab-on-chip (Brody et al., 1996; Squires and Quake, 2005), porous media (e.g. Marmur and Cohen, 1997; Siebold, 2000) and soil water repellency (Shirtcliffe et al, 2006). The fundamental principles governing these types of problems are based on balancing the inertial forces, viscous forces, hydrostatic pressure and the capillary forces. Effective use and control of capillary imbibition requires an understanding of the different layers of subtlety that a problem may provide. Thus, there are different time regimes from the very early stage inertia dominated stage, described by Quéré (1997), to the late stage viscous regime of Lucas (1918) and Washburn (1921); the transition between these regimes for capillary rise is discussed by Fries and Dreyer (2008a). For horizontally mounted channels where gravity can be neglected and these regimes are described by the exact analytical Bousanquet solution (Bousanquet, 1923), whose form is valid whether the channel is closed or open (e.g. Bouaidet et al., 2005; Jokinen and Franssila, 2008); the Lucas-Washburn solution is the long time limit of the Bousanquet solution. We define a closed-channel as one whereby all walls are solid and an open-channel as one with a liquid-air interface as the effective wall. Due to its importance in microfluidics, capillary imbibition has previously been considered for a wide range of cross-sectional shape channels, such as circular (e.g. Strage et al., 2003), rectangular (e.g. Ichikawa et al., 2004; Jong et al., 2007; Zhu and Petkovic-Duran, 2010) and grooved/triangular (Yost and Holm, 1995; Romero and Yost, 2006; Baret et al., 2007). Moreover, the same approach has been taken for channels defined by hydrophilic paths on a hydrophobic substrate (Darhuber et al., 2001) and by the space between two parallel plates (Rosendahl et al., 2004) under the assumption of flow with low Reynolds number and liquid imbibing in a tube/slab-like manner. When channels are mounted vertically gravity becomes important and exact analytical solutions for capillary imbibition are no longer possible in general. However, a visco-gravitational solution for time as a function of meniscus position does exist for the equivalent of the Lucas-Washburn regime (e.g. Krotov and Rusanov, 1999; Hamraoui et al. 2000, Hamraoui and Nylander, 2002), including for liquid-liquid systems (Mumley et al, 1986). In these problems, the role of the shape and wetting state of the walls are critical.

Advances in lithographic fabrication techniques are increasing the range of studies in which capillary aspects of imbibition and rise are critical. These advances are leading to studies with microfluidic (e.g. Yang et al, 2011) and nanofluidic capillaries widths of a few tens of nm (Han et al., 2006) or with depths as small as 6 nm (Oh et al, 2009). Whilst non-constant channel cross sections have been a focus of study experimentally and theoretically (Legait, 1983; Staples and Shaffer, 2002, Reysatt et al, 2008; Liou et al, 2009), increased solid-liquid contact area, and hence increased capillary pull can be achieved using a range of in-channel structures. In a series of studies, Bico and co-workers studied imbibition using hemi-wicking, which amplifies the capillary pull using wall roughness (Bico 2000, Bico et al., 2002; Bico and Quéré, 2003; Ishino et al, 2007); ideas recently applied to rough Cu_6Sn_5/Cu intermetallic surfaces (Liu et al, 2011). Their work used

average parameters to characterize the capillary effect of roughness and topographic structures. This has been complemented by modelling studies by Kusumaatmaja et al. (2008) and Mognetti and Yeomans (2009) focused on feature shape and channel filling patterns, finite element modelling and experiments incorporating both capillary and viscous effects of flow through micropost (Srivastava et al., 2010; Byon and Kim 2011), and experimental studies using, e.g. stars, octagons and squares (Chen et al., 2009).

In hemi-wicking, the simplest viewpoint remains a capillary-driven penetration with a leading edge meniscus advancing in a tube/slab-like manner. However, the actual solid-liquid-vapor interface at the leading meniscus can be far more complicated as is known for capillary rise in square cross-section tubes, where the rise of a central meniscus is preceded by liquid fingers rising up the four internal edges. This reduces the equilibrium meniscus height by a factor of $(2+\pi^{1/2})/4$ (Dong and Chatzis, 1995; Bico and Quéré, 2002). These effects are due to the wetting effects in corners and edges (Concus and Finn, 1969; Ransohoff and Radke, 1988; Ramé and Weislogel, 2009, Girardo et al., 2009, 2012; Weislogel at al., 2011). Most recently, Ponomarenko et al. (2011) have studied the capillary rise of wetting liquids in the corners of different geometries and shown that in the viscous dominated regime the meniscus of these fingers rises without limit following a universal $\text{time}^{1/3}$ law, in contrast to the Lucas-Washburn $\text{time}^{1/2}$ law which eventually saturates at an equilibrium height. These geometry induced wetting effects can be expected to impact both on capillary rise and imbibition in microfluidic channels with non-circular cross-sections. There is therefore a need to study capillary-driven imbibition and rise within rectangular cross-section channels and with open and closed boundaries.

In this paper, we first provide in section 2.1 an overview of the theoretical basis of capillary driven rise and imbibition. We do so in a form that brings out the coherence of the equations and their solutions for different channel shapes in different orientations. We develop simple interpolation formulae for the viscous friction associated with open and closed rectangular channels of different aspect ratio. We show how within this formulation different contact angles on the various channel walls can be incorporated using surface free energy changes, including considerations of surface roughness or topography as required for hemi-wicking. Subsequently, in section 2.2 we compare the exact numerical solution for capillary-driven imbibition to the various analytical solutions of the approximate equations with and without gravity. We obtain a condition for the cross-over time and rise height below which the Bousanquet solution is the best approximation and above which the visco-gravitational solution is a more accurate description. In section 2.3, we discuss the sensitivity of imbibition for open rectangular channels to the value of contact angle and the limitations of this approach when corner filling along edges between walls due to wetting is taken into account.

In sections 3 and 4 we present experiments on the capillary rise of polydimethylsiloxane (PDMS) oils in closed square tubes of glass and in open rectangular channels of SU-8. We observe that capillary rise in rectangular channels using PDMS oils involves a rising central meniscus, but with thin fingers spreading in advance of this main rise along the inside corner edges qualitatively

consistent with the type of behaviour described in Ponomarenko et al. (2011). The extent of advance of the fingers is sufficient to completely exit our channels. We find that fits to the numerical solution of the exact differential equation describing capillary rise, neglecting the fingers, up to the point where the fingers reach the ends of the channels can describe the rise of the central meniscus of the liquid in both of these cases. We also find that the friction in the open-channel case is consistent with a non-rigidified liquid-air interface rather than for a rigidified boundary as recently reported for imbibition into horizontally mounted open microchannels (Yang et al., 2011).

2. Theoretical approach

2.1 Model formulation

In this section we review the standard analytical approach to describing capillary driven imbibition to provide a common notation and clarity on the assumptions used, particularly with regards the wetting of the surfaces. Our aim is to consider the structure of the equations for uniform cross-section open and closed channels, but independent of precise geometry.

2.1.1 Momentum and gravity terms

We consider a tube (or "slab") of liquid of density ρ, constant cross-sectional area A_c and length x(t) advancing along a channel displacing a gas phase. The rate of change of momentum is then,

$$\rho A_c \frac{d}{dt}\left(x\frac{dx}{dt}\right) = \rho A_c x\frac{d^2x}{dt^2} + \rho A_c\left(\frac{dx}{dt}\right)^2 \qquad (1)$$

where t is time. The force driving the imbibition (or rise) is the capillary one and those resisting the imbibition are gravity and viscous forces. For a vertically mounted channel the gravitational force is,

$$f_{grav} = -\rho g \sin\varphi\, A_c x \qquad (2)$$

where g=9.81 m s^{-2} is the acceleration due to gravity and φ is the angle of orientation of the channel to the horizontal.

2.1.2 Capillary terms

The capillary terms arise from the interchange or creation of solid-vapor, solid-liquid and liquid-vapor interfaces as the front of the tube of liquid advances. In this simplified model the profile of the solid-liquid-vapor interface is assumed to remain the same as a small advance forward, Δx, occurs. The surface free energy change ΔF as the liquid advances is then caused by changes in the various interfacial areas (Fig. 1),

$$\Delta F = \Delta x\left[\sum_i L_i^{SV\to SL}\left(\gamma_{SL}^i - \gamma_{SV}^i\right) + \sum_i L_i^{LV}\gamma_{LV}\right] \qquad (3)$$

where the γ^i_{SL} and γ^i_{SV} are the interfacial energies per unit area relating to the i^{th} solid wall element, γ_{LV} is the surface tension of the liquid, $L_i^{SV\to SL}$ is the perimeter length of the i^{th} solid wall element on which contact with vapour is replaced by contact with the liquid, and L_i^{LV} is the perimeter length of any liquid-vapor interface created. Since the Young's law contact angle is $\cos\theta^i_e=(\gamma^i_{SV}-\gamma^i_{SL})/\gamma^j_{LV}$ and the capillary force, f_{cap}, is $(-\Delta F/\Delta x)$ in the limit of $\Delta x\to 0$, we obtain,

$$f_{cap} = \gamma_{LV}\left[\sum_i L_i^{SV\to SL}\cos\theta_e^i + \sum_i L_i^{LV}\cos\left(180^o\right)\right] \qquad (4)$$

where $\cos(180^o)= -1$ has been used to show the similarity in the terms when the interface between a liquid and vapour is regarded as a perfectly hydrophobic surface.

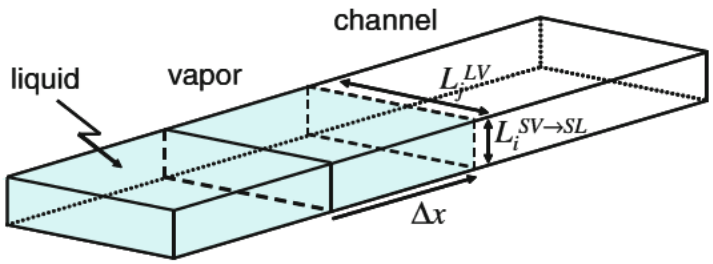

Figure 1. Surface free energy changes as a tube/slab of liquid penetrates into a channel resulting in new solid-liquid and liquid-vapor interfaces.

Figure 2 shows three specific channel geometries: a) circular cross-section tube of radius R, b) closed and c) open rectangular channel of width W and depth H. In each case, it is assumed that the solid surfaces can have different surface chemistries (i.e. contact angles). In the simplest case of a tube, only the first term contributes and the perimeter length is $2\pi R$ so that eq. (4) becomes,

$$f_{cap}^{tube} = 2\pi R\gamma_{LV}\cos\theta_e \qquad (5)$$

In the case of the closed and open rectangular channels, eq. (4) becomes,

$$f_{cap}^{rect} = \gamma_{LV}W\left[\cos\theta_e^B + \cos\theta_e^T + \varepsilon\left(\cos\theta_e^L + \cos\theta_e^R\right)\right] \qquad (6)$$

where ε=H/W and (B, T, L, R) label the contact angles for the bottom, top and left and right hand side surfaces; for the open channel $\theta^T_e=180^o$ is used in eq. (6).

