

The kinetics of wetting: the dynamic contact angle

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Abstract: From measurements of dynamic contact angles, whereby a continuous solid strip is drawn into a large liquid pool, we obtained an operational equation:

$$\cos \theta_d = \cos \theta_o - 2(1 + \cos \theta_o) Ca^{1/2}$$

which predicts that under air entrainment conditions, the velocity is independent from the nature of the strip.

This empirical equation is also applicated to two other methods, namely the wetting of a vertical plate and the spreading of small drops.

Key words: Moving contact line, dynamic contact angle, air entrainment, wetting of a plate, spreading of a drop.

Introduction

The kinetics of wetting are very important for the technical process of coating. But it also is a challenge for a theorist to understand the mechanism of wetting: what about the boundary condition at the moving contact line and the fact that just there the pressure becomes infinite without a slip condition [1]. Until now the theoretical aspect was unresolved. Nevertheless, a large number of papers report measurements on dynamic contact angles [2–8], drawing a solid strip into a liquid [9–18], on spreading of drops on solid [19–21]. Different authors claim that the dynamic contact angle is ruled by macroscopic hydrodynamics [13–18, 22, 23], e. g., the capillary number, while others find it necessary to introduce molecular considerations [9, 10, 24].

In this paper we first present our own experiments, i. e., dynamic contact angle measurements when a continuous solid strip is drawn into a large pool of liquid. Out of these data we distil an operational equation and compare this with reanalyzed published results. In order to show its universality, we apply this equation to two other practical problems: the wetting process of a vertical solid plate for which we use our own results, and the spreading of a liquid drop on a solid, for which we use published data.

Experimental

We used two different methods to determine the dynamic contact angle:

1. A continuous solid strip is drawn into a large pool of liquid. The dynamic contact angle θ_d , i. e., the angle between the solid and liquid at the moving contact line, changes with strip velocity: θ_d is increasing with increasing speed. The apparatus for measuring these dynamic contact angles is similar to the one used by Burley and Kennedy [13, 14]. The liquid profile is illuminated by a Helium Neon laser and dynamic contact angles are photographed in function of the strip velocity. For each liquid this velocity is varied from $v = 0$ till $v = v_{\max}$, which is the velocity where air entrainment sets in. Air entrainment can easily be observed [10–13, 15] because the liquid-solid contact line changes from a straight line into a broken zigzag curve.

The materials used for the continuous strip are: smooth and rougher polyethylene (PE), polyethyleneterephthalate (PET), and for the liquids: aqueous glycerine solutions, aqueous ethylene-glycol solutions and ordinary corn oil.

Surface tensions are measured using the Wilhelmy plate technique and the viscosities using a capillary viscometer.

2. The second series of experiments concern the dynamic contact angle during the wetting of a vertical, initially dry platina Wilhelmy plate. This plate is coupled with a transducer (Gould Statham Universal Transducing cell UC 3 with a level arm, a UL 5 accessory), which is connected with a Gould Digital Storage Oscilloscope (OS 4000 with output unit 4001). The outgoing signal is finally recorded on a strip chart recorder. Since for high viscosity liquids the use of the storage oscilloscope is not necessary, the transducer is directly connected with the pen recorder.

At time $t=0$, when we make contact between the dry plate and the liquid, a trigger signal starts the registration of the change in weight, caused by the climbing of the liquid on the plate. This force profile $F(t)$ is stored by the oscilloscope, after which it is recorded. After a sufficient time $t = \infty$, i. e., when the weight remains constant, we also note $F(\infty)$. It is the ratio between $F(t)$ and $F(\infty)$ which gives information about the dynamic contact angle θ_d ,

$$\frac{F(t)}{F(\infty)} = \cos \theta_d. \quad (1)$$

As liquid we use silicon oils with a viscosity in the range $\mu = 3.5$ P(oise) to 588 P, and a surface tension $\sigma = 20$ dyne/cm.

