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Experimental Study of the Spreading of a Viscous Droplet on a Nonviscous Liquid

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We describe experiments on the spreading of liquid droplets deposited on a (wetable) liquid substrate, when the friction in the droplet dominates. We find that the horizontal radius R increases with the spreading time t like $t^{0.26 \pm 0.02}$ in the capillary regime ($R < \kappa^{-1}$, the interfacial capillary length), and like $t^{0.51 \pm 0.02}$ in the gravity regime. These results are in good agreement with a recent theory.

I. Introduction

(1) Spreading on Solids. The spreading of macroscopic droplets on completely wettable solid substrates has been studied a long time ago by Tanner¹ and Marmur.² In this case, the spreading radius $R(t)$ increases very slowly, like $t^{1/10}$, and does not depend on the spreading coefficient S . These laws have been interpreted theoretically:^{3,4} the free energy S is entirely “burned” inside a precursor film which develops ahead the macroscopic contact line and the driving force pulling the droplet reduces to

$$F = \gamma(1 - \cos \theta) \approx \gamma \frac{\theta^2}{2}$$

where γ is the liquid surface tension and θ the small dynamic contact angle. The dominant viscous dissipation takes place near the contact line (where the velocity gradient is the largest) and can be expressed as

$$T\dot{S} = \frac{\eta}{\theta} \frac{\dot{R}^2}{l}$$

(η is the liquid viscosity, l is a logarithmic factor, and $\dot{R} = dR/dt$ is the velocity of the contact line). Equating $F\dot{R}$ and $T\dot{S}$, one finds that $\dot{R}(t) \propto \theta^3$. One can express θ as a function of Ω , the conserved volume of the nonvolatile liquid droplet, and the radius R : $\theta \propto \Omega/R^3$. This leads to $R(t) \propto t^{1/10}$, in good agreement with experimental data.²

(2) Spreading on Liquids. This situation is far less understood. One major advantage is that the surface of a liquid is nearly perfect (if surfactant impurities are capillary scooped out), compared to the surface of a solid, where roughness and chemical heterogeneity are always present. But the interpretation is more complex, because of the back flows induced in the liquid substrate.^{5,6}

The dissipation now takes place (i) in the droplet ($T\dot{S}_d$) and (ii) in the substrate ($T\dot{S}_s$).

(i) Inside the droplet (viscosity η), for a long time limit, the dynamic contact angle is small, and a lubrication

approximation can be used. The velocity field inside the droplet is two dimensional and is ruled by a 2D Navier–Stokes equation.

In our case, η is larger than the substrate viscosity η_s and the flows are “plug flows”, as shown in ref 6. The velocity gradients are of the order of \dot{R}/R . The viscous dissipation in the droplet is then (ignoring all coefficients)

$$T\dot{S}_d \approx \Omega \eta \left(\frac{\dot{R}}{R} \right)^2 \quad (1)$$

where $\Omega \approx hR^2$ is the constant droplet volume.

(ii) In the substrate (viscosity η_s), the back flows, driven by the spreading drop, are localized in a region of volume $\approx R^3$ and thus

$$T\dot{S}_s \approx \eta_s R^3 \left(\frac{\dot{R}}{R} \right)^2 \quad (2)$$

The comparison of eqs 1 and 2 defines a critical radius R_c at which the two terms become equal

$$R_c = \left(\frac{\eta}{\eta_s} \Omega \right)^{1/3} \quad (3)$$

Two regimes must then be distinguished:

(a) $R > R_c$, Substrate Dominant. All previous studies on liquid/liquid spreading, both theoretical⁶ and experimental⁷ have been concerned with this case, where the dissipation in the substrate is dominant.

The main difficulty, reported in ref 7, is the definition of the radius of the drop, the edge profile being extremely elongated with a very small dynamic contact angle.