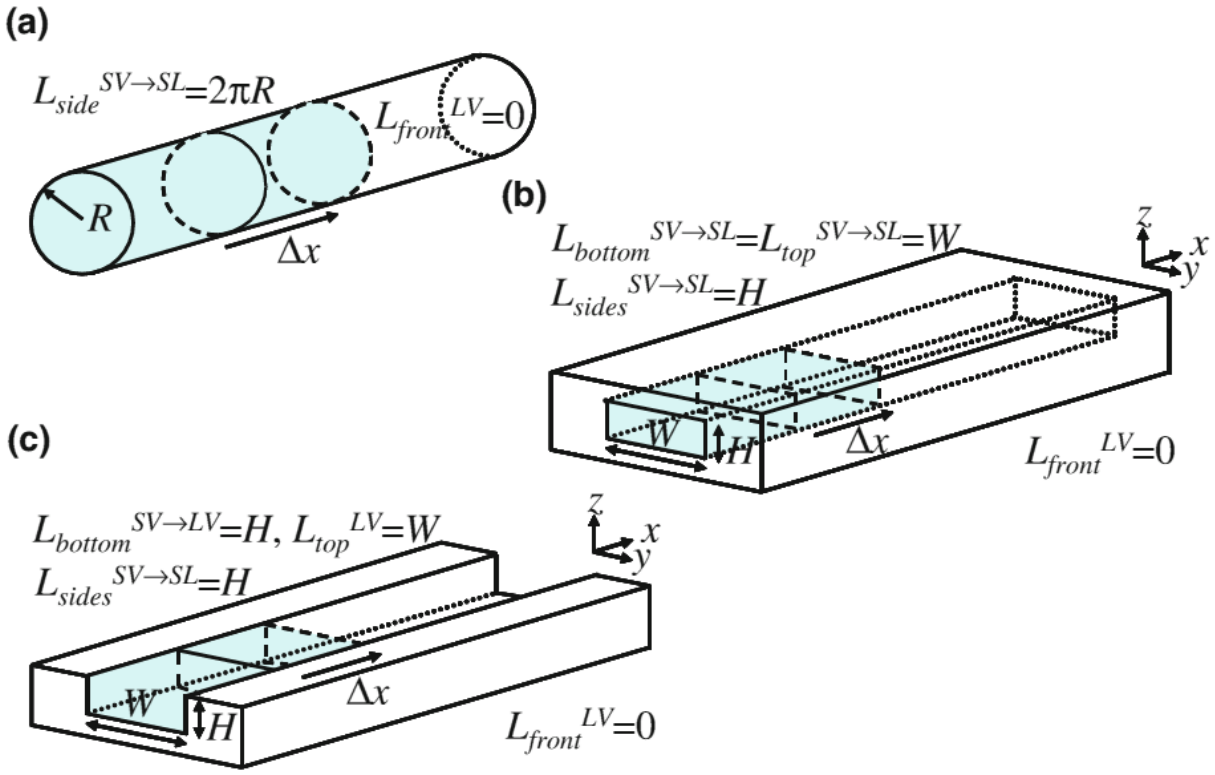

Figure 2. Solid-liquid and liquid-vapor interfaces associated with, a) circular cross-section tube, b) closed rectangular channel, and c) open rectangular channel.

Other shaped channels, such as a tube of elliptical cross-section and V-shaped grooves or triangular channels, can be assessed in the same manner from eq. (4). For example, an open or closed V-shaped channel of width W and depth H gives,

$$f_{cap}^{groove} = \gamma_{LV} W\left[\cos\theta_e^T + \frac{1}{2}\sqrt{1+4\varepsilon^2}\left(\cos\theta_e^L + \cos\theta_e^R\right)\right] \qquad (7)$$

where θ^T_e=180^o gives the open groove result. For the case of flow between two parallel plates with open sides along a path defined by a hydrophilic stripe on the plates, eq. (6) with θ^L_e=180^o and θ^R_e=180^o can be used.

2.1.3 Capillary terms and surface roughness

A slightly more complex situation is when one or more of the surfaces are rough or topographically structured at the small scale. In the Wenzel case the liquid fully penetrates into the surface features whereas in the Cassie-Baxter state the liquid bridges between surface features (Quéré, 2008; Shirtcliffe et al., 2010). When the contact angle is well below 90^o, surface roughness can drive enhanced spreading (e.g. McHale et al., 2004). Using the surface free energy argument, eq. (4) becomes,

$$f_{cap} = \gamma_{LV}\left[\sum_i L_i^{SV\to SL}\cos\theta_T^i + \sum_i L_i^{LV}\cos\left(180^o\right)\right] \qquad (8)$$

where the Young's law contact angle, $\theta^i{}_e$, is replaced by the Wenzel or Cassie-Baxter contact angle, $\theta^i{}_T$ with $\theta^i{}_T=\theta^i{}_W$ or $\theta^i{}_T=\theta^i{}_{CB}$, and $L_i{}^{SV\to SL}$ is the planar projection of the perimeter length of the i^{th} solid wall element across which the liquid advances. The Wenzel and Cassie-Baxter contact angles are defined by,

$$\cos\theta_W = r_s\cos\theta_e \qquad (9)$$

and

$$\cos\theta_{CB} = \varphi_s\cos\theta_e - \left(1-\varphi_s\right) \qquad (10)$$

where r_s is the roughness at the contact line and φ_s is the solid surface fraction. More generally, a mixed partially penetrating state may exist and $\theta^i{}_T$ then takes on the appropriate value taking into account both surface roughness and solid surface fraction (Shirtcliffe at al., 2010). Thus, eq. (5)-(7) attempt to take into account the effect of roughness or topography on the capillary drive for imbibition simply by the replacement of the contact angle by the appropriate Wenzel, Cassie-Baxter or mixed state one involving both the surface chemistry and surface structure. This approach based on minimizing surface free energy changes does not take into account contact line pinning and hysteresis.

2.1.4 Viscous terms and interpolation formulae

The viscous force for flow down a tube or a channel can be deduced from the flow velocity profile assuming incompressible, Newtonian liquid with a laminar flow, and solving the continuity and Navier-Stokes equations. For the closed rectangular channel geometry Brody et al. (1996) give the general approach and solution for the flow (see also Ichikawa et al., 2004). The non-zero component of the equations relates the flow velocity, u(y,z), in the x-direction to the pressure gradient,

$$\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = \frac{1}{\eta}\left(\frac{dp}{dx}\right) \qquad (11)$$

where η is the viscosity and p(x) is the pressure profile which only depends upon x. This equation can be solved for a channel of arbitrary aspect ratio ε=H/W using a Fourier series approach to obtain a general solution for u(y,z) to which non-slip boundary conditions can then be applied for the upper and lower channel surfaces. To work out the viscous force we first evaluate the depth and width averaged value of the flow velocity of the closed channel, $u^c{}_{ave}$,

$$u_{ave}^{c} = \left(-\frac{dp}{dz}\right)\left(\frac{8H^2}{\eta\pi^4}\right)\sum_{l=0}^{\infty}\frac{1}{(2l+1)^4}\left[1-\left(\frac{2\varepsilon}{(2l+1)\pi}\right)\tanh\left(\frac{(2l+1)\pi}{2\varepsilon}\right)\right] \quad (12)$$

This allows us to write the pressure gradient in terms of the average flow velocity so that the flow profile is,

$$u(y,z) = \left(\frac{48u_{ave}^{c}}{\pi^3\zeta_c(\varepsilon)}\right)\sum_{l=0}^{\infty}\frac{(-1)^l}{(2l+1)^3}\left[1-\frac{\cosh\left(\alpha_l^c\, y/W\right)}{\cosh\left(\alpha_l^c/2\right)}\right]\cos\left(\alpha_l^c\, z/W\right) \quad (13)$$

where $\alpha_l^c = \frac{(2l+1)\pi}{\varepsilon}$ and we have defined an aspect ratio function, $\zeta_c(\varepsilon)$, as

$$\zeta_c(\varepsilon) = \left(\frac{96}{\pi^4}\right)\sum_{l=0}^{\infty}\frac{1}{(2l+1)^4}\left[1-\frac{2\tanh\left(\alpha_l^c/2\right)}{\alpha_l^c}\right] \quad (14)$$

The viscous force on the top, bottom and two walls of the rectangular channel is then,

$$f_{visc}^{c} = 2x\eta\left[\int_{-W/2}^{W/2}\left(\frac{\partial u(y,z)}{\partial z}\right)_{z=H/2}dy + \int_{-H/2}^{H/2}\left(\frac{\partial u(y,z)}{\partial y}\right)_{y=W/2}dz\right] \quad (15)$$

which gives,

$$f_{visc}^{c} = -\frac{12\eta x u_{ave}^{c}}{\varepsilon\zeta_c(\varepsilon)} \quad (16)$$

This form makes obvious the relationship between flow in a closed rectangular channel of arbitrary aspect ratio and the one-dimensional result because in the limit of a shallow and infinitely wide channel, i.e. $W\to\infty$, the aspect ratio function $\zeta_c(\varepsilon)\to 1$.

Repeating the previous approach for an open channel gives,

$$u_{ave}^{o} = \left(\frac{8GW^2}{\eta\pi^4}\right)\sum_{l=0}^{\infty}\frac{1}{(2l+1)^4}\left[\frac{\tanh\left((2l+1)\pi\varepsilon\right)}{(2l+1)\pi\varepsilon}-1\right] \quad (17)$$

which allows the pressure gradient to be written in terms of the average flow velocity so that the flow profile is,

$$u(y,z) = -\left(\frac{12u_{ave}^{o}}{\pi^3\varepsilon^2\zeta_o(\varepsilon)}\right)\sum_{l=0}^{\infty}\frac{(-1)^l}{(2l+1)^3}\left[\cosh\left(\alpha_l^o z/H\right) - \tanh\alpha_l^o \sinh\left(\alpha_l^o z/H\right) - 1\right]\cos\left(\alpha_l^o y/H\right) \tag{18}$$

where $\alpha_l^o = (2l+1)\pi\varepsilon$ and we have defined an aspect ratio function, $\zeta_o(\varepsilon)$, as

$$\zeta_o(\varepsilon) = \left(\frac{24}{\pi^4\varepsilon^2}\right)\sum_{l=0}^{\infty}\frac{1}{(2l+1)^4}\left[1 - \frac{\tanh\alpha_l^o}{\alpha_l^o}\right] \tag{19}$$

The viscous force on the bottom (but not top) and two walls of the rectangular channel is then,

$$f_{visc}^{o} = -\eta\left[\int_{-W/2}^{W/2}\left(\frac{\partial u(y,z)}{\partial z}\right)_{z=0}dy + 2\int_{0}^{H}\left(\frac{\partial u(y,z)}{\partial y}\right)_{y=W/2}dz\right] \tag{20}$$

which gives,

$$f_{visc}^{o} = -\frac{3\eta x u_{ave}^{o}}{\varepsilon\zeta_o(\varepsilon)} \tag{21}$$

In a similar manner to the closed rectangular channel result, eq. (16), this form makes obvious the relationship between flow in an open rectangular channel of arbitrary aspect ratio and the one-dimensional result because in the limit of a shallow and infinitely wide channel, i.e. $W\to\infty$, the aspect ratio function $\zeta_o(\varepsilon)\to 1$. It should be noted that alternative, but equivalent Fourier series solutions for the flow in an open rectangular exist, such as that in Baret et al. (2007) and Yang et al. (2011).

