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Electroviscous effects in capillary filling of nanochannels

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We theoretically examine the widespread hypothesis of an electroviscous origin of the increase in apparent viscosity observed in recent experiments on capillary filling of nanochannels. Including Debye-layer corrections to the hydraulic resistance, we find that the apparent viscosity reaches a maximum in the mesoscopic regime where the channel height (or more generally the hydraulic radius) is comparable to the screening length. However, for realistic estimates of central parameters, we find that the electroviscous contribution to the apparent viscosity is at most a 1% effect.

Of particular importance is to achieve a more complete understanding of fluid dynamics in the mesoscopic regime, where relevant length scales and phenomena associated with this crossover include the Debye screening length $\lambda_D$ (typically of the order 10 nm), the zeta surface potential $\zeta$ (typically sub-$k_BT$ and of the order meV), and the issue of slip versus no slip on the intermolecular subnanometer length scale $\delta$.\textsuperscript{7}

This mesoscopic regime is typically entered when capillaries with cross-sectional dimensions of approximate 100 nm and below are infilled with buffer solutions with an ionic strength relevant for carrying typical biological samples, e.g., DNA. A typical salinity in micrometers is filled with liquid from an attached reservoir by capillary action. The length of the fluid plug—the position of the liquid meniscus—while still exceeding the molecular length scale, i.e., $\delta<\lambda_D\approx h$. This mesoscopic regime is typically entered when capillaries with cross-sectional dimensions of approximate 100 nm and below are infilled with buffer solutions with an ionic strength relevant for carrying typical biological samples, e.g., DNA. A typical salinity in the millimole range results in $\lambda_D\sim 10$ nm.\textsuperscript{7}

This has motivated several basic nanoscale experimental investigations on the classical problem of capillary filling, see Fig. 1, thus testing the classical Washburn formula,\textsuperscript{8}

$$x^2(t) = \frac{yh \cos \theta}{3\eta} t,$$

which is known to provide a well-established description of the filling dynamics in capillaries with cross-sectional dimensions of millimeter size and down below 1 $\mu$m. Here, $x$ is the length of advancement along the channel of the liquid front, $\gamma$ is the water-air surface tension, $\theta$ is the contact angle, and $\eta$ is the viscosity. The Washburn formula is derived within the framework of the Stokes equation for a charge-neutral liquid where no surface charging and electro-osmotic phenomena occur. Equation (1) implicitly relies on the continuum hypothesis which limits its validity for fluid dynamics at the intermolecular length scale, while it is still expected to work in the mesoscopic regime where physical mean fields remain well defined and continuum formalism applies.

Experimental observations support an unexpected increase in the filling time, beyond the predictions of Eq. (1), in shallow nanoslit devices for slit heights of approximately 100 nm and below.\textsuperscript{9,10} In all reported experiments, a systematic deviation from the behavior predicted by the Washburn formula is observed: Although the observed dynamics maintain the proportionality between $x^2$ and $t$, the constant of proportionality $a$ does not scale linearly with the channel height $h$ for slit channel heights of approximately 100 nm and below.

In the absence of a detailed theoretical model, different possible interpretations have been presented for the unexpected height dependence of $a(h)$. Tas \textit{et al.} speculated that the phenomena is of an electroviscous origin,\textsuperscript{9} while Thamdrup \textit{et al.} showed that in their experiments the phenomena correlate with the formation of air bubbles.\textsuperscript{10} Both interpretations implicitly assume that changes in hydraulic resistance $R_{\text{hyd}}$ play a central role. For this reason, the changes in observed filling time are naturally presented in terms of an increase in apparent viscosity $\eta_{\text{app}}$ entering the Washburn formula.

In this letter we work out the electroviscous correction to the apparent viscosity $\eta_{\text{app}}$ and discuss the result and conse-

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The corrections from a finite zeta potential follow from our recent general linear-response theory of combined mass and charge transport in long straight channels\cite{11,12} with the electrolyte being subject to the application of an external pressure drop $\Delta p$ and voltage drop $\Delta V$ along the channel. These potential drops result in a liquid flow rate $Q$ and an electric current $I$ given by the $2 \times 2$ conductance matrix $G$ as

$$G = \begin{pmatrix}
G_{11} & G_{12} \\
G_{21} & G_{22}
\end{pmatrix},$$

with the matrix being subject to an Onsager relation, $G_{12}=G_{21}$. In the absence of a zeta potential we of course have $G_{12}(\zeta=0)=G_{21}(\zeta=0)=0$ so that Eq. (2) becomes

$$\eta_{\text{app}} = \left[ 1 - \frac{G_{12}G_{21}}{G_{11}G_{22}} \right]^{-1},$$

where we have used that $R_{\text{hyd}}(\zeta) = R_{11}(\zeta)$ with the resistance matrix $R = G^{-1}$ given by the inverted conductance matrix. In applying the result in Eq. (3) to the present problem of capillary filling, we have implicitly utilized that the time scale for charge transfer and charging of the Debye layer is several orders of magnitude smaller than the time scale for moving the meniscus further the distance of one Debye length. This difference in time scales secures that at any instant the charge distribution has reached its equilibrium, and consequently the electric current is zero, $I=0$.

