

# Wetting Kinetics of a Drop on a Horizontal Solid Surface under a Viscous Ambient Liquid

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The wetting kinetics of a drop on a horizontal solid surface covered by a viscous liquid has been investigated. Theory indicates the rates of movement behave similarly for cases when the ratio of the ambient fluid viscosity to the drop viscosity  $\chi$  is very high to very low. The case where the above viscosity ratio is low is well-known, since spreading rates are usually measured in air. The experimental data for  $\chi \sim 1$  are provided here. The extent of spreading is proportional to time raised to a power which is closer to  $1/7$  than the expected value of  $1/10$ . Contact line instability was also observed in that the contact lines were seen to be wavy. It is suggested here that the deviation seen in the power is related to the contact line instability.

## Introduction

Whereas the kinetics of spreading of a drop on a solid surface with air as the ambient fluid has seen a lot of both experimental and theoretical investigations as reviewed by Lin et al. (1996), little work has been done for the case where the ambient fluid is a viscous liquid. The key variable is the viscosity ratio  $\chi = \mu_a/\mu$ , of ambient fluid viscosity  $\mu_a$  to the drop viscosity  $\mu$ . When the ambient fluid is air  $\chi \approx 0$ , the drop assumes the shape of a segment of a sphere

$$V = \frac{\pi(1 - \cos \theta)(2 + \cos \theta)r_0^3}{3 \sin \theta(1 + \cos \theta)} \quad (1)$$

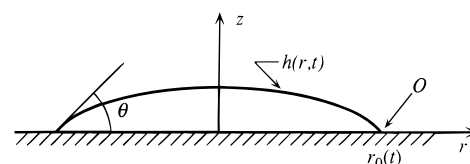
where  $V$  is the drop volume,  $r_0$  is the basal radius, and  $\theta$  is the apparent dynamic contact angle shown in Figure 1. When the drop is thin and moves slowly under the effects of surface tension, one also observes that

$$r_0/V^{1/3} = a(c + t/V^{1/3})^{1/10} \quad (2)$$

In that limit, eq 1 becomes  $V \approx \pi\theta r_0^3/4$ , which can be used to relate  $\theta$  to time leading to Tanner's law where  $\theta$  falls with time. All of these quantitative information apply only to wetting liquids.

For the case where  $\chi \gg 1$  another rate characteristic has been discovered. Brochard-Wyart and de Gennes (1994) obtained a critical value of the dynamic contact angle  $\theta_{cr} = \chi^{-1}$ . For  $\theta > \theta_{cr}$  they show that  $r_0$  is proportional to time  $t$ . This critical value corresponds to  $r_0$  of  $(4V\chi/\pi)^{1/3}$ . Of course,  $r_0$  must be less than this value for the new rate rule to apply. Above this value the wetting kinetics follows the one-tenth power rule. This result that the one-tenth power will hold at sufficiently large times for all viscosity ratios is quite important here.

Experimental results supporting such a theory have been given earlier by Foister (1987) but the data are confined to wetting or spreading times less than 2 s, where the linear dependence occurs for both small and



**Figure 1.** The drop showing the coordinate system and the chief features.

large  $\chi$ . It is more conventional to measure the spreading rates of drops at large times (using contact angle goniometers). The fluid mechanics in this case are analyzable using lubrication theory approximation. Considerable work already exists for the case  $\chi = 0$  by Neogi and Miller (1982a,b) and has led to eq 2. Other cases are more complex, but the case where  $\chi \gg 1$  can be treated, and as shown below also leads to eq 2 as expected from the results of Brochard-Wyart and de Gennes (1994).

Liquid–liquid systems are interesting also because of the contact line instability that could occur. The instability would show up in the form of a scalloped contact line discussed later. In the absence of heat and mass transfer, interfacial instability of this kind will take place when a viscous fluid displaces a more viscous liquid ( $\chi > 1$ ) and the observed phenomenon is referred by a very descriptive name of viscous fingering and discussed by Miller (1978). Evidently, viscous fingering can also happen at the contact line and for the same reasons as shown by Joanny and Andelman (1987).

