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Contact angles and wetting velocity measured electrically

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We describe two new measurement techniques for studying the wetting behavior of a liquid on a surface. First, we measure the contact angle of a droplet, by measuring the capacitance between a conducting droplet and a subsurface counter electrode. The estimated error in the measured contact angle is 2% for contact angles in the range between 60° and 120°. In the second measurement technique, we detect the current as a function of time, which provides information about the dynamics of a droplet wetting the substrate. The time-integrated current is related to the base area of the droplet. Consequently, we can derive the radial velocity of the three-phase line of the droplet. The time resolution of the measurement technique is limited by the charging time of the initial capacitance, in our case approximately 0.5 ms. © 1999 American Institute of Physics.

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I. INTRODUCTION

Ever since Young derived his contact-angle equation in 1805,\textsuperscript{1} contact angles have been measured to study surface and interface energies.\textsuperscript{2} Methods of contact-angle measurement are typically optical or, less commonly, tensiometric.\textsuperscript{3,4} In optical measurements an angle accuracy better than 1° can be achieved by solving the Laplace equation for the observed shape.\textsuperscript{5,6} However, optical measurements are complicated by optical distortions and are laborious, which limits the number of measuring points by time constraints.

In this article, we show that the contact angle of a liquid on a solid surface can be derived from a capacitance measurement. The technique requires a subsurface electrode and a conducting liquid. In this geometry, we can relate the capacitance between the droplet and the subsurface electrode to the droplet base area. We can express the contact angle of the droplet in terms of the droplet base area, knowing the droplet shape and volume. The shape of a droplet is determined by the surface tensions and the gravitational force. For small droplets, the surface tensions dominate and the droplet resembles a cap of a sphere. For larger droplet volumes gravity becomes significant, which can be accounted for numerically. As an example, we use the capacitance-based measurement to study voltage-induced changes of contact angle, so-called electrowetting.\textsuperscript{7–11}

Finally, we demonstrate an electrical method to derive the radial velocity of a spreading droplet. We show that we can study droplet dynamics by measuring the current flowing to the droplet as a function of time. The electrical measurements facilitate the data analysis significantly, as compared to the optical measurements, where a high-speed camera and extensive image analysis are needed.

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II. STATIC DROPLET EXPERIMENTS

An electric potential is applied between the conducting liquid droplet and the subsurface counter electrode, schematically shown in Fig. 1. By measuring the capacitance of the droplet, we derive the droplet base area which relates to the contact angle if the droplet shape and volume are known. First, we discuss the relation between the capacitance and the base area of the droplet. After that, we discuss the shape of a droplet and the relation between the droplet base area and the contact angle. Finally, we apply the capacitance-based measurement technique to measure the voltage-induced changes of contact angle in an electrowetting experiment.\textsuperscript{7–11}

A. The capacitance of a droplet

The potential applied to a droplet in the geometry of Fig. 1 induces charge in the droplet and an image charge on the solid electrode. The capacitance is defined as the charge on each of the two conductors divided by their potential difference. The main contribution to the capacitance of the droplet system can be modeled as a parallel-plate capacitor ($C_{\text{par}}$). A second contribution is the stray capacitance $C_{\text{str}}$, originating from fringing fields at the edge of the droplet. The capacitance can be written as

$$ C = C_{\text{par}} + \frac{\varepsilon_r \varepsilon_0 A}{d} + C_{\text{str}}. \quad (1) $$

where $A$ is the base area of the droplet, $d$ is the insulator thickness and $\varepsilon_r$ is the dielectric constant of the insulator. The serial capacitances of the diffuse ionic double layers at the wire/liquid and the liquid/insulator interfaces are sufficiently large to be neglected.

For a 10 μl droplet with a contact angle of 90° (radius 1.7 mm), $\varepsilon_r=2.7$ and $d=10 \ \mu m$, we find $C_{\text{par}}=21 \ \text{pF}$. As explained in Appendix A, using the same parameters, we find $C_{\text{str}}=0.36 \ \text{pF}$, so 1.7% of $C_{\text{par}}$. The ratio of $C_{\text{str}}$ to $C_{\text{par}}$ increases for increasing contact angles. For $\theta$ ranging between 60° and 120°, the ratio $C_{\text{str}}/C_{\text{par}}$ increases from 1% to less than 3%.