(b) $R < R_c$, Droplet Dominant. The present paper is focused on this new regime where the dissipation in the droplet is dominant. As usual the spreading is driven by capillary forces for small drops and by gravity for large ones. The crossover radius between these two regimes is the interfacial capillary length

$$\kappa^{-1} = \sqrt{\frac{\tilde{\gamma}}{\tilde{\rho}g}}$$

where $\tilde{\gamma}$ is an effective interfacial tension

$$\tilde{\gamma}^{-1} = \gamma_{ds}^{-1} + \gamma^{-1}$$

(γ_{ds} is the interfacial tension between the droplet d and the substrate s, while γ is the d surface tension) and $\tilde{\rho}$ is

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Table 1. Interfacial Tension and Viscosity of the Glycerol/Water Mixture

	γ_{ds} (mN/m)	η_s (mPa·s)
glycerol/water, 1/1	36.4	5.97
glycerol/water, 5/1	33.2	45.9

the effective density

$$\tilde{\rho} = \rho \left(1 - \frac{\rho}{\rho_s} \right)$$

(ρ , ρ_s are the droplet and substrate densities, respectively).

These theoretical predictions for the spreading have been given in ref 8. The main results are the following:

(i) $\kappa R < 1$, Capillary Regime. This regime is soluble exactly in the lubrication approximation. The profile is a spherical cup of horizontal radius

$$R = \left(\frac{16}{\pi} \Omega \frac{\tilde{\gamma}}{\eta} \right)^{0.25} t^{0.25} \quad (4)$$

The exponent can be easily understood by equating the dissipation in eq 1 with the work of the capillary driving force.

$$\{\tilde{\gamma}(1 - \cos \theta)\} 2\pi R \dot{R} \cong \tilde{\gamma} \theta^2 R \dot{R}$$

The height of the droplet is $h \cong \theta R$ and the (fixed) volume is $\Omega \cong h R^2$; hence $R \cong t^{0.25}$. The dynamic contact angle θ is related to the velocity \dot{R} of the contact line by the (exact) relationship

$$\frac{\tilde{\gamma}}{\eta} \theta = \dot{R} \quad (\theta \ll 1) \quad (5)$$

Thus, in this case, θ is finite and the contour of the droplet is sharp.

(ii) $\kappa R > 1$, Gravitational Regime. Here we have only a scaling prediction. The droplets are nearly flat, of thickness h , except near the edge, which has an angle θ given by the contact line motion eq 5.

Equation 1 remains valid, but the pulling force is now gravitational and equal to $^{1/2} \tilde{\rho} g h^2$ (per unit length of the contact line), hence

$$R \cong \left(\frac{\tilde{\rho} g}{\eta} \right)^{0.5} t^{0.5} \quad (8)$$

II. Experiments

(1) Materials. We deposit a droplet of poly(dimethylsiloxane) (PDMS) (referred as liquid d) on the surface of a glycerol/water mixture (liquid s) contained in a parallelepiped trough (length 65 mm, depth 10 mm). Three molecular weights of PDMS are used, giving three values of the viscosity η_d (29 310, 58 620 and 97 700 mPa·s) and a constant surface tension ($\gamma_d = 21$ mN·m⁻¹). The proportion of water in the mixtures allows us to vary the viscosity η_s of the substrate. This viscosity was measured at ambient temperature with a capillary viscometer (Ubbelohde). Each mixture also gives a different value for the interfacial tension γ_{ds} , which we measure by the Wilhelmy method. These values are displayed in Table 1. The mixtures which are used are all completely wettable by PDMS.

(2) Droplet Deposition. We take a small amount of liquid d with a sharp glass needle covered with a Teflon spray: this treatment makes the glass surface hydrophobic. Then the liquid can flow along the vertical needle and forms a small droplet which eventually falls by gravity. Different needle diameters give different droplet sizes (in the order of 1 mm). The droplet mass is obtained by measuring the weight of the tube before and

