

# Time-resolved, three-dimensional quantitative microscopy of a droplet spreading on solid substrates

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## Summary

A polarized microscope was used to study the spreading of mercury droplets on thin silver films. Using the differential interference contrast (DIC) method and semi-quantitative measurements of the optical path difference (OPD), the three-dimensional shape of the liquid droplet that wets the solid surface was constructed with an angle resolution of  $1^\circ$ . The evolution of the droplet shape was determined with a time resolution of 0.04 s. The quantitative results are compared with other wetting-reaction systems. In particular, it is demonstrated that the droplet has a spherical-cup shape during the entire wetting-reaction process.

## Introduction

The light microscope is an excellent tool for collecting 2D information. There is a wide range of stereo-techniques available, however, the limit of conventional light microscopy for 3D qualitative and quantitative information is a long-standing problem. The limited field depth prevents simultaneous qualitative information, i.e. a full 3D image in one view. Moreover, the nature of projected view prevents the 3D quantification of the object. Various methods have been recently developed to overcome this problem. The scanning electron microscope (SEM) that has a large field depth is most popular for 3D imaging. It also enables quantitative 3D evaluation by stereo-coupled images. Other well-known methods are the confocal microscope and the atomic force microscope (AFM). These methods enable the gathering of 3D information, but suffer from several limitations. One limitation is the long acquisition time of the quantitative 3D information (order of minutes), and hence time-resolved microscopy by these methods is limited to these time scales.

Here we demonstrate the feasibility of a differential interference contrast (DIC) light microscope for time-resolved (TV rate) image acquisition combined with 3D quantitative evaluation of a liquid droplet as it interacts with a planar substrate. This method is most relevant for studies of wetting phenomena.

The wetting of solid surfaces by liquid droplets is an important process in material science and technology, with a diverse range of applications, e.g. soldering and painting. Liquids wet solids, completely or partially, depending on the surface tension coefficients of the materials. The equilibrium contact angle,  $\theta_{eq}$ , for partial wetting is given by:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta_{eq} \quad (1)$$

where  $\gamma_{ij}$  is the surface tension coefficient between phase  $i$  and phase  $j$  (solid, liquid or vapour), respectively. Recent studies (Landry & Eustathopoulos, 1996; de Ruijter *et al.*, 1997, 1999; Eustathopoulos, 1998; Liu & Chuang, 2000) have focused on the dynamics of the droplet towards reaching its final state. Assuming partial wetting ( $0^\circ < \theta < 180^\circ$ ), as the initial state of the droplet, it will spread (prior to equilibrium), as long as  $S = \gamma_{sv} - \gamma_{lv} - \gamma_{sl}$  ('power' of the spreading) is positive. In the case of a complete ( $\theta = 0^\circ$ ) wetting, one has  $\gamma_{sl} + \gamma_{lv} < \gamma_{sv}$  and Eq. (1) is not satisfied, i.e.  $S \geq 0$ . Note that Eq. (1) refers only to the contact angle and not to the entire droplet's shape and its evolution with time. Theoretical studies (de Gennes, 1985; de Ruijter *et al.*, 1997, 1999) assume that for small droplets, i.e. where gravity is negligible, and for small angles ( $\theta \ll 1$ ), the droplet has a spherical-cup shape. Under the spherical-cup shape approximation the evolution of the droplet shape is described either by its time-dependent radius  $R(t)$ , or by the time-dependent angle of contact  $\theta(t)$ , which are related through:

$$H_0(t) = R(t) \cdot \tan \frac{\theta(t)}{2}, \quad (2)$$

and for small angles ( $\theta < 30^\circ$ )

$$H_0(t) = \frac{1}{2} R(t) \cdot \theta(t), \quad (3)$$

where  $H_0(t)$  is the height of the centre of the droplet. The radius  $R(t)$  and the angle of contact  $\theta(t)$  of the advancing droplet, were found, in both experimental and theoretical studies (de Gennes, 1985; de Ruijter *et al.*, 1997, 1999), to obey a power law with two major regimes:  $R(t) \sim t^{1/7}$  and  $\theta(t) \sim t^{-3/7}$  at the early stages, and  $R(t) \sim t^{1/10}$  and  $\theta(t) \sim t^{-3/10}$  during long-time relaxation to the equilibrium stage.

