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1990 J. Phys.: Condens. Matter 2 SA421

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## The spreading of drops on solid surfaces

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Received 14 August 1990

**Abstract.** We present a detailed study of the macroscopic spreading kinetics of a non-volatile liquid, polydimethylsiloxane, on model solid surfaces of continuously adjustable spreading power, with special attention paid to the immediate vicinity of the zero spreading parameter value. We establish the existence of new spreading regimes which are, we think, the signature of non-monotonic interactions versus thickness laws.

The spreading of a liquid on a solid surface influences a large number of practical situations. The underlying physical mechanism, however, has only just started to be elucidated. This is mainly because very often the spreading process leads to the formation of thin liquid films. Both the static and the dynamic physical properties of these thin films are different from those of the bulk liquid, the interaction between the molecules being perturbed by the presence of the interfaces. A detailed study of the spreading may thus help us to gain a better understanding of the liquid state. Starting from the simple physical situation (an everyday experiment) where a small drop is deposited on a solid surface, we may ask two basic questions.

- (i) When does the drop spread?
- (ii) How does it spread? (What is its shape, what are its kinetics of evolution, etc?)

We all know the nineteenth-century answer to the first question: when a liquid drop is deposited on a solid, three interfaces come into play, and the three corresponding interfacial tensions  $\gamma_{SG}$ ,  $\gamma_{SL}$  and  $\gamma$  (the solid–gas, solid–liquid and liquid–gas interfacial tensions, respectively) measure the free energy (per unit area) associated with an increase in the corresponding interface [1]. The spreading parameter  $S = \gamma_{SG} - \gamma_{SL} - \gamma$  is the energy gained when covering one unit area of the dry solid with a flat liquid film of macroscopic thickness.

If  $S$  is negative, the situation where the solid is covered by a liquid film is not favourable. The equilibrium shape of the drop is a spherical cap (if small enough to ensure that gravity is negligible compared with capillarity), characterized by its equilibrium contact angle  $\theta$ , the solution of Young's [2] equation  $\cos \theta = (\gamma_{SG} - \gamma_{SL})/\gamma$ .

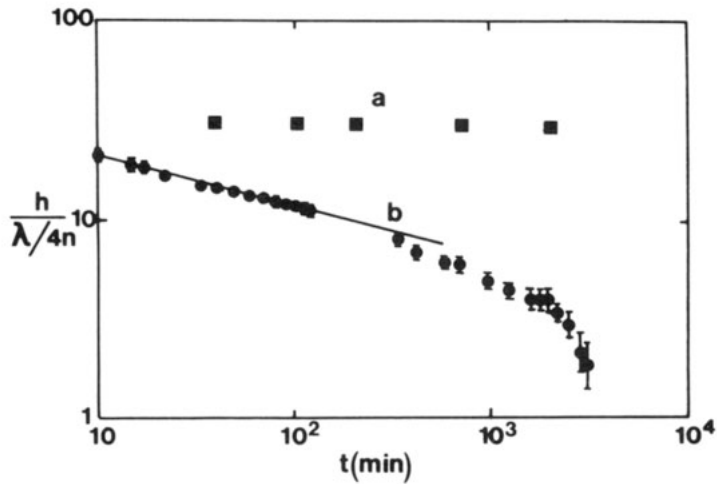
If  $S$  is positive, the liquid spreads and tends to cover the maximum solid surface.  $S = 0$  thus appears as an obvious criterion to distinguish between partial and total wetting. For total wetting situations the nineteenth-century answer to the second question, 'How does the drop spread?', leads to a paradox: assuming Poiseuille flow of the

liquid under excess Laplace pressure [1] associated with the curved liquid–gas interface of the drop yields Tanner’s [3] laws. These laws correctly describe the evolution with time of the macroscopic parameters of the drop such as its size  $R(t)$ , its maximum height  $h(t)$  or its apparent contact angle  $\theta_a(t)$  [4] but are unable to explain why these kinetics are independent of the spreading parameter  $S$  which should be the driving energy of the spreading process [5].

