Precursor films in wetting phenomena

M N Popescu\textsuperscript{1,2}, G Oshanin\textsuperscript{3}, S Dietrich\textsuperscript{2,4} and A-M Cazabat\textsuperscript{5}

\textsuperscript{1} Ian Wark Research Institute, University of South Australia, Adelaide, SA 5095, Australia
\textsuperscript{2} Max Planck Institute for Intelligent Systems, Heisenbergstraße 3, 70569 Stuttgart, Germany
\textsuperscript{3} Laboratoire de Physique Théorique de la Matière Condensée (UMR CNRS 7600), Université Pierre et Marie Curie, 4 place Jussieu F-75252, Paris Cedex 05, France
\textsuperscript{4} Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany
\textsuperscript{5} Laboratoire de Physique Statistique (UMR CNRS 8550), Université Pierre et Marie Curie and Ecole Normale Supérieure, 24 rue Lhomond 75231 Paris Cedex 05, France

E-mail: Mihail.Popescu@unisa.edu.au, oshanin@lptmc.jussieu.fr, dietrich@is.mpg.de and anne-marie.cazabat@upmc.fr

Received 9 January 2012, in final form 23 April 2012
Published 25 May 2012
Online at stacks.iop.org/JPhysCM/24/243102

Abstract

The spontaneous spreading of non-volatile liquid droplets on solid substrates poses a classic problem in the context of wetting phenomena. It is well known that the spreading of a macroscopic droplet is in many cases accompanied by a thin film of macroscopic lateral extent, the so-called precursor film, which emanates from the three-phase contact line region and spreads ahead of the latter with a much higher speed. Such films have been usually associated with liquid-on-solid systems, but in the last decade similar films have been reported to occur in solid-on-solid systems. While the situations in which the thickness of such films is of mesoscopic size are fairly well understood, an intriguing and yet to be fully understood aspect is the spreading of microscopic, i.e. molecularly thin, films. Here we review the available experimental observations of such films in various liquid-on-solid and solid-on-solid systems, as well as the corresponding theoretical models and studies aimed at understanding their formation and spreading dynamics. Recent developments and perspectives for future research are discussed.

Contents

1. Introduction 2
2. Droplets on solid substrates: equilibrium versus non-equilibrium 3
2.1. Partial wetting 3
2.2. Complete wetting 4
3. Spreading of non-volatile droplets 4
3.1. Non-volatile droplet spreading at macroscopic scales 5
3.2. Non-volatile droplet spreading at mesoscopic scales: mesoscopic films 6
3.3. Non-volatile droplet spreading at microscopic scales: ultrathin molecular films 8
4. Experimental studies of spreading of microscopic precursor films 8
4.1. Molecularly thin precursor films in liquid-on-solid systems 8
4.2. Ultrathin precursor films in metal-on-metal systems 12
5. Models for the dynamics of spreading of microscopic precursors 14
6. Numerical studies of ultrathin precursors 18
6.1. Monte Carlo simulations 18
6.2. Molecular dynamics simulations for simple or polymeric liquids 19
6.3. Molecular dynamics simulations for metal-on-metal systems 22
1. Introduction

Wetting of a solid by a liquid is a very common natural phenomenon. Morning dew on the grass, rain drops on plant leaves or windows, a coffee spill staining a table cloth, the water rising in the capillaries of a tree, the lubricating film covering the eye, or the oil drops on a non-stick frying pan are examples of wetting in day-to-day life. As well as being a ubiquitous natural phenomenon, wetting is at the core of many technologies and technological processes vital for various industries [1–3], e.g., the protective spin coating of surfaces (CDs, DVDs, glass lenses, car mirrors and windows), the development of water-resistant fabric, ink-jet printing, wall-painting, froth flotation [4] or acid heap leaching [5] in mineral recovery.

The theoretical analysis of wetting phenomena was started more than 200 years ago by Young [6], Laplace [7] and Plateau [8]. Their descriptions and the related subsequent developments are usually referred to as classical capillarity. Based on the seminal work by Gibbs [9], the theory of molecular liquids in terms of statistical physics led to a good (and still progressing) understanding of their bulk equilibrium properties [10, 11]. The theoretical description of the structure and properties of free liquid–vapour interfaces [12–15], as well as of the equilibrium wetting transitions occurring at an inert wall exposed to a fluid which is in a thermodynamic state close to bulk liquid–vapour coexistence, have also reached a mature state [16–19]. (For relatively recent developments see [20–23] and references therein.)

These contributions have put forward a thermodynamic and mechanical description of capillarity which is successful in explaining a large number of phenomena such as capillary rise, the shape of sessile or pendant drops and the shape of a meniscus, at least as long as only macroscopic phenomena are involved. The physicochemical parameters controlling the thermodynamic wettability of solid surfaces were clarified through the careful work of Zisman [24] and colleagues (see, e.g., [1]).

In the last two decades, significant efforts have been made towards understanding wetting phenomena at mesoscopic and microscopic scales. This was facilitated by the development of modern experimental techniques, capable of probing interfacial structures down to molecular scales, together with the fast paced technological progress in the fabrication of patterned surfaces possessing lateral wetting properties tailored on the micron- or even nano-scale through surface chemistry or topography. In this review, we focus solely on one particular subject in this area, i.e. the spreading of molecularly thin precursor films emanating from droplets deposited on solid substrates.

Since the late 1980s much progress has been achieved, both experimentally and theoretically, towards the understanding of the spreading dynamics of such films. Not only has their occurrence in various liquid-on-solid systems been reported in numerous studies, but also various details about their spatiotemporal structure have been revealed. Moreover, molecularly thin precursor films have been discovered in metal-on-metal systems, including even the case of films emerging from solid clusters. The rich behaviour observed in these latter systems, which includes surface alloying, is at present a topic of active investigations. The rapidly developing nano-fluidics chip technology keeps the interest in such films high by raising new questions, such as the spreading behaviour of sub-micron scale drops or their motion induced by such precursor films [25]. On the theoretical side, a number of models have been proposed in order to explain the experimentally observed behaviour.

However, these results are scattered in the literature and to date no attempt has been made to present a comprehensive review. In particular, [26], which dates back to 1991, covered only the few results concerning the dynamics of microscopic precursor films available during the short period from 1989, when the first reports on this topic appeared [27–30]. The recent review of dynamics of wetting in [31] has only briefly touched this subject because it was not within its main scope. Here we strive to overcome this dearth by collecting and assessing the large body of available experimental results, for both liquid-on-solid and solid-on-solid systems, and by discussing the various attempts at theoretical and numerical modelling of the spreading of microscopically thin precursor films.

This review is outlined as follows. In section 2 we briefly recall certain general thermodynamic criteria for the thermodynamic equilibrium of a macroscopic (but sufficiently small for the capillary forces to dominate external ones, such as gravity) liquid drop on a solid substrate. In section 3 we focus on spontaneous spreading of a droplet. In order to put the subject into a broader context (and in order to avoid referring an interested reader to the seminal original papers too often), there we concisely discuss the characteristic features of the spreading of the macroscopic part of the droplet, the emergence of a mesoscopic precursor film, and its dynamics. Size constraints do not permit us to provide a more detailed discussion of all seminal contributions. An interested reader can find such a description in comprehensive reviews [16, 26, 31]. Next, in section 4 we turn to the subject of interest here and we overview experimental data on spreading of microscopically thin precursor films in different liquid-on-solid and solid-on-solid systems. Section 5 presents various theoretical models of microscopic precursor films, while section 6 focuses on numerical simulations of these systems. Section 7 presents the recent developments in this area. Finally, in section 8 we provide a summary and an outlook.

---

6 Unfortunately size constraints make it impossible to do justice to all the numerous important contributions to the understanding of equilibrium wetting phenomena. The interested reader is encouraged to consult the extended bibliography lists in, e.g., [13, 16, 18].
is determined by Young’s equation
\[ \sigma_{lv} \cos \theta_{\infty} = \sigma_{sv} - \sigma_{sl}. \] (1)
Note that \( \theta_{\infty} \) is understood to be measured macroscopically, on a scale large compared with the range of long-ranged intermolecular forces. In terms of the so-called spreading coefficient (also often called the spreading ‘power’)
\[ S = \sigma_{sv} - \sigma_{lv} - \sigma_{sl}, \] (2)
one can rewrite equation (1) as
\[ \cos \theta_{\infty} = 1 + \frac{S}{\sigma_{lv}}, \] (3)
which relates the equilibrium contact angle to \( S \).

