A Study on Capillary Flow under the Effect of Dynamic Wetting

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Abstract
A theoretical model was proposed to consider the dynamic contact angle from a macroscopic viewpoint. A slight convex profile of liquid surface is assumed to avoid the divergence of viscous stress near the three-phase contact line on the wall. The theoretical results of the dynamic contact angle are dependent on the parameter \( \varepsilon \), the ratio of surface area occupied by the defects on the solid surface. The movement of liquid column in a capillary is investigated experimentally. The modified Lucas-Washburn equation including the effect of dynamic wetting represents well the measured results. The theoretical model can approximate the measured dynamic contact angles within the experimental uncertainty.

Key words
Capillary Tube, Dynamic Wetting, Contact Angle, Surface Tension, Viscous Stress

1. Introduction
The wetting behavior between solid and liquid phases has an important topic in various engineering fields treating small amount of liquid on a solid surface. When the three-phase contact line at the tip of the liquid surface on the solid wall moves with a finite velocity, one can observe that the contact angle changes with the velocity. When the capillary number, i.e., the ratio between viscous force and surface tension is larger than roughly \( 10^{-4} \) at which the velocity may be typically \( 0.1 \text{ mm/s} \), the effect of dynamic wetting should be taken into consideration to discuss the liquid motion on the solid surface. Many theoretical or experimental studies have discussed the velocity dependence of contact angle [1,2]. There are two kinds of theoretical models to express the dynamic contact angle, one of which is called hydrodynamic model to consider the viscous dissipation in the wedge of liquid near the contact line, and the other is called molecular kinetic theory (MKT) to consider the molecular movement at the contact line [1,2]. In the former model, the liquid motion is analyzed from the theory of fluid dynamics under the assumption of slip condition at the contact line. In order to avoid stress divergence at the contact line where the thickness of liquid layer becomes zero, the no-slip condition is discarded and the slip length is introduced so that the integral of viscous stress on the wall can be determined. The dynamic contact angle is then related to the viscous force. In the latter, back or forward jump of liquid molecules at the contact line is considered based on the Frenkel-Eyring theory of liquid transport which is applied to the determination of viscosity and so on. The excess surface tension caused by the contact angle change was related to the statistical average of molecular motion, i.e., the macroscopic velocity. Both models include some properties relating to molecular length scale. Although those theories have succeeded in some degree to explain the experimental results for the velocity dependence of contact angles, it is still not clear whether they represent the correct mechanism of dynamic wetting or not.

If we consider the wetting phenomenon on a real solid surface with roughness or defects with much larger scale than molecules, it seems natural that the behavior of apparent contact angle should be controlled mainly by the macroscopic characteristics on the solid surface. In this report, first a theoretical model is proposed to estimate the dynamic contact angle from a macroscopic viewpoint. In order to discuss the velocity dependence of contact angles, the viscous stress is estimated during the stick-slip motion of the contact line between the defects on the solid surface.

Next we discuss the behavior of liquid column in a capillary tube as the real system influenced by the dynamic wetting. The capillary phenomenon is related to many applications in science, industry and daily life, e.g., the movement of liquid in a small gap in heat pipes, the rise of blood in the blood sugar level sensor, and so on. However very few reports have investigated the liquid motion in the capillary based on a systematic experiment to measure precisely the behavior of the liquid column or the dynamic contact angle [2,3,4]. In this report, the liquid height and the dynamic contact angle are measured simultaneously in a glass capillary. The results are compared with the modified Lucas-Washburn equation for the movement of liquid column including the effect of dynamic wetting. The theoretical model for the dynamic contact angle proposed here is validated through comparison with the measured results in this experiment.