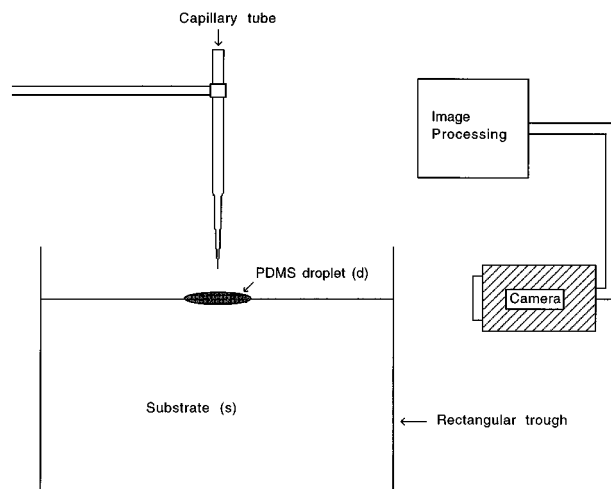


Figure 1. Experimental setup.

after droplet emission. The droplet weight is in the range of milligrams and is measured with an accuracy of 10 μ g ($\approx 1\%$).

(3) Experimental Setup (Figure 1). The droplets are filmed laterally with a CCD camera through the glass side wall of the trough. The spatial resolution is 35 μ m. Since the refraction indices of d and s are very close, the droplets can be seen only by using an oblique light source nearly parallel to the camera (Figure 2). The images are then digitalized and the drop radius is measured using a video analysis software. For small droplets ($R < 1.5$ mm), the edge is relatively sharp and the relative uncertainty is

$$\Delta R/R \approx 6\%$$

For large droplets, the edge is more fuzzy and we estimate

$$\Delta R/R \approx 9\%$$

III. Results

The radius $R(t)$ has been plotted against the spreading time t on Figure 3a, for different liquid pairs. The novel feature is the observation of two distinct slopes with a crossover at a certain radius $R = R^*$.

R^* ranges between $0.85\kappa^{-1}$ and $1.01\kappa^{-1}$, where κ^{-1} is the interfacial capillary length (see Table 2). This tends to confirm the existence of a transition between capillary and gravity regimes.

(1) Capillary Regime ($\kappa R < 1$). When $R(t)$ is monitored, the initial time is arbitrarily chosen as the instant of first contact between the drop and the substrate. We derive the numerical coefficient

$$a = \frac{16}{\pi} \Omega \frac{\tilde{\gamma}}{\eta}$$

from surface tension, viscosity, and mass measurements. We then adjust the power exponent α and the effective initial time t_0 assuming that the time dependence follows a power law

$$R = \alpha^\alpha (t - t_0)^\alpha$$

We find $t_0 = 1 \pm 0.5$ s, which is comparable to the fall time of the drop and $\alpha = 0.26 \pm 0.02$, which confirms the theoretical prediction $\alpha = 0.25$ (eq 4).

(2) Gravity Regime ($\kappa R > 1$). Here we adjust β and b to get the best fit for the radius of the flattened droplet

$$R(t) = b^\beta (t - t_0)^\beta$$

assuming the same initial time $t_0 \approx 1$ s. We find that β

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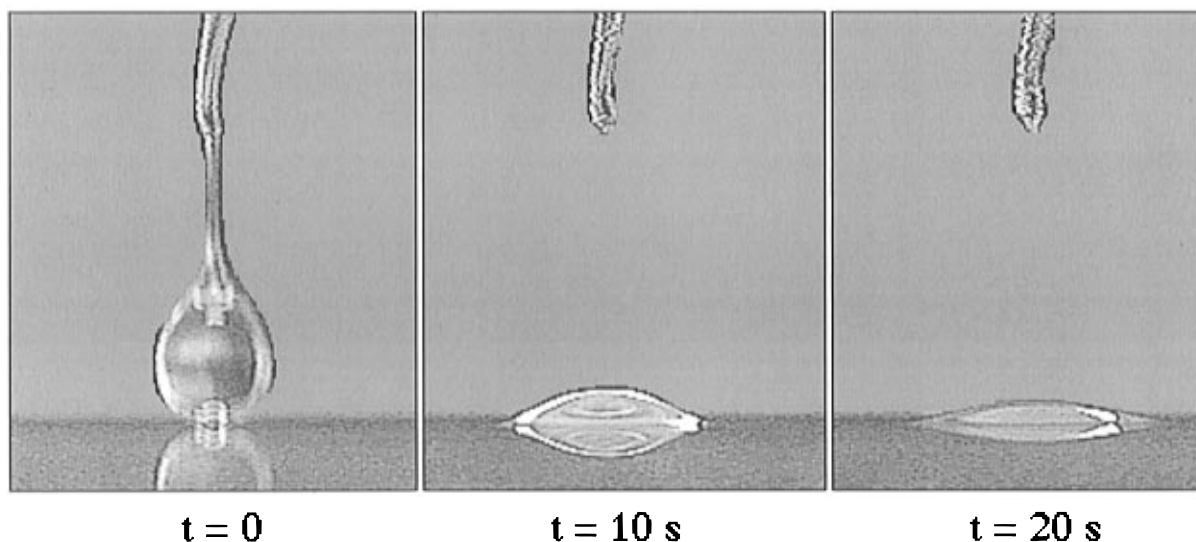


