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Forces, pressures and energies associated with liquid rising in nonuniform capillary tubes

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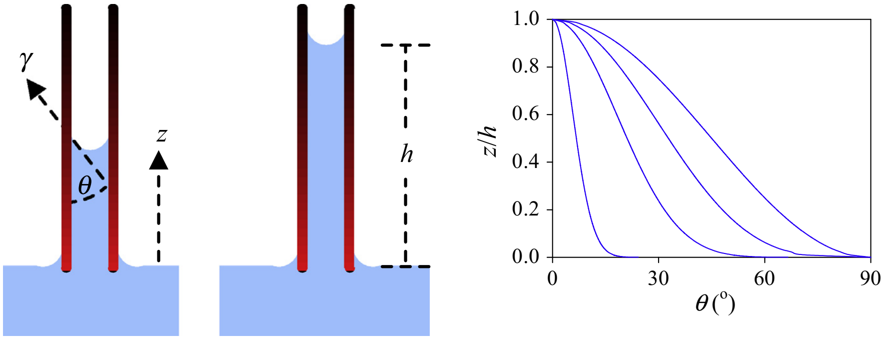
GRAPHICAL ABSTRACT



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ABSTRACT

In this theoretical study, the forces, pressures, energies and kinetics for liquid rising in three types of capillary tubes were analyzed: one type was chemically homogeneous and the other two were nonuniform with chemical gradients. The tubes with chemical gradients were "designed" such that the liquid would still rise and attain the same ultimate height as an equivalent homogenous tube, but as shown here, the energies and kinetics of these inhomogeneous tubes are anticipated to be quite different from their homogeneous counterpart.

1. Introduction

Some of the biggest names in modern science have studied and contributed to our understanding of capillary rise: da Vinci, Boyle, Newton, Young, Laplace, Gauss, Maxwell and Einstein, to name a few [1]. The earliest investigators attempted to elucidate the seemingly spontaneous rise of liquids in small diameter tubes [1a,2], but also, more broadly, the character and range of molecule interactions [1a,1e]. These pioneering studies were often framed in terms of forces and pressures. Analyses of energies [3] and kinetics [4] came later.

More recently investigators have considered capillary rise or imbibition in the absence of gravity [5], in tilted tubes [6], in non-circular tubes [7], in tapered tubes [8], in rough tubes [5b], in tubes where inertia dominates [4d,9], in tubes where the contact angle [5b,10] or viscosity [11] depends on rise velocity, in tubes with surfactants solutions [12], as well as in various types of porous media [13].

With all that has been done, there still are unanswered questions. For instance, how would the capillary rise differ if the tube were chemically heterogeneous? There are undoubtedly many

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scenarios that could be considered. One could imagine inhomogeneities inside a tube that would completely impede the rise of liquid. On the other hand, if certain types of nonuniformities allowed liquid to rise, would liquid reach the same height as in an otherwise equivalent homogeneous tube? How would forces, pressures, energies and kinetics be affected?

These questions are not solely of academic interest. A wide variety of industrial products, such as filters, purifiers, gas contactors and various micro-fluidic devices, rely on controlling the wettability inside hollow fibers and other porous materials. In order to accurately characterize and control wettability inside porous materials, it is necessary to understand the role of chemical heterogeneities.

Thus, in this study, the rise of liquid in nonuniform capillary tubes with chemical gradients is examined. First, the forces, pressures and energies associated with a wettable, homogeneous tube are analyzed. Next, the same quantities are evaluated for two types of tubes that exhibit chemical gradients, yet still allow liquid to rise to the same level as a wettable, homogeneous tube of the same diameter. The kinetics of some of these nonuniform tubes is also explored.

2. Theory

2.1. Capillary rise in a smooth vertical tube

Consider the vertical capillary tube shown in Fig. 1. It is smooth with a constant, inner diameter of D. The capillary is brought into contact with a liquid of surface tension γ, density of ρ, and viscosity of μ, such that its bottom just touches the liquid, Fig. 1a. The liquid wets the tube with an advancing contact angle of θ. If D is small and $\theta < 90°$, then a concave meniscus forms inside the tube. The curvature of the meniscus and the surface tension of the liquid create an upward “Laplace” pressure (p_c),