2. Theoretical Consideration
2.1 Dynamic contact angle
Based on the hydrodynamic model stated in section 1, Cox discussed the dynamic wetting and obtained the following relation for the dynamic contact angle [5].

\[
\theta_d = \left( \theta_s^3 + 9D \cdot Ca \right)^{1/3}
\]  (1)

where \( \theta_d \) and \( \theta_s \) indicate the dynamic contact angle and the static contact angle, respectively. \( D \) is an experimental constant defined as:

\[
D = \ln \left( \frac{L}{S} \right)
\]  (2)

where \( L \) is the typical length scale of the system and \( S \) is the slip length. In Eq. (1), \( Ca \) is the capillary number defined as:

\[
Ca = \frac{\mu U}{\sigma}
\]  (3)
\( \mu, U \) and \( \sigma \) indicate viscosity, velocity of contact line and surface tension, respectively. Cox discussed the liquid flow near the contact line separately in three regions, i.e., inner region where the slip condition is applied, intermediate region and outer region of macroscopic scale. Equation (1) was derived from the solution obtained by the method of matching asymptotic expansions. Here, we try to propose an approximate model to discuss the dynamic wetting on the solid surface having roughness or defect whose scale is much larger than the microscopic slip length.

Figure 1 shows the schematic of contact line movement on the solid surface with defects such as roughness or patch of adsorbed foreign molecules. Although we consider the receding of the contact line as shown in Fig. 1, the mechanism discussed below can be directly applied to the advancing case. In the practical wetting behavior, it is observed that the contact line movement is not continuous but shows a stick-slip type behavior even in the macroscopically quasi-static movement, i.e., the contact line is once trapped at the defect as shown in Fig. 1, then it moves irreversibly with a finite velocity to the next defect [6]. When the contact line is trapped at the defect, the liquid surface is distorted and some excess work is necessary to move over the defect. This energy is dissipated during the slip motion and is considered as the cause of the contact angle hysteresis (i.e., the static contact angle is dependent on the moving direction of the contact line) [7]. When the contact line moves with a macroscopically finite velocity \( U \), \( U \) is just added to the slip velocity during the irreversible motion, which leads to the increases of viscous drag on the wall \( \tau_W \) compared with the quasi-static case. In the present model, this drag increase is related to the difference between the static and the dynamic contact angles.

As shown in Fig. 1(b), the viscous drag is estimated during the slip motion after the contact line is released from the defect. Since very large wall shear stress concentrates mainly near the contact line, the resultant of frictional force may be estimated in the region of \( \lambda \), the characteristic distance between defects as shown in Fig. 1(b). de Gennes calculated the viscous dissipation in the straight wedge region near the contact line, which has often been treated as the lubrication problem [8]. When the wall shear stress is integrated, the slip length should be introduced to avoid the stress divergence at the contact line. If we consider the irreversible slip motion, the contact angle may be different from the static equilibrium angle at the edge of the contact line. In the present model, a slight convex profile of liquid surface is assumed instead of the straight line as shown in Fig. 1(b). The origin of the coordinate system is taken at the edge of the defect. \( x \) and \( y \) coordinates are taken in the horizontal and the wall-normal directions, respectively. The liquid surface profile \( b(x) \) is approximated by the following expression as:

\[
\frac{b}{\lambda} = \tan \theta_d \left( \frac{x - \epsilon}{1 - \epsilon} \right)^{1/3}
\]

(4)

where \( \bar{x} = x / \lambda \) and \( \epsilon \) is the ratio occupied by the defect. The above profile satisfies the following geometrical conditions.

\[
\bar{x} = \epsilon : b = 0, \quad \bar{x} = 1: \frac{b}{\lambda} = \tan \theta_d, \quad \frac{db}{dx} = \tan \theta_d
\]

(5)

Equation (4) means that the liquid surface is assumed to be distorted by \( \epsilon \lambda \), i.e., the scale of defect. The velocity distribution \( u(y) \) in the liquid is simply approximated by the following equation to satisfy the boundary conditions at the wall and the liquid surface.

\[
\frac{u}{U} = \frac{3}{2} \left( \frac{2y - y^2}{x} \right)
\]

(6)

where \( \bar{y} = y / b \).