In thermal equilibrium \( S \) is either negative or zero (Antonov’s rule [18]). The case \( S < 0 \), which implies \( 0^\circ < \theta_{\infty} \leq 180^\circ \), is referred to as partial wetting. It corresponds to drops, surrounded by a microscopically thin film adsorbed at the surface. Classical capillarity predicts the essential features of the shape of such drops. If the drop is small enough so that gravity can be neglected (i.e., the characteristic length scale of the drop is much smaller than the capillary length \( \chi \)), the hydrostatic pressure rapidly equilibrates inside the drop; the drop then adopts the shape of a spherical cap in order to obey Laplace’s law (i.e., the pressure difference between the liquid drop and the surrounding vapour is balanced by the surface tension \( \sigma_{lv} \) multiplied by the mean curvature of the drop shape) and the in-plane isotropy\(^8\).

Statistical mechanics studies of wetting phenomena in the grand canonical ensemble reveal that in the case of partial wetting (i.e. at bulk liquid–vapour coexistence on the vapour side and at a temperature \( T \) below the wetting transition temperature \( T_w \)) the substrate is covered by a microscopically
\[ \sigma_{lv} \cos \theta_{\infty} = \sigma_{sv} - \sigma_{sl}. \] (1)
Note that \( \theta_{\infty} \) is understood to be measured macroscopically, on a scale large compared with the range of long-ranged intermolecular forces. In terms of the so-called spreading coefficient (also often called the spreading ‘power’)
\[ S = \sigma_{sv} - \sigma_{lv} - \sigma_{sl}, \] (2)
one can rewrite equation (1) as
\[ \cos \theta_{\infty} = 1 + \frac{S}{\sigma_{lv}}, \] (3)
which relates the equilibrium contact angle to \( S \).

In thermal equilibrium \( S \) is either negative or zero (Antonov’s rule [18]). The case \( S < 0 \), which implies \( 0^\circ < \theta_{\infty} \leq 180^\circ \), is referred to as partial wetting. It corresponds to drops, surrounded by a microscopically thin film adsorbed at the surface. Classical capillarity predicts the essential features of the shape of such drops. If the drop is small enough so that gravity can be neglected (i.e., the characteristic length scale of the drop is much smaller than the capillary length \( \chi \)), the hydrostatic pressure rapidly equilibrates inside the drop; the drop then adopts the shape of a spherical cap in order to obey Laplace’s law (i.e., the pressure difference between the liquid drop and the surrounding vapour is balanced by the surface tension \( \sigma_{lv} \) multiplied by the mean curvature of the drop shape) and the in-plane isotropy\(^8\).

Statistical mechanics studies of wetting phenomena in the grand canonical ensemble reveal that in the case of partial wetting (i.e. at bulk liquid–vapour coexistence on the vapour side and at a temperature \( T \) below the wetting transition temperature \( T_w \)) the substrate is covered by a microscopically
\[ \sigma_{lv} \cos \theta_{\infty} = \sigma_{sv} - \sigma_{sl}. \] (1)
Note that \( \theta_{\infty} \) is understood to be measured macroscopically, on a scale large compared with the range of long-ranged intermolecular forces. In terms of the so-called spreading coefficient (also often called the spreading ‘power’)
\[ S = \sigma_{sv} - \sigma_{lv} - \sigma_{sl}, \] (2)
one can rewrite equation (1) as
\[ \cos \theta_{\infty} = 1 + \frac{S}{\sigma_{lv}}, \] (3)
which relates the equilibrium contact angle to \( S \).

In thermal equilibrium \( S \) is either negative or zero (Antonov’s rule [18]). The case \( S < 0 \), which implies \( 0^\circ < \theta_{\infty} \leq 180^\circ \), is referred to as partial wetting. It corresponds to drops, surrounded by a microscopically thin film adsorbed at the surface. Classical capillarity predicts the essential features of the shape of such drops. If the drop is small enough so that gravity can be neglected (i.e., the characteristic length scale of the drop is much smaller than the capillary length \( \chi \)), the hydrostatic pressure rapidly equilibrates inside the drop; the drop then adopts the shape of a spherical cap in order to obey Laplace’s law (i.e., the pressure difference between the liquid drop and the surrounding vapour is balanced by the surface tension \( \sigma_{lv} \) multiplied by the mean curvature of the drop shape) and the in-plane isotropy\(^8\).

Statistical mechanics studies of wetting phenomena in the grand canonical ensemble reveal that in the case of partial wetting (i.e. at bulk liquid–vapour coexistence on the vapour side and at a temperature \( T \) below the wetting transition temperature \( T_w \)) the substrate is covered by a microscopically
thin liquid-like film, the thickness $h_{\infty}$ of which (see the inset in figure 1(a)) is temperature dependent and exhibits wetting transitions [18, 32]. In the case of a first-order wetting transition, for $T \to T_\text{w}$, $h_{\infty}$ jumps to a macroscopic value, whereas $h_{\infty}$ diverges continuously for a second-order wetting transition (also known as critical wetting [18]). For bounded systems these singularities are smeared out. The spherical cap-like shape of the liquid–vapour interface, which for a suitably large drop is indeed valid far away from the substrate, is distorted in the vicinity of the substrate due to the effective interaction between the liquid–vapour interface and the substrate and smoothly connects to the uniform equilibrium film thickness far away from the drop [18, 33]. The deviations of this actual shape from that of a spherical cap cut by the substrate contribute to the line tension [33–41], i.e. the excess free energy, associated with a line-like inhomogeneity, within the decomposition of the excess free energy into bulk, surface and line contributions [9].

2.1.2. Non-equilibrium behaviour. If a droplet is deposited on an initially dry substrate, it is typically not in equilibrium and the equilibrium can be reached only via certain dynamical processes. The way the relaxation towards equilibrium takes place depends significantly on the volatility of the liquid under ambient conditions. If the liquid is volatile, the equilibrium with the ambient gas can be established relatively fast via condensation of vapour onto the substrate. In contrast, if the liquid is non-volatile under ambient conditions (i.e. if it has a very low vapour pressure), the evolution of the drop shape towards equilibrium will proceed via two-dimensional evaporation and motion of liquid molecules on the substrate surface. Usually, these are much slower processes and in many cases the time required to approach equilibrium after contact with the ‘dry’ substrate can be more than a few hours, or even days.

The pertinent quantity for the dynamics is the initial spreading coefficient

$$S_0 = \sigma_{\text{lg}} - \sigma_{\text{lg}} - \sigma_{\text{sl}},$$

(4)

where $\sigma_{\text{lg}}$ is the surface tension of the dry solid substrate in contact with the gas. The surface tension $\sigma_{\text{lg}}$ is typically larger than $\sigma_{\text{sv}}$; assuming that $\sigma_{\text{lg}} \approx \sigma_{\text{lv}}$, which is appropriate for an inert gas (i.e. which has a low solubility in the liquid and which does not act as a surfactant) and for temperatures sufficiently far from the critical point, it follows that $S_0 \geq S$. (Note that $\sigma_{\text{lg}}$ is not a measurable quantity; it can be computed assuming the constrained equilibrium that the gas density is constant up to the substrate surface without the formation of a liquid-like wetting film.) The initial $S_0$ can be positive or negative, but whenever $S_0 < 0$ $S$ is also negative. Hence, for non-volatile liquids and for $S_0 < 0$ the drop will relax towards an equilibrium configuration which displays a non-zero static (equilibrium) contact angle.

9 Instabilities of droplets caused by line tension have been critically discussed in [42].

2.2. Complete wetting

If the equilibrium spreading coefficient vanishes, i.e., $S = 0$, one has complete wetting. The corresponding equilibrium contact angle of a volatile liquid is zero, i.e., $\theta_\infty = 0$, so that the solid–vapour interface consists of a macroscopically thick wetting layer, which implies that the solid–vapour surface tension is equal to the sum of the solid–liquid and liquid–vapour surface tensions.

For a drop of a non-volatile liquid deposited on an initially dry substrate $S_0$ is positive (although its equilibrium spreading power $S = 0$), and therefore the drop will spread while preserving its volume. This volume conservation constraint is essential for describing both the spreading dynamics and the final state of non-volatile liquid drops. This explains why in certain situations a non-volatile liquid drop does not spread down to an unbounded film of uniform thickness, but that spreading stops when the drop eventually takes on a ‘pancake’-like shape of thickness $e(S_0) = a\sqrt{3\sigma_{\text{lg}}/(2S_0)}$ (where $a$ is a molecular length [16] specific to non-retarded van der Waals interactions, $a = \sqrt{-A/(6\pi \sigma_{\text{lg}})}$, with $A < 0$ being the Hamaker constant). This occurs if short-ranged interactions promote dewetting, even though the overall situation is that of complete wetting. Such structures have been theoretically predicted and analysed in [16, 43, 44], and indeed observed later experimentally (see, e.g., [45]).