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the actual value. We have fitted the relation between base area and contact angle as a quadratic series \( \theta = c_0 + c_1 A + c_2 A^2 \) with the constants \( c_0 \), \( c_1 \) and \( c_2 \) given in Appendix C.

C. Static contact-angle measurements by capacitance

A droplet on a horizontal substrate spreads until it reaches a minimum in potential energy. This is determined by the cohesion forces in the liquid and the adhesion of the liquid with the substrate. The phenomena of surface and interfacial tensions are explained in terms of \( \gamma \), the surface tension [N m\(^{-1}\)] or surface free energy [J m\(^{-2}\)]. By applying a potential, we can alter the surface free energy of the droplet and therefore the contact angle. The relation between the contact angle and the applied potential is derived by, for instance, Welters and Fokkink\(^{10}\)

\[
\cos \theta(V) = \cos \theta_0 + \frac{1}{2} \frac{\epsilon_0 \epsilon_r}{d \gamma_{LV}} V^2.
\]

where \( \theta_0 \) is the contact angle at 0 V, \( \gamma_{LV} \) is the surface tension of the liquid/vapor interface and \( V \) is the voltage applied to the counter electrode.

In Fig. 3(a) we show the dependence of the capacitance on the applied potential. The material system was a silicon wafer coated with an aluminum layer as metal electrode, an insulating parylene-N layer and a highly fluorinated AF1600 layer as a hydrophobic top coating. The liquid was demineralized water with 0.1 mol \( \text{K}_2\text{SO}_4 \). We placed a 10 \( \mu \text{L} \) droplet\(^{13}\) on the sample and applied a voltage to the aluminum electrode. We decreased the voltage from zero to \(-250 \text{ V}\) and the droplet spreads out as a result. Next, the voltage was increased to 0 V and the droplet contracts. Finally, we increased the potential to \(+250 \text{ V}\) and decreased it to 0 V. We covered the entire voltage range in 100 steps. The complex impedance was measured using a HP4192A impedance analyzer. On top of the bias voltage, an ac signal was added; we used a 700 Hz oscillation frequency with an amplitude of 5 \( V_{\text{rms}} \), a signal that does not affect the droplet shape. The measurement precision of the impedance analyzer was about 1%. For all measurements, the out-of-phase signal (capac-
be in agreement with measurements with an Alfa Step 200
an accuracy of 1%. Results of interferometry were verified to
area.15 The thickness of the AF1600 layer was about 25 nm,
in agreement with a measurement of the capacitance per unit
parylene-N. 14 The resulting value of
performing the experiments in an environment saturated with
causes a decrease of the droplet volume at a rate of
parylene layer behaves as a good insulator and that the liquid
~
resistive current
was nearly two orders of magnitude larger than the in-phase signal (resistive current). This indicates that the
parylene layer behaves as a good insulator and that the liquid
has a sufficiently high electrical conductivity. Evaporation
causes a decrease of the droplet volume at a rate of
0.5%–1% per min. The recording of one complete curve
takes less than 2 min. Evaporation can be suppressed by
performing the experiments in an environment saturated with
water vapor.

The contact angle can be obtained from the base area
using Eq. (C2). We used the parallel-plate approximation
(Cair is neglected) to relate the base area to the capacitance.
The thickness of the parylene insulator was determined by
interferometry (Nanospec/AFT), yielding \( d = 9.9 \, \mu m \), with
an accuracy of 1%. Results of interferometry were verified to
be in agreement with measurements with an Alfa Step 200
(Tencor instruments). The dielectric constant is \( \epsilon_r = 2.65 \) for
parylene-N.14 The resulting value of \( \epsilon_r / d \) was verified to be
in agreement with a measurement of the capacitance per unit
area.15 The thickness of the AF1600 layer was about 25 nm,
orders of magnitude smaller than the thickness of the parylene layer. Figure 3(b) shows the contact angle measured by
capacitance as a function of applied potential. The solid line
is the theoretical curve, calculated using Eq. (4). In the
voltage range \(-200 < V < 200 \, V\), the measured contact-angle
modulation differs less than \( 2^\circ \) from the theoretical contact
angle. The plot confirms that electrowetting is independent
of the polarity of the applied voltage. In the geometry of Fig.
1, we have also determined the contact angle using the com-
mon optical method for contact-angle detection. The abso-
lute initial contact angle at 0 V varied between \( 104^\circ \) and
\( 119^\circ \) for different measurements on the same sample. The
measurements appeared to be very sensitive to changes of
optical alignment and angle of observation. The contact
angles derived from a capacitance measurement fell in the
range \( 120 \pm 1^\circ \).

