Correlation for Dynamic Contact Angle

TSUNG-SHANN JIANG, SOO-GUN OH, AND JOHN C. SLATTERY

Department of Chemical Engineering, Northwestern University, Evanston, Illinois 60201

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A correlation is suggested for available experimental measurements of the advancing dynamic contact angle measured through the liquid phase during the displacement of a liquid–gas interface through a glass capillary tube. This same correlation is shown to describe the advancing contact angle as a wire enters a liquid from a gas, so long as the effects of inertia and gravity appear to be negligible. This suggests that experimental measurements of the dynamic contact angle may be independent of the macroscopic geometry.

Hoffman (1) observed the advancing dynamic contact angle Θ_m measured through the liquid phase during steady-state displacement of liquid–air phase interfaces through a glass capillary tube. Conditions were such that the effects of inertial forces, gravity, and adsorption upon the tube wall in the immediate neighborhood of the moving common line could be neglected. He presented his results in the form of a correlation for Θ_m as a function of the capillary number $Ca = \eta V/\gamma$, which is the ratio of viscous forces to interfacial forces at the liquid–gas interface, and a shift factor, which in turn was a function of the static contact angle Θ_s. Here η is the viscosity of the liquid, V is the speed of displacement of the interface, and γ is the liquid–air surface tension. Unfortunately, a relationship for the shift factor that could be used a priori was not given. To be able to predict Θ_m as a function of Ca, it would be necessary to have one or more measurements of Θ_m as a function of Ca so that the shift factor could be determined by comparison with Hoffman's master curve.

As summarized in Table I, a least-square-error fit of the data for the five fluids studied by Hoffman (1) gave

$$\frac{\cos \Theta_s - \cos \Theta_m}{\cos \Theta_s + 1} = \tanh (4.96\ \mathrm{Ca}^{0.702}). \qquad [1]$$

(The two parameters in Eq. [1] resulted from a nonlinear regression in which we minimized the sum of the squares of the percentage errors $(\Theta_{calc} - \Theta_{meas})/\Theta_{meas} \times 100$.) We also present in Table II a comparison between Eq. [1] and the data of Hansen and Toong (2) and of Rose and Heins (3) for basically the same geometry.

A number of other techniques have been used to study the effect of the speed of displacement of the common line upon the contact angle.

(1) Ablett (4) used a partially immersed rotating cylinder. The depth of immersion was adjusted to give a flat phase interface, which in turn allowed the contact angle to be easily calculated.

(2) Coney and Masica (5) studied displacement in a tube with a rectangular cross section.

(3) Schonhorn *et al.* (6) and Radigan *et al.* (7) examined the spreading of sessile drops.

(4) Ellison and Tejada (8), Inverarity (9) and Schwartz and Tejada (10, 11) photographed a wire entering a liquid–gas interface.

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TABLE I

Comparison of Eq. [1] with Portion of Hoffman's (1) Data upon Which It Is Based

Fluid	η (poise)	γ (dyn/cm)	Θ_s (deg)	Tube diameter (cm)	No. points	Error[a] (%)
GE silicone fluid SF-96	9.58	21.3	0	0.195	17	15.0
Brookfield std. viscosity fluid	988	21.7	0	0.195	23	3.1
Dow Corning 200 fluid	24,300	21	12	0.195	3	3.0
Ashland Chem. Admex 760	1,093	43.8	69	0.195	13	3.5
Santicizer 405	112	43.4	67	0.195	8	5.7

[a] Defined as $(\Theta_{calc} - \Theta_{meas})/\Theta_{calc} \times 100$; $\pm$ unless noted otherwise.

(5) Burley and Kennedy (12–14) studied a plane tape entering a liquid–gas interface.

(6) Johnson *et al.* (15) measured both advancing and receding contact angles using the Wilhelmy plate.

(7) Elliott and Riddiford (16, 17) observed both advancing and receding contact angles in radial flow between two flat plates. Johnson *et al.* (15) found considerably different results in examining similar systems with the Wilhelmy plate. Wilson (18) has discussed the instabilities associated with radial flow between plates.

The static contact angle is independent of measurement technique or, equivalently, geometry. At this writing, the effect of geometry upon dynamic measurements of the contact angle is unsettled. Dussan V. (19) and Huh and Mason (20) suggest that experimentalists normally have observed the dynamic contact angle too far away from the common line for their measurements to be geometry independent. No one has yet demonstrated that the same dependence of the contact angle upon the speed of displacement of the common line can be observed in two distinctly different geometries.