Whilst eq. (14) and eq. (19) are exact, it is useful for fitting to experimental data to have simple interpolation formulae. For channels with aspect ratios in the range ε=0.0 to 2.0, we find suitable interpolations with limits of unity as $\varepsilon\to 0$ are given by,

$$\zeta_c^{-1}(\varepsilon) \approx 1 + 0.362374\varepsilon + 1.020980\varepsilon^2 \tag{22}$$

and

$$\zeta_o^{-1}(\varepsilon) \approx 1 + 0.671004\varepsilon + 4.169711\varepsilon^2 \tag{23}$$

Figure 3 shows the exact summations given by eq. (14) and eq. (19) and the interpolations from eq. (22) and eq. (23). Below aspect ratios of 0.60, the agreement is good to around 3% or better and above this aspect ratio up to ε=2.0 is better than 1% (as shown in the inset of fig 3). A similar approach could also be adopted for flow in other shapes of channels, such as triangular grooves (Ayyaswamy et al, 1974).

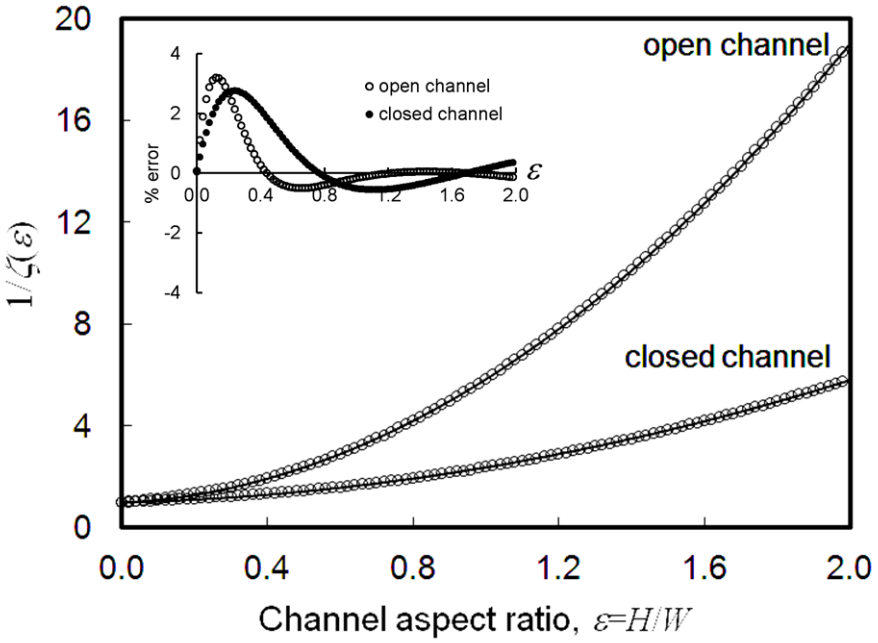

Figure 3.Geometric factors in the viscous force for flow in open and closed rectangular channels with aspect ratio ε=H/W between 0 and 2.0. The symbols are the exact results and the solid lines are the interpolation formulae. The inset shows the corresponding % error between the two.

For completeness, we note the standard expression for viscous force for flow in a circular cross-section tube,

$$f_{visc}^{tube} = -8\eta\pi x u_{ave}^{tube} \tag{24}$$

2.1.5 Defining equation and its assumptions

The equation describing capillary-driven imbibition is given by combining eqs. (1), (2) and (8) with eqs. (16), (21) or (24) as appropriate for the channel or tube and assuming u_{ave}=dx/dt can be used,

$$\frac{1}{2}\frac{d}{dt}\left(\frac{dx^2}{dt}\right) = b - g\sin\varphi\, x - a x\left(\frac{dx}{dt}\right) \tag{25}$$

In this equation, the viscous coefficient a has dimensions of inverse time (s^{-1}) and is defined for the tube, closed rectangular channel and open rectangular channel as,

$$a = \begin{cases} 8\eta/\rho R^2 \\ 12\eta/\rho H^2\zeta_c(\varepsilon) \\ 3\eta/\rho H^2\zeta_o(\varepsilon) \end{cases} \tag{26}$$

and the capillary coefficient term b has dimensions of speed^2 (m^2s^{-2}) and is defined in these three cases as,

$$b = \frac{\gamma_{LV}}{\rho A_c}\left[\sum_i L_i^{SV\to SL}\cos\theta_T^i - \sum_i L_i^{LV}\right] = \begin{cases} 2\gamma_{LV}\cos\theta_e/\rho R \\ \gamma_{LV}\left[\cos\theta_e^B + \cos\theta_e^T + \varepsilon\left(\cos\theta_e^L + \cos\theta_e^R\right)\right]/\rho H \\ \gamma_{LV}\left[\cos\theta_e^B + \cos\theta_e^T + \varepsilon\left(\cos\theta_e^L + \cos\theta_e^R\right)\right]/\rho H \end{cases} \quad (27)$$

For closed channels with smooth surfaces and the same contact angle on all surfaces θ_e, $b = 2\gamma_{LV}\cos\theta_e(1+\varepsilon)/\rho H$. For open rectangular channels, the free surface vapor boundary acts as a perfect hydrophobic surface (i.e $\theta_e^T=180^o$), and if all other contact angles are the same, $b = \gamma_{LV}\left[\cos\theta_e(1+2\varepsilon)-1\right]/\rho H$. The capillary coefficient b (eq. (27)) can thus be written for the three cases as:

$$b = \begin{cases} 2\gamma_{LV}\cos\theta_e/\rho R \\ 2\gamma_{LV}\cos\theta_e(1+\varepsilon)/\rho H \\ \gamma_{LV}\left[\cos\theta_e(1+2\varepsilon)-1\right]/\rho H \end{cases} \quad (28)$$

Equation (25) is well-known in the theory of capillary driven imbibition, but is written here in a form that emphasizes the similarities between circular cross-section tubes, closed and open rectangular channels of arbitrary aspect ratio. Moreover, it allows the key assumptions to be easily identified and their influence on the structure of eq. (25) to be assessed. For example, using the open form for viscous dissipation in an open rectangular channel assumes that momentum can be transferred across the liquid-vapor interface as liquid flows up the tube of liquid to extend itself. However, as indicated by Yang et al. (2011) in their study on the capillary flow in horizontally oriented shallow open rectangular channels (H=19 μm and W=15, 25, 50 and 75 μm) a rigidified liquid-vapor interface can occur due to contaminants or surfactants on the liquid-vapor interface. Their fitting therefore used the viscous parameter a from eq. (26) for a closed rectangular channel with the capillary b parameter from eq. (27) for an open rectangular channel.

The assumptions in the approach in sections 2.1.2 and 2.1.3 taken to derive the capillary terms is that they include a quasi-equilibrium advancing state and this leads to the Young's law equilibrium contact angle, θ_e. Many authors have questioned this and replaced the contact angle by either the advancing contact angle or the velocity dependent dynamic contact angle Hoffman's formula (Siebold et al., 2000; Chebbi, 2007) or molecular-kinetic theory (Hamraoui et al, 2000; Hamraoui and Nylander, 2002; Blake and de Coninck, 2004) or have considered a range of possible dynamic contact angle relationships (e.g. Popescu et al., 2008). It is also possible that a quasi-equilibrium meniscus shape may be achieved, but only after an initial capillary penetration. Even after the initial penetration, a further assumption is that the profile of the liquid meniscus advances in a tube/slab-like manner without change and this we examine further in section 2.3 using wetting concepts commonly used for corner filling problems. Possibly one of the most limiting aspects in complex shape channels is that a given wetting state, such as a Cassie-Baxter, Wenzel or mixed

state arising from minimum surface free energy change considerations, is not known a priori. Moreover, the extent of hysteresis and asymmetric imbibition properties can be linked to complex topographies (e.g. Kusumaatmaja et al., 2008). Thus for capillary filling in channels of complex shapes alternatives to a purely analytical (with numerical solution) approach that have been considered include the Lattice Boltzmann approach (e.g. Kusumaatmaja et al., 2008; Clime et al., 2012), numerical simulation using diffuse interface models (e.g. Mehrabian et al., 2011), smoothed particle hydrodynamics (e.g. Tartakovsky & Meaking, 2005) and molecular-dynamics (e.g. Ahadian et al., 2009; Stukan et al., 2010).

2.2 Exact and approximate solutions

Equation (25) predicts that experiments on capillary-driven imbibition/rise into channels of different cross-sectional shapes and with open and closed surfaces will show the same type of behaviour, but each will have its own length and timescales determined by the appropriate form of the two parameters a and b. Whilst it cannot be solved exactly, approximate solutions can be obtained for the different characteristic length and time scales. Fries and Dreyer (2009) discuss a systematic approach to obtaining dimensionless scaling for the case of a cylindrical tube and porous media using the Buckingham π theorem.

2.2.1 Bousanquet solution for a horizontal capillary

To obtain a dimensionless form of eq. (25) we scale the position and time coordinates as $T=at$ and $X=ax/(2b)^{1/2}$,

$$\left(\frac{\mathrm{d}^2\mathrm{X}^2}{\mathrm{dT}^2}\right)=1-\mathrm{G}\sin\varphi\,\mathrm{X}-\left(\frac{\mathrm{dX}^2}{\mathrm{dT}}\right) \tag{29}$$

where we have defined a dimensionless constant $G=g(2/b)^{1/2}/a$. Using eq. (26) and eq. (28) the tube, closed and open channel cases are,

$$\mathrm{G}=\begin{cases} \sqrt{\dfrac{\mathrm{g}^2\rho^3\mathrm{R}^5}{64\eta^2\gamma_{\mathrm{LV}}\cos\theta_{\mathrm{e}}}} \\ \sqrt{\dfrac{\mathrm{g}^2\rho^3\mathrm{H}^5\zeta_{\mathrm{c}}^2(\varepsilon)}{144\eta^2(1+\varepsilon)\gamma_{\mathrm{LV}}\cos\theta_{\mathrm{e}}}} \\ \sqrt{\dfrac{2\mathrm{g}^2\rho^3\mathrm{H}^5\zeta_{\mathrm{o}}^2(\varepsilon)}{9\eta^2\gamma_{\mathrm{LV}}\left[(1+2\varepsilon)\cos\theta_{\mathrm{e}}-1\right]}} \end{cases} \tag{30}$$

The dimensionless form given in eq. (29) corresponds to the Fries and Dreyer (2009) case 3 where the basic parameter is gravity and the scaling parameters are inertia and viscosity. Our definitions of

X and T are not identical to their scaled variables in the case of a tube, but our controlling parameter G is simply related to their Ω by $G=2^{1/2}/\Omega$. When $G\sin\varphi\rightarrow 0$ so that the capillary is horizontally oriented, the solution to eq. (29) is the Bousanquet solution (1923),

$$X^2(T) = T - \left[1 - \exp(-T)\right] \tag{31}$$

At long timescales when T>>1 (i.e. t>>1/a), eq. (31) gives $X(T)\approx T^{1/2}$ or $x(t)=(2b/a)^{1/2}t^{1/2}$, which is the Lucas-Washburn solution when the viscous term dominates; effectively the first term in eq. (29) can be ignored. At short timescales when T<<1 (i.e. t<<1/a), eq. (31) gives $X(T)\approx T/\sqrt{2}$ or $x(t)=b^{1/2}t$, which is the inertial solution of Quéré (1997) with a linear imbibition with time; effectively the last term in eq. (29) can be ignored.