III. DYNAMIC DROPLET EXPERIMENTS

A. Deriving the droplet velocity from the current

By studying the current flowing to the droplet as a func-
tion of time, we can obtain important information about the
dynamics of the droplet during wetting. For instance, we can
determine the velocity of the three-phase line.

The current \( I \) is defined as the differential of the charge
to time. Let us consider the droplet system to be an ideal
capacitor. Since \( Q = CV \), with \( Q \) the charge on the capacitor
and \( C \) the capacitance of the droplet, we can write

\[
I(t) = \frac{dQ}{dt} = C \frac{dV}{dt} + V \frac{dC}{dt}.
\]

The first term represents the charging of the initial capaci-
tance of the droplet. The second term represents the current
needed to charge the changing capacitance, for example, be-
cause the droplet spreads out or contracts. The time \( \tau \) re-
duced to charge the initial capacitance is given by the re-
response time of the voltage source as well as the response
time of the electric polarization of the insulating layer. For
times higher than the charging time \( \tau \), we have the following
relation between the current and the droplet area:

\[
I(t) = V \frac{dC}{dt} = V \frac{\mu_0 \epsilon_r \, dA}{d} \quad (t > \tau),
\]

where we used the parallel-plate approximation. Integration
gives

\[
A(t) = A_0 + \frac{d}{\epsilon_0 \epsilon_r \, V} \int_0^t I(t') \, dt',
\]

where \( A_0 \) is the initial base area of the droplet. In principle,
we can derive the contact angle from \( A \), when the droplet
shape and volume are known (see Sec. II). The radius of the
droplet as a function of time, \( r(t) \), is related to the base area
by \( A = \pi r^2 \). We differentiate \( r(t) \) to find the velocity of the
three-phase line in radial direction

\[
\nu(t) = \frac{d}{dt} \left( \frac{1}{\sqrt{\pi}} \frac{d}{dt} \, \sqrt{A(t)} \right).
\]

B. Velocity measurements by current

Dynamic experiments were performed on glass samples
with a layer of indium–tin–oxide as metal electrode, an ins-
ulating parylene layer and a hydrophobic AF1600 top coat-
ing. We used a function generator to provide a step function,
which was amplified to \(-225 \, V\) and applied to the subsur-
face electrode. We used a custom built high-voltage ampli-
ifier for which the voltage deviates no more than 1% of its
final voltage within \( 100 \, \mu s \). The current was determined by
measuring the potential drop across a 100 k\( \Omega \) resistor. A
digital oscilloscope averaged the signal 16 times to enhance
the signal to noise ratio. We used five different time and
voltage scales in order to acquire the current between 0.1 and
50 ms and still have sufficient resolution. One measurement
involves about 100 switching cycles in total, due to the averaging and changing of scales. We verified that the system was not modified irreversibly during the measurement, by comparing a measurement of the capacitance as a function of voltage before and after the complete \( I(t) \) measurement.

Figure 4 shows the absolute value of the current on double logarithmic scales for both a freely spreading droplet and a droplet constrained in a spacer. The latter cannot move and, therefore, the difference between the curves is due to the increasing base area of the free droplet. We see that for \( t \approx 20 \mu s \), the current increases. This is caused by the response of the voltage source \( (dV/dt \neq 0) \). Until \( t = 0.1 \) ms the two curves are similar, showing that the current mainly results from the charging of the initial base area. For \( t > 0.1 \) ms, the current of the freely spreading droplet is larger because of its increasing base area. The inset shows the current versus time on linear scales, illustrating the difference between the curves.

We plotted the radial velocity of the three-phase line as a function of time in Fig. 5, using Eqs. (7) and (8). The velocity is of the order of 0.1 m s\(^{-1}\), approaching zero after about 15 ms. The inset in Fig. 5 is a plot of the integrated velocity, i.e., the radius of the droplet. The radius increases from 1.5 to 2.1 mm, in agreement with static capacitance measurements at 0 and \(-225\) V, respectively. For \( t > 0.5 \) ms, we conclude that the measured points represent the actual velocity, with an overestimation of less than 10% due to the charging current of the initial capacitance. Minor inaccuracies are added because we use several different voltage and time scales of the oscilloscope.