Figure 2. Spreading sequence of a droplet of PDMS ($\eta_d = 58\,620$ mPa·s) on a surface of glycerol/water: 5/5 ($\eta_s = 5.97$ mPa·s). The screen size is 5 mm.

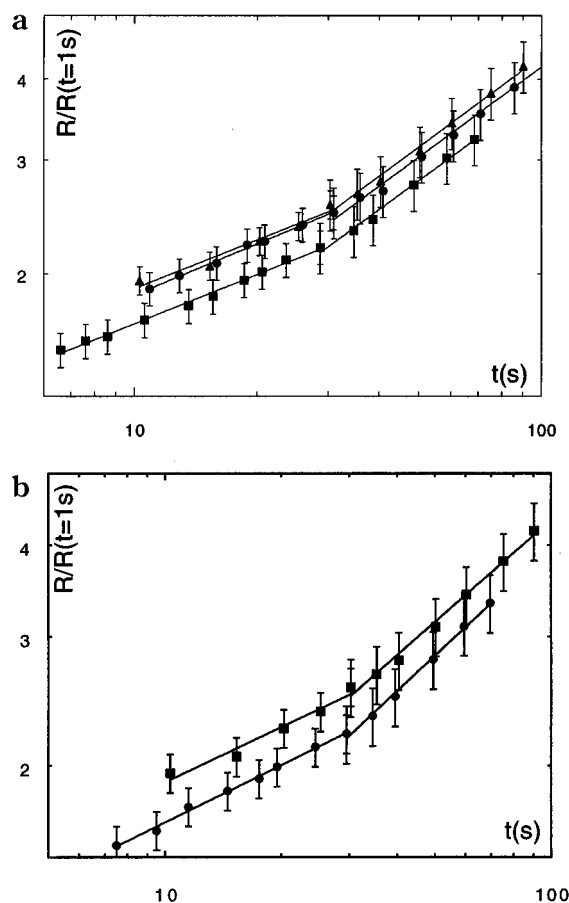


Figure 3. Radius versus spreading time of a PDMS droplet deposited on a glycerol/water mixture in reduced units $\hat{R}(t)/\hat{R}(t=1s)$. (a) Influence of the droplet viscosity η_d , $\eta_s = 5.97$ mPa·s: ●, $\eta_d = 29\,310$ mPa·s; ■, $\eta_d = 58\,620$ mPa·s; ▲, $\eta_d = 97\,700$ mPa·s. (b) Influence of the substrate viscosity η_s , $\eta_d = 97\,700$ mPa·s: ■, $\eta_s = 5.97$ mPa·s; ●, $\eta_s = 45.9$ mPa·s.

$= 0.51 \pm 0.02$, which is also in good agreement with the theoretical predictions (eq 6).

For both regimes, we can check in Figure 3b that, in our case, the spreading kinetics is actually independent of η_s . The slight mismatch between the two curves is due to a differences between the values of the crossover radius R^* induced by variations on $\bar{\rho}$ and $\bar{\gamma}$ when the substrate is changed.