It has been shown (Bain *et al.*, 1994; Domingues do Santos & Ondarcuhu, 1995; Landry & Eustathopoulos, 1996; de Gennes, 1998; Eustathopoulos, 1998; Be'er *et al.*, 2000; Liu & Chuang, 2000) that during the interaction of a metal droplet on a metal substrate, both wetting and chemical reactions govern the dynamics of the process. In such cases, the time dependence of the radius and the angle of contact do not obey a power law. Moreover, a single function can hardly describe the full range of such wetting curves, and a wetting regime corresponding to  $R(t) \sim t$  is observed for a part of the spreading time (Landry & Eustathopoulos, 1996; Eustathopoulos, 1998; Liu & Chuang, 2000). In this context we have found (Be'er *et al.*, 2000) that Hg droplets tend to propagate spontaneously on Ag surfaces causing a nearly complete wetting formation, i.e.  $\theta \rightarrow 0^\circ$ .

Several methods have been used to detect the shapes of such droplets, but none of them can follow the evolution of the droplet shape with time.

- 1 In a top view of transparent droplets on transparent substrates, such as oils on glass, the droplet is considered as an optical lens (Aveyard *et al.*, 1999). By knowing the index of refraction and the focal length of the droplet-lens, one can infer the exact three-dimensional shape of the droplets.
- 2 A side view of opaque droplets (de Ruijter *et al.*, 1997). This method gives limited information due to the depth of focus and to the projected view.

In this paper we demonstrate that quantitative polarized-light microscope measurements can be used to determine the 3D shape of an opaque metal droplet (Hg) that wets an opaque substrate (Ag). The shape is determined in one view-frame. Accordingly, it is possible to follow its evolution at a standard (TV) rate.

## Materials and methods

We studied the evolution of the shape of small Hg droplets (100  $\mu\text{m}$  in initial diameter) on thin Ag films (200 nm). The Ag films were thermally deposited on microscope slides in a vacuum chamber. Well-controlled smooth clean surfaces along relatively large distances are achieved when using thin Ag films rather than thick Ag foils (0.1 mm). The Hg droplet was placed on the silver substrate at room conditions within a few minutes to a few hours after the evaporation. The droplet propagation involves a wetting process combined with a chemical reaction and an intermetallic compound is formed. The formula of the metallic-compound is the  $\epsilon$  phase  $\text{Ag}_4\text{Hg}_3$  (the detailed proof will be published elsewhere). During this process, which takes a few minutes, the droplet changes its angle of contact. A polarized light microscope

(Axioskop-ZEISS) equipped with a DIC accessory and a colour CCD camera was used to analyse the 3D shape of the droplet and its evolution with time.

The principles of qualitative polarized-light microscope are described in detail by Robinson & Bradbury (1992). It is emphasized that visible colours are actually a result of a reduction of the intensity of some wavelengths, due to destructive interference. This method (DIC) enables the detection of steps in the specimen surface, in the order of  $1/20$  of the incident wavelength. Using white halogen light as a source, steps of about 20 nm are detectable. As an auxiliary object, a lambda plate changes the grey values into colours again.

Because of the high reflectivity of the metallic droplet, the white light is reflected. Moderate slopes of a specimen that cause small length difference between partial beams will show different colours than steeper slopes. Extremely steep slopes reflect the light out of the objective, so that in such regions the specimen appears dark. A typical view of the droplet, with different colours representing the differences in local slopes, is shown in Fig. 1(a). Quantification of the colours can indicate quantitatively the local slope.