We now proceed by calculating the conductance matrix elements by analytical means. For $h \ll w$ the problem becomes quasi-one-dimensional and within the Debye–Hückel limit it can be solved exactly. In particular, we have

$$G_{11} = \frac{h^2w}{12L\eta},$$

$$G_{12} = G_{21} = -\frac{hw\epsilon\zeta^2}{L\eta\lambda_D^2} \left[ 1 - \frac{2\lambda_D}{h} \tanh \left( \frac{h}{2\lambda_D} \right) \right],$$

$$G_{22} = \frac{hw}{L} \frac{\epsilon\zeta^2}{\eta\lambda_D^2} \frac{1 + \cosh \left( \frac{h}{\lambda_D} \right)}{1 + \cosh \left( \frac{h}{\lambda_D} \right)},$$

where $L$ is the length of the channel, $\sigma=\epsilon D/\lambda_D^2$ is the conductivity of the liquid, $D$ is the diffusion constant of the ions, and $\epsilon$ the dielectric function of the liquid. Long, but tedious manipulations then leads to

$$\eta_{\text{app}} = 1 + 12 \left( \frac{\lambda_D}{h} \right)^4 \frac{\left( \frac{h}{\lambda_D} - 2 + \left( \frac{h}{\lambda_D} + 2 \right) e^{-h/\lambda_D} \right)^2}{1 + e^{-h/\lambda_D}} \chi^2,$$

which is correct to lowest order in the dimensionless parameter

$$\chi = \frac{\epsilon\zeta^2}{\eta\sigma\lambda_D^2} = \frac{\epsilon\zeta^2}{\eta D} = \frac{\mu_{\text{eo}}^2}{\epsilon D}$$

expressing the square of the ratio between the electro-osmotic mobility and the viscous mobility. The latter form of $\chi$ is perhaps most appropriate from an experimental point of view, as the electro-osmotic mobility $\mu_{\text{eo}}=\epsilon\zeta/\eta$ can be determined by measurements easier than the zeta potential $\zeta$ itself.
In Fig. 2 we show the apparent viscosity for increasing values of $\chi$. Most importantly it should be emphasized that the electro-viscous correction is maximal for $h \approx 3.212 \lambda_D$, which is a value that can be found numerically. This is the mesoscopic regime where the Debye screening length $\lambda_D$ becomes comparable to the channel height $h$, while still exceeding the intermolecular length scale $\delta$.

The plot also includes experimental data reproduced from Refs. 9 and 14 for both a 0.1\textit{M} NaCl solution with $\lambda_D \sim 1$ nm (Refs. 9 and 14) as well as for demiwater with $\lambda_D \sim 200$ nm. While the experiments with a NaCl solution belong to the supmesoscopic regime with $h > \lambda_D$ the demiwater experiments are in the opposite submesoscopic limit with $h < \lambda_D$. As seen, the demiwater results are not consistent with the hypothesis of a correction of an electroviscous origin as derived above. We note that this conclusion is quite solid, since the demiwater data would belong to the submesoscopic regime (to the left of the peak) even if we for some reason would allow for a one order of magnitude reduction in the estimate of the screening length, i.e., $\lambda_D \sim 200 \rightarrow 20$ nm. The dashed line shows a fit of Eq. (6) to the NaCl data with $\chi \sim 16$ used as fitting parameter. However, we emphasize that this high value of $\chi$ is completely unrealistic and, in fact, for a zeta potential in the meV range, we find that $\chi \lesssim 10^{-3}$, thus leaving the estimated relative electroviscous correction a sub-1% effect at most.

Nanofluidic capillaries have recently been used in optofluidics and in applications for stretching of DNA molecules. The majority of these experiments employ nanochannels with roughly a square cross section. The above quasi-one-dimensional results may be generalized to more arbitrary two-dimensional (2D) channel cross sections with an aspect ratio of order unity. Following Ref. 12 we straightforwardly arrive at the approximate result,

$$\frac{\eta_{\text{app}}}{\eta} \approx 1 + \frac{8I_n^2}{\alpha^2} \left( \frac{R}{\lambda_D} \right)^2 \lambda_D \chi^2,$$  \hspace{1cm} (8)

where $I_n$ is the modified Bessel function of the first kind of order $n$ and $R = 2A/P$ is the hydraulic radius with $A$ being the cross-sectional area and $P$ being the length of the perimeter. For a circular cross section with radius $a$ we have $R = a$ and Eq. (8) is exact in the limit of a small $\chi$. Likewise, for a square channel with side length $a$ we get $R = a/2$. Equation (8) gives rise to the same qualitative dependence on $R/\lambda_D$ as in Fig. 2 and our above estimates and conclusions remain unchanged for nanochannels with a true 2D electrohydrodynamic flow profile.

While we are confident that the electroviscous effect would reveal itself in a clean experiment (i.e., in the absence of other competing effects) with a true nanoscale slit ($h \sim 3\lambda_D$), the strength of the effect is far too weak to account for the experimental observations. This strongly supports the existence of other dominating effects, as also observed in recent studies where the apparent viscosity was found to correlate with the presence of air bubbles which tend to increase the hydraulic resistance. In conclusion, our calculation of the Debye-layer correction shows that for realistic estimates of central parameters, the electroviscous contribution to the apparent viscosity is below a 1% level.

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