3. Spreading of non-volatile droplets

The issue of a non-volatile drop spreading on a substrate from an initial non-equilibrium configuration with $S_0 > 0$ towards its equilibrium shape in situations in which $S = 0$ has been the subject of extensive experimental and theoretical investigations. The results of this analysis have been reviewed thoroughly in [16, 26, 31, 46–48]. Here we shall focus only on those main findings which are of interest in the present context. Moreover, we constrain ourselves to the late stages of spreading (and hence sufficiently small dynamical contact angles) when all transient behaviours and memory effects of the initial non-equilibrium shape have died out. (Some recent experimental results on the transient inertial regime at very early stages of spreading can be found in [49, 50].)

In figure 1(b) we sketch a typical configuration for a non-volatile liquid droplet spreading on a solid substrate. The drop can be divided into the following two main regions: (i) a macroscopic bulk and (ii) a precursor film, the thickness of which may be on a mesoscopic or a microscopic scale. Note that figure 1(b) is schematic and the relative sizes of these regions are not drawn to scale. The non-equilibrium, time-dependent parameters $\theta(t)$ and $h(t)$, which are expected to obey $\theta(t \to \infty) \to \theta_{\infty}$ and $h(t \to \infty) \to h_{\infty}$, require further discussion. During spreading, the shape of the macroscopic part of the drop does not necessarily have to be a spherical cap because spreading is a non-equilibrium process. (Although very often a spherical cap shape is employed in the interpretation of experimental or computer simulation results concerning droplet spreading or dynamic wetting (see, e.g., [51]), one should keep in mind that...
it remains an assumption which should be at least checked for validity in each particular instance.) Therefore, we shall define the parameters \( \theta_i \) and \( h_i \) without reference to a particular shape. As shown in figure 1(b), far away from the substrate the shape of the drop has a negative curvature, while at the precursor film the curvature is approaching zero from above. Therefore, there is an inflection point, at a distance from the substrate of the order of the range of the effective interface potential, where the curvature of the shape changes from negative (corresponding to the macroscopic part) to positive (corresponding to the region of the foot and precursor film). Therefore, it is a natural choice to define the macroscopic part of the drop as that part of the shape exhibiting negative curvature up to the inflection point and the ‘dynamic’ contact angle \( \theta_i \) as the angle formed by the tangent to the drop shape at this inflection point (see also [52]). The foot of the drop is defined as that part of the drop shape where the curvature is positive and attains zero from above upon approaching the almost flat precursor film. Accordingly, \( h_i \) is defined as the maximum thickness of the film extending ahead of the foot region. Note that for very small or very flat drops (i.e. small equilibrium contact angles) these definitions involving a dynamic macroscopic shape of the drop and a foot region are obviously of limited value because they increasingly depend on the experimental resolution and, moreover, the inflection point becomes inadequate as a relevant experimental parameter. In contrast, the definitions of the equilibrium observables \( \theta_\infty \) and \( h_\infty \) remain on solid ground as long as the amount of liquid is sufficient to limit the fluctuations around a mean shape.

3.1. Non-volatile droplet spreading at macroscopic scales

The key parameter characterizing the spreading of the macroscopic part of the non-volatile drop is the so-called capillary number \( Ca = \eta U/\sigma \), where \( U \) is the velocity of the advancing liquid wedge and \( \eta \) is the viscosity of the liquid. An early experimental analysis of the relation between the dynamical contact angle \( \theta_i \) and the capillary number has been carried out by Hoffman [53], who studied a forced spreading (with velocities varying over five decades) of a liquid in a capillary, measuring a dynamical contact angle by a photographic technique. In a series of experiments with silicon oils, he obtained conditions of complete wetting and found a fairly universal relation between \( Ca \) and \( \theta_i \); in particular, in the limit of low \( Ca \) and \( \theta_i \) he found that his data can be represented as a power law

\[
Ca = \text{constant } \theta_i^\alpha ,
\]

where \( \alpha = 3 \pm 0.5 \). Cox [54] treated analytically the rather general problem of one fluid displacing another one on a solid surface for any viscosity ratio and contact angle. He solved the hydrodynamic equations to first order in \( Ca \) assuming that the macroscopic wedge with angle \( \theta \) ends in a zone of molecular extension where slip is allowed. In the complete wetting case and for small contact values his analysis confirmed the result in equation (5) with \( \alpha = 3 \). We note that a relation of this type was first derived theoretically by Fritz [55], but for the slightly different problem of a liquid spreading on a wet surface. In comparison with Cox’s analysis, in this case the viscosity of the displaced phase (i.e. vapour) is negligible and the conceptual difficulties arising due to the movement of the contact line on a solid substrate are bypassed by considering a surface covered by a liquid film. A detailed analysis of the relation in equation (5) has also been carried out by Teletzke et al [56].

Voinov [57] and Tanner [58] derived analytically the relation in equation (5) with \( \alpha = 3 \) solving the hydrodynamic equations in the lubrication approximation. They have also used the result in equation (5) in order to obtain the time evolution of the base radius \( R_i \) and the dynamical contact angle \( \theta_i \) of a spreading droplet of a non-volatile liquid under the assumption that the droplet shape is that of a spherical cap at all times during spreading. In this case \( R_i \) and \( \theta_i \) are coupled due to the constraint of fixed volume \( V \). This leads to the so-called Tanner’s laws [57, 58] according to which for sufficiently large \( R_i \) and small \( \theta_i \) these quantities are given by

\[
R_i \sim V^{3/10} \left( \frac{\sigma \eta}{\eta} \right)^{1/10} \quad (6)
\]

and

\[
\theta_i \sim V^{1/10} \left( \frac{\sigma \eta}{\eta} \right)^{-3/10} . \quad (7)
\]

Thus the spreading of the macroscopic part of the droplet is rather slow; it would take a very long time to completely spread a macroscopic droplet. Note that equations (6) and (7), together with the fixed volume constraint, predict that the final state (i.e. at \( t \to \infty \)) of the spreading drop is a two-dimensional gas. However, this is not necessarily so. The validity of the relations (6) and (7), which are based on classical continuum hydrodynamics, breaks down at a crossover time \( T_0 \), at which the height of the spreading drop reaches the range of the effective interface potential (which describes the effective interaction between the substrate and the liquid–gas interface).

The behaviours given in equations (6) and (7) have been observed in a number of thorough experimental studies (see, e.g., the detailed analysis of the full shape of a spreading drop by using laser light interferometry reported by Chen and Wada [59] and the review by Marmur [60]). On the other hand, some significant deviations have been observed for spreading liquids with very low viscosity (see, e.g., [61]). However, such deviations have been explained in [62] by the influence, at intermediate times, of the dissipation at the macroscopic contact line [63], which is unaccounted for in the hydrodynamic description of spreading.

We finally point out the remarkable feature in equations (6) and (7) that neither the radius nor the dynamic contact angle of the macroscopic part of the droplet depend on the initial spreading power \( S_0 \). This shows that in conditions in which the liquid completely wets the solid the macroscopic spreading turns out to be independent of the wettability (i.e. the value of \( S_0 \)) of the solid surface. A consistent explanation for this feature is due to Hervet and de Gennes [16, 64], who have shown that (i) the macroscopic
behaviour described by equations (5)–(7) stems from the interplay of the hydrodynamic dissipation in the wedge of the macroscopic part of the droplet and the ‘driving force’ for spreading provided by the free energy of the drop due to its shape not being the equilibrium one, i.e., a two-dimensional gas or a flat ‘pancake’ (see section 3.2.2), and that (ii) $S_0$ is entirely dissipated in the mesoscopic part of the drop. These arguments have been used further in [52, 65] in order to account for the effects of the line tension on the late-stage (i.e. post-Tanner) spreading of a macroscopic droplet. For simple liquids, the conclusion reached in these references was that in the late stages of spreading a positive line tension is responsible for the formation of pancake-like structures, whereas a negative line tension tends to lengthen the contact line and to induce an accelerated spreading (i.e., there is a crossover to a faster algebraic increase of $R_t$ than in the Tanner stage) [52].

3.2. Non-volatile droplet spreading at mesoscopic scales: mesoscopic films

3.2.1. Experimental evidence. The first reported observation of an ‘invisible’ film spreading ahead of the edge of a macroscopic drop stems from the pioneering work by Hardy [66, 67], who studied the behaviour of drops of water, acetic acid, and various other polar organic liquids on clean surfaces of glass and steel. Hardy realized that a film of liquid about one micron thick is pushed out and spreads from a drop, and that, importantly, this process may or may not be followed by spreading of the drop itself\(^\text{10}\).