Results and discussion

1. The dynamic contact angle for a strip drawn into a large pool of liquid

For a smooth PE strip and the aqueous glycerol solutions we plotted $\cos \theta_d$ as a function of the square root of the strip velocity $v^{1/2}$; an example is shown in Fig. 1. It is seen that a linear relationship is obtained. At $v = 0$, the curve extrapolates to the static advancing contact angle; $\theta_d = \theta_o$ [25]. At $\cos \theta_d = -1$, i. e., $\theta_d = \pi$, the curve extrapolates to a velocity v_π , which corresponds to the velocity at which air entrainment sets in, or in other words $v_\pi \approx v_{\max}$. This is in agreement with the findings of other authors [10, 13, 18]. For 10 other viscosities lying in the range from $\mu = 0.104$ P to 1.84 P, and with almost the same surface tension $\sigma \approx 63$ dyne/cm, we obtain analog graphs. The slopes, $k = -d \cos \theta_d / v^{1/2}$, from each of these curves

are calculated and plotted as a function of the square root of the viscosity $\mu^{1/2}$ (Fig. 2). Again a linear relation between k and $\mu^{1/2}$ is obtained, suggesting that the dynamic contact angle depends on the square root of the capillary number, $Ca^{1/2} = (\mu v / \sigma)^{1/2}$. All the results with the smooth PE strip and the aqueous glycerol solutions are taken together in a $\cos \theta_d$ vs. $Ca^{1/2}$ graph (Fig. 3.). This linear relationship is expressed in the next equation

$$\cos \theta_d = \cos \theta_o - \gamma Ca^{1/2} \quad (2)$$

with $\gamma = -d \cos \theta_d / d Ca^{1/2}$, being the corresponding slope.

An analog analyzing method is used for other combinations of the different strips with the different liquids. The final results are given in Table 1.

We can conclude from this that:

i) $\cos \theta_d$ decreases linearly with the square root of the capillary number as shown in Eq. (2).

ii) At $v = 0$, the dynamic contact angle extrapolates to the static advancing one obtained through the method of Wolfram [25, 26]. In Table 2, where we compare this extrapolated value θ_o to the static ones θ_A , we find good agreement.

iii) At $\cos \theta_d = -1$, i. e., $\theta_d = \pi$, the extrapolated velocity v_π corresponds to the directly observed velocity v_{\max} .

iv) The slopes γ , given by the linear relationship of Eq. (2), are not constant but are a function of the extrapolated contact angle θ_o . In Fig. 4, where, beneath our own data, the results of other investigators are shown,

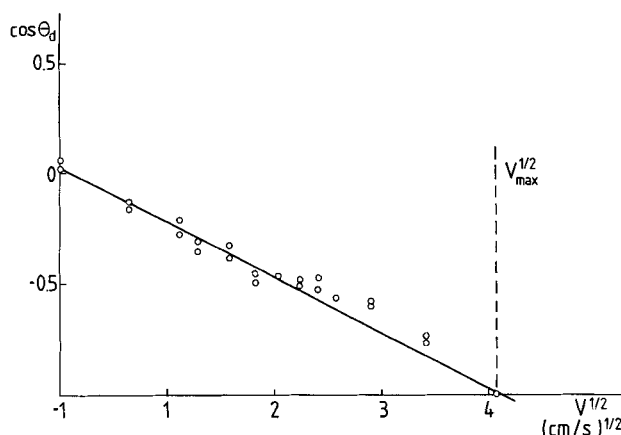


Fig. 1. Smooth polyethylene strip drawn into an aqueous glycerol solution: $\mu = 1.506$ P, $\sigma = 63$ dyne/cm. $\cos \theta_d = (0.02 \pm 0.04) + (-0.25 \pm 0.01) v^{1/2}$; $\theta_o = 89^\circ \pm 2^\circ$; regression coefficient = 0.96

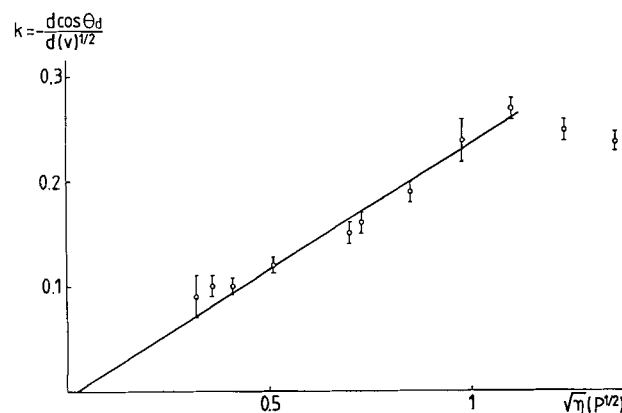


Fig. 2. Smooth polyethylene strip drawn into aqueous glycerol solutions. $\cos \theta_d = \cos \theta_o - 0.23 \pm 0.01 (\mu v^{1/2})$; regression coefficient = 0.98

