Liquid-liquid capillary rise

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Abstract. We study the dynamics of capillary rise of a liquid-liquid interface using two immiscible liquids. By adjusting the height of the less dense fluid column, we measure the rise of the ensemble in the tube. A theoretical model is proposed that captures the time dependence of the position of the interface. Particular attention is given to the dynamics of the oil-water interface. Different types of flow regimes are identified and compared with previous theoretical and experimental findings. The theoretical model was found to be in good qualitative agreement, even though the contact angles of the two interfaces do not remain constant during the elevation of the fluid.

1. Introduction

When a capillary tube is put in contact with a liquid, a column is seen rising inside of it. This is known as capillary rise and it is due to capillary forces, which become dominant when length scales are smaller than the capillary length. Capillary action has many applications in biotechnology, biology and medicine [1-3], immunocytochemistry [4] and heat transfer [5]. It can also be found in nature, certain small sized birds relying on capillarity in order to drink [6]. The phenomenon has received a lot of attention, several papers investigate the dynamics of different liquids [7], the effect of surfactant solutions [8], the effect of geometry or coating of the capillary tube [9, 10, 11]. The dynamics of the rising column is generally described by the following model

\[
\pi D \cos \theta - mg = \rho \pi D^2 / 8 \left( dz / dt \right)^2 - \tau_{visc} \pi D z = \left( m + m' \right) dz / dt^2
\]

(1)

where \( \pi D \cos \theta \) is the capillary force, \( mg \) is the gravitational force, \( \rho \pi D^2 / 8 \left( dz / dt \right)^2 \) is the force due to dynamic pressure and \( \pi D \tau_{visc} \) is the viscous force [12]. As the liquid column rises, it undergoes several regimes: gravitational, inertial and viscous, the latter being split into early viscous and late viscous.

The dynamics of the capillary rise of a low viscosity liquid, undergoing purely inertial flow, or of a very high viscosity liquid, undergoing purely viscous flow, as well as the transitions between them have been the subject of several past papers [13, 14]. After going through these different regimes, the column reaches an equilibrium height, which is prescribed by Jurin's law.

In this paper, we study and visualize the capillary rise of one viscous liquid, but also of two immiscible liquids, by adding into the tube another less dense liquid. A theoretical model is proposed in order to capture and describe the capillary rise of the ensemble.
2. Experimental details

The experimental setup is composed of a glass capillary tube, having an inner diameter of $D = 1.1$ mm and a glass tank. First, the experiments are performed using only one liquid, by putting in contact the empty capillary tube with the sunflower-seed oil, which was kept in the glass tank. The sunflower-seed oil has the following material properties: density $\rho = 920$ kg/m$^3$, viscosity $\eta = 55$ mPa·s and surface tension $\sigma = 0.032$ N/m. The contact angle of the oil-air ensemble was found to be approximately $68.5^\circ$. The dynamics of the oil-air interface is depicted in figure 1. A high-speed camera is used to capture the phenomenon, a Photron FASTCAM Mini UX100 high-speed camera at a working frame rate of 1000 fps.

![Figure 1. Capillary rise of an oil-air interface showing the inner diameter of the capillary tube and the flow direction.](image)

The experiments are then performed with two working liquids, the glass tank containing the heavy liquid. The less dense liquid (sunflower-seed oil) was placed in the tube using the same method as before, by adjusting the contact time with the liquid bath of oil. The heavy liquid in all experiments is water, of density $\rho = 1000$ kg/m$^3$, viscosity $\eta = 1$ mPa·s and surface tension $\sigma = 0.072$ N/m. The capillary tube holding the column of sunflower-seed oil is then put in contact with the water, as depicted in figure 2. The phenomenon was recorded with the use of the high-speed camera and the data was analysed with an in-house routine implemented in MATLAB that allowed us to measure the position of the meniscus in the capillary tube. The interfacial tension between oil and water was found to be $\sigma = 0.025$ N/m and the contact angle between the two is approximately $72.5^\circ$.