It has been recognized recently that the formation of thin liquid films during the spreading process gives an explanation for this apparent paradox [6, 7]. Whenever a liquid film becomes thinner than the range of the molecular interactions the two interfaces which limit the film can no longer be considered as independent and an additional free energy term  $P(e)$  (with  $e$  the film thickness) has to be taken into account;  $\pi(e) = -dP(e)/de$  is the disjoining pressure introduced by Derjaguin [8] to describe thin liquid films. If we consider a simple van der Waals fluid and solid, total wetting situations are obtained if the polarizability of the solid is larger than that of the liquid to ensure that  $S > 0$ .  $P(e)$  is then positive ( $P(e) = A/12\pi e^2$ , where  $A$  is the effective Hamaker constant of the system) and thus opposes spreading. Using these ideas, de Gennes [7] and Joanny [9] have predicted that, for liquids of low enough volatility (‘dry spreading’) to ensure that no efficient transport of liquid molecules towards the solid surface occurs though the vapour phase, the spreading should stop when a liquid ‘pancake’ of thickness  $e_c$  is formed.  $e_c$  is given by a balance between the spreading and disjoining pressure terms; for van der Waals liquids,  $e_c \approx a\sqrt{3\gamma/2S}$  (where  $a$  is the molecular size) [7]. It should be noted that this final ‘pancake’ corresponds to a metastable situation rather than to true thermodynamic equilibrium for which the vapour should be saturated. The additional  $P(e)$  term also plays a role during the transient stages of spreading; it is responsible for the formation of the precursor film which progressively develops ahead of the macroscopic edge of the drop [7, 9]. All the interfacial energy gained during the spreading is burned by friction in this precursor (for ‘dry spreading’), an explanation of the apparent independence of the macroscopic spreading kinetics with respect to the spreading parameter.

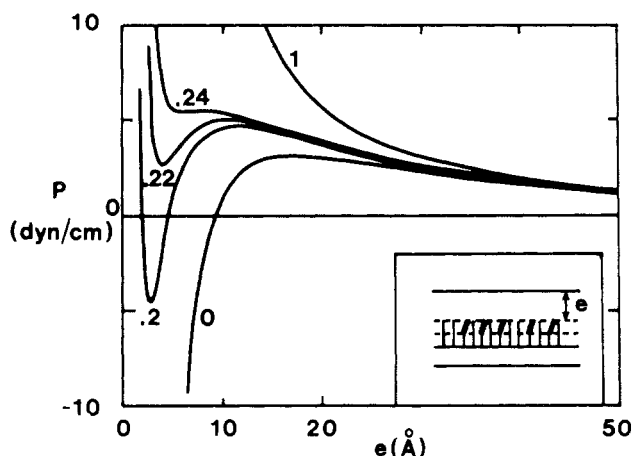
Recent experiments on model systems have been undertaken to test these ideas. They have established the existence of the precursor film in clearly ‘dry-spreading’ situations [5] and have shown qualitative agreement between de Gennes’ and Joanny’s predictions and the precursor film profiles and evolutions [10]. However, detailed studies of the late stages of spreading have revealed a rather complex situation; on a substrate of low spreading parameter a ‘pancake’ has been observed [11–13] but of a thickness comparable with the molecular size, while on higher-energy surfaces the same liquid loses its cohesion, forming a film of molecular thickness made of molecules not densely packed [12–14]. These molecular films render any further comparison with theory difficult. Layering of the transient films has also been observed [15], indicating a spreading process more complicated than first thought.

We report here results of a series of spreading experiments undertaken on model substrates of continuously adjustable spreading parameter, with special attention paid to the immediate vicinity of  $S = 0$  for which thick final ‘pancakes’ were predicted. The model substrates are obtained by chemical modification of the silica surface of silicon wafers using self-assembled monolayers formed by a mixture of saturated tetradecyltrichlorosilane (TTs)  $\text{Cl}_3\text{—Si—(CH}_2\text{)}_{13}\text{—CH}_3$  and unsaturated tetradecyltrichlorosilane (u-TTs)  $\text{Cl}_3\text{—Si—(CH}_2\text{)}_{12}\text{—CH=CH}_2$ . The details of the grafting procedure are reported elsewhere [16, 17].



**Figure 1.** Spreading kinetics of the macroscopic drop as monitored through its macroscopic height  $h$  (scaled unit:  $\lambda$  is the wavelength of light used and  $n$  the index of refraction of the liquid) as a function of time  $t$  on logarithmic scales for two slightly different surface polarizabilities: curve a,  $\beta_0 < \beta < \beta_1$ , very slow spreading; curve b,  $\beta_1 < \beta < \beta_2$ , Tanner's law  $h \sim t^{-0.2}$  is asymptotically followed at short times. Departure from this classical behaviour is observed when a large enough precursor film is formed. This transient thick film is clearly visible in ellipsoccontrast (lower panel).

