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Short Communication

## Festoon instabilities of slightly volatile liquids during spreading

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**Résumé.** — Nous avons observé deux régimes d'étalement pour de grandes gouttes plates d'huiles silicones (degré de polymérisation  $N < 20$ ) déposées sur des pastilles de silicium nues : i) d'abord, le contour de la goutte est parfaitement régulier et le rayon  $R$  croît en temps comme  $R \sim t^{0.15}$ , ii) en dessous d'une épaisseur seuil  $h_c$ , un bourrelet se forme à la ligne de contact qui ondule et développe une instabilité en festons. En même temps, l'étalement s'accélère et  $R$  croît comme  $R \sim t^{1/3}$ . Nous interprétons ces résultats par l'effet Marangoni produit par le gradient de tension superficielle, induit au bord de la goutte par l'évaporation du liquide.

**Abstract.** — We have observed two stages in the spreading of large, flat, droplets of silicone oils (degree of polymerization  $N < 20$ ) deposited on bare silicon wafers : i) at first, the drop contour is perfectly circular and the drop radius  $R$  increases with time as  $R \sim t^{0.15}$ , ii) below a critical thickness  $h_c$ , a rim is formed at the contact line and the contour develops spectacular festoons. At the same time, the spreading speeds up and the radius increases as  $R \sim t^{1/3}$ . We have interpreted these results in terms of Marangoni driven instabilities induced by the surface tension gradient generated at the drop edge by liquid evaporation.

Fingering instabilities of advancing liquid fronts submitted to external forces — centrifugal force, gravity, thermal gradient — have been intensively studied during the last few years [1-8]. Periodic modulations of the contact line have been observed whenever the driving forces tend to induce a liquid rim near the contact line. The rim is usually unstable towards peristaltic deformations and the contour first undulates. Fingers are then formed when the external forces impose larger velocities to the thicker parts of the rim.

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We study here the spontaneous instabilities observed with no external thermal gradient during the spreading of slightly volatile silicone oils. The first observations of anomalous spreading were performed by Bascom *et al.* [9], monitoring the spreading of squalane on steel plate. They observed that volatile impurities increase drastically the rate of spreading and lead to the formation of a ridge at the advancing edge. Later Williams [10] observed digitation or liquid undulation of the contour for small droplets of slightly volatile silicone oils. He noticed that a Marangoni contribution must exist for the most volatile liquids. However, he suggested alternatively an inherent instability of the advancing contact line, independent of any gradient, which is probably ruled out. In this paper, we perform systematic spreading experiments for a series of slightly volatile silicone oils (molecular weights ranging from 400 to 1 400 Daltons). The contour is unstable in the late stages of spreading (for large radii, with drops flattened by gravity). For relatively high molecular weights (index of polymerization  $> 20$ ), the contour remains circular (and this rules out Williams's suggestion). In section 1, we describe our experiments. In section 2, we interpret our results in terms of a Maragnoni effect : the surface tension gradients are generated by evaporation near the contact line. We call this instability « festoons ». The festoons are very different from the fingering observed for a drop placed in an external gradient [5, 6].

