Forced Imbibition - a Tool for Determining Laplace Pressure, Drag Force and Slip Length in Capillary Filling Experiments

D. I. Dimitrov\textsuperscript{1,3}, A. Milchev\textsuperscript{1,2}, and K. Binder\textsuperscript{1}

\textsuperscript{(1)} Institut für Physik, Johannes Gutenberg Universität Mainz, Staudinger Weg 7, 55099 Mainz, Germany
\textsuperscript{(2)} Institute for Chemical Physics, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
\textsuperscript{(3)} University of Food Technologies, 4002 Plovdiv, Bulgaria

When a very thin capillary is inserted into a liquid, the liquid is sucked into it: this imbibition process is controlled by a balance of capillary and drag forces, which are hard to quantify experimentally, in particularly considering flow on the nanoscale. By computer experiments using a generic coarse-grained model, it is shown that an analysis of imbibition forced by a controllable external pressure quantifies relevant physical parameter such as the Laplace pressure, Darcy’s permeability, effective pore radius, effective viscosity, dynamic contact angle and slip length of the fluid flowing into the pore. In determining all these parameters independently, the consistency of our analysis of such forced imbibition processes is demonstrated.

Flowing fluids confined to pores with diameters on the $\mu$m to $nm$ scale are important in many contexts: oil recovery from porous rocks\textsuperscript{(1)}; separation processes in zeolites\textsuperscript{(2)}; nanofluidic devices such as liquids in nanotubes\textsuperscript{(3)}; nanolithography\textsuperscript{(4)}; nanolubrication\textsuperscript{(5)}; fluid transport in living organisms\textsuperscript{(6)} and many other applications\textsuperscript{(1)}. However, despite its importance for so many processes in physics, chemistry, biology and technology, the flow of fluids into (and inside) nanoporous materials often is not well understood: the effect of pore surface structure on the flowing fluid\textsuperscript{(5,7,8)} is difficult to assess, although very beautiful experiments have recently been made (e.g.\textsuperscript{[11,12]}), more information is needed for a complete description of the relevant microfluidic process.

In the present work, we propose to use \textit{forced imbibition} with the external pressure as a convenient control parameter to obtain a much more diverse information on the parameters controlling flow into capillaries than heretofore possible. Extending our recent study of imbibition at zero pressure\textsuperscript{(13)}, we concisely describe the theoretical basis for this new concept, and provide a comprehensive test of the concept in terms of a “computer experiment” on a generic model system (a fluid composed of Lennard-Jones particles flowing into a tube with a perfectly crystalline (almost rigid) wall and spherical cross-section, see Fig.\textsuperscript{1}). We also provide a stringent test of our description by having estimated all parameters of the theory in independent earlier work\textsuperscript{(13)}, and hence there are no adjustable parameters whatsoever. We emphasize that our procedures and analysis could be followed in experiments with real materials fully analogously.

We briefly summarize the pertinent theorem. On a macroscopic scale the rise of a fluid meniscus at height $H(t)$ over the entrance of a capillary with time $t$ is described (at zero external pressure) by the well-known Lucas-Washburn equation\textsuperscript{(14)}

$$H^2(t) = \frac{(\gamma_{LV} R \cos \theta)}{2\eta} t + H_0^2. \quad (1)$$

Here $\gamma_{LV}$ is the liquid-vapour surface tension of the liquid, $\eta$ the shear viscosity of the fluid, $R$ the pore radius, $\theta$ the contact angle, and $H_0$ a constant (which accounts for the fact that Eq.\textsuperscript{14} holds only after some transient time when inertial effects have already vanished). Eq.\textsuperscript{14} follows when one balances the viscous drag force $\frac{8\eta H(t)^2 dH(t)}{dt}$ with the Laplace pressure $P_L = 2\gamma_{LV} \cos(\theta)/R$. 

![Figure 1: A snapshot of the capillary during imbibition](image)
The applicability of Eq. (1) for ultrathin pores has been rather controversial \[16, 17, 18\]. This debate was clarified \[13\] by recalling that on the nanoscale the slip length \(\delta\) \[19, 20\] must not be neglected. According to the definition of this length, the drag force under slip flow conditions in a tube of radius \(R\) and slip length \(\delta\) is equal to the drag force for a no-slip flow in a tube of effective radius \(R + \delta\). Thus one ends up with a modified Lucas-Washburn relationship:

\[
\frac{2\gamma_LV \cos(\theta)}{R} + P_{\text{ext}} = \frac{8\eta}{(R + \delta)^2} H(t) \frac{dH(t)}{dt}. \tag{2}
\]

On the left hand side of Eq. (2) we have now also included an external pressure term \(P_{\text{ext}}\). If one uses Darcy’s permeability \[21\] \(k = (R + \delta)^2/8\), Eq. (2) can be written in a form which does not depend on the capillary radius anymore, introducing also the rate \(v(P_{\text{ext}}) = \frac{dH^2(t)}{dt}\),

\[
P_L + P_{\text{ext}} = \frac{\eta}{k} H(t) \frac{dH(t)}{dt} = \frac{1}{2} v(P_{\text{ext}}) \frac{\eta}{k}. \tag{3}
\]

