

Contact angle determined by spontaneous dynamic capillary rises with hydrostatic effects: Experiment and theory

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Abstract

We investigate spontaneous dynamic capillary rises of liquids. While the liquid front rises spontaneously and vertically in a capillary, hydrostatic effects become more and more important. We theoretically derive new equations for capillary rises with hydrostatic effects, in order to describe the relation between the liquid front height and time, which enables us to experimentally measure contact angles of capillary tube surfaces directly. Excellent agreement between our theory and experiment shows the validity of the proposed method. Thus, it becomes possible to measure the wettability of small particles as well as porous materials.

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1. Introduction

The wetting of small particles and porous materials is a very important aspect of nature phenomena and practical surface chemistry, especially in chemical and pharmaceutical technologies which all require the knowledge of small particle wettability for product designs and production processes [1–4]. For such materials, there are a number of studies to measure contact angles directly on particles with diameters in the micrometer range, such as the film trapping method [5], the gel trapping method [6], a method based on an atomic force microscopy by measuring the force acting on a single spherical particle which is pushed through the liquid interface [3,7], and so on. Although more methods for measuring contact angles become available, capillary rise methods are still a practical approach widely used to characterize such systems by measuring the rate of liquid penetration within the porous structure, due to its handleability and feasibility [8,9].

The dynamics of fluids in a porous structure is a problem related to many disciplines and has been a subject of much interest [2,10]. The flow takes place at the level of

pores (about 1 μm or less) but the quantity of interest is the flow averaged over the whole macroscopic sample. The detailed description of liquid flow through a porous medium is greatly complicated by the many time-scales and length-scales that are involved. The simplest way to illustrate imbibition is capillary rises. Washburn [11] and Lucas [12] elucidated the dynamics of capillary rises by using the Poiseuille equation with the driving force for rises described by the Laplace equation for the pressure difference across the invading liquid meniscus. In a typical capillary rise experiment, a tube which is closed by a filter at the tube bottom is filled with small powder particles. The bottom of the tube is brought into contact with the liquid. For the capillary effect of the aperture between the powder particles, the liquid can rise in the tube. According to the rising speed, the contact angle may be calculated. The Lucas–Washburn equation for the penetration of a liquid into a horizontal cylindrical capillary is

$$x^2 = \frac{r\gamma_{lv} \cos \theta}{2\eta} t, \quad (1)$$

where x denotes the distance penetrated by the liquid, γ_{lv} the surface tension of the liquid of viscosity η , θ the contact angle between the liquid and the capillary surface, r the internal radius of the capillary, and t the time.

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Assuming that the powder behaves like a bundle of capillaries [13], a modified Lucas–Washburn equation $x^2 = (c\bar{r})\gamma_{lv} \cos \theta t / 2\eta$ is used to analyze resulting data of the capillary rise method. Here c stands for a constant that accounts for orientation of the capillaries and \bar{r} the mean capillary radius in the bulk. There are two unknown terms involved in this equation, namely, $(c\bar{r})$ and θ . The common way to solve this problem is to use a perfect liquid ($\theta = 0$) to calculate $(c\bar{r})$. However, in a practical measurement, it is difficult to get a kind of perfect wetting liquids for each sample, and it is also difficult to prepare a couple of samples which have the same value of the coefficient $(c\bar{r})$. In this work, we shall take into account hydrostatic effects of capillary rises and obtain a new expression. As a result of hydrostatic effects, we may further avoid the above-mentioned difficulties in the capillary rise method by using the Lucas–Washburn equation.

2. Theory

In general terms, for a cylindrical capillary, we assume that only laminar flow exits in the capillary and neglect any air resistance for the moment, the overall balance of forces on the liquid in the capillary takes the following form [14],

$$\frac{8\eta x}{r^2} \frac{dx}{dt} + \rho \left[x \frac{d^2x}{dt^2} + \left(\frac{dx}{dt} \right)^2 \right] = \sum P, \quad (2)$$