In fitting experimental data for imbibition into horizontal channels, the full Bousanquet solution (eq. (31)) can be used provided data is captured across both the long and short timescales as determined by 1/a. If data for only short or only long timescales is captured then either the Quéré (Inertial) or Lucas-Washburn (Viscous) solutions should be used.

2.2.2 Viscous solution for a vertical capillary

When T>>1 and the inertial term can be ignored, but gravity cannot be neglected, eq. (29) becomes,

$$0 = 1 - G\sin\varphi\, X - \left(\frac{dX^2}{dT}\right) \tag{32}$$

As shown by Washburn (1921), and discussed by Fries and Deyer (2008b) (see also Mumley et al., 1986 and Krotov and Rusanov, 1999), this has an analytical solution, but for time as function of position rather than for position as a function of time. By rearranging eq. (32) to,

$$\frac{2X}{1 - G\sin\varphi\, X}\left(\frac{dX}{dT}\right) = 1 \tag{33}$$

an exact integration can be performed to get the visco-gravitational solution,

$$T = \frac{-2}{(G\sin\varphi)^2}\left[G\sin\varphi\, X + \log(1 - G\sin\varphi\, X)\right] \tag{34}$$

where X=0 at T=0 has been assumed. When $G\sin\varphi X\rightarrow 0$, the $\log(1-G\sin\varphi X)$ can be expanded and this gives $T\approx X^2$, which is the Lucas-Washburn solution. As $G\sin\varphi X\rightarrow 1$, the logarithm diverges so that $T\rightarrow\infty$ and so at equilibrium the capillary rise height is $X_e=1/(G\sin\varphi)$, i.e. $x_e=b/(g\sin\varphi)$. Fries and Dreyer (2008b) discuss the problems of inverting eq. (34) and also provide an analytic solution in

terms of the Lambert W(x) function defined by w=W(w)exp(W(x)). Eq. (34) can be rewritten in terms of x and t as

$$t = -\frac{ab}{(g\sin\varphi)^2}\left(\frac{x}{x_e} + \ln\left(1-\frac{x}{x_e}\right)\right) \tag{35}$$

In fitting experimental data for imbibition into vertical channels (φ=90^o) the viscous-gravitational solution (eq. (34) or eq. (35)) can be used provided data is captured including both the early Lucas-Washburn stage $T\approx X^2$ and the approach to equilibrium as determined by $x\rightarrow b/g$. The fact eq. (35) is an analytical solution with time as a function of position, which cannot be easily inverted, does not prevent fitting of experimental data since time can be fitted as a function of measured position as easily as position as a function of measured time.

2.2.3 Inertial solution for a vertical capillary

When T>>1 and the viscous term can be ignored, but gravity cannot be neglected, eq. (29) becomes,

$$\left(\frac{d^2X^2}{dT^2}\right) = 1 - G\sin\varphi\, X \tag{36}$$

There is no obvious closed form solution to eq. (36), but a perturbation solution can be constructed for X as a power series in $G\sin\varphi$ (Quéré, 1997). When $G\sin\varphi$=0 the zeroth order solution is $X_o^2(T)=T^2/2$. We then write $X(T)\approx X_o + G\sin\varphi X_1$ and substitute into eq. (36) and keep first order terms in $G\sin\varphi$,

$$\left(\frac{d^2(TX_1)}{dT^2}\right) \approx -\frac{T}{2} \tag{37}$$

This has a solution $X_1(T)=-T^2/12$, which gives a gravity modified inertial solution of,

$$X(T) \approx \frac{T}{\sqrt{2}}\left(1-\frac{\sqrt{2}G\sin\varphi T}{12}\right) \tag{38}$$

or in non-scaled quantities,

$$x(t) \approx \sqrt{bt}\left(1-\frac{g\sin\varphi t}{6\sqrt{b}}\right) \tag{39}$$

Equation (38) can also be inverted to give,

$$T(X) \approx \sqrt{2}X\left(1+\frac{G\sin\varphi\, X}{6}\right) \qquad (40)$$

2.2.4 Cross-over between Bousanquet and visco-gravitational solutions

Equation (29) can be solved numerically for any value of $G\sin\varphi$ using the inertial approximation for the initial boundary conditions $X(0)=0$ and $(dX^2/dT)_{T=0}=0$. Figure 4 shows the behavior of X(T) as a fraction of the equilibrium height, X_e, for G=0.1 and $\varphi=90^o$ together with the, Bousanquet, Lucas-Washburn and inertial approximations. Perhaps surprisingly even at capillary rise heights up to 20% of the equilibrium height both the Lucas-Washburn and the viscous-gravitational approximations show substantial differences from the exact solution. Moreover, this is not significantly improved using the first order gravitational correction to the inertial approximation. Numerically the initial rise height is best described by the Bousanquet solution (eq. (31)) until it crosses over with the visco-gravitational solution (eq. (34)) at around $(T,X/X_e)=(6.5,0.22)$. Above this cross-over the visco-gravitational solution ever more closely agrees with the exact numerical solution as the rise height tends to its equilibrium value; however, it always lies above the exact numerical solution. Since the curve exponentially approaches equilibrium as $(X-X_e)/X_e \sim \exp(-G^2T/2)$, fitting experimental data taken in the long time limit using eq. (34) could force better agreement by overestimating G.

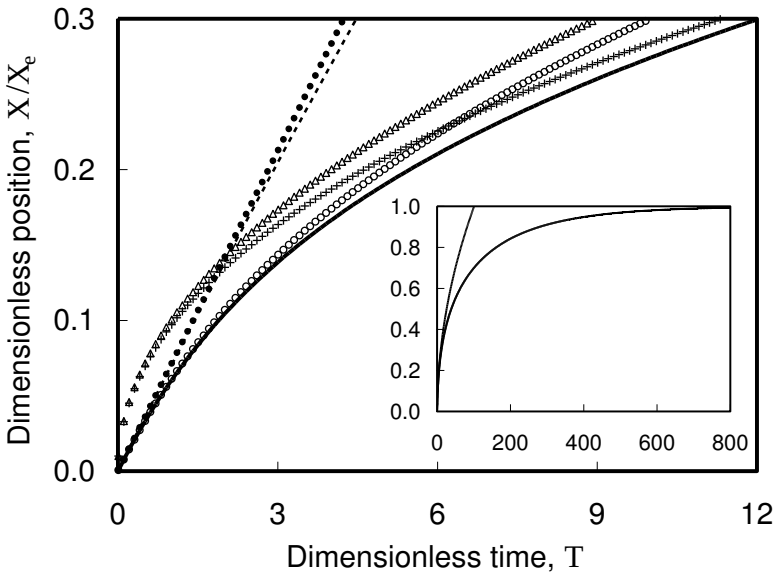

Figure 4. Comparison of approximate analytical solutions for Bousanquet (ooo), visco-gravitational (+++), Lucas-Washburn (ΔΔΔ), inertial (●●●) and inertial with gravity correction (- - -) to the exact numerical solution (solid line) for G=0.1 and $\varphi=90^o$. The capillary rise height X is shown as a fraction of the equilibrium rise height, X_e. The inset shows the long time behaviour for the exact solution and the Bousanquet solution. On this scale the visco-inertial cannot be distinguished from the exact solution and the Lucas-Washburn approximation cannot be distinguished from the Bousanquet solution on the longer time scale.

The derivative dX/dT can be calculated for each of eq. (31) and eq. (34) and this shows that in the Bousanquet case the initial slope of X(T) is $1/\sqrt{2}$ whereas in the visco-gravitational case the initial slope tends to infinity as 1/2X. Since in both cases the slopes are positive at all positive T and in the visco-gravitational case $X \to X_e = 1/(G\sin\varphi)$ whereas in the Bousanquet case $X \to \infty$, there is one and only one cross-over point (T_c, X_c).at which the two curves meet. The cross-over time, T_c, can be calculated numerically as a function of $G\sin\varphi$ by equating the Bousanquet solution (eq. (31)) to the visco-gravitational solution (eq. (34)). For a vertical channel with $\varphi = 90^o$ this is shown in fig. 5 (ooo symbols and left hand y-axis) as a function of $G = 1/X_e$. A numerical interpolation of this function accurate to 3.7% in T_c over the range $G = 1\times10^{-7}$ to 1.0 is given by a 2/3^{rds} power law,

$$T_c(G) \approx \frac{1.341}{G^{2/3}} = 1.341 X_e^{2/3} \qquad (41)$$

The validity of the 2/3^{rds} power law can be shown analytically for small G although the pre-factor in eq. (41) is found to be $(3/2)^{2/3}=1.3104$. Numerically, using 1.3104 is accurate to 4% in the range of G up to 0.1, to 1% in the range of G up to 0.01, and 5.8% in the range of G up to up to 1.32. A best fit interpolation for the numerically calculated rise height at which the crossover, X_c, occurs over the range up to G=0.25 is given by $1.07025/G^{1/3}$; the exact numerical calculation is shown in fig. 5 by the ΔΔΔ symbols (right hand y-axis) and the interpolation is the dotted line. An improved estimate is given by using the interpolation for T_c in the Bousanquet solution (eq. (31)) and this is shown as the solid line passing through the ΔΔΔ symbols.

To derive the 2/3^{rds} power law for T_c we expand the log term in the visco-gravitational approximation (eq. (34)) to 3rd order and regroup terms to get,

$$\frac{X^2}{(T - X^2)^{2/3}} \approx \left(\frac{3}{2G\sin\varphi}\right)^{2/3} \qquad (42)$$

From the Bousanquet solution (eq. (31)), we then note that,

$$\frac{X^2}{(T - X^2)^{2/3}} = T_c\left[\frac{1-(1-e^{-T})/T}{(1-e^{-T})^{2/3}}\right] = Tf(T) \qquad (43)$$

which defines a function f(T). Combining eq. (42) and eq. (43) at $(T, X)=(T_c, X_c)$ then gives,

$$T_c\, f(T_c) \approx \left(\frac{3}{2G\sin\varphi}\right)^{2/3} = \left(\frac{3Xe}{2}\right)^{2/3} \qquad (44)$$

when the cross-over time is large $f(T_c)\rightarrow 1$ and when it is small $f(T_c)\rightarrow 0.5T_c^{1/3}$ so that the power law changes from 2/3 to 1/2 as T_c becomes small. Since large T_c corresponds to small $G\sin\varphi$ (i.e. large X_e) we obtain the numerically observed 2/3rd power law with the pre-factor of $(3/2)^{2/3}= 1.3104$. This also suggests that the fractional crossover rise height for small $G\sin\varphi$ will be,

$$\frac{X_c}{X_e} \approx \left(\frac{3}{2X_e^2}\right)^{1/3} = \frac{1.1447}{X_e^{2/3}} \qquad (45)$$

and this is shown in fig. 5 as the dashed line (referenced to the right hand side y-axis).