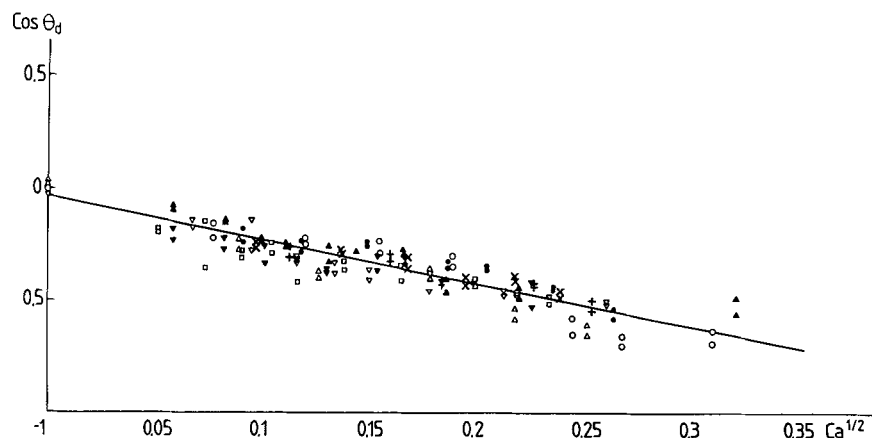


Fig. 3. Smooth polyethylene strip drawn into aqueous glycerol solutions. $\mu = 1.214$ P: Δ ; $\mu = 0.910$ P: \circ ; $\mu = 0.723$ P: \times ; $\mu = 0.533$ P: \bullet ; $\mu = 0.492$ P: $+$; $\mu = 0.265$ P: \blacktriangle ; $\mu = 0.173$ P: ∇ ; $\mu = 0.130$ P: \blacktriangledown ; $\mu = 0.104$ P: $\cos \theta_d - (-0.03 \pm 0.06) = -1.95 \pm 0.06 Ca^{1/2}$; $v_{\max} = 15.5 \pm 0.9 \text{ cm} \cdot \text{s}^{-1} / \mu \text{ tot } \mu = 1.2 \text{ P}$; $\theta_o = 92^\circ \pm 3^\circ$; regression coefficient = 0.87

Table 1. Results from $\cos \theta_d - Ca^{1/2}$ analysis method: $\cos \theta_d = \cos \theta_o - \gamma Ca^{1/2}$

	$\theta_o \pm \text{SD}$	$\gamma \pm \text{SD}$
aqueous glycerol solutions:		
pe, smooth	$92^\circ \pm 3^\circ$	1.95 ± 0.06
pe, rough	$97^\circ \pm 2^\circ$	1.61 ± 0.05
pet	$77^\circ \pm 5^\circ$	2.62 ± 0.05
aqueous ethyleneglycol solutions:		
pe, smooth	$80^\circ \pm 4^\circ$	2.17 ± 0.05
pe, rough	$84^\circ \pm 4^\circ$	2.03 ± 0.06
pet	$65^\circ \pm 5^\circ$	2.69 ± 0.07
corn oil:		
pe, smooth	$37^\circ \pm 10^\circ$	3.7 ± 0.2
pe, rough	$45^\circ \pm 7^\circ$	3.9 ± 0.2
pet	$66^\circ \pm 4^\circ$	2.3 ± 0.2

^a) Experimental results from Blake [10] for five viscosities are also considered in this case.

Table 2. Comparison between the static advancing angle θ_A and the extrapolated value θ_o . θ_Y is the Young contact angle and α is a measure of the roughness of the substratum, both obtained using the tilted plate method [25, 26]

	θ_Y	α	$\theta_A = \theta_Y + \alpha$	$\theta_o \pm \text{SD}$
aqueous glycerol solutions:				
pe, smooth	82°	13°	95°	$92^\circ \pm 3^\circ$
pe, rough	82°	20°	102°	$97^\circ \pm 2^\circ$
pet	65°	8°	72°	$77^\circ \pm 5^\circ$
aqueous ethyleneglycol solutions:				
pe, smooth	63°	13°	76°	$80^\circ \pm 4^\circ$
pe, rough	63°	20°	83°	$84^\circ \pm 4^\circ$
pet	48°	8°	56°	$65^\circ \pm 5^\circ$

corn oil: no experiments with the tilted plate method are available

we have plotted γ vs. $\cos \theta_o$, and again we get a linearity which can be written as

$$\gamma = 2(1 + \cos \theta_o). \quad (3)$$

So, Eq. (2) becomes

$$\cos \theta_d = \cos \theta_o - 2(1 + \cos \theta_o) Ca^{1/2}. \quad (4)$$

Here refer here to Tanners equation [27], which gives a relation between small dynamic contact angles θ_d and the capillary number Ca :

$$\theta_d = (3\Phi)^{1/3} Ca^{1/3} \quad (5)$$

with Φ nearly constant, being a logarithmic function of Ca . Tanner [27] also gives some theoretical evidence for spreading on a dry as well as on a wet surface, making use of the lubrication method for thin films.