Because the polarizability of the terminal vinyl group of u-TTS is slightly higher than that of the terminal TTS methyl, the polarizability of the surface can be continuously adjusted by varying the fraction  $\beta$  of u-TTS in the grafted monolayer. On such surfaces, whose quality has been checked using x-ray reflectivity techniques and contact angle measurement with dodecane as a reference liquid [16], we have characterized the spreading kinetics of polydimethylsiloxane (PDMS) narrow molecular weight fractions ( $M_w \approx 18\,000$  and  $26\,500$ ,  $M_w/M_n \approx 1.1$ ). The typical volumes of the deposited drops are in the range  $\Omega \approx 10^{-9}$ – $10^{-8}$  cm<sup>3</sup> and extreme care is taken to avoid dust and pollution by working under a dry controlled nitrogen atmosphere [16].



**Figure 2.** Evolution of the film free energy  $P(e)$  with the fraction of unsaturated bonds in the grafted monolayer, calculated for a stratified solid substrate illustrated in the inset, assuming additive van der Waals interactions.

For very small u-TTS concentrations ( $\beta < \beta_0$ ,  $\beta_0 \approx 24\%$ ), PDMS partially wets the surface; the drop reaches its static advancing contact angle in a time from milliseconds to several hours when the contact angle becomes very small. Then the process stops and no further evolution can be detected over very large periods of time (6 months).

If the polarizability of the surface is slightly increased ( $\beta_0 < \beta < \beta_1$ ,  $\beta_1 \approx 26\%$ ) a total wetting regime is observed and very small drops ( $\Omega \approx 10^{-10} \text{ cm}^3$ ) totally spread. Very surprisingly, however, the kinetics of evolution of the macroscopic cap of larger drops are much slower than for a drop of comparable volume on high-energy surfaces and no longer follow Tanner's laws as can be seen in figure 1, curve *a*, where the maximum height of the drop  $h$  is reported as a function of time (on logarithmic scales). Moreover these slow spreading kinetics appear to be highly sensitive to the surface polarizability and decrease drastically when  $\beta \rightarrow \beta_0$ , again in contradiction with previously observed behaviours. If the surface polarity is further increased, with  $\beta_1 < \beta < \beta_2$ ,  $\beta_2 \approx 27\%$ , the situation is that in figure 1, curve *b*; the macroscopic drop asymptotically follows Tanner's law, but a thick film ( $e \approx 500 \text{ \AA}$ ) clearly visible when observed by ellipsocontrast [5] (figure 1, lower panel) develops all around the drop. When the volume of liquid involved in that film is no longer negligible compared with  $\Omega$ , the kinetics depart from Tanner's law. When the spreading contrives, this film thins and becomes too thin to be visible under the microscope. The film is only transitory at this thickness and we do not observe a very thick 'pancake'.

Increasing the surface energy ( $\beta > \beta_2$ ) again, a high-energy-type spreading comparable with what has previously been reported [5] is recovered.

We think that these surprising spreading behaviours are indicative of the recently predicted pseudo-partial wetting regime [18]. Because  $P(e)$  may contain many other contributions apart from van der Waals (especially short range) and because  $S = P(e \rightarrow 0)$ ,  $S$  and the effective Hamaker constant of the system are independent parameters. They may even have opposite signs and yield a spreading criterion far more complex than first thought, especially when a minimum or oscillations appear in the liquid film free energy versus distance law. It is interesting to note that the experimental

system that we have used can be modelled by a homogeneous stratified medium (see the inset in figure 2). This can give rise to such situation as illustrated in figure 2, where  $P(e)$  has been calculated as a function of  $\beta$  assuming the additivity of the interactions [19].

The appearance of a minimum at finite distance for a small range of  $\beta$  renders plausible the interpretation of the strange spreading behaviour that we have observed in terms of pseudo-partial wetting. Further investigations especially on microscopic length scales are at present under way which aim to establish this point fully.

In conclusion, by continuously varying the surface energy by chemical modifications, we have demonstrated the existence of a new spreading regime, distinct from partial wetting because very small drops totally spread, and distinct from the previously reported total wetting regime because the macroscopic spreading kinetics of the drop appear to be highly  $S$  sensitive and incompatible with Tanner's laws. This behaviour may be indicative of the recently predicted pseudo-partial wetting regime and, if this is confirmed by further experiments, spreading kinetics could become a very sensitive tool to characterize interaction versus distance laws.

### Acknowledgments

We thank J J Benattar and J Daillant (CEA, Saclay) for having performed the x-ray reflectivity characterizations of our substrates. One of us (PS) acknowledges St-Gobain for financial support.

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