### 1. Experimental observations.

We have studied the dynamics of spreading of droplets of silicone oils (PDMS, Petrarch System) deposited on horizontal silicon wafers. The wafers, purchased from Siltronix, are used in their bare (oxidized-covered) « clean » state. The wafer diameter is  $\varnothing = 101.6$  mm and the thickness  $e = 500$   $\mu\text{m}$ . A silicone oil wets completely the wafer. The droplet radius,  $R$ , always larger than the capillary length  $\kappa^{-1} = \sqrt{\frac{\gamma}{\rho g}} \sim 1.5$  mm, was monitored by a video system : a CDD camera (Sony XC-77 CE) with a telephotolens (magnifying power  $\times 20$ ) and a T.V. monitor with 1 000 lines resolution. We now describe the different stages of the spreading for a PDMS silicone oil (volume 2  $\mu\text{l}$ , molecular weight 410 Daltons). During the first two minutes, the drop spreads in a circular fashion. Then a liquid rim appears at the wedge, together with colored interference fringes. Periodic modulations of the moving front begin to form (Fig. 1). The number of these sinusoidal contact line oscillations remains constant as the drop flattens. We have studied the dynamics of spreading of silicone oils of different molecular weights, characterized by : i) the variation  $R(t)$  of the radius with time and ii) the onset of the festoon at a critical radius  $R_c$ . Since the radius is always at least ten times larger than the amplitude of the contact line oscillations,  $R(t)$  is a well defined quantity. A typical variation of  $R(t)$  for a PDMS droplet (volume 5  $\mu\text{l}$ , molecular weight 770) is plotted in figure 2 in logarithmic coordinates over four decades. One clearly sees two spreading regimes : i) a *slow* regime with  $R(t) \sim t^{0.15 \pm 0.03}$ , below a critical radius  $R_c$ , previously observed with high molecular weights [12] and ii) a *fast* regime, where  $R(t) \sim t^{0.34 \pm 0.01}$ . The cross-over radius  $R_c$  between the two regimes is the critical radius of the festoon instability. We have studied  $R_c$  as a function of the molecular weight,  $M_w$  and volume,  $\Omega$ , of the sessile droplets. For each molecular weight, we have monitored the variation of  $R_c$  with  $\Omega$  and found  $R_c \sim \Omega^{0.45 \pm 0.15}$ . For the flat droplets considered here,  $\Omega = \pi R^2 h_0$ . We conclude that the instability appears at a critical thickness  $h_c$ ,  $h_c = \frac{\Omega}{\pi R_c^2}$ , independent of the volume  $\Omega$  and depending only on molecular weight. We found  $h_c = 40 \pm 5$   $\mu\text{m}$  for  $M_w = 410$ ,  $h_c = 14 \pm 2$   $\mu\text{m}$  for  $M_w = 770$  and  $h_c = 10 \pm 3$   $\mu\text{m}$  for  $M_w = 1 250$ .

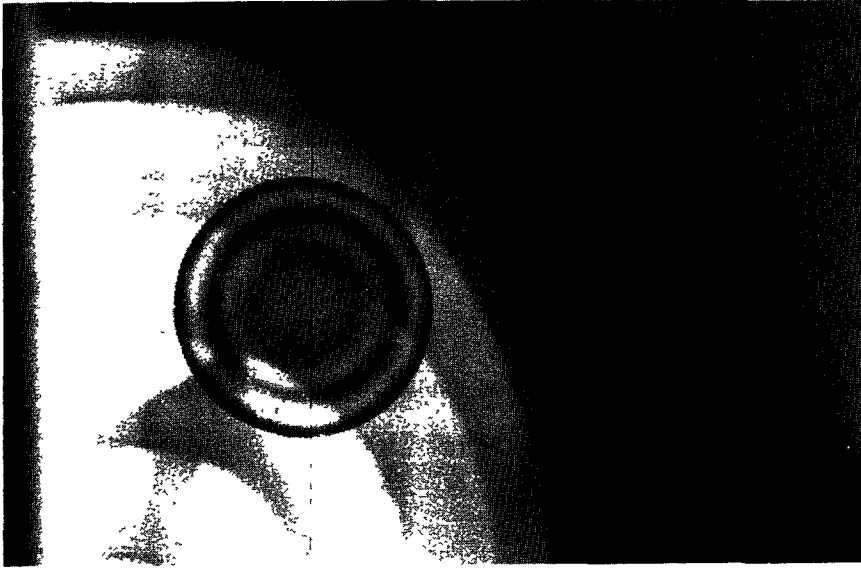


Fig. 1. — Snapshot of the spreading for a PDMS silicone oil droplet ( $\Omega = 2 \mu\text{l}$ ,  $M_w = 410$  Daltons) : we can see colored interferences on the drop surface. A liquid rim is formed at the drop periphery and the contact line is periodically modulated.