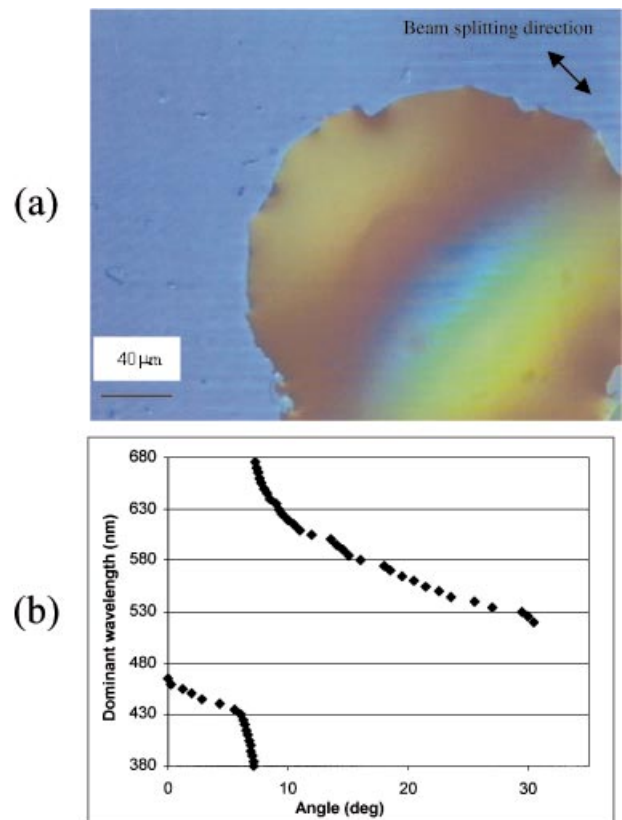


Fig. 1. (a) A top view of the Hg droplet at  $t = 20$  s. Different angles result in different colours, the blue background being the horizontal Ag substrate. The beam splitting direction is marked. (b) A related colour-angle chart. The size of the experimental spots indicates the experimental error ( $\sim 1^\circ$ ).