Large time spreading data in liquid–liquid systems do not exist and are reported here for the first time. The theory described earlier and one special case considered below all indicate directly or indirectly that  $r_0 \propto t^{1/10}$  at large times, and this was verified but with some modifications. Finally, the contact line instabilities are observed.

## Spreading Kinetics at Very High $\chi$

When a thin drop is spreading very slowly, lubrication theory approximation applies and the quasistatic approximation can be made. Under lubrication theory approximation, applicable when the drop has spread

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sufficiently that the slope of its profile  $|\partial h/\partial r| \ll 1$ , it can be assumed that the flow is like that between two parallel flat plates, hence simplifying enormously the fluid mechanics. The drop geometry and the coordinates are shown in Figure 1, where  $h$  is the local drop thickness and a function of the radial position  $r$  and time  $t$ . A special boundary condition is

$$v_r|_{z=0} = -\frac{l}{3\mu} \frac{\partial p}{\partial r} \quad (\text{slip}) \quad (3)$$

at the solid-liquid interface where  $l$  is the slip length, related to the surface roughness if the surface is rough as in Neogi and Miller (1982b) and to the surface diffusion if the surface is smooth as in Neogi and Miller (1982a). For very high  $\chi$  the velocity boundary condition at the liquid-liquid interface is

$$v_r|_{z=h} = 0 \quad (4)$$

where  $h$  is the local drop height, a common approximation when the ambient fluid is very viscous. (In contrast, for very low values of  $\chi$ , the condition at  $z = h$  becomes that of zero shear.) The normal stress boundary condition is the Laplace pressure

$$p = -\gamma_\infty \left[ \frac{\partial^2 h}{\partial r^2} + \frac{1}{r} \frac{\partial h}{\partial r} \right] \quad \text{at } z = h \quad (5)$$

where the terms within brackets denote the approximate form of the curvature when the slope of the drop profile is small and  $\gamma_\infty$  is the liquid-liquid interfacial tension. The resultant tangential velocity

$$v_r = \frac{1}{\mu} \frac{\partial p}{\partial r} \left( \frac{z^2}{2} + \frac{zh}{3} - \frac{zh}{2} - \frac{l^2}{3} \right) \quad (6)$$

shows that the shear stress at the contact line is infinite. This happens because even though we have used a slip at the solid-liquid interface at the contact line to eliminate the contact line singularity, we have reintroduced the singularity by imposing no slip at the liquid-liquid interface. Nevertheless, the tangential velocity averaged over the local drop thickness

$$\langle v_r \rangle = \frac{\gamma_\infty}{12\mu} \frac{\partial}{\partial r} \left( \frac{\partial^2 h}{\partial r^2} + \frac{1}{r} \frac{\partial h}{\partial r} \right) (h^2 + 2l^2) \quad (7)$$

is well-behaved at the contact line.

The remaining development mirrors the previously solved case of a spreading drop under air by Neogi and Miller (1982a,b), since eq 7 only differs from that case by its constants. The continuity equation and the boundary conditions on the drop profile remain unchanged. Hence the rate of spreading is identical to eq 2 with

$$a = 1.056 \left\{ \frac{\gamma_\infty}{\mu V^{1/3}} \left[ \ln \left| \frac{1}{\epsilon} \right| \right]^{-1} \right\}^{1/10} \quad (8)$$

where  $\epsilon = 1/(3V/4\pi)^{1/3}$ . Thus, the tenth-power dependence of the extent of spreading as a function of time remains the same for  $\chi \gg 1$  as for  $\chi = 0$ .