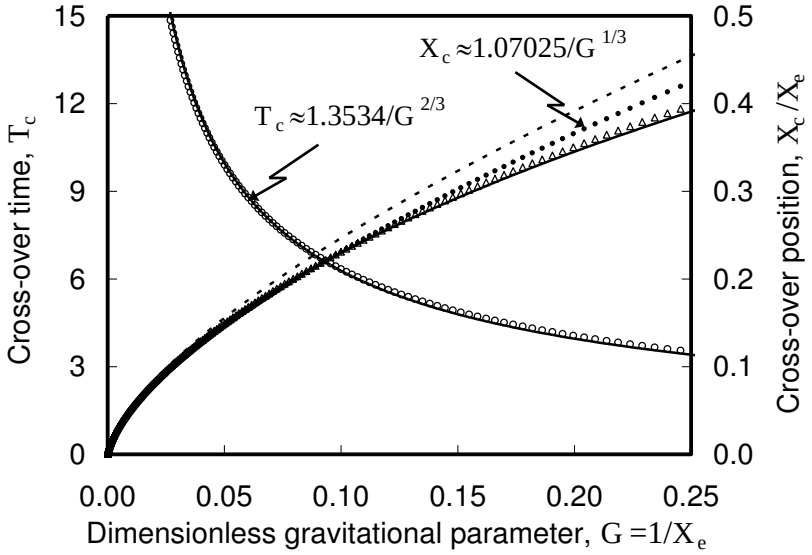

Figure 5. Cross-over time, T_c, at which the visco-inertial solution better approximates the exact numerical solution than the Bousanquet solution (ooo symbols and left hand y-axis); the solid line is the interpolation $T_c \approx 1.3534X_e^{2/3}$ optimized for G up to 0.25 with $\varphi=90^o$ (left hand y-axis). Capillary rise height X_c/X_e at the cross-over calculated numerically ($\Delta\Delta\Delta$ symbols) and an interpolation using $X_c \approx 1.07025/G^{1/3}$ (dotted line). Using the interpolation of T_c in the Bousanquet equation gives an improved estimate of X_c (solid line through $\Delta\Delta\Delta$ symbols); the dashed line shows the analytical approximation $X_c \approx (3/2)^{1/3}X_e^{1/3}$.

The Bousanquet and visco-gravitational solutions can be combined to provide an overall approximate solution by using the former solution when $T<T_c$ and the latter solution when $T>T_c$ (i.e. the solution predicting the lower capillary rise X(T)). This provides a broad time range approximate solution as shown in fig. 6 for G=0.1. Figure 6 also illustrates the percentage error between the exact solution and this approximate solution for a vertical capillary with $\varphi=90^o$, which has a maximum error of 6.7% at T=6.3 when $X_c/X_e=0.216$. For G=0.0283, corresponding to a cross-over at $X_c/X_e=0.1$, the maximum error is 3.2% and for G=0.814, corresponding to a cross-over at $X_c/X_e=0.7$, maximum error is around 17%.

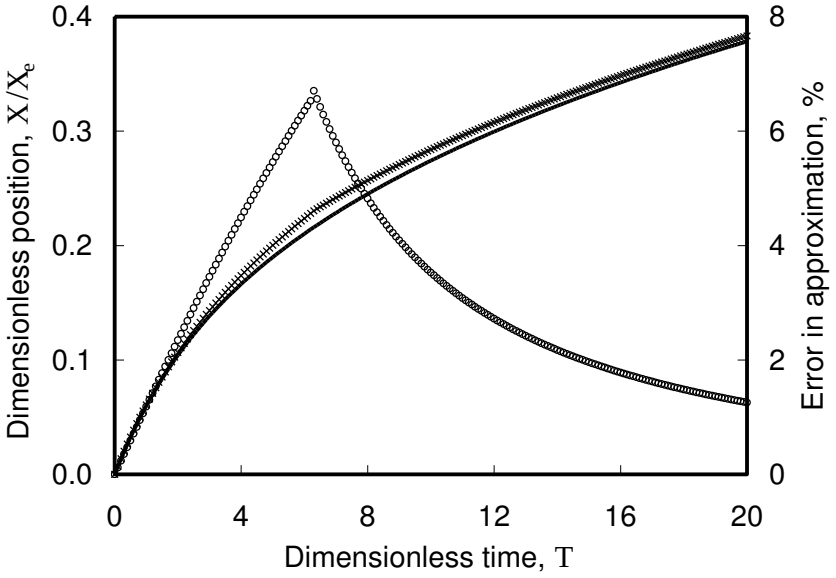

Figure 6 The exact solution for G=0.1 and φ=90^o (solid curve and left hand y-axis) and the approximation obtained using the lower value for X taken from the Bousanquet and the visco-gravitational solutions (xxx and left hand y-axis). The percentage error using the approximation peaks at T_c (ooo and right hand y-axis).

2.3 Filling conditions and capillary fingers

According to the approach in section 2.2, for capillary-driven imbibition to commence it has to be energetically favourable for the liquid to enter the channel, i.e. the surface free energy change in eq. (3) must satisfy $\Delta F<0$, or equivalently the capillary force in eq. (4) must satisfy $f_c>0$ and the b parameter in eq. (27) must be positive. Thus, for an open or closed rectangular channel,

$$\cos\theta_e^B + \cos\theta_e^T + \varepsilon\left(\cos\theta_e^L + \cos\theta_e^R\right) > 0 \qquad (46)$$

For a closed channel with smooth surfaces and the same contact angle on all surfaces this simply means the contact angle must be less than 90^o. However, for an open rectangular channel θ_e^T=180^o and so the condition becomes,

$$\cos\theta_e > \frac{1}{1+2\varepsilon} \qquad (47)$$

as noted by previous authors. Therefore as the aspect ratio of a rectangular channel reduces imbibition becomes increasingly difficult and lower contact angles corresponding to more wetting liquids are required. For example, aspect ratios of ε=10, 0.6, 0.3 and 0.2 require contact angles below 78.5^o, 63.0 ^{o}, 51.3 ^{o} and 44.4 ^{o}. Effectively the capillary pull required is principally from the wall area which becomes relatively less as the width of channel increases.

From an experimental perspective the accuracy of quantitative estimates of the capillary coefficient b parameter in both the inertial (Quéré) and viscous (Lucas-Washburn) regimes from the

initial imbibition data become more difficult for open rectangular channels. In these cases data is typically analyzed using plots of (x,t) and (x^2,t), respectively, and in these cases the slopes, k, will be proportional to $b^{1/2}$ and b. Indeed, examining the exact Bousanquet solution for capillary-driven imbibition, eq. (31), which describes horizontal channels over all times, T, and approximately vertical channels at times $T<T_c$, shows that the contact angle dependence in $x^2(t)$ arises from an overall factor proportional to b. Thus, if we write $x^2(t)=bf(a,t)$ where f(a,t) is a function not involving the contact angle, a plot of $x^2(t)$ versus f(a,t) will have a slope of k=b. The sensitivity of the slope, k, to small changes in the contact angle can be evaluated as a fractional error in the slope on these plots. For the case of closed and open channels with the same contact angle on each surface, the error in the slope for the Lucas-Washburn and Bousanquet plots is,

$$\left|\frac{\delta \mathrm{k}}{\mathrm{k}}\right| \Big/ \delta\theta = \left|\frac{\delta \mathrm{b}}{\mathrm{b}}\right| \Big/ \delta\theta = \begin{cases} \tan\theta_{\mathrm{e}} \\ (2\varepsilon+1)\sin\theta_{\mathrm{e}} \,/\, [(2\varepsilon+1)\cos\theta_{\mathrm{e}} - 1] \end{cases} \qquad (48)$$

As shown by fig. 7, the error given by eq. (48) as a percentage change in slope per degree is large and changes rapidly for contact angles close to the transition to imbibition; a small uncertainty in contact angle results in large changes in the slope and hence estimates of b from experimental data. Experimentally, for open channels there is therefore an incentive to work with liquids that wet the surfaces effectively and therefore have contact angles below that determined by the critical angle for imbibition arising from the aspect ratio. However, this then leads to increasing risks that the assumption that imbibition occurs in a tube like manner with a meniscus of constant profile will not be accurate as discussed below.

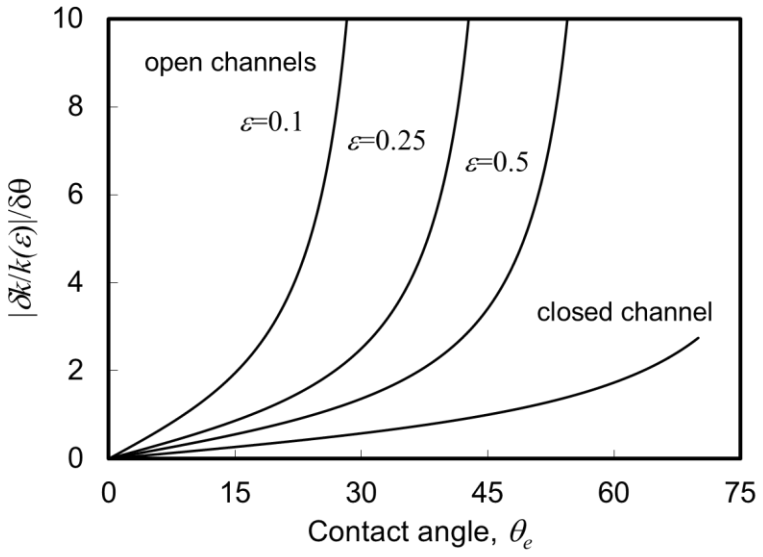

Figure 7 The sensitivity of the fractional change in slope per degree in the Lucas-Washburn equation to small changes in contact angle for closed and open rectangular channels; aspect ratios of ε=0.1, 0.25 and 0.5 are shown.

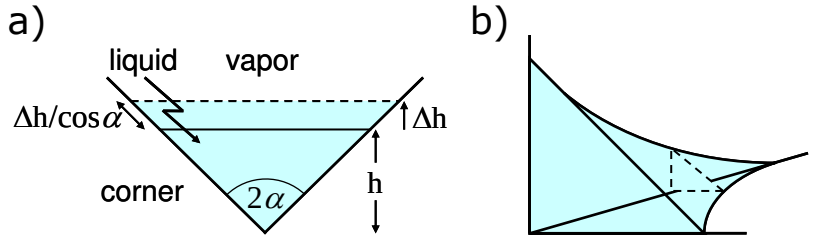

Figure 8. Surface free energy changes as a tube/slab of liquid penetrates into a channel resulting in new solid-liquid and liquid-vapor interfaces. a) Two-dimensional corner viewpoint, and b) an edge viewed as a sequence of two dimensional corners.