At least part of the problem appears to be that entirely comparable experiments have rarely been carried out in two different geometries.

Gravity plays an important role in at least a portion of the experiments of Ablett (4), Ellison and Tejada (8), Schwartz and Tejada (10, 11) and Johnson *et al.* (15). The principal motions are parallel with gravity.

Inverarity (9) unfortunately reports the equilibrium contact angle rather than the static advancing contact angle. Since these two contact angles are in general different, there is no basis for comparing his data with those of others.

TABLE II

Comparison of Eq. [1] with Other Data

Ref.	Fluid	η (poise)	γ (dyn/cm)	Θ_s[a] (deg)	Tube diameter (cm)	No. points	Error[b] (%)
(2)	Nujol	1.77	30.4	22	0.238	8	+8.4
(2)	Nujol	1.77	30.4	36	0.121	17	+8.8
(3)	Nujol	1.05	30.1	23	0.066 and 0.110	29	10.2
(3)	Oleic acid	0.256	32.5	32	0.066 and 0.10	17	10.6

[a] Given by Hoffman (1).

[b] Defined as $(\Theta_{calc} - \Theta_{meas})/\Theta_{calc} \times 100$; $\pm$ unless noted otherwise.

Johnson *et al.* (15) concluded that effects of adsorption on the solid in the immediate neighborhood of the moving common line might be present in the studies of Elliott and Riddiford (16, 17).

In the study of spreading drops by Schonhorn *et al.* (6), the rate of spreading appears to be controlled by a kinetic process at the moving common line. This is indicated by their observation that the rate of spreading was unchanged when the drop was inverted. This kinetic process may have been controlled by the movement of a very small precursor layer similar to those observed by Radigan *et al.* (7) and by Williams (21).

The effects of both inertia and gravity are significant in the studies of Burley and Kennedy (12–14).

Coney and Masica (5) considered displacement over a previously wet wall, which sets their work apart from others.

As one exception, it appears that there is a basis for comparing Hoffman's (1) data with selected experiments of Schwartz and Tejada (10), who measured the dynamic contact angle formed as a wire entered a liquid–gas interface. Table III shows a comparison of Eq. [1] with that portion of their data for which $We < 10^{-3}$. Here

$$We \equiv \frac{\rho V^2 L}{\gamma}$$

is the Weber number, which is the ratio of inertial forces to interfacial forces at the liquid-gas interface; ρ is the density of the liquid; L a characteristic dimension of the system, chosen here to be the static meniscus height as estimated using the computations of Huh and Scriven (22). The error is 15% or less, so long as $Bo < 10^{-1}$, where

$$Bo \equiv \frac{\rho g L^2}{\gamma}$$

is the Bond number, which is the ratio of gravity to interfacial forces, and g is the acceleration of gravity.

TABLE III

Comparison of Eq. [1] with Data for Contact Angle Measured on Cylinder Entering Liquid–Gas Interface (10). In All Cases, $We < 10^{-3}$

System[a]	Bo	Θ_s (deg)	No. points	Error[b] (%)
Water/Nylon	5.55×10^{-3}	70	14	−13.9
DOS[c]/Teflon	2.07×10^{-2}	61	19	−5.9
Methylene iodide/ Nylon	6.04×10^{-2}	41	11	−15.4
n-Octane/Teflon	9.59×10^{-2}	26	1	−29.7
α-Bromonaphthalene/Nylon	1.20×10^{-1}	16	7	−92.7

[a] All solid surfaces are smooth.
[b] Defined as $(\Theta_{calc} - \Theta_{meas})/\Theta_{calc} \times 100$.
[c] Di(2-ethylhexyl) sebacate.

This suggests that Eq. [1] may be applicable to any macroscopic geometry so long as the effects of gravity, of inertia, and of adsorption all appear to be absent.

If Eq. [1] is applicable to any macroscopic geometry, then the experimentally observed dynamic contact angle is independent of the macroscopic geometry in which the measurement is made and dependent only upon the properties of the materials involved and the speed of displacement of the common line. Additional experimental studies will be required for a definitive answer to this question.

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