where ρ is the density of the liquid and $\sum P$ is the total effective pressure which forces the liquid to move along the capillary. The total effective pressure $\sum P$ contains three separate pressures: the unbalanced atmospheric pressure P_A , the hydrostatic pressure P_x , and the capillary pressure P_s . For such cases, P_A is always taken as a constant. For P_x and P_s , one takes $P_x = \rho g x$ and $P_s = 2\gamma_{lv} \cos \theta / r$. The first term on the right-hand side of Eq. (2) gives the viscous resistance of the liquid in the capillary, and the remaining terms describe the inertial resistance. When the capillary radius is very small, viscous forces are dominant, and thus the inertial effects can be neglected. In the mean time, if the effect of the hydrostatic pressure P_x and the unbalanced atmospheric pressure P_A can be neglected, one only has to solve the following equation:

$$\frac{8\eta x}{r^2} \frac{dx}{dt} = \frac{2\gamma_{lv} \cos \theta}{r} \quad (3)$$

with the initial condition $x = 0|_{t=0}$. The integration of Eq. (3) leads to the Lucas–Washburn equation (Eq. (1)). In the early stages of penetration or when r is large or η small, the inertial effects [15] are usually significant (the inertial effects can lead to a preferential invasion of small pores) and the hydrostatic effects are trivial. With the penetration of liquid into capillary, the inertial effects, however, become trivial, too. In this situation, the term of inertial effects can be neglected, and then Eq. (2) can be written as

$$\frac{8\eta x}{r^2} \frac{dx}{dt} = P_A - \rho g x + \frac{2\gamma_{lv} \cos \theta}{r}. \quad (4)$$

Let us neglect the effect of the unbalanced atmospheric pressure P_A and integrate Eq. (4), and then we obtain,

$$\frac{\rho g r^2}{8\eta} t + x = -\frac{2\gamma_{lv} \cos \theta}{\rho g r} \ln \left(1 - \frac{\rho g r x}{2\gamma_{lv} \cos \theta} \right). \quad (5)$$

If the hydrostatic effects are very insignificant, i.e., $\rho g x \ll 2\gamma_{lv} \cos \theta / r$, the term $\rho g r x / (2\gamma_{lv} \cos \theta)$ in Eq. (5) can be neglected, and then the question reduces to the Lucas–Washburn equation (Eq. (1)). However, with the penetration of liquid into a capillary, the hydrostatic effects become more and more significant. In this case, the term $\rho g r x / (2\gamma_{lv} \cos \theta)$ in Eq. (5) plays a role, and then we achieve the following equation

$$\frac{x^2}{\gamma_{lv} \cos \theta} + \frac{\rho g r x^3}{3\gamma_{lv}^2 \cos^2 \theta} = \frac{rt}{2\eta}. \quad (6)$$

After differentiating this equation, we obtain

$$v = \frac{\gamma_{lv}^2 \cos^2 \theta r}{2\rho g \eta x^2 r + 4\gamma_{lv} \cos \theta \eta x}, \quad (7)$$

where $v = dx/dt$ represents the velocity of the front of the liquid rise in the capillary. After differentiating Eq. (6), we obtain

$$x^3 + \frac{3\gamma_{lv} \cos \theta}{\rho g} \frac{x^2}{r} - \frac{3\gamma_{lv}^2 \cos^2 \theta}{2\rho g \eta} \cdot t = 0, \quad (8)$$

$$\gamma_{lv}^2 \cos^2 \theta = \frac{2\rho g \eta}{3} \frac{x^3 v}{x - 2tv}, \quad (9)$$

$$r = \frac{6\eta \gamma_{lv} \cos \theta x^2}{-2\rho g \eta x^3 + 3\gamma_{lv}^2 \cos^2 \theta t}. \quad (10)$$

Here only contact angle θ is an unknown parameter, and the velocity of the liquid front $v = dx/dt$ can be deduced from the height-time experimental data (e.g., see Section 3). Consequently, using Eq. (9), we are allowed to measure the contact angle θ between the capillary and the liquid (which is beyond perfect liquids ($\theta = 0$)). It is worth remarking that perfect liquids have to be used for the feasibility of the Lucas–Washburn equation).

3. Experiment

We observed the liquid front rising in vertical capillary tubes. Two different diameters (0.3 mm and 0.4 mm) of capillary were used in our study, and both tubes are made of the same kind of glass. Before conducting the experiment, the tubes were immersed for 48 h in the mixture of acetone, ethanol, and water, and blown dry with nitrogen. And then they were immersed for several hours in concentrated sulfuric acid with an oxidant (potassium dichromate) added, washed with deionized water, and finally blown dry with nitrogen again. This procedure substantially reduced the uncontrolled chemical heterogeneities on the tube inner surface. To observe the delicate motion of the liquid front, a

microscope is used to view it horizontally. The images were captured by using a CCD camera attached to the microscope, and then recorded by a computer at a series of time intervals.