Developing Eq. (4) for small angles, i. e., $\theta_d \approx 1 - \theta_d^2/2$, we get

$$\theta_d = \Omega Ca^{1/4} \quad (6)$$

with $\Omega = \Omega(\theta_o)$ a function of the static contact angle θ_o and $\Omega(\theta_o = 0) = \sqrt{6}$.

We can say that Eqs. (5) and (6) are comparable for small capillary numbers Ca .

The first very important practical consequence of the operational Eq. (4) is that under air entrainment conditions, i. e., $\cos \theta_d = -1$ and $v = v_{\max}$,

$$v_{\max} = \frac{\sigma}{4\mu}. \quad (7)$$

v_{\max} , the air entrainment velocity is independent of the nature of the solid strip. This important conclusion is

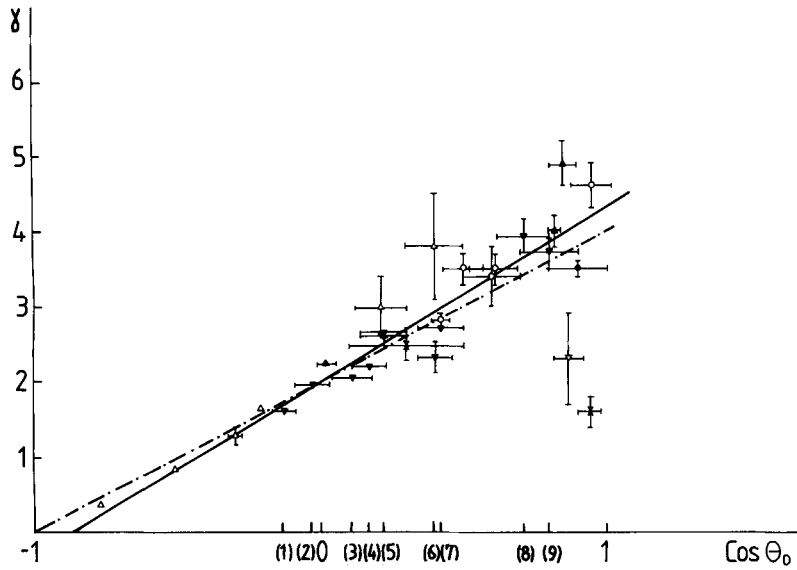


Fig. 4. —: $\cos \theta_d - \cos \theta_o = -2(\cos \theta_o + 1) Ca^{1/2}$ (4); $v_{\max} = \sigma/4\mu = 15.8 \text{ dyne} \cdot \text{cm}^{-1}/\mu$. pe, smooth: \square , pet: \times , pet 1: \circ , pet 2: \bullet , pet 3: \blacksquare , triacetat: $+$; pet 1, pet 2, and pet 3 are polyethyleneterephthalate with different gelatin layers

also stated by Burley et al. [14, 17] and Gutoff et al. [18]. The intrinsic value of Eq. (7) is also pointed out in Fig. 5 where we have plotted v_{\max} vs. μ for different