With the experimental techniques available at that time, a direct observation of such a film—called by Hardy the ‘primary’ film—was not possible. He was able to detect its presence only indirectly, via its lubricating effects, by observing a significant drop of the static friction of the surface both far away and close to the three-phase contact line. Hardy stated that he is unable to conceive a mechanism by which the film is pushed out of the drop and proposed that spreading of the film occurs via a process involving a steady condensation of vapour\(^\text{11}\).

Two decades later, Bangham and Saweris [70], analysing the spreading behaviour of numerous polar and apolar liquids on freshly cleaved mica, demonstrated that primary films do also occur even in the absence of any vapour in the gas. This suggests that the evaporation/condensation scheme (proposed by Hardy and clearly confirmed by [69]) is not the only possible physical mechanism producing the film. The conclusion drawn from their experiments is that the primary film can also form by surface diffusion of molecules from the edge of the drop. Recently, these findings have been re-examined and confirmed [71]. The experiments in [71] employed pairs of drops of water/alcohol, water/acetic acid, and PDMS/ trans-decaline, the first two involving volatile liquids, placed on glass or mica substrates. The occurrence of drop motion has been explained as the result of a surface tension gradient at the solid–gas interface due to the formation of precursor films [71, 72], which, in case of volatile components, form either via an evaporation–condensation mechanism or by spreading on the surface out of one of the drops (PDMS). It was also noted that the thickness of these films is different (although no precise characterization of the thickness was provided): ultrathin (invisible) in the first case, and mesoscopically thick (visible) in the latter.

In 1964, Bascom et al [73] investigated the spreading of the primary film from a more quantitative point of view using ellipsometry and interferometry techniques. They examined the behaviour of various hydrocarbons on clean, horizontal or vertical metal surfaces in the presence of either vapour saturated and vapour unsaturated air. By monitoring the late stages of spreading via ellipsometry it was concluded that a primary film is present in all the cases studied. Making the air saturated or unsaturated with vapour, roughening the surface, and purifying the liquids did not eliminate the occurrence of the film, but only affected the spreading speed. The thickness of the film was found to depend sensitively on the kind of liquid/solid pair under study but generally it amounted to a few hundred Å.

A decade later Radigan et al [74] showed that the appearance of such films is not specific to the drop being bona fide liquid. Scanning electron microscopy studies of an inorganic molten glass spreading on a Fernico metal (i.e. a Fe–Ni–Co alloy with a coefficient of linear expansion close to that of hard glass) at 1000 °C revealed a spreading film with an average height of the order of one micron. To our knowledge, this was the first publication in which the notion of a ‘precursor film’ was used.

Finally, Ghiradella et al [75] detected a mesoscopic precursor film for a hydrochloric solution rising in a glass vessel on a vertical wall. The existence of the film was demonstrated by monitoring the changes in electrical resistance across the wall. Ausserrè et al [76] were the first to directly visualize the precursor films with thicknesses of several hundred Å by using polarized reflection microscopy for the spreading of non-volatile high molecular weight polydimethylsiloxane (PDMS) on smooth horizontal silicon wafers. The density profiles of these films were studied by ellipsometry in [77] and the final stages of spreading of small PDMS droplets in [78].

3.2.2. Theoretical concepts. We now turn to the theoretical analysis of the time evolution of the mesoscopic part of the drop (see figure 1(b)), focusing on scales from about 30 Å to 1 μm. At such scales, a continuum picture is still applicable, but certain long-ranged forces become relevant, mainly van
der Waals forces for organic liquids, or double-layer forces for water. Accordingly, interfacial tensions alone become insufficient to describe the free energy of the system. An additional free energy term $\omega(h)$ has to be included, which takes into account the interactions between the two interfaces (solid–liquid and liquid–gas for the liquid-on-solid spreading); $h$ is the local film thickness. This additional free energy contribution, known as the effective interface potential $\omega(h)$, has a pressure counterpart, which is the disjoining pressure $\Pi(h) = -\partial \omega / \partial h$. This was introduced by Derjaguin [79] in order to describe the dynamics of thin liquid films.$^{12}$

Within the lubrication approximation [40, 79, 80], the spreading of a thin, non-evaporating liquid film on a solid substrate ahead of the macroscopic edge of the drop, which moves with velocity $U$ along the $x$-direction, is governed by the conservation law

$$\frac{\partial h}{\partial t} = -\frac{\partial}{\partial x}(hU), \quad (8)$$

and the dynamic equation

$$\eta U = \frac{h^2}{3} \frac{\partial}{\partial x} \left( \frac{\partial^2 h}{\partial x^2} + \Pi(h) \right), \quad (9)$$

which holds for mesoscopically thin films in the absence of gravity and surface tension gradients.

Capitalizing on the ideas of Derjaguin [79], Hervet et al [16, 26, 64, 81, 82] and Teletzke et al [56] have provided a description of mesoscopic precursor spreading which includes the contribution of the long-ranged forces. This has stimulated a strong activity in the field, both theoretically and experimentally. Following the analysis in [82], below we shall briefly outline some basic theoretical concepts and results concerning the spreading of mesoscopic precursor films. According to this analysis, explicit results can be obtained in two limiting cases: first, if the velocity $U$ of the macroscopic edge varies very slowly in time (adiabatic case, in which the drift of the edge contributes to the spreading of the precursor), and second, if $U \to 0$ (diffusive case, in which the motion of the macroscopic edge has stopped and the expansion of the film is controlled solely by the spreading power $S_0$ and the disjoining pressure).

(A) Adiabatic films. The theoretical analysis of equations (8) and (9) shows that a so-called adiabatic film emanates from a liquid wedge which is advancing with a constant (or slowly varying) velocity $U$. Under the additional assumptions that curvature effects are negligible and that this film is stationary, i.e., that its shape reaches a stationary shape very rapidly at timescales which are much shorter than the scales at which the velocity of the macroscopic wedge varies (thus the name ‘adiabatic’), the spreading equation (equation (9)) of the film along the $x$-coordinate reduces to [79, 82, 83]:

$$\eta U = \frac{h^2}{3} \frac{\partial \Pi}{\partial x} = \text{constant}, \quad (10)$$

$^{12}$Note that $S_0 = \int_0^\infty dh \Pi(h)$, while $S = \int_0^\infty dh \Pi(h)$, where $h_\infty$ is the equilibrium film thickness.

which renders the film profile. The latter equation can be solved, e.g., for the common case of a non-retarded van der Waals disjoining pressure $\Pi(h) = -A/(6\pi h^3)$, where $A < 0$ denotes the Hamaker constant. For this case a simple analysis [82] shows that for $S_0 > 0$ the distance $l_a$ from the macroscopic wedge to the point at which the height of the adiabatic film is that of a ‘pancake’, i.e., $h(l_a) = e(S_0) = \sqrt{-A/(6\pi S_0)}$, is given by

$$l_a = \frac{-A}{6\pi \eta U e(S_0)} \sim \sqrt{S_0}. \quad (11)$$

Hence, the lateral size of the adiabatic film is proportional to $\sqrt{S_0}$. This shows that, while the macroscopic properties of a spreading droplet are independent of the spreading coefficient, the mesoscopic properties, e.g., the length of the adiabatic film and the thickness of the pancake, do depend on $S_0$. In particular, the adiabatic film is longer and thinner the larger $S_0$ is.

As we remarked at the end of section 3.1, in the macroscopic picture [16] the Young capillary force $f_y = S_0 + \sigma_g(1 - \cos(\theta_l))$ per unit length of the contact line is compensated by the overall viscous force $f_{\text{visc}} = \int (\eta U^t h) \, dx$. This viscous force can be split into two parts: the viscous force in the macroscopic wedge which stems from hydrodynamic dissipation in the bulk of the droplet, and the viscous force in the precursor. By integrating both sides of equation (10) along the $x$-axis from the location $x = 0$ of the macroscopic wedge to the tip $x = l_a$ of the precursor film one finds that for arbitrary expressions of the disjoining pressure the viscous force (per length) in the precursor is exactly equal to $S_0$. This shows that the entire spreading power $S_0$ is dissipated in the film. This remarkable result due to Hervet and de Gennes [16, 64] resolved the long standing paradox that under complete wetting conditions the spreading of the macroscopic part of the drop is independent of the value of the spreading power $S_0$. This is so because this way the driving force of spreading equals $\sigma_g(1 - \cos(\theta_l))$ and it is exactly balanced by the hydrodynamic dissipation in the bulk so that $S_0$ drops out of the dynamics.