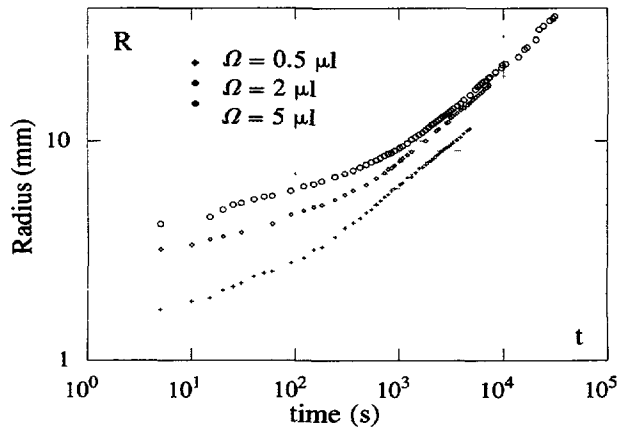


Fig. 2. — Log-log plot of the radius variation *versus* time for a PDMS droplet of molecular weight 770. The different symbols correspond to the three different volume droplets : (+) :  $\Omega = 0.5 \mu\text{l}$  ; ( $\diamond$ ) :  $\Omega = 2 \mu\text{l}$ , (O) :  $\Omega = 5 \mu\text{l}$ .

**2. Interpretation of the spreading regimes.**

2.1 SLOW SPREADING ( $h > h_c$ ). — The spreading of the large drop ( $R \gg \kappa^{-1}$ ) before the onset of the instability is controlled by gravity. In previous works [11, 12], we studied the dynamics of wetting and the shape of the so-called « heavy » droplets (because gravitational forces are dominant). We showed the existence of a new regime of spreading for droplets

radius between  $\kappa^{-1}$  and  $R_g^{(1)} = 3 \kappa^{-1} \ln \frac{\kappa^{-1}}{a}$  ( $\sim$  cm), where  $a$  is a molecular size. In this regime, (the most important one in practice), the viscous dissipation in the wedge of the drop, near the contact line, is dominant. The central part of the drop relaxes faster, and the drop has a quasi-static shape. It can be pictured as a flat disk of thickness  $h_0$ , terminated by a liquid wedge of contact angle  $\theta_d (\ll 1)$ , and size  $\kappa^{-1}$ . The relationship between  $h_0$  and  $\kappa^{-1}$  is (as for a static droplet flattened by gravity [14]) given by :

$$h_0 = \kappa^{-1} \theta_d. \quad (1)$$

This has been checked experimentally in reference [12].

The spreading velocity  $U_s = \frac{dR}{dt}$  of the contact line is given by the Tanner law [13] :

$$U_s = \frac{dR}{dt} = \frac{V^*}{9 \ln} \theta_d^3 \quad (2)$$

where  $V^* = \frac{\gamma}{\eta}$  is a typical wetting velocity and  $\ln$  a logarithmic factor describing the divergence of the dissipation in a wedge ( $\ln \sim \ln \frac{\kappa^{-1}}{a} \sim 10$ ).

The volume conservation for a flat gravity pancake is written as :

$$\Omega = \pi R^2 h_0 \quad (3)$$

and equations (1, 2) lead to the spreading velocity :

$$U_s = \frac{dR}{dt} = \frac{V^*}{9 \ln} (\kappa h_0)^3 \sim \frac{V^*}{9 \ln} \kappa^3 \frac{\Omega^3}{\pi^3 R^6} \quad (4)$$

and to  $R(t)$  by integration [11] :

$$R^7 = \frac{V^*}{\ln} \frac{\kappa^3}{\pi^3} \Omega^3 t. \quad (5)$$

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(1) The threshold  $R_g$  is obtained by comparing two velocities : i) the spreading velocity  $U_g$  under gravity, ignoring the wedge :

$$U_g = \kappa^2 V^* \frac{h_0^3}{3R}.$$

ii) the velocity of the contact line, given by the Tanner law :

$$U_s = \frac{dR}{dt} = \frac{V^*}{9 \ln} \theta_d^3 = V^* \frac{(\kappa h_0)^3}{9 \ln}$$

The quasi-static regime shows up if  $U_s < U_g$ , i.e.  $R < R_g = 3 \kappa^{-1} \ln \frac{\kappa^{-1}}{a}$

2.2 ONSET OF THE INSTABILITY ( $h = h_c$ ). — A surface tension gradient  $\frac{d\gamma}{dx}$  is induced near the contact line by the liquid evaporation, which induced a stress  $\sigma_{xz} = \frac{d\gamma}{dx}$  at the liquid free surface, and a Marangoni flow [5, 6, 9]:

$$U_M = \frac{1}{2} V^* \left( \frac{1}{\gamma} \frac{d\gamma}{dx} \right) h_0. \quad (6)$$