## Experimental Section

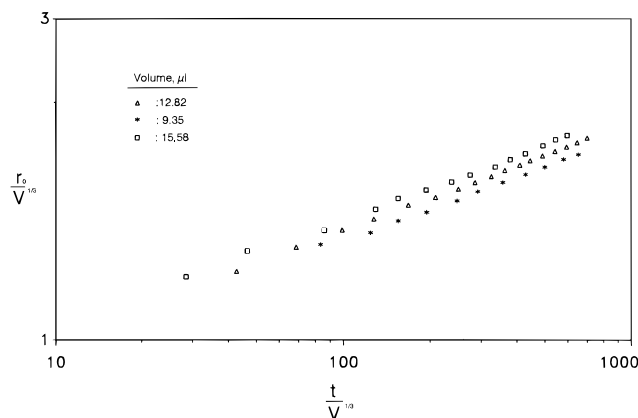
The rates of spreading of a drop of viscous liquid under another viscous liquid on the horizontal upper

surface of a solid were measured using a Ramé-Hart contact angle goniometer. In spreading experiments, the extent of spreading  $r_0$  and the apparent dynamic contact angle  $\theta$  were followed as functions of time  $t$ . An environmental chamber was set on the stage and filled with ambient viscous liquid. On the stage was placed a glass slide and the upper surface of which could be seen through a quartz viewing window. On the slide was glued (cyanoacrylate) a freshly cleaved mica sheet, and it was mildly baked to drive off the volatiles. This was used as a smooth surface. This surface was wetted by microfiltered, deionized water and in the previous work with an electron microscope had failed to show surface imperfections in the case of Lin et al. (1996). In other cases glass slides were used as an example of rough surfaces. These were cleaned with *n*-propanol and KOH solution and washed with deionized water. Previously we had undertaken a more thorough cleaning procedure, but found as far as wetting by our purified water was concerned the above propanol-KOH wash followed by a wash in deionized water was sufficient. The wetting characteristics on the two surfaces have been contrasted earlier by Lin et al. (1996). All experiments were carried out at room temperature (22–23 °C).

The environmental chamber containing the substrate was filled with the ambient liquid, and a drop of a second liquid,  $\sim 1\text{--}10 \mu\text{L}$ , was then layered on the substrate using a microsyringe and  $r_0$  and  $\theta$  were measured with time.  $V$  was calculated using eq 1 and remained constant within experimental error (up to 10%).

A range of systems where  $\chi \gg 0$  and the liquid drop is wetting was extremely difficult to find. If  $\omega = \rho_a/\rho$  is the density ratio where  $\rho_a$  is the ambient liquid density, then for small drops used here the behavior when a drop is layered onto the substrate should be independent of  $\omega$  and gravity. However, the drops under this condition could not be made small enough. If  $\omega$  was greater than 1.0, the drops could not even be made to coalesce with the substrate. (When a drop is deposited on a solid surface, a thin film of ambient fluid is trapped between the drop and the solid. The film thins and eventually breaks, and the drop coalesces with the solid. It is in this form that the drop spreads on the solid and displaces the ambient liquid.) There are a number of ways of overcoming this problem, but even when the drop was "tricked" into assuming the desired initial configuration, it did not stay in place but streamed away from the surface. Only when the density ratio  $\omega$  was less than 1, could we form drops that spread. That is, gravity is important in determining the stability of the liquid-liquid interface. However, for the small drops used here, gravity is unimportant in determining at least the evolving shapes of the drop. This can be inferred from the fact that the calculated drop volumes using a segment of sphere profiles are correctly found to be a constant independent of time. If gravity were a factor, then one would have to use other means such as Bashforth-Adams tables (Miller and Neogi, 1985) to calculate a time-independent volume. It will be discussed later that the rate of wetting also does not show the effects of gravity.