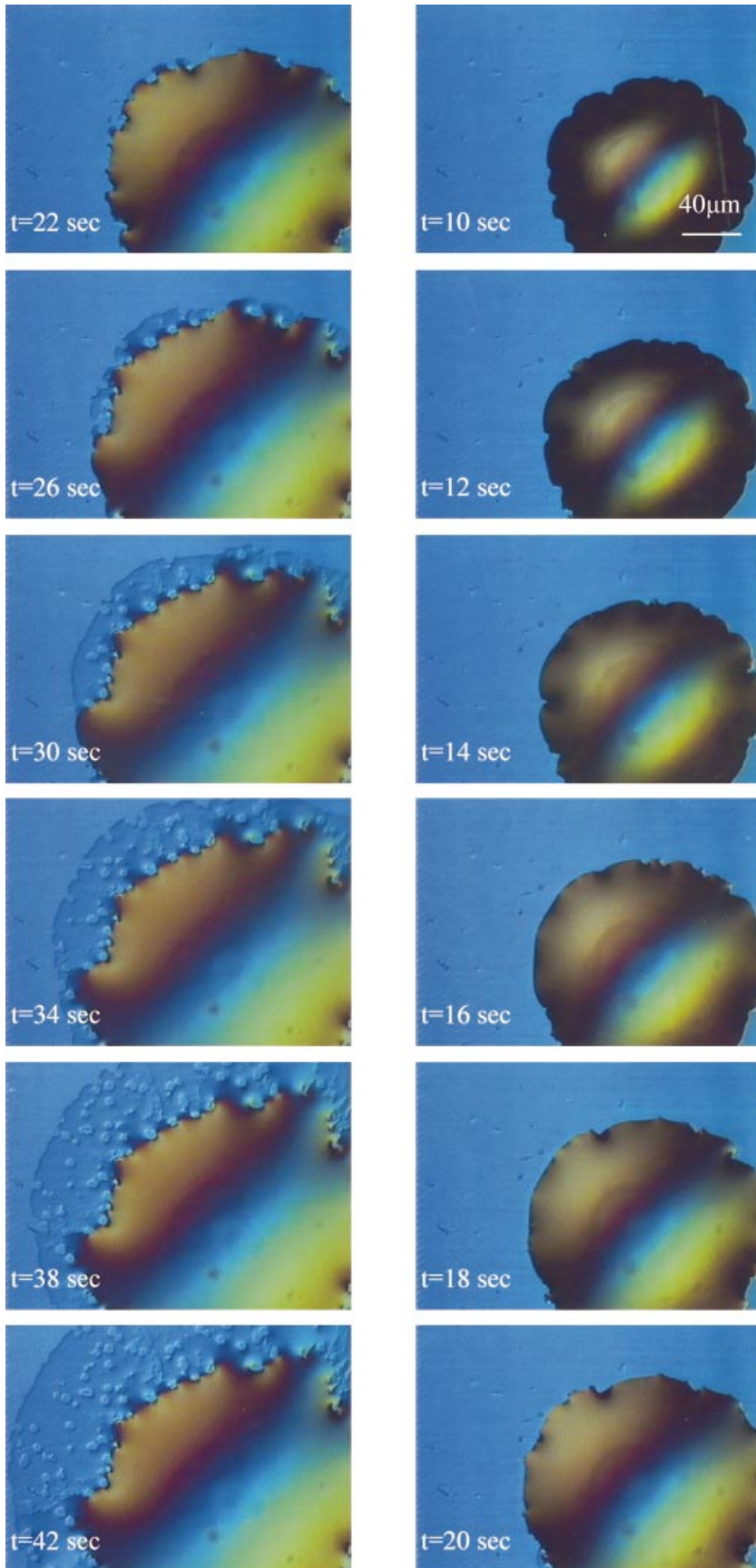
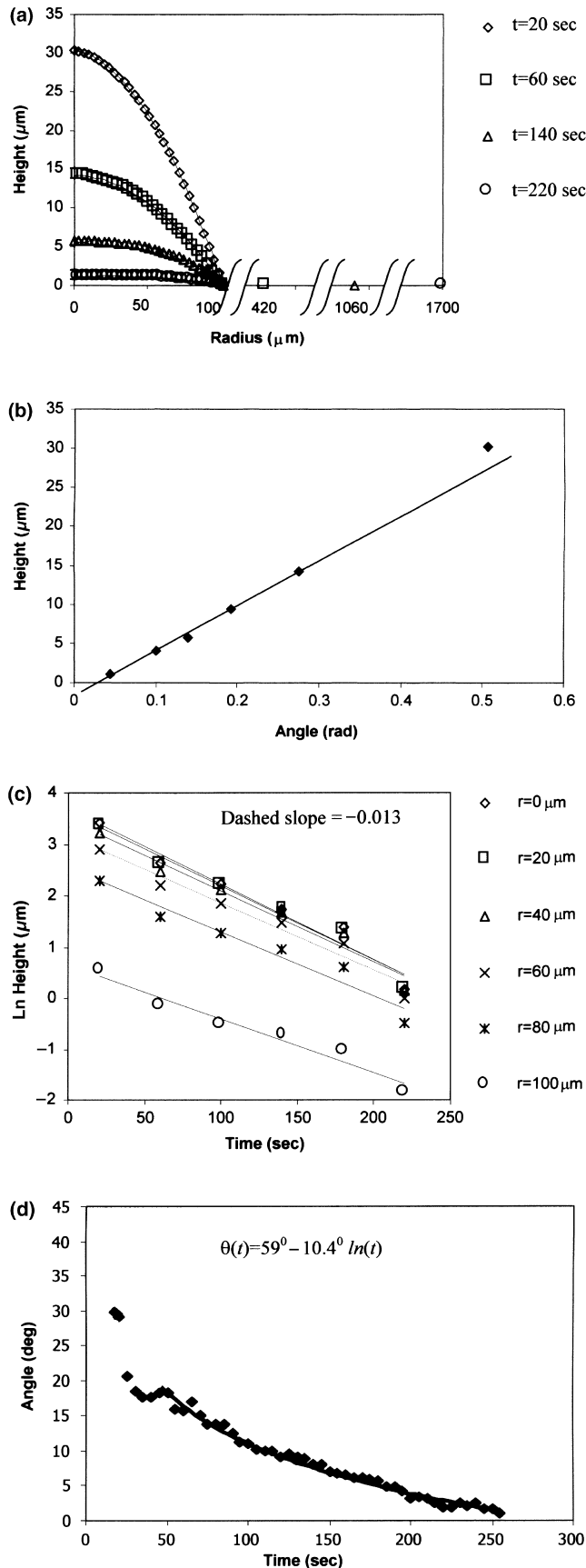


Fig. 2. A series of top-view snapshots of the propagating droplet. The first six pictures belong to the transient regime, whereas the last six pictures belong to the major regime.