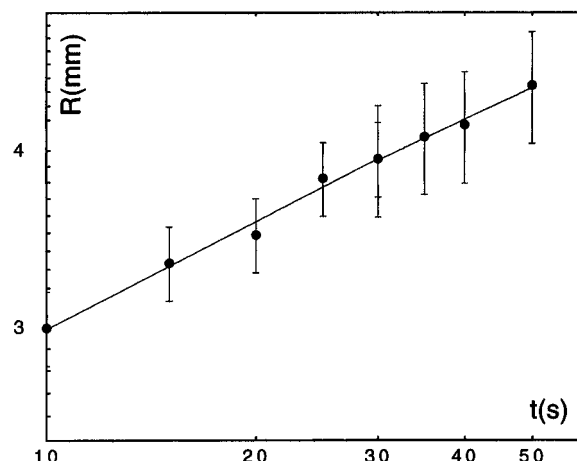


Figure 4. Spreading of a PDMS droplet ($\eta_d = 58\,620$ mPa·s) on a glycerol substrate ($\eta_s = 934$ mPa·s).

Table 2. Interfacial Capillary Lengths of the Glycerol/Water Mixture

(a) 1:1 Glycerol/Water			
PDMS	29 310 mPa·s	56 620 mPa·s	97 700 mPa·s
R^* (mm)	3.00	3.37	3.00
κ^{-1}	3.33	3.33	3.3
κR^*	0.90	1.01	0.90
(b) 5:1 Glycerol/Water			
PDMS	97 700 mPa·s		
R^* (mm)	2.28		
κ^{-1}	2.69		
κR^*	0.85		

IV. Discussion

(1) Our d/s liquid pairs have been chosen to be systematically in the regime of dominant droplet dissipation. This implies $\kappa^{-1} \ll R_c$. There is one marginal case, namely that of pure glycerol for which $R_c \approx \kappa^{-1}$ (Figure 4). Indeed, in this case, we do not see a cross over (see point 2 below).

(2) Our case is rather unique in that β is strongly different from α ; thus the transition is easy to exhibit. For comparison, remember the case of a solid substrate, where the transition from the capillary to gravity drive changes the exponent from 1/10 to 1/8!⁹ Similarly, with a viscous

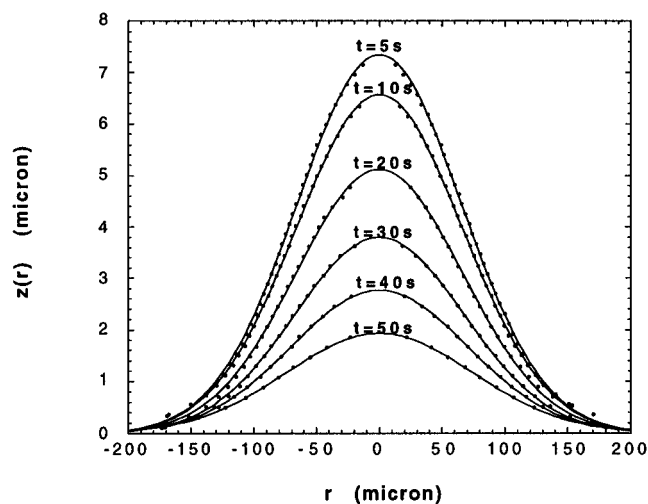


Figure 5. Profiles of a spreading droplet of ultraviscous PDMS ($\eta_d = 2\,445\,000\text{ mPa}\cdot\text{s}$) at different times fitted by a Gaussian.

liquid substrate ($R > R_c$) the exponents shift only from $1/7$ to $1/5$.⁶ This is why we do not see any conspicuous accident in the case of pure glycerol: the exponent varies from 0.25 to 0.20.

(3) We have ignored the precursor film, which always develops in complete wetting. We can actually demonstrate its existence by following the motion of talc particles deposited on the free surface. But the precursor film does not seem to alter the macroscopic hydrodynamics. (Measurements on the precursor film are under way.)

(4) In the limit of very viscous PDMS ($2.5\text{ M mPa}\cdot\text{s}$), we find that the shape of the spreading drop is no longer a spherical cap. The profile, shown in Figure 5 at different times, is well fitted by a Gaussian (of width constant with time t whereas the height decreases as $1/t$). The volume of the macroscopic drop is not conserved since the liquid flows into a microscopic film which develops ahead. These flows can be as well visualized by the motion of small particles deposited on the substrate. This entirely different regime will be published separately.

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