Finally, note the oscillation of the velocity. By stroboscopic illumination, we verified that the droplet indeed shows an overshoot as well as oscillations in the radial velocity. Figure 6 shows two photographs of a droplet in motion. The droplet shape differs from the static droplet shape, indicating that capillary waves have been excited. From capillary wave theory, it is expected that the oscillations occur later in time for larger droplet volumes, which was confirmed experimentally. We have also noticed that an increase of the viscosity reduces the amplitude of the velocity oscillation but does not affect the spreading time.

IV. DISCUSSION

A. Static measurements

We have introduced a capacitance-based method to measure contact angles of a droplet. We derived a relation between the base area of a droplet and the contact angle in the presence of gravity. For a 10 \( \mu l \) aqueous droplet, residing on an insulator with a thickness of 10 \( \mu m \), we deduced that the influence of fringing fields from the sides of the droplet to the total capacitance is less than 2% for contact angles around 90°. Knowing the thickness of the insulator and the dielectric constant, we can calculate the base area from the capacitance and consequently derive the contact angle. We showed experimental data of the contact angle as a function of the potential applied between the droplet and the counter electrode. The data are in agreement with electrowetting theory. The estimated error in the contact angle is 2% in the range between 60° and 120°. The main contribution to the error is due to the stray capacitance. The capacitive measurement of contact angle gives the averaged contact angle of the entire droplet. This is in contrast with optical measurements, where just one point of the contact line is sampled. The capacitance-based measurement is fast, easy to use and it facilitates data analysis.

B. Dynamic measurements

We have shown that measuring the current as a function of time provides a fast and convenient method to acquire information about a droplet while it is wetting the substrate. We measured the radial velocity of the three-phase line of the spreading droplet. In our situation, the time resolution of the measurement was 0.5 ms, after which the difference be-
APPENDIX A: STRAY CAPACITANCE

We calculate the contribution of the stray capacitance to the total capacitance for the case that the droplet is a semi-sphere at potential \( V \) on a plane at zero potential. In Jackson, the potential \( \Phi \) is given for the case of a sphere with radius \( a \) consisting of two hemispheres at opposite potential, with a plane of zero potential at \( z = 0 \). Using the same coordinate system as Jackson, the potential is given by

\[
\Phi(r, \theta, \varphi) = \frac{V}{4\pi} \int_0^{2\pi} d\varphi' \int_0^1 d(\cos \theta') \left[ \frac{1}{r} d(\cos \theta') - \int_1^a d(\cos \theta') \right] \frac{a(r^2 - a^2)}{(a^2 + r^2 - 2ar \cos \gamma)^{3/2}}
\]

with

\[
\cos \gamma = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\varphi - \varphi').
\]

The stray charge on the \( 0 \ V \) plane at \( z = 0 \) is given by the fringing electric field integrated over the \( z = 0 \) plane. At \( z = a \), \( E \) goes to infinity, since at that point there is a step in the potential. In reality, the thickness of the insulating layer removes the singularity in the electric field. We define an angle \( \delta \), by \( \sin \delta = d/a \). To find the electric field, we integrate to \( \pi/2 - \delta \) instead of \( \pi/2 \). The integral expression for \( E \) at \( z = 0 \) is then given by

\[
E(x) = \frac{3V}{\pi a} \int_0^\pi d\varphi' \int_0^{\pi/2 - \delta} d\theta' \left( \frac{x^2 - 1}{x^2 - 2x \sin \theta' \cos \varphi'} \right)^{3/2},
\]

with \( x = r/a \). For \( \delta = 0.01 \), we plotted the electric field as a function of the normalized radius in Fig. 7. The electric field of the parallel-plate capacitor equals \( V/d = V/(a \sin \delta) \approx 100 \cdot V/a \). From the figure, we see that at \( x = 2 \), the fringe field is less than 1% of the parallel-plate electric field. For \( x < 1 + \delta \), the fringing field decreases, as in that region the field is mainly generated by the parallel-plate charges instead of the stray charges.