In order to reduce the dominant (yellow and red) wavelengths of the white source, we used a blue (470 nm) filter so that the uniformity of the spectrum is improved. Calibration of colours vs. slopes has been achieved by allowing a thin Ag film to change its position with respect to the microscope in steps of  $0.5^\circ$ . The measurements were taken in a diametric section of the droplet parallel to the beam-splitting direction. The tilting for calibration was obtained in the same direction. It should be emphasized that the camera and the video recorder are concerned with the visible colours and not with wavelengths. However, it is straightforward to translate the visible colour of each pixel in the image, which is a triple variable function, into a dominant wavelength, which is a single variable function, by using the HSL (hue saturation luminosity) triplet and the CIE (Commission Internationale de l'Eclairage, Cambridge) 1931 chromaticity diagram. This procedure enables one to obtain the calibration chart of angles vs. dominant wavelength. A similar procedure that correlates polarization colours with crystal birefringence is known as the Michel-Levy chart. We found that this procedure is capable of resolving shape angles to  $1^\circ$ . The results are given in Fig. 1(b). The chart is periodic and should contain several orders of colours. However, no signal returns from slopes that are steeper than  $30^\circ$ , therefore only one order of colours is observed. The chart is shifted according to the orientation of the lambda plate so that it contains colours from consecutive orders and a discontinuity between them. The chart in Fig. 1(b) is for a specific orientation of the lambda plate that was chosen to meet the best colour response of the colour CCD camera. In this specific chart the discontinuity between red to violet is at about  $7^\circ$ .

### Discussion and conclusions

The optical system described above was used to study the interaction of the Hg droplets with Ag surface. The interaction is divided into two time regimes: (a) a transient regime (about 30 s), in which the droplet spreads on the film in a compact shape with a constant velocity ( $\approx 8 \mu\text{m s}^{-1}$ ); (b) the major regime (about 200 s), in which the droplet no longer propagates, but 'feeds' the Ag film with a thin Hg layer. A series of 12

Fig. 3. (a) A cross-section of the droplet at various times:  $t = 20, 60, 140, 220$  s. Note the corresponding marks of the thin layer to the right of the drop. (b) The slope of the straight line is approximately  $54 \mu\text{m}$ , which is about half of the radius observed in (a), and fits Eq. (3). The highest point does not fall on the line as the angle to which it belongs is relatively large ( $29^\circ$ ) with respect to the spherical-cup shape approximation. (c) The height of the given droplet,  $H(r; t)$  ( $100 \mu\text{m}$  in diameter) shows an exponential decay in time, which is radially independent.  $r = 0$  corresponds to the centre of the spreading droplet where  $H(r; t)$  is relatively large, whereas  $r = 100 \mu\text{m}$  is close to the edge of the droplet in which the local height is small. (d) The angle of contact vs. time. For the last 200 s presented here, a logarithmic function was best fitted for the angular decay.

top-view snapshots of the propagating droplet are shown in Fig. 2. This Hg film interacts with the Ag substrate, forming an intermetallic compound with a thickness of 0.1  $\mu\text{m}$ . The propagation and the geometry of the thin layer has been reported elsewhere (Be'er *et al.*, 2000, 2001). As the Hg bulk 'feeds' the Ag surface with a thin layer, its mass reduces with time and therefore its shape evolves. Here we report quantitatively on the evolution of the droplet shape.

The shape of a Hg droplet, 100  $\mu\text{m}$  in diameter, was analysed quantitatively by the above-mentioned procedure. This experiment was repeated 20 times and the results shown here belong to a typical experiment. As the colour determines  $\theta$ , we know the angle for each  $R$ . At the interface between the droplet and the substrate the height is zero. Each pixel has a different colour and thus a different angle. We also know that each pixel corresponds to a certain length in micrometres; thus, we can calculate the exact shape of the whole droplet. It is now possible to check whether Eq. (3) is satisfied.