$$p_c = \frac{4\gamma}{D}\cos\theta. \tag{1}$$

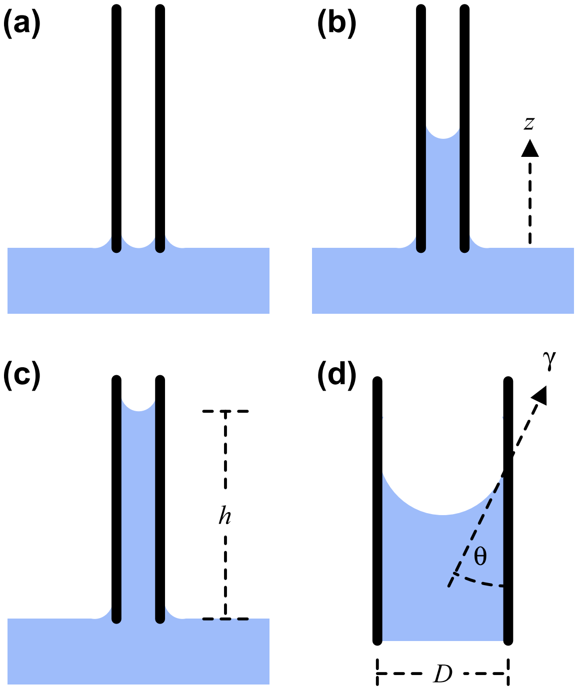

Fig. 1. Depiction of capillary rise in a small diameter tube. (a) The tube contacts the liquid and forms a concave meniscus inside the tube. (b) Liquid rises vertically. (c) The liquid stops at an equilibrium height of h. (d) A close-up view of the meniscus.

The Laplace pressure causes the liquid to rise in the vertical or z direction, Fig. 1b. As the liquid rises, the magnitude of the hydrostatic pressure inside the tube (p_h) increases with the transient height of the liquid column (z),

$$p_h = \rho g z, \tag{2}$$

where g is the acceleration due to gravity. The hydrostatic pressure is directed downward, acting against the Laplace pressure. The difference between Laplace and hydrostatic pressures (Δp),

$$\Delta p = p_c - p_h = \frac{4\gamma}{D}\cos\theta - \rho g z, \tag{3}$$

determines the rate of rise and the extent of energy dissipation within the liquid column. Flow ceases where $\Delta p = 0$ and $z = h$, Fig. 1c. Thus, from Eq. (3), the final rise height (h) can be estimated as [1a,1d,1e,14]

$$h = \frac{4\gamma\cos\theta}{\rho g D}. \tag{4}$$

If $\theta = 0°$, then Eq. (4) reduces to

$$h = \frac{4\gamma}{\rho g D}. \tag{5}$$

2.2. Wettability of the model tubes

Several wetting profiles, shown in Fig. 2, were used to explore variations in forces, pressures, energies and kinetics as liquid rises in a capillary tube. The tube shown in Fig. 2a is homogeneous and wettable with $\theta = 0°$ along its entire length. Fig. 2 also portrays two types of nonuniform tubes that exhibit a wetting gradient. The walls of these tubes are smooth with a constant diameter of D, but θ varies along their length. These tubes are relatively lyophobic near their bottoms where $z = 0$ and their wettability increases with z until $\theta = 0°$ where $z/h = 1$. Fig. 2b shows the profile of a nonuniform tube where θ varies exponentially as

$$\cos\theta = e^{z/h-1}, \tag{6}$$

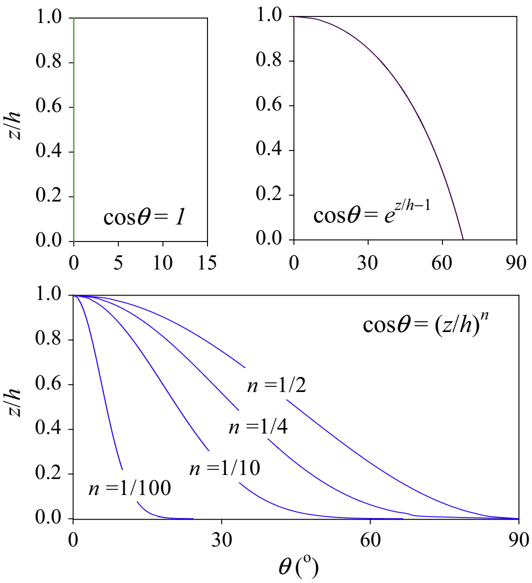

Fig. 2. Contact angle profiles inside of three types of capillary tubes: one type with homogeneous wettability where $\cos\theta = 1$ ($\theta = 0°$) and two types of heterogeneous tubes with chemical gradients where the wettability varies either as $\cos\theta = e^{z/h-1}$ or as $\cos\theta = (z/h)^n$.