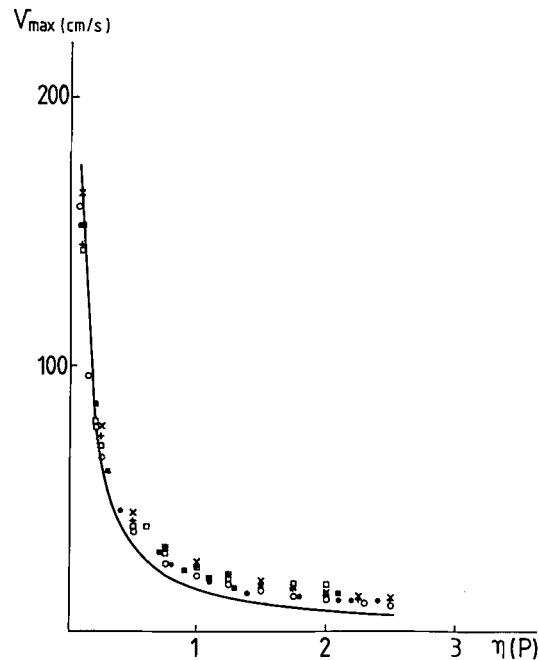


Fig. 5. —: Linear regression, $y = (2.3 \pm 0.1) \cos \theta_o + (2.0 \pm 0.2)$; regression coefficient = 0.94; - - - : $y = 2(\cos \theta_o + 1)$. [18]: \circ , [5, 6]: \bullet , [6]: \times , [10, this work]: $+$, [4]: $*$, [14, 16, 17]: Δ , [8]: \blacktriangle , [3]: ∇ , [this work]: \blacktriangledown . Our experimental results: 1) rough pe/aq. glycerol, 2) smooth pe/aq. glycerol, 3) rough pe/aq. ethyleneglycol, 4) smooth pe/aq. ethyleneglycol, 5) pet/aq. glycerol, 6) pet/corn oil, 7) pet/aq. ethyleneglycol, 8) rough pe/corn oil, 9) smooth pe/corn oil

strip materials drawn into an aqueous glycerol solution. For aqueous ethyleneglycol solutions we get an analog result.

Without going into details it should be noted that these empirical findings cannot be applied on the rougher PE strip for viscosities larger than about 1 P. Since Eq. (7) does not explain either the minimum in the $v_{\max} - \mu$ curve or the increasing evolution for $\mu > 1$ P. Burley and Jolly [14] also reported anomalous behavior for surfaces of a certain roughness.

2. The wetting of a vertical solid plate

For a strip drawn into a large liquid pool, Burley and Kennedy [16] showed that for dynamic contact angles less than $\pi/2$ the correct liquid profile is obtained by only taking gravitational and surface forces into account. This means that viscous forces in the bulk may be neglected. De Gennes [28] comes to the same conclusion; he stated that all the free energy S , i. e., $S = \sigma_s - \sigma_{s1} - \sigma_1$, is "burned up" in the precursor film. This means that the height of the liquid on a vertical plate is given by

$$h = h_L (1 - \sin \theta_d)^{1/2} \quad (8)$$

with $h_L = (2\sigma/\rho g)^{1/2}$, the Laplace length, and ρ is the liquid density, and g is the gravitational acceleration.

The viscosity is implicitly included in the dynamic contact angle θ_d given by Eq. (4), which can be regarded as the boundary condition of the wetting problem. Furthermore, we consider the dynamic contact angle

θ_d as a macroscopic reflection of all molecular considerations.

The rate of wetting is given by Eq. (4)

$$v = \frac{dh}{dt} = \left[\frac{\cos \theta_d - \cos \theta_o}{2(1 + \cos \theta_o)} \right]^2 \frac{\sigma}{\mu} \quad (9)$$

and also be Eq. (8)

$$\frac{dh}{dt} = -h_L \frac{\cos \theta_d}{2(1 - \sin \theta_d)^{1/2}} \frac{d\theta_d}{dt}. \quad (10)$$

After equalizing Eq. (9) to Eq. (10) and taking into account that at $t = 0$, $\theta_d = \pi/2$, we find

$$T = \int_{\theta_o}^{\pi/2} \frac{(1 + \sin \theta_d)^{1/2}}{2(\cos \theta_d - \cos \theta_o)^2} d\theta_d \quad (11)$$

with $T = t/\tau_R$ the dimensionless time, τ_R being the relaxation time given by

$$\tau_R = 4\mu (1 + \cos \theta_d)^2 \left\{ \frac{2}{\rho g \sigma} \right\}^{1/2}. \quad (12)$$

Equation (11) can be solved by numerical integration.

In our case where the platina Wilhelmy plate is completely wetted by the silicon oils, i. e., $\theta_o = 0$ and thus, $\cos \theta_o = 1$, we have to rewrite Eqs. (11) and (12) as

$$T = \int_0^{\pi/2} \frac{(1 + \sin \theta_d)^{1/2}}{2(\cos \theta_d - 1)^2} d\theta_d \quad (13)$$

$$\tau_R = 16\mu \left\{ \frac{2}{\rho g \sigma} \right\}^{1/2}. \quad (14)$$

The relaxation time for water is extremely small, i. e., $\tau_R = 8.5 \cdot 10^{-4}$ s. Thus, in order to prove Eq. (13) experi-

mentally, we have to use rather high viscosity fluids. Therefore, we have chosen silicon liquids with their wide range of viscosities and their low surface tension. The experimental results, presented in Fig. 6, match very well with the theoretical Eq. (13). The fact that at low viscosities, i. e., $\mu < 3$ P, the experimental points lie under the theoretical ones is due to the slowness of our measuring device (especially to the Statham transducer).