The material properties of the working liquids are determined by means of standard methods. By weighting a known volume of liquid, we obtained the density with a simple mass-per-volume method. The viscosity was measured using a rotational rheometer, Anton Paar Physica, using a cone-plate geometry. To determine the surface tension, respectively the interfacial tension, we adopted the pendant drop method, which is based on assessing the shape factor of the droplet by measuring two diameters within the drop.

![Figure 2. Schematic representation of the experimental setup and relevant parameters of the working liquid-liquid system.](image)
3. Results and discussion

We analysed the situation of only one working liquid, it being the sunflower-seed oil, having a viscosity 55 times larger than pure water. The first two regimes, the inertial and gravitational regime, have a very small characteristic time scale, thus they cannot be observed. In this case, the theoretical model is adapted for the viscous regime as following

\[ 2\sigma_1 R \cos \theta - 8\eta_1 \cdot \frac{dz}{dt} - \rho g R^2 z = 0 \]

where \( R \) is the radius of the tube, \( \theta \) is the contact angle, \( z \) is the height of the column, which is a function of time \( t \). The theoretical and experimental findings are then compared. A comparison between the two is shown in figure 3. It can be observed that the prediction and the experimental data settle at the same equilibrium height. Theoretical model also predicts a higher velocity of elevation for the liquid column. The experimental results show that the column of liquid rises slower than the prediction especially in the beginning, the relative difference becoming smaller as the column reaches equilibrium. The distinction between the two is due to the time variation of the contact angle, a feature not included in the model.

For the two working liquids, water and sunflower-seed oil, we extended the Lucas-Washburn-Rideal equation [15]. Due to the high viscosity of the oil phase, we can consider the flow to be described by the pure viscous regime, as the other regimes take too little time to be observed. It takes approximately 20 ms for viscous effects to diffuse across the capillary tube and to initiate a Hagen-Poiseuille flow. Therefore, the model becomes:

\[ 4\left( \sigma_{12} \cos \theta_2 + \sigma_z \cos \theta_z \right) + \rho g h_0 D - \left( z \rho + \rho z \eta_2 H \right) gD - 4\left( z \eta_1 + \eta_2 H \right) \frac{dz}{dt} = 0 \]

where \( D \) is the diameter of the capillary tube, \( h_0 \) is the level to which the tube is immersed in the glass tank and \( H \) is the established height of the column of sunflower-seed oil. The capillary tube was immersed in the water tank by \( h_0 = 5 \) mm. Using the same MATLAB routine, we measured the meniscus rise of the oil-water ensemble.

The comparison between the prediction and experiment, as well as the flow regimes, is presented in figure 3-b. The dissimilarity between the theoretical model and the experimental data is caused by the variation in time of the contact angle, which the prediction does not take into consideration. Despite this limitation, theoretical predictions and experimental data are in good qualitative agreement.

The interface between the two immiscible liquids shows the change in contact angle as the column rises (see figure 3-b). This can be clearly seen in the start-up flow regime, immediately after the capillary

![Figure 3](image_url)

**Figure 3.** a) Height of the liquid column as a function of time; experimental data vs. theoretical predictions given by equation (2) for sunflower-seed oil. Several snapshots of columnary rise are also showed. b) Height of the liquid column as a function of time for a two-liquid system. Theoretical predictions are given by equation (3).
touches the liquid bath. The interface between these two immiscible liquids becomes concave, but as the column advances it changes curvature. The concave shape of the meniscus will maintain during the early viscous regime. At the equilibrium, the meniscus settles to a convex shape. We expect the transition from the early viscous to the late viscous regime to take place when the water-oil meniscus changes curvature.

The shape of the meniscus at start-up flow can be seen in figure 4. At early times, the shape of the interface does not change dramatically as shown in figure 4-d. The interface advances, as the heavier liquid is invading the capillary tube, taking the shape of a spherical cap. Immediately after the capillary touches the liquid bath, the interface curves abruptly and it appears to deviate from the shape of a spherical cap. We would like to assess the pressure difference causing this alleged difference in shape. Since the time taken for viscous effects to diffuse from the wall is approximately 20 ms, Poiseuille flow settles immediately. If one reduces the problem to a planar geometry and Poiseuille flow for both liquids, the normal stress balance at the interface will be given by

\[ -p_1 + 2\eta_1 \frac{\partial V_1}{\partial r} + p_2 - 2\eta_2 \frac{\partial V_2}{\partial r} = \sigma_{12} \text{div} \mathbf{n} \]  \hspace{1cm} (4)