(B) Diffusive films. In view of equation (11), the adiabatic films may have a noticeable spatial extent only for very small velocities of the macroscopic wedge. In practice, as soon as the length of the adiabatic film becomes greater than a few micrometres, another process comes into play. Since the thickness of this film is not constant spatially, there is a gradient of the disjoining pressure along the film. This causes a non-stationary film—the so-called ‘diffusive’ film—to develop ahead of the adiabatic film. When the length $l_\ell$ of such a diffusive film becomes sufficiently large, the film becomes nearly flat so that curvature effects are negligible. As a result, from equations (8) and (9) one finds that the profile $h(x, t)$ of the spreading diffusive film solves the differential equation [81, 84]

$$\frac{\partial h}{\partial t} = \frac{\partial}{\partial x} \left( \left( -\frac{h^2}{3\eta} \frac{\partial \Pi}{\partial h} \right) \frac{\partial h}{\partial x} \right). \quad (12)$$
This is a non-linear diffusion-type equation with an effective ‘diffusion coefficient’

\[ D(h) = -\frac{h^3}{3\eta} \frac{\partial \Pi}{\partial h} \]  

(13)

which depends on the local height of the mesoscopic film. In the presence of dispersion forces \( \Pi(h) \sim h^{-3} \) and thus \( D(h) \) increases as the height decreases. A straightforward analysis shows \([81, 82, 84]\) that, when the diffusive film becomes much longer than the adiabatic one, the length \( \ell_t \) of such a film increases ‘diffusively’, i.e. in proportion to the square root of time:

\[ \ell_t \sim \sqrt{D(e(S_0))t}, \]  

(14)

where \( e(S_0) \) is the thickness of the equilibrium pancake shape of the whole drop. Hence, \( D(h = e(S_0)) \) is the largest possible value of the diffusion coefficient. In the case of a van der Waals liquid, \( D(e(S_0)) \) as given by equation (13) is comparable with the Stokes diffusion coefficient of a sphere of radius \( e(S_0) \), i.e. about \( 10^{-9} \text{ m}^2 \text{ s}^{-1} \).

Thus the phenomena occurring at the macroscopic and mesoscopic scales, where hydrodynamics is applicable, can be summarized as follows. In the case of complete wetting a macroscopic non-volatile drop spreads very slowly (equation (6)) due to the balance between the hydrodynamic viscous dissipation in the bulk and the ‘driving’ Young force (see the end of (A) above). It gradually empties into a mesoscopically thin film, which is formed by the lateral gradient of the disjoining pressure during the spreading process and serves as a lubricant for the macroscopic part of the trailing droplet. (This process also removes a singularity in the hydrodynamic dissipation at the three-phase contact line.) The entire initial spreading power \( S_0 \) is dissipated by viscous friction in this film. The mesoscopic film flattens as it spreads. When the entire volume of the droplet leaks into the film the spreading process stops and an equilibrium ‘pancake’ is formed. This description remains valid as long as the thickness \( e(S_0) \) of this final pancake shape is significantly larger than the molecular size.

### 3.3. Non-volatile droplet spreading at microscopic scales: ultrathin molecular films

As noted above, the mesoscopic films cannot provide a complete picture for the spreading of a non-volatile liquid droplet. The continuum hydrodynamic description explicitly presumes that the thickness of the liquid film stays within the mesoscopic range, which means that the thickness \( e(S_0) \) of the pancake should be much larger than the molecular scale. This imposes constraints on the values of the surface tension \( \sigma_1 \) and of the spreading power \( S_0 \). Accordingly, the hydrodynamic description might hold for low energy substrates, but may break down for intermediate or high energy surfaces, for which the pancake thickness drops below the size of the liquid molecules\(^{13}\). In this context, the challenging experimental observation \([27, 28]\) that spreading of non-volatile droplets of squalane or PDMS on silicon wafers is accompanied by the occurrence of a film of a microscopic, not mesoscopic, thickness called for new experimental approaches and theoretical concepts. These will be reviewed in sections 4, 5 and 6.

### 4. Experimental studies of spreading of microscopic precursor films

#### 4.1. Molecularly thin precursor films in liquid-on-solid systems

The experimental analysis of films with thicknesses of the order of only a few molecular diameters became possible with the advent of advanced experimental techniques such as spatially resolved ellipsometry. Ellipsometry is an optical method allowing for the measurement of the local thickness of very thin films which are deposited on substrates with an optical index of refraction \( n \) different from that of the film. If the contrast between the indices of refraction is large (such as for silica or silicon oil \( n = 1.4 \) for red light) on a silicon substrate \( (n = 3.8) \), effective film thicknesses as small as 0.1 Å can be measured \([28, 85]\); the lateral resolution remains usually in the range of micrometres. Here it is important to emphasize that, in fact, ellipsometric measurements yield ‘effective’ thicknesses, which are equal to the actual thickness multiplied by the local number density (averaged across the film at a certain lateral position) divided by the bulk number density. In other words, the effective thickness is the actual thickness multiplied by the ratio \((n_{\text{loc}} - 1)/(n_0 - 1)\), where \( n_0 \) is the bulk index of refraction for the liquid and \( n_{\text{loc}} \) is the local index of refraction (also averaged across the film at a certain lateral position). This local thickness has the property that it vanishes if there is no film, i.e., \( n_{\text{loc}} = 1 \). In consequence, effective thicknesses below the molecular diameter can be observed in ellipsometry, which signifies that the film becomes a diluted, two-dimensional surface gas, rather than a dense fluid.

Employing spatially resolved ellipsometry with modulated polarization, as developed by Drévillelon et al \([85]\) and Beaglehole \([28]\), a systematic analysis of spreading speeds of ultrathin precursor films has been carried out by Heslot et al \([27]\). They focused on the temporal evolution of the shapes of rather small drops (with a volume of about \( 10^{-4} \mu l \)) of non-volatile liquids (squalane and PDMS) spreading (in the complete wetting regime) on silicon wafers. First, the authors did not observe a ‘pancake’ as the final stage of spreading but rather they detected a gradual transition to a surface gas due to molecular diffusion on the substrate surface. Second, their analysis revealed a precursor film of nearly molecular molecular crystals (bound by van der Waals forces, or in some special cases, by hydrogen bonds). Hard solids have ‘high energy surfaces’ \((\sigma_1 \sim 0.5-5 \text{ N m}^{-1})\), while molecular solids (and also molecular liquids) have ‘low energy surfaces’ \((\sigma_1 \sim 0.05 \text{ N m}^{-1})\). Here \( \sigma_1 \) denotes surface energies, i.e. half of the work needed to separate an infinite piece of material into two half-spaces and take the two emerging solid–vacuum planar interfaces far from each other.

\(^{13}\) According to the classification of Zisman \([24]\) there are two main types of solid: (i) hard solids (covalent, ionic, or metallic), and (ii) weak
thickness, the radial extent of which, $\ell_i$, increases in time as

$$\ell_i \approx \sqrt{D_1 t},$$  

(15)

where the subscript ‘1’ indicates that, distinct from equation (13), $D_1$ is the ‘diffusion coefficient’ related to a molecularly thin precursor film.

Beaglehole [28] analysed the profiles of the microscopic precursor of a spreading drop of siloxane oil on glass, fused silica, and freshly cleaved mica. He also observed that the mean radial extent $\ell_i$ of the precursor at late stages follows equation (15). (Late times means that they are much larger than the single molecule diffusion time, i.e. the time it would take an isolated molecule to move by diffusion over a distance equal to its diameter, with the lateral extent of the precursor being orders of magnitude larger than this molecular size, yet small enough that the drop remains large and can act as a particle reservoir.)

Using ellipsometry and x-ray reflectometry in a controlled atmosphere of dry and filtered N$_2$, Heslot et al [29] (see also [47]) studied the spreading speed and the number density profiles normal to the substrate of a molecularly thin precursor film emanating from a macroscopic meniscus in a capillary rise geometry in which a vertical silicon wafer covered by a natural oxide is immersed in a light silicon oil (PDMS). They observed a film climbing up the vertical wall the extent of which—after 56 h—attained macroscopic values of about 10 mm (see figure 2). The film number density varied in a step-like manner in the direction normal to the substrate surface. For the major part of the film in the lateral direction the effective film thickness was nearly constant, with a value of about 6 Å. Near the tip of the film its effective thickness decreases smoothly. Since PDMS is a worm-like polymer with the size of the monomer of the order of 6 Å, the observations have been interpreted such that the major part of the film is a compact monolayer of disentangled PDMS molecules lying flat on the solid surface. The region near the tip, where the measured effective thickness falls to a value corresponding to a submonolayer regime, can be viewed as one populated by a surface gas of PDMS molecules. (Note that this effective thickness can take values below the size of a PDMS molecule.) The lateral extent $\ell_i$ of the film (denoted as $L$ in figure 2) was measured at various times and it was found to be in agreement with equation (15) with $D_1 \approx 3 \times 10^{-11} \text{ m}^2 \text{s}^{-1}$.