The force balance on the area ABC shown in Fig. 1(b) is now considered. The solid-gas and solid-liquid interfacial tensions, \( \sigma_s \) and \( \sigma_{sl} \) act on the contact line \( \Lambda \) while the liquid-gas surface tension \( \sigma \) acts on the liquid surface at C with the dynamic contact angle \( \theta_d \) as shown in the figure. Since the Reynolds number should be quite small, the influence of inertial force can be neglected. As a result, the resultant of each interfacial tension stated above balances the viscous force on the wall AB shown in Fig. 1(b). The integral of wall shear stress \( F_s \) on AB can be calculated by use of Eqs. (4) and (6) as:

\[
F_s = \int_0^\lambda \left( \frac{du}{dy} \right)_y \; dx = \frac{3 \mu U (1 - \epsilon)^{1/3}}{\epsilon \tan \theta_d} \int_0^\lambda \frac{dx}{(x - \epsilon)^{1/3}}
\]

(7)

It is noted that we can calculate the integration by use of Eq. (4) without divergence under the no-slip condition. On the
other hand, the resultant of interfacial tensions in the
tangential direction can be calculated as follows.

\[ F_i = \sigma \cos \theta_d - \sigma_s + \sigma_{sl} = \sigma (\cos \theta_d - \cos \theta) \]  

(8)

Note that the Young’s equation for the equilibrium contact
angle \( \theta \) was used to obtain the above relation as:

\[ \sigma_s - \sigma_{sl} = \sigma \cos \theta \]  

(9)

Equating Eq. (7) to Eq. (8) leads to the following relation to
estimate the macroscopic dynamic contact angle \( \theta_d \).

\[ |\cos \theta_d - \cos \theta| = \frac{3(1-\varepsilon)}{\varepsilon \tan \theta_d} \cdot Ca \]  

(10)

It is noted that Eq. (10) can be applied to both receding and
advancing of the contact line if \( Ca \) is defined as positive
value. The solution of nonlinear Eq. (10) can easily be
calculated by a numerical manner. We can obtain the
dynamic contact angle if an appropriate value of \( \varepsilon \) is
assumed to fit the experimental results.

Equation (10) apparently includes only macroscopic
parameter, i.e., \( \varepsilon \), rather than \( S \) in Eq. (2). It is noted that Eq.
(10) cannot be applied to the limits, i.e., \( \varepsilon \to 0 \) or \( \varepsilon \to 1 \). In the
former limit, Eq. (10) shows a divergence and \( \theta_d \to \theta \) in the
latter. As mentioned in 2.1, the present model assumes the
defect much larger than the slip length \( S \). When \( \varepsilon \)
approaches zero, i.e., the surface is completely smooth, the
dynamic contact angle should be calculated by another
model such as Eq. (1) instead of the present model. The
other limit \( \varepsilon \to 1 \) actually does not occur because the contact
line is not trapped everywhere but it should move with a
finite velocity on some regions of smaller roughness. \( \varepsilon \)
should have a limit less than unity. It is noted that the
proposed model should be recognized as an approximate
one to represent the effect of macroscopic defects in a
reasonable range of \( \varepsilon \). In practice, however, the microscopic
phenomenon also may give an influence on the dynamic
wetting behavior. In order to construct a more rigorous
model, we should include both macroscopic and
microscopic effects. This problem will be considered in the
future study.

### 2.2 Movement of liquid column in the capillary

The movement of liquid column in a capillary can be
described by the well-known Lucas-Washburn equation
which considers the force balance between the surface
tension and other opposite forces [2]. Figure 2
schematically represents the capillary flow and various
forces acting on the liquid column. Modified Lucas-
Washburn equation considering the dynamic contact angle
can be written as follows:

\[ \rho R^2 \left( \frac{dh}{dt} \right)^2 + \rho R^2 h \frac{d^2 h}{dt^2} - 2R \sigma \cos \theta_d \]

\[ + 8 \mu h \frac{dh}{dt} + \rho g R^2 h = 0 \]  