Figure 4. a) Parabolic fit (eqn. 5) of the water-oil interface at start-up. The fitting parameter is the pressure jump at the interface \( \Delta p \); b) Columnary rise near start-up showing the concave shape of the water-oil interface. c) Parabolic fit (continuous line) vs. spherical cap fit (broken line) of the water-oil interface at start-up; d) Shape of the interface for several moments in time near start-up.

where \( \mathbf{n} \) is the unit normal. After linearization one obtains a second order differential equation for the shape of the interface having the following solution

\[ z(r) = \frac{\Delta p}{2\sigma_{12}} \left( R_0^2 - r^2 \right) \]  \hspace{1cm} (5)

The fit of data present in figure 4-a, shows a pressure difference of \( \Delta p = 95.5 \) Pa. The model has a major limitation since we have neglected the second principal radius of curvature by using the planar approximation. Due to the complicated interaction near the wall, it is difficult to approximate the shape of the interface with a spherical cap (see figure 4-c). We find the parabolic approximation more suitable at start-up, only to provide a qualitative measure of the pressure jump.
4. Conclusions
This paper investigates the capillary rise of two immiscible liquids. By using a liquid 55 times more viscous than water, the column inside the capillary tube goes through an almost pure viscous regime. The inertial start-up regime has a small characteristic time scale, since viscous effects take very little time to diffuse across the capillary tube and to establish a Hagen-Poiseuille flow.

Theoretical models of capillary rise seldom consider the time variation of the contact angle. Despite this limitation, such models are found to be in good qualitative agreement, especially when considering the equilibrium height. The water-oil interface shows a curvature change, starting with a concave shape at start-up and then settling to a convex surface when approaching equilibrium.

At start-up, due to the complex interaction between the wall and the liquid-liquid interface, the concave interface is better fitted by a parabolic approximation rather than by a spherical cap, which can be used later, as the column advances. Only a convex shape was found for the oil-air interface during the rise of the liquid column.

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References
[1] Sauer-Budge, A. F., Brookfield, S. J., Janzen, R., McGraw, S., Boardman, A., Wirz, H., & Pollock, N. R., PloS one, 12(8) (2017)
[2] Berthier, J., Brakke, K. A., Furlani, E. P., Karampelas, I. H., Poher, V., Gosselin, D., ... & Pouteau, P., Sens. Actuat. B: Chem, 206 (2015).
[3] Roelofs, K. G., Wang, J., Sintim, H. O., & Lee, V. T. PNAS, 108(37) (2011).
[4] Brigati, D. J., Budgeon, L. R., Unger, E. R., Koebler, D., Cuomo, C., Kennedy, T., & Perdomo, J. M., J. Histotechnol, 11(3) (1988).
[5] Weibel, J. A., & Garimella, S. V., Adv. Heat Transf. 45 (2013).
[6] Kim, W., & Bush, J. W., J. Fluid Mech., 705 (2012).
[7] Walls, P. L., Dequidt, G., & Bird, J. C., Langmuir, 32(13) (2016).
[8] Zhmud, B. V., Tiber, F., & Hallstensson, K., J. Colloid, 228(2) (2000).
[9] Wu, P., Zhang, H., Nikolov, A., & Wasan, D., J. Colloid, 461 (2016).
[10] Lim, H., Tripathi, A., & Lee, J., Langmuir, 30(31) (2014).
[11] Stange, M., Dreyer, M. E., & Rath, H. J., Phys. Fluids, 15(9) (2003).
[12] Wu, P., Nikolov, A. D., & Wasan, D. T., Langmuir, 33(32) (2017).
[13] Quéré, D., EPL, 39(5) (1997).
[14] Fries, N., & Dreyer, M., J. Colloid, 327(1) (2008).
[15] Wu, P., Nikolov, A. D., & Wasan, D. T., Langmuir, 33(32) (2017).