Significant progress has been made in [30], which reports the striking phenomenon of ‘terraced wetting’ (see figure 3). Using spatially resolved and time-resolved ellipsometry, it was shown that liquid drops (PDMS or tetraakis(2-ethylhexoxy)-silane (TK)) spreading on silicon wafers exhibit a strong, dynamical layering in the vicinity of the solid surface such that a spreading droplet advances via a series of distinct molecular layers, and the $k$th layer expands proportional to $\sqrt{t}$ with its own ‘diffusion coefficient’ $D_k$ ($\cdots > D_{k-1} > D_k > D_{k+1} > \cdots$). A similar effect has been observed for spreading of TK in the capillary rise geometry [86]. Since the latter terraced spreading occurred for a system seemingly similar to the one in [29], for which it was not observed, this behaviour has been further scrutinized in [87], which focused on the effects of the surface energy on precursor film spreading. It was found that ‘terraced wetting’ occurs on so-called ‘high energy’ substrates (such as UV-ozone cleaned silicon wafers used for the experiment immediately after cleaning). As long as the macroscopic part of the drop acts as a reservoir, up to five such molecular layers are observed, each expanding over macroscopic distances proportional to the square root of time. When the drop starts to run out of material, the top layers are observed to empty themselves into the lower ones, down to the first one. In contrast, for low energy substrates (such as silicon wafers prepared by monolayer deposition of a fatty acid using the Langmuir–Blodgett technique, see [87]), typically only a single molecularly thin precursor film has been observed to advance proportional to the square root of time [87].

The terraced spreading phenomenon was further studied in [45, 88, 89], which present a remarkable catalogue of many diverse forms which a spreading ‘terraced’ droplet can adopt under a variety of conditions for various liquid-on-solid systems. A diversity of profiles of the film thickness has been observed, with either a gradual (if any) variation of the thickness as function of the distance from the macroscopic

![Figure 2.](image-url)
drop or a fairly strong lateral variation. These studies revealed that the ‘terraced wetting’ phenomenon results from an intricate interplay between the surface energy and friction, and that it occurs for liquids which are non-volatile both in 3D and in 2D. At room temperature this is the case for PDMS oils with a viscosity larger than 0.02 Pa s and for the silicon derivative TK, and at temperatures below 5 °C for squalane.

Perfectly terraced droplets with terraces possessing flat tops and sharp edges have been observed by Daillant et al [90, 91] for the liquid crystal 8CB spreading on a (400) silicon wafer and by Betelů et al [92] for the liquid crystal 755 spreading on an oxide covered (100) Si wafer. Using ellipsometry, for perfluoropolyalkylether (PFPE) films on carbon surfaces Ma et al [93] have also observed a complex terraced spreading with an increase of the size of the individual layers proportional to the square root of time, while by using surface plasmon resonance Lucht and Bahr [94] have revealed a terraced structure on gold for the spreading of a liquid-crystalline smectic-A droplet. Similar observations (i.e. terraced spreading or single monolayer spreading of the precursor with an expansion proportional to $\sqrt{t}$) have been further reported for a variety of complex liquids, such as liquid crystals or alkanes, in contact with bare silicon wafers or ones which are grafted with polymer brushes [91, 95–97]. Naturally, in such systems the details of the spreading behaviour, such as the prefactor $D_1$, differ and the structure of the various spreading monolayers is significantly more complicated.

The influence of the surface energy has been analysed in detail by Voué et al [98], who examined the dependence of $D_1$ for the precursor monolayer next to the substrate on the surface energy characterized by the so-called critical surface energy $\gamma_c$ (obtained for alkane series as the abscissa of the point at which the extrapolated linear relation $\cos \theta = \gamma_c / \gamma$ versus $\sigma_{lv}$—the so-called Zisman plot—intercepts the line $\cos \theta = 1$). By using spatially resolved ellipsometry, these studies showed that $D_1$ is equal to zero up to a certain threshold value of the surface energy followed by a non-monotonic dependence on the surface energy, exhibiting a pronounced maximum for intermediate surface energies (see figures 4 and 5 and section 5).

The effect of the droplet size on the dynamics of such ultrathin films has been studied by Leiderer et al [99]. Using the method of optically excited surface plasmon resonance, they determined the density profiles of submonolayer films during spreading of picolitre volumes of PDMS on a silver substrate. The results showed that the spreading of the film is described by the $\sqrt{t}$ dependence on time, which may become significantly slower if the drop is too small to act as a reservoir for the emanating precursor film.

By using scanning micro-ellipsometry and scanning x-ray photoemission spectroscopy, Novotny investigated the spreading behaviour of droplets of perfluoropropylene polymers, which are widely used in magnetic recording applications [100]. He observed microscopic precursor films with a sharp edge and spreading in accordance with equation (15). He systematically analysed the dependence of $D_1$ on the molecular weight $M$ and concluded that it can be described effectively by an algebraic law $D_1 \sim M^{-\alpha}$ with $\alpha \approx 1.7$. Fraysse et al [101] (see also [89]) studied the spreading speeds of low molecular weight PDMS precursor films on bare oxidized silicon wafers, used without cleaning, or on wafers bearing loosely grafted trimethyl layers. Their analysis confirmed that the radial extent of the film grows proportionally to the square root of time (equation (15)) and it showed that $D_1$ is inversely proportional to the bulk viscosity $\eta(M)$ of the PDMS liquid. Since for this range of molecular weights the best fit of the PDMS viscosity is given by $\eta(M) \sim M^{1.7}$ [101], the observations made in [101] appear to agree rather well with the experimental results obtained by Novotny [100]. Further on, O’Connor et al [102, 103] and Min et al [104] studied the spreading behaviour of PFPE (perfluorinated polyether, terminated with hydroxyl groups), AM2001 (piperonyl groups), and Ztetraol (propylene glycol ether groups) on silica surfaces as a function of the end group functionality, molecular weight, temperature, and humidity. The square root of time law for the growth of the radial extent of the film has been observed for all liquid-on-solid systems studied in [102–104]. However, the dependence of $D_1$ on the molecular weight $M$ turned out...
The height of the droplet placed in a measurement chamber for 24 h. The atmosphere were cleaned by oxygen flow under UV illumination and then spreading on hydrophilic oxidized silicon wafers. The wafers equation (15) for molecularly thin precursor films of PDMS Figure 4. J. Phys.: Condens. Matter D[106], who studied the molecular weight dependence of the open circles, see [98] for details; note that the triangle corresponding to the case labelled by HDMZ24 falls nonetheless on this line. This is, however, not surprising because the surface treatment used to produce this substrate (see below) does not make the HDMZ24 surface too different from those of the original wafers, although it lowers the surface energy due to a trimethyl layer grafted on the native silicon oxide. The data, represented by open circles and triangles, correspond to chemically different and differently treated substrates: ‘uncleaned’ denotes bare wafers used without any cleaning procedure; ‘UV O3 unprotected’ wafers were UV–ozone cleaned wafers (1 h under a dry O2 flow plus 20 min under an O2 flow saturated with H2O); ‘UV O3 protected’ wafers were wafers cleaned according to the same procedure but protected after cleaning by aluminum foils and stored under nitrogen in the presence of silica gel to prevent a fast contamination of the reaction sites; ‘C16’ wafers are surfaces obtained by chemical grafting a 3.4 nm thick layer of hexadecyltrichlorosilane; ‘HDMZ24’ surfaces are obtained by exposing a UV–ozone cleaned wafer to hexamethyldisilazane vapour for 24 h at room temperature (this procedure results in grafting a 0.4 nm thick trimethyl layer) and finally ‘OTS’ wafers are obtained by chemically grafting octadecyltrichlorosilane on a UV–ozone cleaned wafer (this procedure results in a 3.2 nm thick layer). LB denotes a Langmuir–Blodgett wafer which has a behaviour completely different from the others, showing that the associated ω-tricosenoic acid layers drastically modify the chemistry of the surface. (Figure 9 in [98]. Reproduced with permission from [98]. Copyright 1998 American Chemical Society.)

to be somewhat weaker; i.e., the observed values of the exponent α seem to be smaller than 1.7. (However, one should keep in mind the merely effective character of this power law.) For example, ellipsometry measurements of ultrathin (i.e. less than 10 Å thick) PFPE precursor film spreading on cleaned silicon wafers with a native oxide layer rendered α ≈ 0.5 [104], which does not agree with the results of Novotny [100] and Fraysse et al [101].