Deionized Water and dimethyl silicone oil (H-201) $[(\text{CH}_3)_3\text{SiO}(\text{Si}(\text{CH}_3)_2\text{O})_n\text{Si}(\text{CH}_3)_3]$ (kinematic viscosity $50 \text{ mm}^2/\text{s}$ and $500 \text{ mm}^2/\text{s}$) were used as the liquids in capillary. In the case of deionized water, the rising front moves too fast to be a meniscus shape. Owing to its comparably smaller surface energy and higher dynamic viscosity, the silicone oil gets a smaller velocity and yields a comparative smooth front which may be conveniently captured and analyzed.

4. Results and conclusion

Fig. 1 displays our experimental results of spontaneous capillary rise of the dimethyl silicone oil with kinematic viscosity $\nu_1 = 500 \text{ mm}^2/\text{s}$ (density $\rho = 980 \text{ kg/m}^3$, oil–air surface tension $\gamma_{lv} = 21.1 \text{ mN/m}$ at 25°C), and kinematic viscosity $\nu_2 = 50 \text{ mm}^2/\text{s}$ (density $\rho = 960 \text{ kg/m}^3$, oil–air surface tension $\gamma_{lv} = 20.6 \text{ mN/m}$ at 25°C), respectively. In detail, Fig. 1a experimentally shows the relation between height x and time t . Fig. 1b shows x^2 as a function of time t for the data presented in Fig. 1a. The process of capillary rise behaves like $x^2 \propto t$ that represents the (approximate) Lucas–Washburn equation (Eq. (1)). We perform Eq. (9)