We integrate the electric field over the entire \( x, y \) plane outside the sphere \((x > 1)\) to find the total stray charge due to fringing fields. As the capacitance is equal to the charge divided by the potential, we find

\[
C_{str} = \frac{\epsilon_0}{V} \int_a^\infty 2\pi r dr E_z = 6 \epsilon_0 a \int_x^\pi dx \int_0^\pi d\varphi' \int_0^{\pi/2 - \delta} d\theta' \times \left( \frac{(x^2 - 1) \cos \theta' \sin \theta'}{(1 + x^2 - 2x \sin \theta' \cos \varphi')} \right)^{3/2}.
\]

A plot of the stray capacitance versus \( \delta \) is shown in Fig. 8. We notice that the stray capacitance depends only weakly on \( \delta \). Thus, the contribution of the electric field in the region \( 1 < x < 1 + \delta \) to the total capacitance is negligible. Note that the magnitude of \( C_{str} \) is rather close to \( 4 \pi \epsilon_0 a \), the capacitance of a sphere of radius \( a \) in vacuum.

APPENDIX B: DROPLET SHAPE IN ABSENCE OF GRAVITY

For small droplets, when the capillary constant [Eq. (3)] is much longer than the radius, the gravitational force can be neglected and a droplet is shaped as a cap of a sphere. We can write the base area \( A \) in terms of the droplet volume \( V \) and the contact-angle \( \theta \)

\[
A = \pi \sin^2 \theta \left( \frac{V}{(2/3) \pi [1 - (3/2) \cos \theta + (1/2) \cos^3 \theta]} \right)^{2/3}.
\]

Using two new variables

\[
\alpha = \frac{A}{[\pi(9/4) \chi_{1/3}]} \quad \beta = [16 + 8 \alpha^3 + \alpha^6 + 2(4 + \alpha^3)^{3/2}]^{1/3},
\]

we find the following expression for the contact angle:

\[
\cos \theta = -1 + \frac{\alpha^2}{\beta} + \frac{\alpha \beta}{4 + \alpha^3}.
\]
This equation is the exact solution in the absence of gravity. Hence, by calculating the base area of the droplet from the capacitance measured, we can directly obtain the contact angle.

APPENDIX C: INFLUENCE OF GRAVITY ON THE DROPLET SHAPE

Gravitational forces change the droplet shape from a cap of a sphere to a more flattened oval-like shape. The droplet shape is determined by equating the Laplace equation and the hydrostatic pressure, as given by O’Brien and van den Brule:

$$\gamma_{LV} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \rho g z + p^*, \quad (C1)$$

where $R_1$ and $R_2$ are two principal radii of curvature of the droplet, $\rho$ is the liquid density, $g$ the gravitational constant and $p*$ is the pressure difference at the liquid/vapor interface at the top of the droplet ($z = 0$) as shown in Fig. 9. We solve this equation using the same method as O’Brien used, by writing the shape parameters as a converging series. We calculated the shape parameters numerically to the third order. In zeroth order, gravity is neglected and the resulting parameter description is that of the cap of a sphere. Higher order solutions deviate from this spherical result, increasingly for higher droplet volumes.

We integrate the parameter description over angles from zero to the contact angle ($\theta$) to find a relation between the principal radii of curvature, the contact angle and the volume. The base area depends on the radii of curvature. Therefore, for a set volume, the relation between the contact angle and the base area can be calculated if the droplet shape and contact angle and, thus, the relation between the volume and the radii of curvature is known.

We have calculated the solution of Eq. (C1) up to the third order and related the contact angle of the droplet to the base area. From the convergence of this series, we conclude that the maximum error in the contact angle for a volume of 10 $\mu$l is less than 1%. A plot of the contact angle versus the droplet base area in zeroth and third order approximation is shown in Fig. 2 for a 10 $\mu$l droplet of water, with $\gamma_{LV} = 0.072$ N m$^{-1}$, $\rho = 10^3$ kg m$^{-3}$. The graph for the third order can be fitted by a quadratic curve, with an accuracy better than 1%. For an aqueous 10 $\mu$l droplet, we find the relation between the contact angle and the base area $A$ to be

$$\theta = c_0 + c_1A + c_2A^2, \quad (C2)$$

where $c_0 = 2.381 \times 10^{11}$, $c_1 = -1.1214 \times 10^{7}$ m$^{-2}$ and $c_2 = 174.97$ m$^{-4}$. This gives a convenient calibration function to calculate the contact angle for any given base area.