Rectangular and many other cross-sectional shape channels differ in their wetting properties from flat and smoothly circular surfaces, precisely because two walls meet at an angle. This effect, the corner filling condition, can be understood by a simple two-dimensional model. Consider two walls joining at an angle 2α with a liquid initially partially filling the corner to a depth h (fig. 8a). When the corner fills with liquid by an additional amount Δh, the surface free energy change is given by,

$$\Delta F = 2\Delta h\left[\frac{(\gamma_{SL}-\gamma_{SV})}{\cos\alpha}+\gamma_{LV}\tan\alpha\right]=\frac{2\Delta h\gamma_{LV}}{\cos\alpha}\left[\sin\alpha-\cos\theta_e\right] \qquad (49)$$

where Young's law has been used to replace the combination of interfacial tensions by $\cos\theta_e$. Thus, the change in surface free energy is zero or negative whenever $\cos\theta_e \geq \sin\alpha$, which gives,

$$(\alpha+\theta_e)\leq 90^o \qquad (50)$$

as the corner filling condition. In the case of a flat surface, $\alpha=90^o$ and a surface wets when the contact angle vanishes, and. in the case of parallel plates, $\alpha=0^o$ and the surface wets between the plates whenever $\theta_e \leq 90^o$. Thus, eq. (46), which is the condition for imbibition assuming a tube of liquid advancing in a channel, must be considered alongside eq. (50).

Whilst this was a two-dimensional argument, an edge can be viewed as a sequence of two-dimensional corners (fig. 8b) and so the same condition, eq. (50), will apply. For example, for the open rectangular channel the side walls meet the bottom surface at 90^o so that the corner filling condition is $\theta_e \leq 45^o$, whereas eq. (47) suggests imbibition will only occur for channel aspect ratios, ε, larger than 0.207. Thus, fingers of liquid can imbibe into open channels at aspect ratios lower than might otherwise be expected. Bico and Quéré (2002) have shown that corner filling leads in square cross-section capillary tubes to fingers of liquid rising along the internal edges against gravity in advance of the central meniscus, which itself rises to an equilibrium height which is a factor $(2+\pi^{1/2})/4$ less than would be the case without the fingers. Moreover, Ponomarenko et al. (2011) have recently used scaling arguments to show that in the viscous regime of capillary rise

against gravity and independent of specifics of the geometry the fingers spread faster than the main meniscus which follows a Lucas-Washburn law.

Thus, for good capillary-driven imbibition in open and closed rectangular channels with reduced sensitivity to the precise value of contact angle, eq. (46) implies it is better to use low contact angle liquids. However, doing so is likely to lead to increasingly stronger effects from liquid fingers spreading along the edges between walls at lower contact angles and higher intrusion rates. From the point of view of microfluidics and lab-on-a-chip, the consequences of this are potentially serious with fingers of liquid spontaneously spreading in advance of the bulk liquid and potentially causing contamination. An interesting question is whether the capillary-drive imbibition/rise in open and closed rectangular channels of the main meniscus can still be accurately described by eq. (31) and (34). The experimental consideration of this is given in section 4.

3. Experimental methods

To test the theory on the influence of capillary shape experiments were conducted on the capillary rise of polydimethylsiloxane (PDMS) oils in three cross-sectional geometries, circular glass capillary tubes, square glass capillary tubes, and SU8 open rectangular cross section channels. The liquid-air interface in open-channels is essentially completely hydrophobic/oleophobic and so a strongly wetting liquid, such as PDMS with its low equilibrium contact angle (θ_e=0) is needed to ensure complete wetting. This choice also eliminates any sensitivity to the precise value of θ_e for liquid penetration into open channels discussed in section 2.3. For each geometry, four PDMS oils (Dow Corning Xiameter PMX-200) of viscosities η=96.0, 48.0, 19.2 and 4.8 mPa s (±5%) and corresponding densities of 960, 950, 930 and 913 kg m^{-3} were investigated. The surface tension of these oils is constant at 19.8 mN m^{-1}. The details of the tubes/channels used are given in table 1.

Table 1. Physical dimensions of channels and experimental parameters.

Channel	Size (μm)	Aspect ratio ($\varepsilon = H/W$)
Circular glass tube	$R = 650$	–
Glass square tube	$H \times W = 600 \times 600$	1
	$H \times W = 400 \times 400$	1
SU8 open rectangular channels	$H \times W = 135^a \times 600^b$	0.225
	$H \times W = 135^a \times 400^b$	0.338

[a] ±5 μm

[b] ±5 μm

The open SU8 channels were fabricated on glass slides using photolithography. After a slide was cleaned, a 20 μm thick SU8 base layer (SU8-10 MicroChem) was spin coated, pre-baked (65ºC for 2 min then at 95ºC for 2 min), UV exposed through a mask, and then post-baked at 65ºC for 30 min. A second SU8 layer (SU8-50 MicroChem), of a nominal thickness of 135 μm, was then spin coated, pre-baked, UV exposed and then post-baked (65 ºC for 30 min then at 95º C for 30 min) to

form the side walls of the channels; this ensured that all three faces of the channels were constructed of SU8. The photoresist was then developed to leave open rectangular channels. The depths of the channels were measured with a stylus profilometer. Variability in the depths of the channels was observed between samples. The data presented in this report are for channels with depths in the range 130-140 μm, and for each channel the measured depth value is used when comparing the data with theory. Commercially available square glass capillary tubes of sides 400 μm and 600 μm were also used in the experiments together with a 650 μm radius circular glass capillary tube for calibration and comparison. SEM characterisations found the internal wall surfaces of the circular and square glass capillaries to be smooth and free from striations.

Each tube/channel was cleaned in isopropylalcohol (IPA) and dried at 100°C for one hour prior to measurements. A small amount of blue dye was used to increase contrast; control experiments without the dye did not show any differences in the dynamics of capillary rise. The sample was mounted vertically next to a rectangular grid which provided a length calibration. PDMS oil from a large reservoir was brought up into contact with the tube/channel very slowly until spontaneous filling started. A high speed camera (NAC Hotshot 512SC) was used to capture videos of the rise of the liquid at 50 frames per second. The videos were analysed after the experiment and the position of the central meniscus measured in ImageJ from the corresponding frames at a set of predetermined time intervals. The initial time t = 0 was defined as the time the liquid first appeared to enter the tube/channel; this was determined to within one frame (i.e. 20 ms). The spatial resolution can be estimated from the field of view of the camera and the pixel resolution and is around 0.02 mm. Each sample/tube was used once only, but measurements were repeated on samples with the same physical dimensions several times and under the same conditions to check for reproducibility.

4. Results and discussions

As discussed in section 2.3, flow in non-circular channels can be expected to be accompanied by advancing liquid fingers that develop with time, increase in prominence and progress ahead of the main meniscus of the liquid. These fingers were visible in the closed square glass tubes (with aspect ratio ε=1) along all four of the internal edges defined by were two walls meet at 90^o. These liquid fingers were very thin and confined to the edges where the walls of the tubes meet making them difficult to clearly image in our experimental set up (fig. 9a). These observations are consistent with those of Girardo et al. (2009) for similar aspect ratio, but in open channels. In contrast, the fingers in our open rectangular SU8 channels with aspect ratios ε=0.225 and 0.338, which propagated along the internal edges defined by where the bottom of the channel and a side wall meet, were very prominent and extended far beyond the main meniscus of the liquid (fig. 9b). They were found to progress much faster than the main front of the liquid, to such an extent as to eventually exit from the end of the channels completely. The dependence of the shape of the fingers on ε is consistent with the measurements of Seemann et al. (2005) of static liquids in open rectangular channels, who found that their shape was determined by contact angle and aspect ratio, and that, for completely wetting liquids (θ_e =0), thick and extended fingers occurred when the

height of channels was sufficiently small compared to their width for ε <0.5, whereas thin fingers, restricted to the corners of the channels, were observed for ε >0.5.

Figure 9. .Micrographs of the shapes of the meniscus of the liquid in rectangular channels/tubes. The arrows show liquid fingers which develop with time and advance ahead of the main meniscus. a) Closed square tubes: fingers are thin and are confined to the four edges where the walls of the tube meet. b) Open rectangular channels with ε=0.225 (also 0.338): fingers are thick and extended and propagate along the internal edges defined by where the bottom of the channel and a side wall meet.

In our experimental conditions, the cross over time for the imbibition of the main body of liquid above which the visco-gravitational solution is a better approximation than the Bousanquet solution (discussed in section 2.2) occurs within the first 25 ms after liquids enter the tubes/channels for all viscosities, which, in all our measurements, takes place within the first measurement time interval. The viscous-gravitational solution is, therefore, the best analytical approximation for our experiments. For each measurement, the variation of the position of the meniscus with time was fitted to both the exact numerical solution (eq. (25)) and analytical solution (eq. (35) with φ=90^o). Both fits were performed within Mathematica® (Wolfram research) using three fitting parameters, a, b and t_0, where the viscous coefficient (a) and capillary coefficient (b) are defined by eq. (26) and eq. (28), respectively. Fitting at the very early stages of imbibition was found to be sensitive to the initial time offset parameter t_0 which was, in practice, found to be less than one to, occasionally, two measurement time intervals. In all fits, a constant contact angle value of θ_e= 0 was assumed, and for the open rectangular channels data analysis was restricted to the part of the experiment during which the wetting fingers remained in the channels.

The solid symbols in fig. 10 show the variation with time (t) of the capillary rise height (x) of the 19.2 mPaS oil in a) 650 µm radius glass tube, b) 400 µm square tube, c) 600 µm square tube, d) 400 µm open microchannel, and e) 600 µm open microchannel. The data show good reproducibility in circular and square tubes. However, some variability between samples (up to 10%) was observed for open channels. The most likely reason for this is the variation in depth of the channels between samples. The solid lines in fig. 10 are the numerical solutions (eq. (25)), whilst the dashed lines are the fits obtained using the approximate visco-gravitational solution (eq. (35)). The data can be fitted accurately (to within 5%) using both solutions, albeit a discrepancy at the very early stage of imbibition (seen in figs 10c, 10d and 10 e). This is, perhaps, not surprising since our analysis assumes a constant contact angle and does not take into account of any dynamic contact

angle changes during the initial entry into the tubes/channels. Moreover, the parameters obtained from fitting using the exact numerical solution and the approximate analytical visco-gravitational solution agree to within 10% for the viscous coefficient a and 3% for the capillary coefficient b. Thus, either the numerical or the visco-gravitational solution can be used to fit the position of the meniscus for our closed tubes and open channels. Moreover, the existence of liquid fingers advancing ahead of the main meniscus of liquid do not seem to prevent the theory from describing the advance of the meniscus for the main body of liquid for values of channel aspect ratio ε considered in our work.