The second difficulty involves viscosity. When a drop of water was made to spread under squalane, it spread too rapidly to obtain any useful measurements. Al-



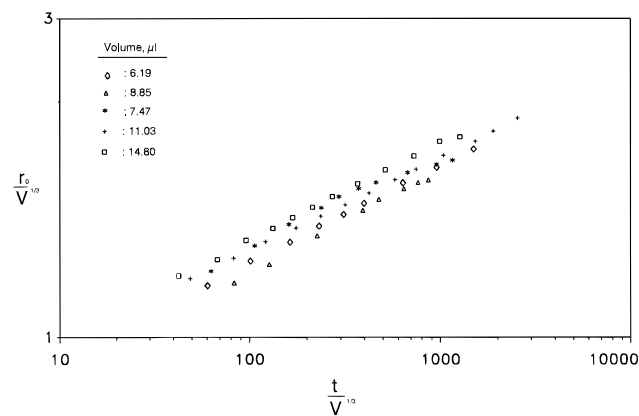
**Figure 2.** Wetting kinetics of poly(dimethylsiloxane) on mica under squalane. The terms  $r_0$  and  $V^{1/3}$  are in cms and  $t$  is in seconds here and elsewhere.

though the current video capture technology can measure such rates, the point to make here is that for high spreading rates the inertial forces surely affect the fluid mechanics, which only complicates the theory developed here and does not allow comparisons to be made. Consequently, we are not only looking for high  $\chi$  but also a drop with high-viscosity  $\mu$ . The high-viscosity condition was met, but  $\chi$  could only be kept at about 1.0.

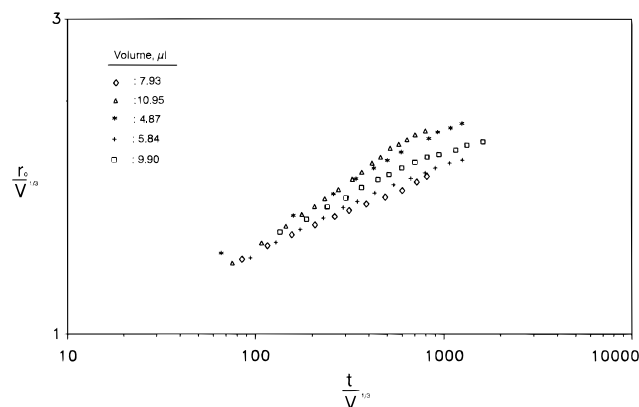
The last difficulty is that due to wettability. That is, the drop will have to wet the substrate preferentially over the ambient liquid. This condition could only be met with poly(dimethylsiloxane) drops with squalane as the ambient liquid. It is noteworthy that Foister (1987) used poly(dimethylsiloxane) drops with only one exception. Poly(dimethylsiloxane) is known to be surface active. Similarly the only suitable ambient liquid for poly(dimethylsiloxane) drops was found to be squalane which gave the highest  $\chi$ , estimated at around 1. Other feasible ambient liquids gave values of  $\chi$  much less than 1. To vary the viscosity of squalane,  $n\text{-C}_{17}$ , a waxy solid, was added. It actually decreased the viscosity of squalane somewhat but gave unexpected results as discussed in the next section. Hydrocarbons are mutually miscible but practically insoluble in poly(dimethylsiloxane). A hydrocarbon (squalane, including sometimes  $n\text{-C}_{17}$ , 35% or 70% by weight) and poly(dimethylsiloxane) were emulsified with a homogenizer. The mixture was then de-emulsified in a centrifuge and again left standing overnight before use. Hence the system studied was poly(dimethylsiloxane) drops spreading under a single-phase squalane- $\text{C}_{17}$  mixture where the two phases were mutually saturated with one another. Hence, no mass transfer and no Marangoni effects would occur.