We remark that our present theory and experiments apply to the wetting of a clean but dry, vertical plate. The rate of wetting is, as expected, much faster for a prewetted plate. This explains the deviation from the previous results of Rillaerts and Joos [4], who performed their experiments in a prewetted capillary (Fig. 5).

3. Spreading of a small drop on a solid

Making use of Eq. (4), we can perfectly describe the spreading of a drop on a solid substrate. For small drops the effect of gravity is negligible and we can use the spherical approximation. The use of large drops does not make the situation different but complicates only the calculations.

We express here the same point of view as in the previous paragraph, that is that the viscosity effects are implicitly included in the dynamic contact angle and can be neglected in the bulk liquid.

A small spherical drop with radius r_o and volume V is placed on a solid surface. This drop spreads from an initial contact angle $\theta_d = \pi$ until an angle $\theta_d = \theta_o$. Because the volume V remains constant, and from geometric arguments, the radius of the drop becomes after a time t

$$r = 4^{1/3} r_o \sin \theta_d [(1 - \cos \theta_d)^2 (2 + \cos \theta_d)]^{-1/3}. \quad (15)$$

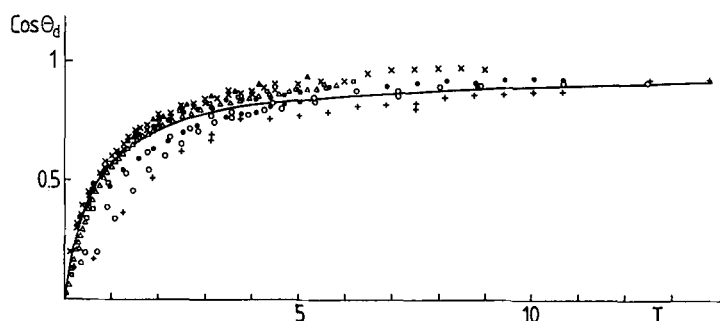


Fig. 6. Climbing of silicon liquids on a platina Wilhelmy plate: $\mu = 3.43$ P: \circ , $\mu = 4.85$ P: $+$, $\mu = 9.7$ P: \bullet , $\mu = 10$ P: \square , $\mu = 122.5$ P: \times , $\mu = 294$ P: Δ , $\mu = 588$ P: \blacktriangle ; —: Eq. (13)

The rate of spreading is given by

$$\frac{dr}{dt} = -4^{1/3} r_o \frac{(1 - \cos \theta_d)^2}{[(1 - \cos \theta_d)^2 (2 + \cos \theta_d)]^{4/3}} \frac{d\theta_d}{dt} \quad (16)$$

Equalizing Eq. (16) to Eq. (9), we get

$$T = \int_{\theta_o}^{\pi} \frac{d\theta_d}{[(1 - \cos \theta_d)^2 (2 + \cos \theta_d)]^{1/3} (2 + \cos \theta_d) (\cos \theta_o - \cos \theta_d)^2} \quad (17)$$

with the relaxation time τ_R given by

$$\tau_R = 4^{1/3} \frac{4\mu}{\sigma} r_o (1 + \cos \theta_o)^2. \quad (18)$$

Under complete wetting conditions, i. e., $\theta_o = 0$ and thus $\cos \theta_o = 1$ Eq. (17) and Eq. (18) become

$$T = \int_{\theta}^{\pi} \frac{d\theta_d}{[(1 - \cos \theta_d)^2 (2 + \cos \theta_d)]^{4/3}} \quad (19)$$

$$\tau_R = 4^{1/3} \frac{16\mu}{\sigma} r_o. \quad (20)$$

We did not perform our own experiments because there are enough data on the spreading of small drops available in literature. We remark that all authors started their experiments by $\theta_d = \pi/2$.