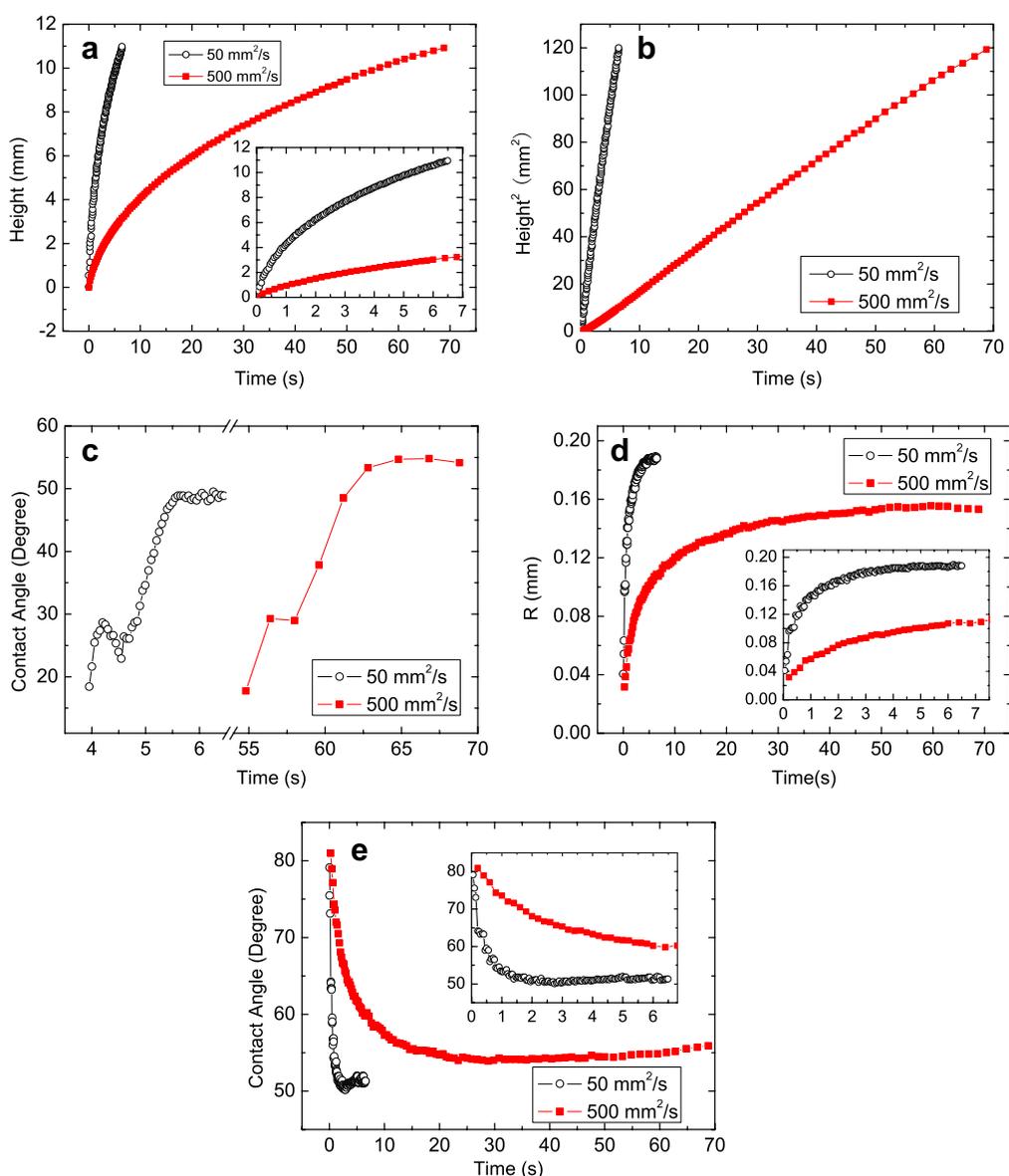


Fig. 1. (a) Experimental data of spontaneous capillary rise of dimethyl silicone oil. (b) The square of height x^2 versus time t for the data in (a). (c) The Contact angle deduced from the experimental data in (a) according to Eq. (9). (d) The capillary tube radius deduced from the experiment data in (a) according to Eq. (10). (e) The contact angle deduced from the experimental data in (a) according to Lucas–Washburn equation assuming the capillary tube radius is 0.15 mm for $500 \text{ mm}^2/\text{s}$ silicone oil and 0.18 mm for $50 \text{ mm}^2/\text{s}$ silicone oil, respectively.

to deduce the contact angle θ according to the experimental data presented in Fig. 1a. The contact angle reaches a plateau value equal to 54° for $500 \text{ mm}^2/\text{s}$ silicone oil and 51° for $50 \text{ mm}^2/\text{s}$ silicone oil, respectively, see Fig. 1c. With these plateau values of the contact angle, Fig. 1d shows the capillary tube radius deduced from the data set in Fig. 1a, according to Eq. (10). We find that the capillary tube radius tends to 0.155 mm for $500 \text{ mm}^2/\text{s}$ silicone oil and 0.187 mm for $50 \text{ mm}^2/\text{s}$ silicone oil, respectively. Fig. 1e shows the contact angle calculated with Lucas–Washburn equation (Eq. (1)) using the known experimental parameters and assuming the capillary tube radius $r = 0.15 \text{ mm}$ according to $500 \text{ mm}^2/\text{s}$ silicone oil, and $r = 0.18 \text{ mm}$ according to $50 \text{ mm}^2/\text{s}$ silicone oil, the contact angle reaches a plateau value equal to 55° for $500 \text{ mm}^2/\text{s}$ silicone oil and 50° for $50 \text{ mm}^2/\text{s}$ silicone oil, respectively.

Though both of the contact angle deduced from Lucas–Washburn equation are close to the results deduced from Eq. (9), we would expect the contact angle of the silicone oil on the glass plane surface equal to about 10° , which has a very surprising difference between the experimental results and the expect results. One of the proposed reason [16] is the contact angle hysteresis. The contact angle calculated using the experimental data is an advancing contact angle, θ_A . It is commonly found experimentally that the advancing contact angle is bigger than the equilibrium contact angle. Another is the dynamic contact angle effects [1]. The common contact angle hysteresis effects assume that liquid movement was sufficiently slow for equilibrium or static values of the advancing contact angle and the receding contact angle to be involved. In capillary rise systems in which liquid flow is relatively fast, the effects of a dynamic advancing contact angle, θ_{AD} , may become apparent. In such situations the advancing contact angle measured will be greater than θ_A . The difference between θ_A and θ_{AD} will generally be found to increase with the speed of liquid flow.

Fig. 1c shows that the contact angle values are calculated from the later experiment data and at the earlier times the contact angle values are not determined. Our approach is mainly taking into account the spontaneous dynamic capillary rises with the hydrostatic effects. At the early times, however, the surface tension is dominant and the hydrostatic effects are trivial, the hydrostatic effects can be neglected. So at the early times the contact angle would not be determined using our approach.