This issue has been revisited by Valignat et al [105, 106], who studied the molecular weight dependence of $D_1$ in equation (15) for molecularly thin precursor films of PDMS spreading on hydrophilic oxidized silicon wafers. The wafers were cleaned by oxygen flow under UV illumination and then placed in a measurement chamber for 24 h. The atmosphere therein contained controlled relative humidity (RH), in order to obtain on the wafer an equilibrated submonolayer of water with controlled coverage, depending on RH. This is motivated by the fact that the substrates used in these experimental studies are chemically heterogeneous and contain different types of surface site. There are low energy siloxane bridges and high energy, chemically active, silanol sites, which may form a hydrogen bond with any of the monomers of a PDMS molecule and thus for the latter represent preferred spots of attachment to the surface. The water molecules have a strong affinity to the silanol sites and effectively screen them, forming molecularly thin islands of water. Hence, exposure to an atmosphere with controlled RH prior to deposition of a PDMS droplet allows one to modify the frictional properties of the substrate by changing the chemical composition of the surface. It was realized that at high substrate friction $D_1$ is controlled by mesoscopic effects, i.e. by the bulk viscosity $\eta(M)$, and thus as noted above the exponent α can be substantially larger than unity. At moderate RH, i.e. at moderate friction, one observes $D_1 \sim 1/M$, while for very high RH, i.e. low friction, $D_1$ (and thus the spreading of the precursor) becomes independent of $M$ [105, 106] (see figure 5, which corresponds to RH = 98% and shows no significant difference between the full and dashed lines, and section 5).

Furthermore, Villette et al [107] focused specifically on the role of water on the spreading of molecular films of PDMS, PDMS with hydroxyl ends (PDMS-OH) and TK on oxidized silicon wafers. Their analysis revealed the
dependence of $D_1$ on RH. In particular, it was realized that for PDMS and PDMS-OH the ‘diffusion’ coefficient $D_1$ shows a distinctly different linear variation with the relative humidity (and, respectively, with the substrate coverage by water) for RH less than or larger than 70%. For moderate RH, $D_1$(RH) has a relatively small slope, which at RH $\approx 70\%$ crosses over to a very steep linear dependence on RH. Overall, within the range of 20%–90% RH, $D_1$ varies by more than two orders of magnitude, attaining the values observed for mesoscopic precursor films. This agrees well with the observations made by Valignat et al [105, 106]. Such a remarkable enhancement of $D_1$ has been explained by the fact that at this value of RH the patches of water on the substrate start to overlap and form a tortuous connected structure on which the spreading of molecules encounters a very low friction. Surprisingly, the dependence of $D_1$ on RH for TK spreading on hydrophilic substrates appears to be more complicated. Similarly to PDMS and PDMS-OH, $D_1$ gradually increases up to RH $\approx 70\%$, followed by an abrupt growth. However, at RH $\approx 80\%$ $D_1$ passes through a maximum and then starts to decrease. At this latter RH one observes signs of a ‘dewetting transition’, in the sense that the previously distinct first, second and third layers in the terraced shape no longer occur and only the first layer spreads, while the rest of the drop does not. For RH larger than 85% the behaviour turns into that for partial wetting: while a monolayer precursor film spreads ahead of the drop, the macroscopic part of the drop attains a non-zero equilibrium contact angle.

Within the complete wetting regime, the $\sqrt{t}$ time dependence of a spreading monolayer has also been observed in the case of PDMS on highly polished silicone wafers coated with a self-assembled monolayer of octadecyltrichlorosilane (OTS) [108]. In this study an interferometric video microscopy technique was employed. (See also [109], in which interferometric microscopy techniques have been employed in order to study the spreading of small drops of very viscous, low volatility liquids on planar smooth substrates.) The authors have been able to accurately reconstruct the shape of the drop during spreading; from the shape, the volume of liquid in the drop was computed as a function of the time $t$ elapsed since the beginning of spreading. Since under the corresponding experimental conditions the liquid used is practically non-volatile, any change (i.e. decrease) in the volume $V(t)$ enclosed by the drop shape has been attributed to liquid being transferred to a precursor film. Therefore, although such films have not been directly imaged and investigated, their existence and the fact that their linear extent grows in time proportionally to $\sqrt{t}$ could be clearly inferred from the significant changes in $V(t)$ (see figure 8 in [108]).

Finally, we mention several other situations in which spreading ultrathin precursors have been observed for partially wetting liquids. Tiber and Cazabat [110] have studied the spreading behaviour of non-ionic trisiloxane oligo(ethylene) oxide surfactants on high and low energy surfaces. These surfactant molecules have a peculiar ‘hammer’-like structure and consist of a compact hydrophobic trisiloxane group sitting as a ‘hammer head’ on an ethylene oxide, which forms a 35 Å long ‘dangling handle’. It was shown that the spreading of drops of these liquids, if at all, occurs only via an autophobic ultrathin precursor film emanating from the drop (‘autophobic’ in the sense that the drop ‘does not wet its own film’ but rather remains in a partial wetting state on top of the precursor-covered substrate). On low energy surfaces these surfactants self-assemble over the solid into well defined bilayers, the radial extent of which grows proportional to $\sqrt{t}$, and after a few days in humid atmosphere they cover several square centimetres. The thickness of the precursor is virtually constant ($54 \pm 2\,Å$) during the whole spreading process. On high energy surfaces, spreading again occurs via an autophobic precursor, the linear extension of which also grows proportionally to $\sqrt{t}$. However, the shape of the vertical cross section of the precursor is now strikingly different, having a cone-like shape with a very wide opening angle and a rounded tip rather than a compact organized structure. This aspect has been further studied in [111], which focused on spreading of various hammer-shaped and linear-shaped surfactants on low, intermediate and high energy surfaces. It was confirmed that spreading of a non-wettable liquid of surfactants proceeds via a ultrathin precursor film with $\ell_s \sim \sqrt{t}$ and only the shape of the vertical cross section of the precursor film depends on the particular choice of the surfactant and of the solid substrate.

4.2. Ultrathin precursor films in metal-on-metal systems

As discussed above, most of the studies of precursor films have been focused on the spreading of liquids on solid substrates. A decade ago, it has been pointed out that microscopically thin films extending over macroscopic distances also occur for wetting in solid-on-solid systems in the so-called Stranski–Krastanov state (crystallites coexisting with a film; see [112, 113] and references therein). A particular example, which has been the subject of a number of also recent studies [114–119], is that of metal films (Pb, Bi or Pb–Bi alloys) on a metal substrate (mono-crystalline Cu(111), Cu(100) or polycrystalline Cu). As we shall discuss below, these studies have provided evidence for submonolayer precursor films exhibiting the same spreading dynamics (linear extent growing in time as $\sqrt{t}$) as in the cases of liquid spreading. They allowed a clear identification of surface diffusion through the film as the mechanism of precursor formation and spreading.

At not too elevated temperatures (among these metals, at about 544.7 K Bi has the lowest bulk melting point), such systems intrinsically have a very low vapour pressure. The choice of Pb, Bi or Pb–Bi alloys to be deposited on Cu(111) (triangular lattice [114, 116]) or Cu(100) (rectangular lattice [112]) is motivated by the practically negligible bulk solubility of Pb or Bi in Cu. This prevents loss of material via diffusion into the substrate. However, there is a good bulk solubility of Bi in Pb, which allows one to prepare alloys over a wide range of concentrations. Moreover, Bi and Pb atoms are very similar in size, which makes the theoretical interpretation of the results easier. In all
cases, physical vapour deposition from high-purity metal sources under ultra-high vacuum was used to create thick (i.e. hundreds of nanometres) overlayers of metal under very well controlled atmospheric conditions. During the preparation of the experiment several cycles of sputtering have been employed to ensure a contaminant-free surface. The investigation of the emerging precursors has also been performed under high-vacuum conditions. The experiment encompassed a combination of scanning Auger electron spectroscopy (SAM) and scanning tunnelling microscopy (STM) or scanning electron microscopy (SEM). The former method serves to determine the atomic composition; it has a spatial resolution below one micron and requires about 5 min for scanning [114–116]. With the latter methods one can obtain roughly the spatial extent of the film or the shape (i.e. the contact angle) of the Pb or Pb–Bi clusters on the surface.

In the investigations of Pb and of Pb–Bi alloys on Cu(111) [114, 116], an initially thick (i.e. hundreds of nanometres) overlayer of metal was gradually heated up to slightly above the melting point of the material (for Pb this is about 600 K, and for alloys about 538–568 K), which led to dewetting and the formation of drops coexisting with a thin nanometres overlayer of metal was gradually heated up to slightly above the melting point of the material (for Pb this is about 600 K, and for alloys about 538–568 K), which led to dewetting and the formation of drops coexisting with a thin film; this configuration was quenched. Even in the solid state the droplets are observed to maintain a quasi-spherical shape with just a flattened top; the ‘dome’ rather than ‘pyramid’ shape could be the result of solidification under a rapid temperature quench. This observation allows one to assign an approximate contact angle even for the solidified particles. As reported in [115, 116], for temperatures \( T \) in the range 360 \( \leq T \leq 610 \) K, these contact angles are about 40°–45°, indicating a partial wetting situation, with a very weak dependence on temperature and composition. Upon annealing at a desired temperature (note that by varying the temperature one can also control the timescale of the dynamics), by waiting for thermal equilibration and by sputtering off the film (which also ensures a final decontamination), the authors were able to investigate the formation and the spreading of precursor films in contact with liquid drops or solid particles [114–116]. For Bi, a different setup was used, in that the film deposition has been performed on a partially masked substrate, while the remaining steps of the procedure, i.e. annealing and sputtering, were the same. This allowed the study of a precursor formation from a straight contact line [115, 116]. Therefore, both straight and circular configurations of the film have been investigated, in addition to the various possible combinations of liquid or solid drops or films.