(11)

where \( h \) indicates the liquid height at time \( t \), and \( R, \rho \) and \( g \)
are the radius of capillary, density and gravitational
acceleration, respectively. In the left hand side of the above
equation, each term indicates in order, the effect of liquid
momentum entering to the capillary \( (F_M \text{ shown in the}
figure)\), acceleration of momentum in the capillary, surface
tension, viscous force \( (F_v) \) and gravitational force \( (F_g) \),
respectively. The viscous force is estimated for the
developed Poiseuille flow, since the capillary radius is
sufficiently small that we can neglect the inlet length
necessary for the velocity distribution to be developed.
Although many authors have been treating the capillary
flow by experiments or by MD (Molecular Dynamics)
simulations, there is still a controversy whether Eq. (11)
precisely represents the liquid motion or not [2]. Especially
there are only a very few reports in which the change of
liquid height and the dynamic contact angle are measured
systematically. In this paper, both the movement of liquid
column and the dynamic contact angle are measured
simultaneously by a method stated below.

### 3. Experimental Method

Figure 3 shows the schematic of experimental apparatus
used in this study. The upper end of the capillary 1 can be
opened and shut by an electromagnetic valve 4. The profile
of liquid surface in the capillary is photographed by a CCD
camera 3. The capillary is enclosed by a square box of
PMMA 2 filled with the test liquid in order to avoid the
image distortion by the refraction. First the top of liquid
column is carefully set at the level of stationary liquid

![Fig. 2 Schematic of capillary flow](image-url)

![Fig. 3 Experimental apparatus](image-url)
surface by a micro syringe 6 shown in the figure. The signal 
when the valve is open is synchronized with the camera and 
the image is sent to PC from the instance when the liquid 
starts to rise in the capillary. The height of liquid column 
and the dynamic contact angle at each second are measured 
from the image on the PC monitor.

In this experiment, Ethelene glycol of 25°C(σ=48.4mN/m, 
ρ=1112kg/m³, μ = 0.01685Pa s) was used as the test 
liquid and the glass tube with the inner radii 0.502 and 
0.315 mm were used as the capillary. The tube radius was 
carefully measured by a reading microscope. The accuracy 
is within 0.001mm.

The dynamic contact angle was measured from the 
profile of axisymmetric meniscus formed at the head of 
liquid column. Since the liquid velocity is much less than 
0.1 m/s in this experiment and the capillary number defined 
by Eq. (3) is quite small, the meniscus profile should be 
approximated by the solution of the axisymmetric Laplace 
equation as [9]:

\[
\sigma \left[ \frac{(d^2z/dr^2)}{1+(dz/dr)^2} \right] - \frac{dz/dr}{r \sqrt{1+(dz/dr)^2}} = -\rho g z + \Delta P_0 \tag{12}
\]

where \( z \) is the height from the meniscus trough at the pipe 
center and \( r \) is the radius. \( \Delta P_0 \) is the pressure at the trough 
sated above. Equation (12) indicates the force balance 
between the surface tension and the static liquid pressure on 
the gas-liquid interface. The solution of Eq. (12) can be 
obtained easily by a numerical manner using Runge-Kutta’s 
method based on the boundary conditions at the pipe center 
and the wall as:

\[
r=0 : \frac{dz}{dr}=0, z=0, r=R : z=z_w
\]

where \( z_w \) indicates the meniscus height at the wall measured 
by the photograph. It is noted that since Eq. (12) includes 
the unknown parameter, i.e., \( \Delta P_0 \), three boundary conditions 
are necessary to obtain the solution of second-order 
differential equation. The numerical solution of Eq. (12) 
was obtained to satisfy the above boundary conditions by 
correcting \( \Delta P_0 \) repeatedly based on Newton’s method. 
Figure 4 shows an example of comparison of calculated 
meniscus profile with the photograph. As shown by the 
figure, both results agree well with each other. The contact 
angle can be calculated from the tangent of the meniscus 
curve at the wall. The dynamic contact angle was obtained as 
the average of more than six measurements for each 
experimental condition with various velocities. The scatter of 
the measurement was within ±1° in this experiment.