## Results and Discussion

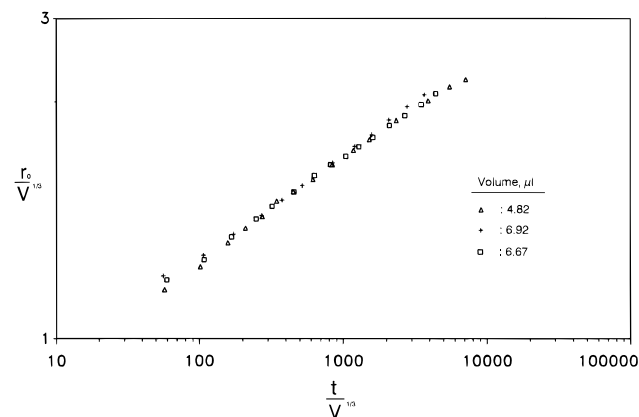
Figure 2 shows the results of poly(dimethylsiloxane) under squalane on mica where a power law appears to be valid. Clearly, Figure 2 shows the larger the drop the faster it travels above the rate predicted by eq 2. The system with squalane containing 35%  $n\text{-C}_{17}$ , Figure 3, shows the curves starting to flatten at large times. This results because the drops were nonwetting and tending toward equilibrium, which was easily verified by waiting for 24 h. The equilibrium contact angles,



**Figure 3.** Wetting kinetics of poly(dimethylsiloxane) on mica under squalane with 35%  $n\text{-C}_{17}$ .



**Figure 4.** Wetting kinetics of poly(dimethylsiloxane) on mica under squalane with 70%  $n\text{-C}_{17}$ .

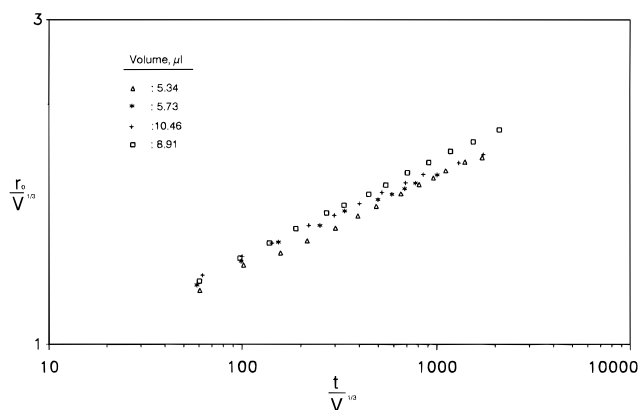


**Figure 5.** Wetting kinetics of poly(dimethylsiloxane) on glass under squalane.

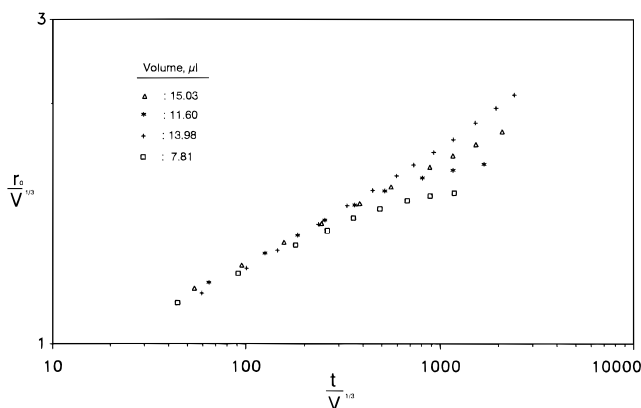
however, were too small to measure. The system with squalane with 70%  $n\text{-C}_{17}$  in Figure 4 clearly shows that the system is nonwetting.

Figures 5–7 show the corresponding systems on glass. Figure 5 is the only case among all the cases investigated here where the volume dependence is fully taken care of using the present choices of dependent and independent variables. Figures 6 and 7 also show that the systems become nonwetting on the addition of  $n\text{-C}_{17}$ . In all cases the equilibrium contact angles were too small to measure.