For constant \(P_{\text{ext}}\), Eq. (3) is easily integrated to

\[
H^2(t) = \frac{2k}{\eta}(P_L + P_{\text{ext}}) t + H_0^2. \tag{4}
\]

Eq. (3) shows that \(v(P_{\text{ext}})\) varies linearly with \(P_{\text{ext}}\), so measuring this relationship yields both parameters \(P_L\) and \(\eta/k\). Instead of using the height \(H(t)\) by observing the meniscus, one may alternatively estimate \(v(P_{\text{ext}})\) from the time variation of the mass of the fluid inside the capillary (i.e. the total number of particles \(N(t) \propto H(t)\) which has entered the capillary up to the time \(t\)). In contrast, the classical experiments on spontaneous imbibition of a fluid, where \(P_{\text{ext}} = 0\), yield only the product \(\kappa P_L\), and hence even if the fluid viscosity \(\eta\) is known, one cannot account the effects due to the driving force \((\propto P_L)\) and due to the drag force \((\propto \kappa)\). Moreover, Eq. (3) suggests the intriguing possibility of applying the present concepts to the most general case of porous media \[1\], irrespective of the particular geometry and topology of the channels in such materials, but this will not be followed up here.

We now present a test of the above concepts by a quantitative analysis of the computer experiment outlined in Fig. 1. We assume also a Lennard-Jones interaction (of strength \(\epsilon_{WL}\) between the wall and the fluid particles (see \[13\] for details on how the wall is atomistically modeled), and study the cases of both nonwettability \((\epsilon_{WL} < 0.65)\) and wettability \((\epsilon_{WL} > 0.65)\) walls. Fig. 2 shows a plot of \(v(P_{\text{ext}})\) vs. \(P_{\text{ext}}\). One can see that there is a broad regime where the variation of \(v(P_{\text{ext}})\) with \(P_{\text{ext}}\) is indeed linear (deviations from linearity for large \(P_{\text{ext}}\) can be attributed to a slight increase of viscosity with increasing fluid density at large pressures). Thus Fig. 2 demonstrates that indeed a rather precise estimation of both \(P_L\) and \(\kappa\) is possible. This is important in many cases, e.g. nanocapillaries or porous media, where neither \(P_L\) nor \(\kappa\) can be reliably predicted theoretically (because information is missing, e.g. the effective channel radius \(R\) or the (dynamic) contact angle \(\theta\) or the slip length \(\delta\) may be unknown).

From the Laplace pressure \(P_L\) one can readily obtain information on the contact angle (if interfacial tension \(\gamma_L\) and pore radius \(R\) are known). Fig. 3 shows the variation of \(P_L\) with \(\epsilon_{WL}\) in our model. By "measuring" the contact angle \(\theta\) dependence on \(\epsilon_{WL}\) in a separate simulation, as well as \(\gamma_L\), we can predict \(P_L\) as \(P_L = 2\gamma_L \cos \theta / R\), as noted above. Fig. 3 shows that the agreement between this prediction and the observations is excellent.

Fig. 4 shows that also the "friction coefficient" of the imbibition (per unit length) \(\eta/2\kappa\) strongly depends on the wettability of the pore wall. The computer experiment has the bonus that it yields insight into the behavior of the system on the nanoscale in arbitrary detail. This is demonstrated by the density profiles of the moving meniscus, shown for \(\epsilon_{WL} = 0.4\) and \(\epsilon_{WL} = 1.2\), respectively. While no layering of the fluid is observed in the case of nonwetting fluids, \(\epsilon_{WL} = 0.4\), for a wettable wall the profile for \(\epsilon_{WL} = 1.2\) indicates significant density oscillations in the vicinity of the wall, i.e. fluid "layering".

Since the shear viscosity \(\eta\) has been determined independently for our system \[13\], \(\eta = 6.34 \pm 0.15\), the ratio
FIG. 3: Plot of the Laplace pressure $P_L$ against the strength $\epsilon_{WL}$ of the wall-liquid interaction. Triangles denote estimates from the meniscus position $H(t)$, squares are derived from the number of particles $N(t)$ that have entered the capillary. Full circles and a dashed line show the theoretical prediction of $P_L = 2\gamma \cos \theta / R$, cf. text. The estimate $\gamma_{LV} = 0.735 \pm 0.015$ was taken from [13].

$\eta/2\kappa$ is readily converted into an estimate for the slip length $\delta$ (Fig. 4b). The gradual decrease of $\delta$ with growing wettability of the wall $\epsilon_{WL}$ is clearly demonstrated.

In conclusion, we have modelled a possible and simple experimental set-up (Fig. 1) by computer simulation and provided a theoretical framework, by slightly extending the Lucas-Washburn approach to include external pressure. As demonstrated, this allows a consistent analysis of resulting data. Such an analysis yields information on the Laplace pressure (if the pore radius is known, the contact angle then can be estimated) as well as the permeability (and hence the slip length). The consistency of our description has been tested by simulations where all these quantities were obtained independently. Thus we have provided a framework which should be a useful guide for both experimental work on capillary filling and further related simulations.

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