Radigan et al. [19] studied at a temperature of 1000 °C the spreading of glass drops of different masses, $m = 0.7$ mg; 4.5 mg and 11.3 mg on Fermico metal. Those authors claim, in contrast to our Eq. (20), that the spreading rate does not depend on the drop size. This conclusion can be blamed on the large scatter of their experimental values. Despite this wide scatter,

we see that in Fig. 7, where we have plotted $\cos \theta_d$ vs. $T - T_{90^\circ}$, some agreement between theory and experiments is achieved. It is also important to mention that they observed, by use of scanning electron microscopy, a precursor film with a height of about 1 μm .

Schonhorn et al. [20] placed small drops of polyethylene and ethylene vinyl acetate copolymers on high-

(alumina and mica) and low-energy (teflon) surfaces. The high-energy surfaces wet completely, i. e., $\theta_o = 0$; for teflon they found a contact angle of $\theta_o = 75^\circ$. Schonhorn et al. defined a sort of relaxation time, namely $1/a_T = L_w \mu / \sigma$, but they claimed as well that L_w is independent of r_o , m , or ρg . Nevertheless, in order to analyze their experiments we put forward that $L_w = 2r_o$. We have plotted $\cos \theta_d$ vs. $T - T_{90^\circ}$ for the high

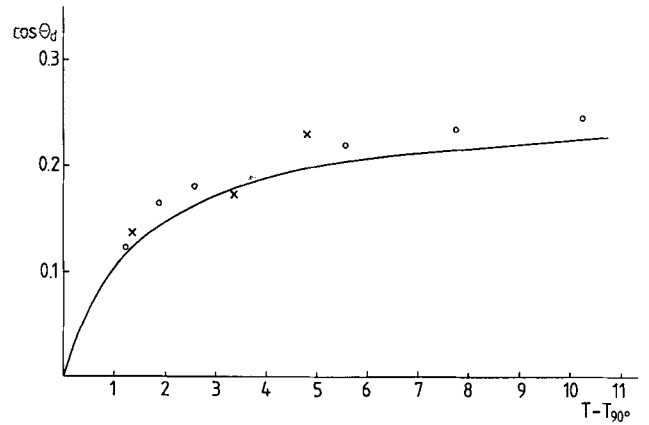


Fig. 8. Spreading of a drop, (from [20]): ○: Elvax 220 op Al: 170 °C; ●: Elvax 220 op Al/ 151 °C; △: Elvax 220 op Al: 123 °C; ▲: Elvax 220 op Al: 118 °C; □: Elvax 220 op Mica: 151 °C; ∆: Dylt PE op Al: 151 °C; —: Eq. (19)

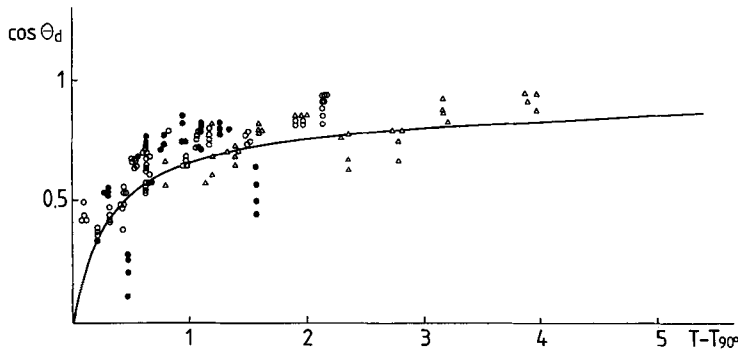


Fig. 7. Spreading of a drop, glass on Fermico metal: 1000 °C, (from [19]): ▲: $m = 0.7$ mg; ○: $m = 4.5$ mg; ●: $m = 11.3$ mg; —: Eq. (19)

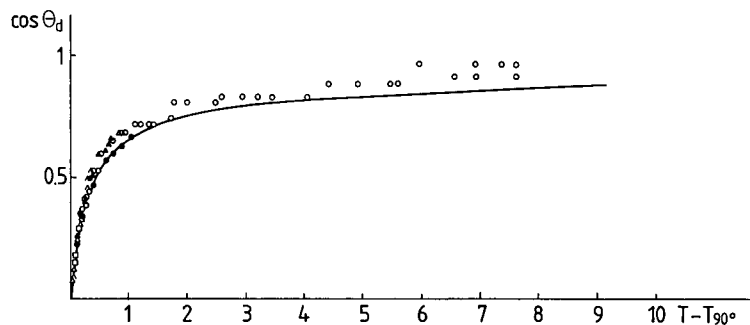


Fig. 9. Spreading of a drop, (from [20]): ○: Elvax 220 op teflon: 170°C; ×: Elvax 220 op Teflon: 151°C; $\theta_o = 75^\circ$; —: Eq. (17)

energy substrata in Fig. 8 and we can say that our theory, i. e., Eq. (19), fits their results well.