Figure 3(a) represents the droplet profiles at four stages. The height of the droplet  $H_0(t)$  and consequently the contact angle  $\theta(t)$  are reduced with time, whereas the radius  $R(t)$  reaches a maximum value  $R_{\text{max}}$  at  $t = 30$  s. On the other hand, a precursor thin film is formed and is continuously expanding, as can be seen by the marked dots along the  $x$ -axis. We have found that Eq. (3) is satisfied, as can be seen in Fig. 3(b), indicating that the droplet has a spherical-cup shape independent of time up to an angle of 0.5 rad.

The evolution of the height of a given droplet at different locations  $r$  ( $0 < r < R_{\text{max}}$ ) as a function of time is shown in Fig. 3(c). It shows that for  $t > 30$  s, the height of the given droplet  $H(r, t)$  depends on time, giving an exponential decay according to:

$$H(r, t) = H(r, 30)e^{-0.013(t-30)} \quad (4)$$

where  $H(r, 30)$  is the height of the bulk at radius  $r$  at  $t = 30$  s.

The dependence of the contact angle  $\theta(t)$  on time was also studied (Fig. 3d) and found to be best fitted with a logarithmic decay:

$$\theta(t) = 59^{\circ} - 10.4^{\circ} \ln(t) \quad (5)$$

Note that below 50 s there is a deviation from this function. However, the standard deviation after this period was found to be  $0.56^{\circ}$ , which is smaller than the experimental error as discussed above. Similar to other wetting-reaction systems (Landry & Eustathopoulos, 1996; Eustathopoulos, 1998), the dependence of  $R(t)$  and  $\theta(t)$  on time, in this experiment, does

not reveal a power law that is expected for simple wetting processes.

## Summary

In conclusion, the results clearly demonstrate the ability of the optical system to construct quantitatively the 3D shape of a metal droplet that spreads on metal substrates, and its evolution with time. To our best knowledge, the present results demonstrate experimentally for the first time that in a reaction-wetting process the liquid droplet has a spherical-cup shape independent of time.

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## References

- Aveyard, R., Clint, J.H., Nees, D. & Paunov, V. (1999) Size-dependent lens angles for small oil lenses on water. *Coll. Surf. A*, **146**, 95–111.
- Bain, C.D., Burnett-Hall, G.D. & Montgomerie, R.R. (1994) Rapid motion of liquid drops. *Nature*, **372**, 414–415.
- Be'er, A., Lereah, Y., Hecht, I. & Taitelbaum, H. (2001) The roughness and growth of a silver–mercury reaction interface. *Phys. A*, **302**, 297–301.
- Be'er, A., Lereah, Y. & Taitelbaum, H. (2000) The dynamics and geometry of solid–liquid reaction interface. *Phys. A*, **285**, 156–165.
- Domingues dos Santos, F. & Ondarcuhu, T. (1995) Free-running droplets. *Phys. Rev. Lett.* **75**, 2972–2975.
- Eustathopoulos, N. (1998) Dynamics of wetting in reactive metal/ceramic systems. *Acta Mater.* **46**, 2319–2327.
- de Gennes, P.G. (1985) Wetting: statics and dynamics. *Rev. Mod. Phys.* **57**, 828–863.
- de Gennes, P.G. (1998) The dynamics of reactive wetting on solid surfaces. *Phys. A*, **249**, 196–205.
- Landry, K. & Eustathopoulos, N. (1996) Dynamics of wetting in reactive metal/ceramic systems: linear spreading. *Acta Mater.* **44**, 3923–3932.
- Liu, Y.M. & Chuang, T.H. (2000) Interfacial reactions between liquid indium and Au-deposited substrates. *J. Elect. Mater.* **29**, 405–410.
- Robinson, P.C. & Bradbury, S. (1992) *Qualitative Polarized-Light Microscopy*. Oxford University Press, Oxford.
- de Ruijter, M.J., De Coninck, J., Blake, T.D., Clarke, A. & Rankin, A. (1997) Contact angle relaxation during the spreading of partially wetting drops. *Langmuir*, **13**, 7293–7298.
- de Ruijter, M.J., De Coninck, J. & Oshanin, G. (1999) Droplet spreading: partial wetting regime revisited. *Langmuir*, **15**, 2209–2216.