Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information for manuscript titled*: "Electro-Capillary effects in Capillary Filling Dynamics of Electrorheological Fluids"*

The purpose of this supplementary material is to provide further discussions on two key concepts associated with the original manuscript. First we derive the modeling of the viscous forces and second we derive the electro-capillary effects on the variation of the static contact angle.

1. Derivation of the lumped parameter equations and viscous forces

We assume a developed pressure driven axial flow model for a general non-Newtonian fluid governed by the Cauchy's Equation of motion

$$0=-\frac{dp}{dx}+\frac{d\tau_{xy}}{dy} \tag{1}$$

Employing the constitutive model of the Bingham fluid is given, as shown in equation 2 (of the original manuscript), and integrating with vanishing stress condition at the centerline and no-slip condition at the channel walls, we have

$$u=-\frac{1}{2\mu}\frac{dp}{dx}\left(H^2-y^2\right)-\frac{\tau_0}{\mu}\left(H-y\right) \tag{2}$$

Now we proceed to obtain the average velocity of the flow profile using the form $\overline{u}=\frac{2\left(\int_0^{y_1}u_1dy+\int_{y_1}^{H}udy\right)}{2H}$, which reads $\overline{u}=-\frac{dp}{dx}\frac{\left(H^3-y_1^3\right)}{3H\mu}-\tau_0\frac{\left(H^2-y_1^2\right)}{2H\mu}$, where y_1 represents the distance from the channel where the plug zone starts to develop. The condition for y_1 can be found by equating the local shear stress with the yield stress, giving the form $y_1=\tau_0\Big/-\frac{dp}{dx}$. Replacing the value of $-\frac{dp}{dx}$ from the average velocity expression, we finally obtain $\left(3y_1H^2-y_1^3-2H^3\right)\tau_0+6y_1\overline{u}\mu H=0$.

The viscous forces on both the wall can be accounted for from the evaluation of the shear stress at the wall using the form $2\left|\left(\tau_{xy}\big|_{y=H}\right)\right|bx$. This can easily be recast into the form of force (using equation A1) as $F_{visc}=2\left|\left(\tau_{xy}\big|_{y=H}\right)\right|bx=-2Hbx\frac{dp}{dx}=3bHx\left(\frac{\tau_0\left(H^2-y_1^2\right)+2\overline{u}\mu H}{H^3-y_1^3}\right)$.

Now we appeal to the basic formulation of the lumped parameter approach, wherein we replace the average velocity by the rate of capillary front advancement, i.e. $\bar{u} = dx/dt$. With this substitution and using the parameter $\bar{y} = y/H$ in order to obtain a dimensionless form, we recover the criteria for plug zone span as given in equation 14 (of the original manuscript) and the viscous force as $\bar{F}_{visc} = \frac{3}{2}\xi\frac{\left(1-\bar{y}_1^2\right)}{\left(1-\bar{y}_1^3\right)}\bar{x} + \frac{3\mathrm{Ca}}{\left(1-\bar{y}_1^3\right)}\bar{x}\left(\frac{d\bar{x}}{d\bar{t}}\right)$.

2. Derivation of the Electro-capillary effects on the contact angle

It is known from a number of previous experimental studies [1] that a column of liquid rises against gravity when a voltage is applied between two parallel electrodes. For a narrow electrode gap, the field practically remains constant. The electric body force acting on the liquid, also known as Korteweg-Helmholtz body force density, is given by [2,3]:

$$f = \rho_f E - \frac{1}{2}E^2\nabla\varepsilon + \nabla\left[\frac{1}{2}E^2\frac{\partial\varepsilon}{\partial\rho}\rho\right] \tag{3}$$

The first term, with ρ_f as the free charge density, has no effect on the net force since we consider the absence of any free charge. The third term, signifying the electrostiction force, becomes negligible since we consider an incompressible fluid, with density ρ. Thus, the above equation predicts a force at the free surface of the liquid between the electrodes, given by $-\frac{1}{2}\nabla\varepsilon E^2$. This force, which can be expressed as $P\cdot\nabla E$, can be attributed to the dipole force acting on the polarized molecules of the liquid due to the fringing of the electric field. Here P is the density of polarization, which is only nonzero when the electric field is non-uniform (which can exist at the liquid-air interface). Now, the height of rise may be determined either by the lumped parameter electromechanics or Maxwell stress tensor. This height, in absence of the surface tension force, for a conductive fluid with a dielectric coating of thickness d and dielectric constant ε_d and channel width of D, comes out to be [3]:

$$h'' = \frac{\varepsilon_d\varepsilon_0 V^2}{4\rho g d D} \tag{4}$$

where V is the total applied voltage. The similar height of rise for the case of a dielectric fluid, of dielectric constant ε_1, confined in the parallel channel of width D and electrodes coated with a dielectric layer of thickness d and dielectric constant ε_d, comes out to be [3]:

$$h'' = \frac{\varepsilon_0 V^2}{2\rho g D\left[2d/\varepsilon_d + D/\varepsilon_1\right]} \tag{5}$$

However, for narrow confinements, one cannot neglect the capillary rise due to surface tension. The expression for this rise reads [3,4]:

$$h' = \frac{2\sigma\cos(\theta_0)}{\rho g D} \tag{6}$$

where θ_0 is the contact angle in absence of the electric field and $\sigma = \sigma_{lv}$ is the surface tension at the liquid-vapour interface. Therefore, the total height becomes:

$$h = h' + h'' = h' = \frac{2\sigma\cos(\theta_E)}{\rho g D} \tag{7}$$

where θ_E is the altered contact angle in presence of the electric field given by $\cos(\theta_E) = \cos(\theta_0) + \frac{\varepsilon_d \varepsilon_0 V^2}{8d\sigma}$. This resembles the Young-Lippmann form of the equation that has been considered in our derivation. Similarly, for the case of dielectrics the Young-Lippmann equations reforms to $\cos(\theta_E) = \cos(\theta_0) + \frac{\varepsilon_0 V^2}{4\sigma[2d/\varepsilon_d + D/\varepsilon_1]}$. Since, we have disregarded the existence of any dielectric layer (which can be thought of as a tiny polarization charge at the electrode due to negligible conductivity of the purely dielectric medium), the form of equation with the assumption of fitting parameter comes out to be

$$\cos\theta = \cos\theta_0 + \frac{\varepsilon H E^2}{w\sigma} \tag{8}$$

where $d = H$ for our study, is the width of the gap between the parallel electrodes. The electric field is $E = V/H$ and w is the fitting parameter used throughout our study. The above expressions can also be derived from the Maxwell stress tensor, as previously derived in the work of Jones [3].

References

1 H. Pellat, *Comptes Rendus l'Académie des Sci.*, 1895, **119**, 691–694.

2 L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media*, Pergamon, Oxford, 1980.

3 T. B. Jones, *Langmuir*, 2002, **18**, 4437–4443.

4 E. W. Washburn, *Phys. Rev.*, 1921, **17**, 273–283.