In the gravity case considered here,  $\frac{d\gamma}{dx} = \kappa \Delta\gamma$ , where  $\Delta\gamma$  is the total surface tension variation over the wedge. For our silicone oils, the evaporation is weak and  $U_M$  is small. However, when  $U_M$  becomes larger than  $U_s$ , the liquid is accumulated just behind the contact line [9]. The resulting liquid rim is unstable with respect to periodic deformations [5, 8, 9] (Rayleigh type instability) [15]. The condition  $U_M = U_s$  gives the critical thickness  $h_c$  for the onset of the instability:

$$h_c^2 = 4.5 \frac{\Delta\gamma}{\rho g} \ln. \quad (7)$$

We can evaluate  $\Delta\gamma$  from the experimental values of  $h_c$  ( $\frac{\Delta\gamma}{\gamma} \sim 2 \times 10^{-5}$  for  $M_w = 410$ ). As the molecular weight of PDMS increases,  $\Delta\gamma$  decreases and the instability is no longer observed. If drops of different volumes are deposited, the instability will show up for critical radii  $R_c$  related to  $h_c$  by equation (3) ( $R_c = \left( \frac{\Omega}{\pi h_c} \right)^{\frac{1}{2}}$ ). The  $\Omega^{1/2}$  dependence agrees with our data. The  $\Delta\gamma$  dependence *via* equation (7) is not tested yet, because  $\Delta\gamma$  is not directly measurable.

2.3 FAST SPREADING ( $h < h_c$ ). — For  $h_0 < h_c$ , the Marangoni flow overcomes spontaneous spreading (driven by gravity) and  $R(t)$  grows faster. Assuming again a surface tension gradient  $\frac{d\gamma}{dx} = \kappa \Delta\gamma$ , which remains constant during the spreading time, we can deduce the evolution  $R(t)$  of the spreading droplet in the Marangoni regime: from equation (6) and the quasi-static assumption <sup>(2)</sup> for the droplet shape (Eq. (1)), we find:

$$\frac{dR}{dt} = \frac{1}{2} V^* \left( \frac{1}{\gamma} \frac{d\gamma}{dx} \right) \frac{\Omega}{\pi R^2} \quad (8)$$

which leads to:

$$R^3 = \frac{3}{2} V^* \kappa \frac{\Delta\gamma}{\gamma} \frac{\Omega}{\pi} t. \quad (9)$$

### Concluding remarks.

Festoon instabilities are clearly the manifestation of a Marangoni flow induced by the liquid evaporation. An early experiment suggesting this was the following: if one illuminates the

<sup>(2)</sup> The quasi-static shape is valid now as long as  $U_M < U_g$ , to assume a fast relaxation of the central part of the drop.

sample with a strong source of light, the threshold thickness  $h_c$  increases. The physical origin of the surface tension gradient can be due either to a thermal gradient generated by the liquid evaporation, or to direct concentration effects: the polymer melt is polydisperse; for the oligomers interested here, the surface tension is larger for the shorter chains. This was observed a long time ago by Gaines *et al.* [16], and interpreted recently by de Gennes [17]. The smaller chains are more depleted by evaporation in the wedge and the surface tension is lower in the thick regions than near the contact line. We are not able to decide between the two mechanisms. A rough estimate of the thermal shift following references [5, 9] on instabilities in external gradients (from  $h_0$  and the oscillation wavelength) or equation (7) for  $\Delta\gamma(h_c)$  leads to  $\Delta T < 0.01$  °C, which would not be easy to measure directly.

The « festoons » are very different from the « fingers » observed in an external thermal gradient. In both cases, we start with a rim which breaks into microdroplets. But, in an external gradient, each microdroplet is driven out at constant velocity and leaves a wet mark in the form of a finger.

Our geometry of large, flat droplets leads to simple spreading laws in the Marangoni regime, because the gradient is localised in the wedge of the droplet, in a region of size  $\kappa^{-1}$ , the capillary length. In the central part which is flat, surface tension is uniform.

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