To confirm the deduced contact angle and the capillary tube radius, while the capillary rise front is stable, a picture was captured by the microscope with a CCD camera. Fig. 2 shows a typical stable capillary rise front of $500 \text{ mm}^2/\text{s}$ silicone oil. The contact angle $\theta = 41^\circ$ and the capillary tube radius $r = 0.15 \text{ mm}$ were obtained from Fig. 2, both of which are close to the result deduced from Eq. (9) and Eq. (10). The difference between the contact angle may come from the dynamic advancing contact angle effects. From the stable capillary rise front picture of $50 \text{ mm}^2/\text{s}$ sil-

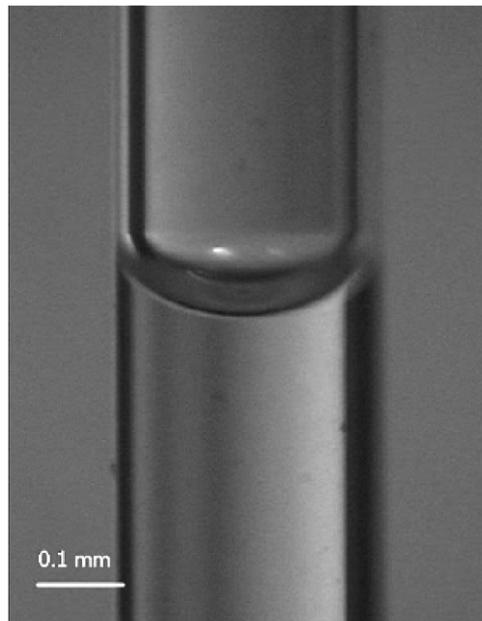


Fig. 2. A picture of a typical stable capillary rise front, captured by the microscopy with a CCD camera. About 50 h later after the capillary rise started, the picture of a stable liquid front was captured.

icone oil, the contact angle $\theta = 39^\circ$ and radius $r = 0.18 \text{ mm}$ were obtained which are also close to results deduced from Eq. (9) and Eq. (10).

Fig. 3 displays Eq. (8) and the Lucas–Washburn equation with the parameters, $\nu = 500 \text{ mm}^2/\text{s}$, $\theta = 54^\circ$ and $r = 0.15 \text{ mm}$, which are both deduced from the data set in Fig. 1a according to Eqs. (9) and (10). Curve (a) shows the experiment data already presented in Fig. 1a. Curves (b) and (c) show the result obtained from our developed theory (Eq. (8)) and the Lucas–Washburn equation, in which the same parameters deduced from curve(a) were adopted. As shown in Fig. 3, apparently the present theory (Eq. (8)) displays a much better agreement with the experimental data.

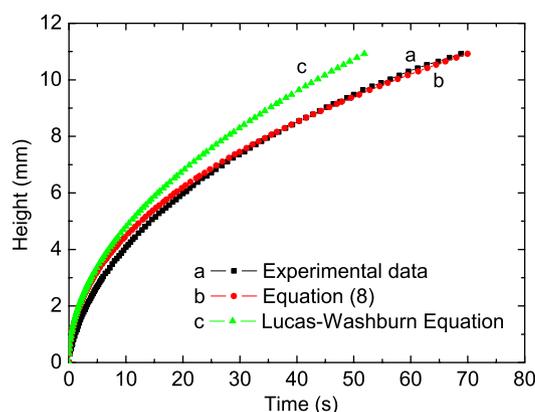


Fig. 3. curve (a) shows the experimental data in Fig. 1a. Curves (b) and (c) show the results obtained from our developed theory (Eq. (8)) and the Lucas–Washburn equation, in which the same parameters deduced from the data in curve (a) were adopted, respectively.

To sum up, we have investigated the hydrostatic effects in the liquid penetration of spontaneous dynamic capillary rises. By taking into account the hydrostatic effects, we have theoretically derived an expression for capillary rises, in order to describe the relation between the liquid front height and time, which enables us to experimentally measure contact angles of capillary tube surfaces directly. Excellent agreement between our theory and experiment shows the validity of the proposed method. Thus, it becomes possible to measure the wettability of small particles as well as porous materials.

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