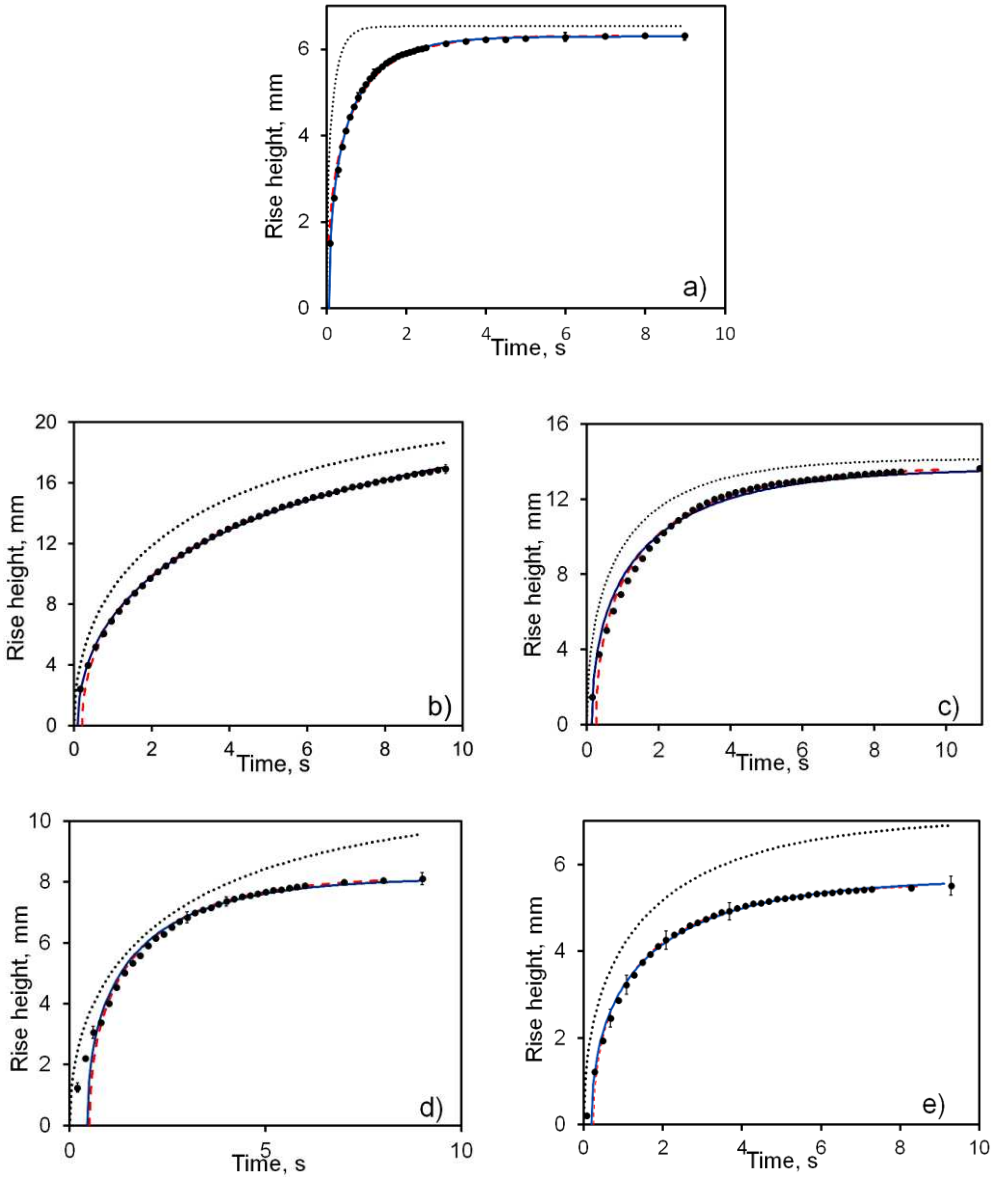

Figure 10. The variation of the rise height with time of the 19.2 mPaS oil in: a) 650 µm radius glass tube, b) 400 µm square tube, c) 600 µm square tube, d) 400 µm open channel and e) 600 µm open channel. The solid symbols represent the experimental data and the solid and dashed lines the numerical and analytical fits respectively. The dotted lines give the expected rise using the nominal device parameters.

In our experiments, we found that the equilibrium capillary rise height was broadly consistent with expectations using the nominal device parameters. The value of the capillary parameter b obtained from the fits agrees very well (to within 2% for circular cross-section tubes) with the experimental observations of the equilibrium height rise x_e ($b=x_e g$). However, the rate at which the liquid approached this equilibrium was always slower than predicted by theory, as is illustrated by the dotted curves in Fig. 10, which represent the expected rise. The value of the viscous coefficient a is larger than predicted by theory for all viscosities and most all tubes and channels except for the 400 μm open channels. We found this parameter to be around 4.2 (±0.2) times larger than the theoretical value for circular tubes and around 1.5 (±0.1) and 1.3 (±0.1) times larger than the theoretical value for 600 μm and 400 μm closed square capillaries, respectively. For the 600 μm and 400 μm wide open channels the fitted values of the viscous coefficient a is around 1.5 (±0.2) and 0.9 (±0.1) times the value predicted from the theory. Preliminary measurements on smaller radius circular cross-section capillary tubes suggests there is a better agreement between fitted and predicted values as the radius reduces to less than a tenth of the capillary length of the liquid. The data for the square tubes and rectangular channels also indicate a better agreement for smaller dimensions with a reasonable agreement for the 400 μm wide open channels.

Retardation of liquid rise in capillaries and tubes has previously been reported by other authors who have suggested a range of possible reasons. These include a possible dynamic contact angle effect during flow (Siebold et al., 2000; Hamdaoui and Nylander; 2002 Chebbi 2007; Xiao et al., 2006; Xue et al 2006), and a possible retardation coefficient arising from an increased frictional dissipation of the moving liquid front (Hamdaoui and Nylander, 2002). A number of different models for how $\cos\theta_e$ in the capillary term b in eq. (28), hence in eq.(25), might be replaced by a dynamic $\cos\theta$ and how that would relate to dissipation were considered in detail by Popescu et al. (2008). They considered four models for a dynamic contact angle including both hydrodynamic (Hoffman, 1975; de Gennes, 1985; Cox, 1986) and molecular-kinetic theory (Blake & Haynes, 1969). In the Hoffman-de Gennes (HdG) approach, the dynamic contact angle, $\theta(t)$, edge speed, dx/dt, relationship is,

$$\left(\frac{dx}{dt}\right) \approx k v^{*} \theta(t)\left(\cos\,\theta_e - \cos\,\theta(t)\right) \qquad (51a)$$

where k is a constant determined by viscous dissipation and $v^*=\gamma_{LV}/\eta$ is characteristic velocity determined by the ratio of surface tension to viscosity. For the linearized form of the molecular-kinetic theory (MKT) model the analogous relationship is,

$$\left(\frac{dx}{dt}\right) = \xi^{-1} v^{*}\left(\cos\theta_e - \cos\,\theta(t)\right) \qquad (51b)$$

where the combination $\xi^{1}v^*$ is a coefficient related to wetting line friction, which depends on both fluid viscosity and solid-liquid interaction (Bertrand et al., 2009; Stukan et al., 2010). If we focus on cylindrical tubes and use $\cos\theta(t)$ from eq. (51a), (51b) in eq. (28) rather than $\cos\theta_e$ to obtain a parameter b_d using the dynamic contact angle, i.e.

(HdG model) $$b \to b_d = 2\gamma_{LV}\cos\theta/\rho R = \frac{2\gamma_{LV}}{\rho R}\left[\cos\theta_e - \frac{1}{kv^*\theta}\left(\frac{dx}{dt}\right)\right] \quad (52a)$$

and

(MKT model) $$b \to b_d = 2\gamma_{LV}\cos\theta/\rho R = \frac{2\gamma_{LV}}{\rho R}\left[\cos\theta_e - \frac{1}{\xi^{-1}v^*}\left(\frac{dx}{dt}\right)\right] \quad (52b)$$

there then arises an additional velocity dependent term. Interestingly, when the dynamic parameter b_d is used in eq. (25) rather than the equilibrium parameter b, the effect can be viewed as retaining the original equilibrium b parameter, but replacing the a parameter by a dynamic a_d parameter,

(HdG model) $$a \to a_d = a\left[1+\left(\frac{R}{4x(t)}\right)\left(\frac{1}{k\theta(t)}\right)\right] \quad (53a)$$

or

(MKT model) $$a \to a_d = a\left[1+\left(\frac{R}{4x(t)}\right)\xi\right] \quad (53b)$$

The additional term in eq. (53a), (53b) is time dependent and vanishes as the imbibition progresses and the dynamic contact angle relaxes to its equilibrium value. This type of term can be expected to cause a slower approach to equilibrium than might be expected from eq. (25) using only a constant contact angle approximated by the equilibrium contact angle. This is consistent with the numerical investigation of Popescu et al. (2008) and with physical expectations that when a vertical tube first comes into contact with the horizontal meniscus of the reservoir the instantaneous contact angle is likely to be 90^o and must relax towards the equilibrium value as imbibition commences. This is also consistent with our preliminary observations that agreement of the fitted a parameter with theoretical expectations improves as the radius of the tube decreases. A similar argument should apply to square capillaries and open channels.

In our case, it is also possible that some of the increased viscous dissipation in the rectangular channels could be induced by the wetting fingers and that their contributions may be dependent on the size and/or aspect ratio ε of the channels. However, Girardo et al. (2012) found that fingers do not seem to induce appreciable extra dissipation in the early stage of microcapillary imbibitions in horizontally mounted smooth microchannels. It is also of note that the fitted values of the viscous coefficient a for the open channels are a factor 2 and 3 lower (for the 400 µm and 600 µm wide open channels) than would be expected for a rigidified liquid-air boundary, as required by Yang et al (2011) to explain the dynamics of capillary flow in their horizontally mounted open narrow microchannels. This indicates that a non-rigidified liquid-air interface best represents the flow in our lower aspect ratio channels. A further detailed quantitative investigation would be needed to clarify the dependence of the viscous coefficient on channel size and aspect ratio on dissipation, but this is beyond the scope of our report.

Whilst the measured equilibrium rise height values are to within 2% of the predicted theoretical value for the circular cross-section tubes, they are around 5% smaller than theoretical predictions for square tubes. We attribute this reduction to the wetting fingers, which are predicted

to reduce the equilibrium height by a value of $(2+\pi^{1/2})/4 = 0.943$ in square geometries (Bico and Quéré, 2002). The equilibrium height is however a factor of 0.83 (±0.03) times smaller than theory for the open channels, although confidence in the exact factor requires some caution since the data has considerable scatter. This is, perhaps, not surprising since the fingers are more prominent, and so may induce a larger reduction in the equilibrium height (Bico and Quéré , 2002).