In most cases the use of  $V^{1/3}$  in the dependent and independent variables following eq 2 is adequate in accounting for much of the volume dependence, and in



**Figure 6.** Wetting kinetics of poly(dimethylsiloxane) on glass under squalane with 35% *n*-C<sub>17</sub>.



**Figure 7.** Wetting kinetics of poly(dimethylsiloxane) on glass under squalane with 70% *n*-C<sub>17</sub>.

**Table 1.** Values from Regression Equation 2<sup>a</sup>

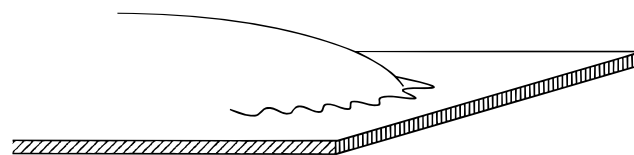
system	exponent	<i>a</i>
Figure 2, PMDS under squalane on mica	0.15	0.72
Figure 3, PMDS under squalane +35% <i>n</i> -C <sub>17</sub> on mica	0.14	0.71
Figure 5, PMDS under squalane on glass	0.15	0.66
Figure 6, PMDS under squalane +35% <i>n</i> -C <sub>17</sub> on glass	0.13	0.72
Figure 7, PMDS under squalane +70% <i>n</i> -C <sub>17</sub> on glass	0.17	0.67

<sup>a</sup> PMDS is poly(dimethylsiloxane). The errors in the fit are no more than 3.5%. The parameter *c* was found to be practically zero.

one case, Figure 5, all of it. The secondary volume dependence in the case of nonwetting liquids is quite complex, but in the case of wetting liquids a higher volume clearly enhances the rate of spreading.

The simplest explanation for the *n*-C<sub>17</sub> induced lack of wetting probably lies in adsorption at the solid–ambient-liquid interface. The fact that contact angles are small suggests that the effect is small. In Figure 7, the plot for *V* = 13.98 μL was taken at about 5 °C above the room temperature (“warm”) and shows significant deviation from the rest in that it appears to make the drop wetting.

The data from the figures were regressed using eq 2 where an adjustable power instead of a fixed 1/10, was used. The last few points were omitted in the region where the power law was not valid. (Again, the power law was not valid in the region where the system was close to equilibrium.) This made us drop Figure 4 altogether. Some individual runs were also removed from consideration for the same reason. The results are shown in Table 1.



**Figure 8.** Schematic diagram of a drop with a wavy contact line.

The values of the power appear to be greater than 1/10 and closer to 1/7. This has also been reported by Dodge (1985) and Cazabat and Cohen Stuart (1986) for drops under air as the ambient fluid, which has led Dodge to question very thoroughly the existing theories. However, these theories approach the problem from very different viewpoints and yet provide answers that agree with one another. As a result, we look for an explanation from other physical features not accounted for in the theory. We note that this deviation cannot be due to the effects of gravity, for it is known from the work of Lopez et al. (1976) that large drops spreading under gravity alone show a 1/8 power dependence. Thus, one would have expected a power between 1/10 (capillarity) and 1/8 (gravity) and not 1/7 which lies outside this range.

The feature in drop spreading, which was easy to see in the experiments, is the contact line instability, that is, with time the contact lines became wavy as illustrated in Figure 8. The waves were uniform in size, easily seen under microscope, and barely visible to the naked eye. They appeared more easily on rough surfaces than on the smooth surfaces, and occurred sooner for drops of smaller volumes. The latter equates to large times, since the time is expressed here as  $t/V^{1/3}$ . In fact this required that we work with larger volumes ~10 μL, although we can work with smaller ones at 2–5 μL. At drop volumes of greater than 25 μL, the drops acquire flat tops, showing the effect of gravity. Nieh et al. (1996) working on rough surfaces with air as the ambient fluid have observed a 1/10 power as well as wavy contact lines, but only for wetting liquids. When we compare their unstable contact lines for a drop spreading under air to those reported here, one obvious observation made is that in liquid–liquid systems the instability manifests far more easily.

It seems possible that the deviation from 1/10 power is linked to the contact line instability. If we follow the arguments of Brochard-Wyart and de Gennes (1994) and equate the surface work to viscous dissipation, it becomes clear that for unstable systems one would have to account for the viscous dissipation from the motion of the waves that develop. This may result in a different expression for the spreading rate.

We will present separately a linear stability analysis of the contact line region and show that the very large curvature in the drop profile at the foot of the drop (and not visible under microscopy) destabilizes the contact line.

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