In Fig. 9 we made the analog graph for the spreading of drops on teflon. Our theory, i. e., Eq. (17), predicts the right progress of the dynamic contact angle in function of time.

Van Oene et al. [21] also performed spreading experiments with Dylt drops on alumina. In contrast with the two other authors his results lead to the conclusion that spreading is depending on the drop radius. We see in Fig. 10 that his results lie on the same master curve if plotted as a function of the dimensionless time. However, the spreading rate is about three times faster as that predicted by Eq. (19). Van Oene also stated that his rate is faster as compared with the similar results of Schonhorn. The reason for this deviation is, in our opinion, that Van Oene modified the surface by his intensive cleaning process so that the spreading coefficient $S = \sigma_s - \sigma_{s1} - \sigma_l$ is larger than zero, $S > 0$. This means that we are in a situation of non-equilibrium and the Young equation is no longer valid.

In previous research [29] we found that there is a limiting value above which the small drops in these systems cannot be referred to as spherical, or in other words, gravitational effects have to be taken into

account. This limiting value is given by $\log V_L^* \approx 0$, with $V_L^* = V_L/a^3$ the dimensionless volume and $a = (\sigma/\rho g)^{1/2}$.

For glass drops, Radigan [19] gives the values: $\rho = 2.21 \text{ g/cm}^3$, $\sigma = 278 \text{ dyne/cm}$, which means that $a = 0.358 \text{ cm}$ and $V_L = 0.046 \text{ cm}^3$. The drops with respective masses $m = 0.7 \text{ mg}$, 4.5 mg , and 11.3 mg have respective volumes of $V = 0.347 \text{ cm}^3$, 2.036 cm^3 , and 5.113 cm^3 , and thus, we cannot neglect the gravitational effect anywhere. This partially explains the deviation between his experiments and our theory (Fig. 7).

For Elvax the limiting volume (V_L) is 0.01 cm^3 , with $a = 0.212 \text{ cm}$. Since Schonhorn [20] used volumes of $V = 0.0067 \text{ cm}^3$, 0.0246 cm^3 , and 0.0282 cm^3 , the spherical approximation can only be applied to the first volume.

Van Oene [21] used for Dylt drops ($\rho = 0.91 \text{ g/cm}^3$, $\sigma = 30 \text{ dyne/cm}$) masses of $m = 0.0015 \text{ g}$ and 0.0167 g , which lead to volumes of $V = 0.0016 \text{ cm}^3$ and 0.0184 cm^3 . With $a = 0.183 \text{ cm}$, the limiting volume becomes $V_L = 0.0061 \text{ cm}^3$ and only the first drop volume is small enough.

Conclusions

The experiments with a strip drawn into a liquid lead to the empirical equation

$$\cos \theta_d = \cos \theta_o - 2(1 + \cos \theta_o) Ca^{1/2}. \quad (4)$$

This formula is tested by comparison with published results, and by application to two other systems, those being the wetting of a vertical solid plate and the spreading of a drop. It is obvious that our empirical approach allows a successful description of different dynamic wetting phenomena. A theoretical base is not available, but we have strong arguments that the viscosity effect can be neglected in the bulk liquid and is

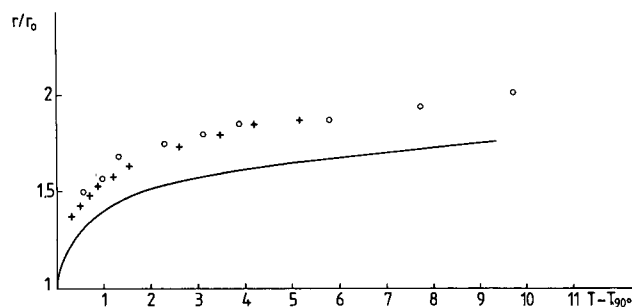


Fig. 10. Spreading of a drop, (from [21]): Dylt drops on alumina: 120°C; small drop: $r_o = 0.073 \text{ cm}$; large drop: $r_o = 0.164 \text{ cm}$; —: Eq. (19)

only intrinsically included as a boundary condition in the dynamic contact angle, given by Eq. (14).

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