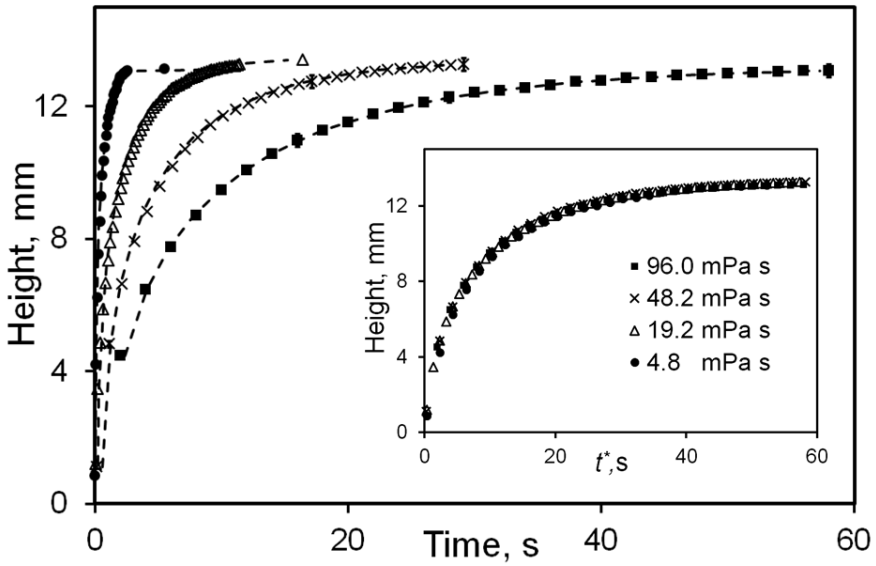

Figure 11. The effect of viscosity on capillary rise for the 600 µm square tube. The dashed lines are the expected rise obtained by taking the fitted value of a for the 96.0 mPa s sample and scaling it according to the ratio of viscosities. The inset shows the data scaled for viscosity. The scaled time t* = 96t/η.

Figure 11 shows the effect of viscosity on the capillary rise in a square tube with sides of 600 µm. As expected, the rise is faster for the lower viscosity oils, but the equilibrium rise height x_e=b/g remains constant as it is independent of viscosity. For the same physical geometry, the visco-gravitational solution predicts that, at a given rise height x, $t \propto ab \propto \eta$ (eq. (35), and eqs. (26) and (28)). It should, therefore, be possible to scale from one viscosity value to another provided the density and surface tension of the liquid are independent of viscosity, which is the case for our liquids to within 5%. To verify this experimentally, the data in fig. 11 are re-plotted with the time for each viscosity data scaled to that of the 96.0 mPa s sample by multiplying it by a factor equal to 96/η (t*= t×96/η); the results are shown in the inset to fig 11. It can be seen that the data scale with viscosity, supporting the above argument. Moreover, this indicates that liquid rise can be predicted for any viscosity value from the experimental data of one given viscosity (taken here to be the 96 mPa s) by scaling the value of a, obtained from the fit to the analytical visco-gravitational solution, according to the ratio of viscosities (dashed lines in fig. 11). Similar results were obtained for 400 µm square tubes (fig. 12a) and round capillaries (fig. 12b). However, our data for the open rectangular channels do not scale as well with viscosity (fig. 12c and fig. 12d). We believe this is due to the variations in the height of channels (130 - 140 (±5) µm) from one sample to another that were difficult to prevent during their fabrication. An improved scaling is obtained (as shown in the

insets of fig. 12c and 12d) if we account for the variations in channel depths between samples at a given channel width as explained in the next paragraph.

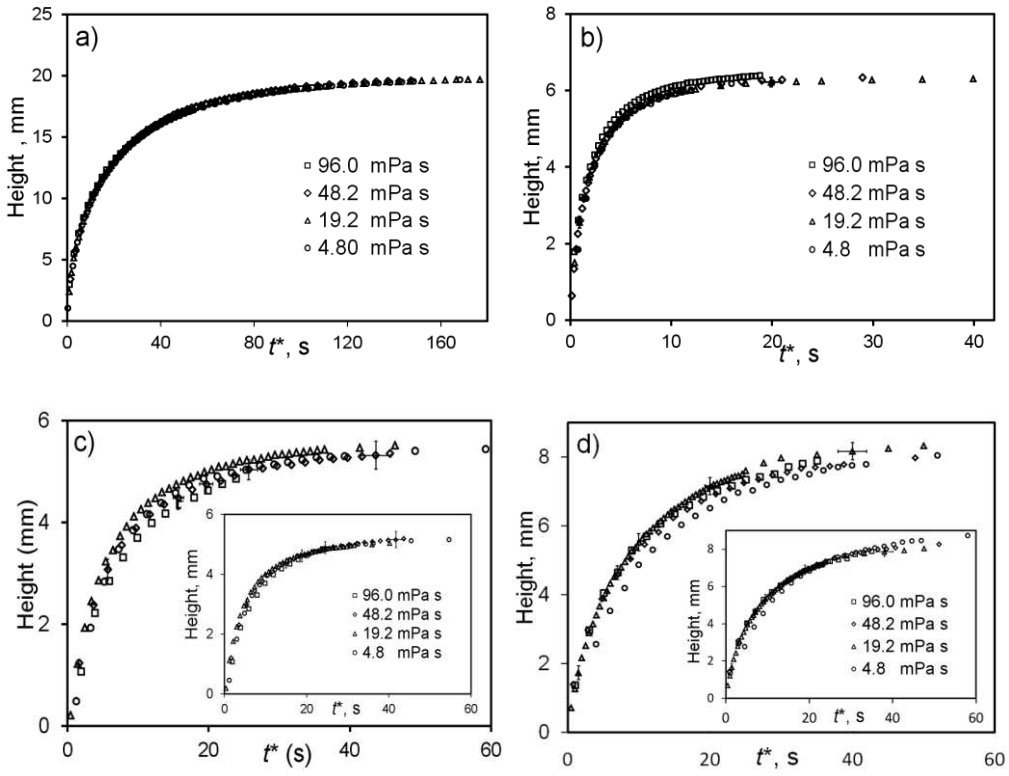

Figure 12. Capillary rise scaled for viscosity in: a) 400 μm square tube, b) R=650 μm circular tube, c) 600 μm open channel and d) 400 μm open channel. The insets to fig 12 c) and fig 12 d) show the data scaled to account for depth variations between samples.

The inset of fig. 13 shows the data from figs 10b and 10c re-plotted to show the effect of the tube dimension on the liquid rise in square tubes (H=W) for the 96 mPa.s oil. As expected the equilibrium rise height $x_{e=}b/g$ scales inversely proportional to H (eq. (28)). For a given x/x_e, the visco-gravitational solution (eq. 35) predicts $t \propto ab \propto \eta/\left(H^3\zeta_c(\varepsilon)\right) \propto \eta H^{-3}$, where $\zeta_c(\varepsilon)= \zeta_c(1)$ is independent of dimension for square tubes. It should, therefore, be possible to scale liquid rise of any sample of dimension H relative to any other given dimension (say 400 μm) both for rise height and time by multiplying x by H/400 and time by $(H/400)^3$. Moreover, time can also be scaled for viscosity in the same way as performed above (fig. 11 and 12a). The results are shown in fig. 13. It is evident that the data cannot be fully scaled for sample dimensions. The reason for this is that theory underestimates viscous dissipation by an amount that is dependent on sample dimension as discussed above. For open channels of varying depths and with θ_e=0, $t \propto ab \propto \eta\varepsilon/\left(H^3\zeta_o(\varepsilon)\right) \propto \eta/\left(WH^2\zeta_o(\varepsilon)\right)$, where $\zeta_o(\varepsilon)$ can be determined using eq. 23. So it should also be possible, in principle, to scale the liquid rise for any sample of known width W, height H (hence ε) and viscosity η relative any other sample with given dimensions and viscosity following the same procedure as for square capillaries. Whilst the data can be scaled for viscosity and small variations in channel depths at fixed channel widths (insets of fig.12c and fig. 12d), it cannot also be

fully scaled for channel width, in the same way as for closed square capillaries, because of the dimension dependent retardation discussed above.

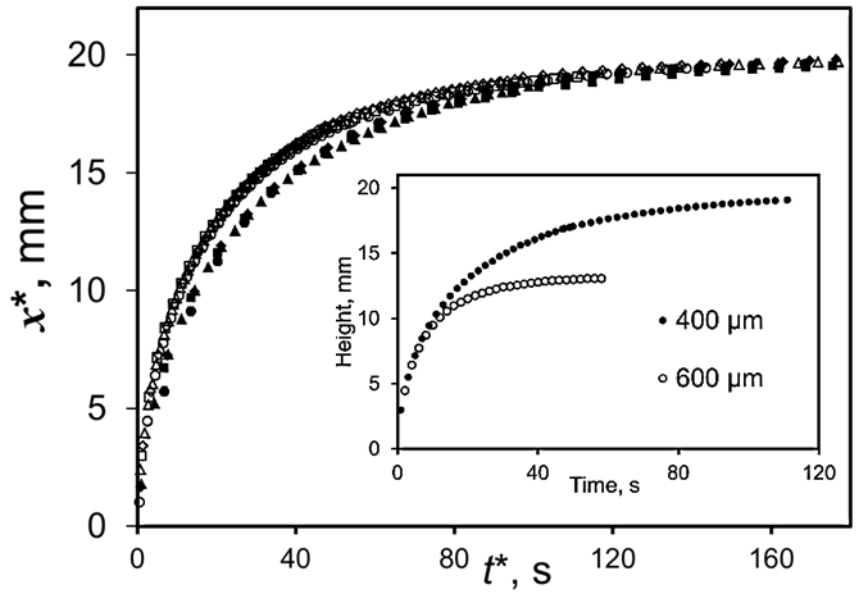

Figure 13. The capillary rise in square tubes scaled for tube dimension and viscosity for 400 μm (empty symbols) and 600 μm (filled symbols). The scaled rise height $x^*=(Hx/400)$ and scaled time $t^*= (H/400)^3 t$. The inset shows the effect of the dimension of square tube on the capillary rise for the 96.0 mPa s oil.

5. Conclusions

In this work, we have presented the theory for capillary driven imbibition into tubes of circular and square cross-sections and into open and closed rectangular channels in a common formalism. The theory can describe tubes and channels at any angle to the horizontal from horizontal to vertical. We have shown that there is a cross-over time and imbibition length below which the exact numerical solution of the equations is best described by the analytical Bousanquet solution and above which by the analytical visco-gravitational solution. We have also highlighted that corner filling wetting ideas lead to the expectation of liquid fingers advancing in square and rectangular tubes and channels in advance of the main meniscus and we have observed this to be the case experimentally. Nonetheless, the theory accurately describes the form of the observed imbibition for capillary rise of PDMS oils in closed square and open rectangular channels of different width cross-sections. We found that the analytical viscous-gravitational solution as an approximation of the exact differential equation for capillary imbibition can be adequately used to fit capillary rise in the systems we studied. From these fits, we found that the viscous friction coefficient is larger than predicted by theory, but that agreement improves for smaller dimension samples, and we attribute this to dynamic contact angle effects. The data indicate that the shapes of the wetting fingers are dependent on the aspect ratio of the samples. For our completely wetting liquids (θ_e=0), the liquid fingers are thin and form near the corner edges for square tubes with aspect ratio ε=1, whereas they are prominent for open channels with low values of ε (0.225, 0.338), in

agreement with observations on static fluids. These fingers may have important implications for the design and performance of microfluidic devices based on liquid imbibition of wetting liquids with contact angles $\theta_e \leq 45°$ in rectangular microchannels. It is possible that they may affect the amount and dynamics of liquid flow, cause contamination between micro-compartments or connect what would otherwise be separate area of liquids.

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