4. Experimental Results

Figure 5 shows the experimental results of dynamic contact 
angles dependent on the velocity of contact line for two 
kinds of glass capillaries. In the figure, the theoretical 
curves are drawn by use of Eq. (1) of Cox’s relation with 
\( D=0.550 \) and Eq. (10) proposed in this study with \( \varepsilon=0.595 \). 
The constants \( D \) and \( \varepsilon \) were determined to fit the 
experimental results by the least squares method. The 
experimental dynamic contact angles are approximated well 
by both theoretical models within the experimental error. As 
shown by the figure, the contact angle dependence on the 
velocity is similar for two kinds of capillaries. This 
indicates the validity of the experiment in this study, i.e., the 
dynamic contact angel is dependent on the characteristics of 
solid wall and test liquid but independent on the capillary 
radius.

The value of \( D=0.550 \) in Cox’s relation seems 
comparatively too small compared with that in other literatures 
like \( D=13 \) [1]. If we take 1 mm as the system length scale 
as \( L \) in Eq. (2), the slip length corresponding to \( D=0.550 \) is 
about 0.58 mm, which should be unrealistically large. It is 
sometimes claimed that the hydrodynamic model based on 
the slip length may not correctly represent the mechanism 
since the experimental results of \( D \) scatter in a wide range 
[2]. On the other hand, the value of \( \varepsilon=0.595 \) seems 
reasonable for real solid surfaces, although more 
sophisticated experimental techniques should be necessary 
to validate the model proposed in this study. The thorough 
discussion for the parameter \( \varepsilon \) will be the subject in the 
future.

Figures 6 and 7 show the experimental results for the 
movement of liquid column in the capillary. Figure 6 shows 
the change of liquid height and Fig. 7 represents the 
velocity of contact line at each second during the movement. 
In Fig. 6, the numerical results of Eq. (11) are drawn for 
two kinds of models stated above. As shown by Figs. 6 and 
7, the experimental results are approximated well by the 
calculated results. We can say that the liquid movement in 
the capillary can be described by the modified Lucas-
Washburn equation in which the effect of dynamic contact 
angle is properly taken into consideration.
5. Summary
A theoretical model was proposed to discuss the dynamic contact angle from a macroscopic viewpoint. The velocity dependence of the contact angle was related to the increase of viscous stress during the slip motion between the defects on the solid surface at which the three-phase contact line is trapped. In order to avoid the divergence of stress integral, a slight convex curve was assumed as the profile of liquid surface near the contact line. The force balance between interfacial tensions and the viscous drag leads to the dynamic contact angle related to the macroscopic velocity of contact line. The contact angle is dependent on the capillary number and the ratio occupied by the defects on solid surface.

The movement of liquid column in capillary tubes was investigated experimentally. The trajectory of liquid height with time and the dynamic contact angles were measured for two kinds of glass capillaries with different inner radii. The measured dynamic contact angles can be approximated by the relation based on the theoretical model proposed in this study. The numerical solution of modified Lucas-Washburn equation to which the above relation is applied agreed well with the experimental results for the movement of liquid column in the capillary.

Nomenclature

- $b(x)$: profile of liquid surface near contact line, m
- $Ca$: capillary number defined by Eq. (3), non-dimensional
- $D$: numerical constant appearing in Eq. (1) and (2), non-dimensional
- $g$: gravitational acceleration, m/s$^2$
- $h$: height of liquid column in capillary, m
- $L$: length scale of system, m
- $R$: inner radius of capillary, m
- $S$: slip length, m
- $t$: time, second
- $U$: velocity of contact line, m/s
- $u(y)$: velocity distribution in the liquid, m/s
- $x$: coordinate in wall-tangent direction, m
- $y$: coordinate in wall-normal direction, m
- $\epsilon$: occupied ratio of defects on solid surface, non-dimensional
- $\theta$: equilibrium contact angle, deg
- $\theta_d$: dynamic contact angle, deg
- $\lambda$: characteristic distance between defects, m
- $\mu$: viscosity, Pa s
- $\rho$: density, kg/m$^3$
- $\sigma$: surface tension, N/m

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References