The results of these experiments revealed that in all cases a precursor film of submonolayer thickness emanates from the drop, and the linear extent \( l_c \) of this film obeys the relation given in equation (15) with the prefactor \( D_1 \) depending on geometry, the metal, the composition of the alloys, and temperature. This is very similar to the features observed in the experiments dealing with the spreading of liquids. Somewhat controversially, changes in the temperature dependence of \( D_1 \) have been interpreted as indicating a change in the state of the film between a disordered (fluid) and a partially ordered (solid) structure [115]. Similar changes would occur due to, e.g., a change in the dynamics induced by a partial surface alloying. However, in the case of pure Pb or Bi, the coverage \( c \) (i.e. an analogue of the effective film thickness \( h \) discussed in section 4.1), where \( c \) is defined such that it takes the value of one (corresponding to a compactly filled monolayer) at the edge of the drop or at the straight contact line, depends strongly on the radial distance \( x \) from the edge of the drop or from the straight contact line (see figure 6(a)). In all these cases, dividing the spatial coordinate by \( \sqrt{D_0 t} \) (\( D_0 \) is the corresponding diffusion coefficient of Pb or Bi atoms on the Cu surface) leads to a collapse of the profiles taken at different times \( t \) onto a single master curve \( \Theta( \lambda = x/\sqrt{D_0 t}; T, \text{metal} ) \), the shape of which depends on the temperature \( T \) and on the materials involved. This scaling is compatible with a surface diffusion mechanism.\(^{15}\)

The master curve \( \Theta( \lambda; \ldots) \) does not necessarily have the shape of an error-function, as would be the case for a simple one-dimensional diffusion process with a fixed concentration source at the origin, but in many cases it exhibits steep drops within certain ranges of coverage [115, 116]. This indicates a coverage-dependent diffusion coefficient, which might be caused by certain surface alloying processes as discussed in detail in [112, 113, 115, 116], but also by attractive interactions between the adsorbed atoms (see section 5). Via a Boltzmann–Matano type analysis [121], from such concentration profiles the coverage dependence of an effective diffusion coefficient \( D(c) \) has been obtained. For both Pb and Bi, the resulting diffusion coefficients \( D(c) \) have a complex structure, with one [114] or even two minima [115] at intermediate coverages and maxima at high coverages (see figure 6(b)). The positions of the minima are compatible with known surface alloying transitions for Pb or Bi on Cu(111). Similar findings have been reported for films of Pb or Bi on Cu(100) [118]. The results for binary alloys are similar, in the sense that a Pb–Bi film spreads on the Cu(111) substrate, but the rate of spreading seems to be dictated by the slower component and the composition of the alloy varies significantly with the distance from the edge of the drop.

Finally, we note that an interesting extension of this system was studied in [117], involving two macroscopic films of Pb and Bi, respectively, which are deposited such that they are separated by a small area of the substrate and give rise to precursor films that ‘collide’. By using SAM, the composition profiles of both Pb and Bi along the direction of mutual approach have been determined. This allows a study of two-dimensional surface interdiffusion of Pb and Bi.

We conclude this section by emphasizing several important features extracted from the experimental analyses of spreading of molecularly thin precursor films.

\(^{14}\)The authors interpreted these observations as ‘pseudo-partial’ wetting. This confusing nomenclature was clarified later [120].

\(^{15}\)Although [115, 116] mention studies of Pb films at temperatures of 600 K and above, for which the film would be in a disordered state and the drop in the liquid state, no coverage profiles at these temperatures are presented.
Precursor films act as a lubricant for the drops in that the precursor films spread from the drop as a result of the dependence of the diffusion coefficient of Pb on Cu(111) at $t^\ast$ and 373 K ($\ast$). (Figure 9(b) 8 h) and for Pb $14$.

Macroscopic part of the drops spreads on a 'prewetted' non-condicio sine qua non principle, occur in addition but it is not only partially wet the solid surface or, in the extreme case, if the drops are actually solidified clusters.

Precursor films spread from the drop as a result of the competition between the gain in entropy and the balance of the attractive interactions between the fluid molecules and the substrate and the attractive interactions among the fluid molecules. Condensation out of the vapour may, in principle, occur in addition but it is not condicio sine qua non for the formation of precursor films.

Precursor films act as a lubricant for the drops in that the macroscopic part of the drops spreads on a 'prewetted' substrate.

At sufficiently large times (but with the drop still being able to act as a reservoir for the precursor film), the radial extent of the film increases proportionally to the square root of time. This dependence holds very generally. Only the prefactor $D_1$ (equation (15)) depends on the particular features of the liquid-on-solid system under study.

One encounters different types of thickness profile. (For submonolayer films the coverage is translated into an effective thickness; see the discussion of figure 2.) In some instances, molecular-sized precursor films are compact and the thickness profile is laterally constant. In other cases, the thickness along the film varies considerably.

These observations are the basis for formulating a theoretical understanding of the spreading of precursor films.

5. Models for the dynamics of spreading of microscopic precursors

The theoretical analyses of the physical mechanisms underlying the seemingly universal $\sqrt{t}$-law and the 'terraced wetting' phenomenon have followed three different lines of thought.

de Gennes and Cazabat [122] proposed an analytical description of the 'terraced wetting' phenomenon, in which the liquid drop on a solid surface was considered as a completely layered structure, the $n$th layer being a quasi-two-dimensional, incompressible fluid of molecular thickness $a$ and with macroscopic radial extent $R_n$ (see figure 7(a)). The interaction energy of a molecule in the $n$th layer with the solid substrate was taken to be of the general form of a negative, increasing (towards zero) function $W_n$ of the distance $n \times a$ from the substrate.

Within this model de Gennes and Cazabat [122] considered, similarly to the behaviour observed in smectic systems, two types of flow: a horizontal, outwardly directed radial particle current and vertical permeation fluxes, one from the neighbouring upper layer and one towards the adjacent layer below. These fluxes are shown to be important only within a thin annulus of small size $\xi$ (comparable to $a$) near each step, resembling a 'permeation ribbon'. Between steps, the viscous effects associated with simple shear dominate. This leads to simple laws for the dilation (or contraction) of the various layers. According to [122], whenever the distinct layers grow laterally at a comparable rate, they all grow proportional to $\sqrt{t}$ with the proportionality factor $\sqrt{(W_{n+1} - W_n)/\zeta_n}$, where $\zeta_n$ is the friction coefficient between the $n$th and the $(n - 1)$th layer. This sheds light on the conditions at which 'terraced wetting' can occur. Such a phenomenon takes place if in several layers close to the substrate the ratios $(W_{n+1} - W_n)/\zeta_n$ have approximately the same value. If, however, the film closest $(n = 1)$ to the solid substrate grows much faster than all the other layers above, i.e. if it decouples from the rest of the drop which then acts as a reservoir for the first layer, this model predicts that the latter grows proportionally to $(t/\ln(t))^{1/2}$ [122]. This is somewhat slower than $\sqrt{t}$, and terraced wetting does not occur in such a situation.

Within the classical framework of non-equilibrium statistical mechanics an alternative description has been worked out by Abraham et al [123, 124] and De Coninck et al [125]. Within this approach, an interfacial model for the non-volatile fluid edge has been developed and analysed in terms of Langevin dynamics for the displacements of...
horizontal solid-on-solid (HSOS) layers \( \{l_j\} \) at increasing heights \( j = 0, 1, \ldots \) from the substrate (see figure 7(b), where \( l_j \) is denoted as \( h_j \)). These have essentially the same meaning as the layers appearing in the de Gennes–Cazabat model [122], and \( l_j \) can be thought of as the radius of the \( j \)th layer. The radii and the heights are measured in units of \( a \) and thus they are dimensionless.

In the model developed in [123–125] one has considered the case \( f(j) = \delta_{i,0} \) (see figure 7(b)), where \( \delta_{i,0} \) is the Kronecker delta, so that the energy \( U(\{l_j\}) \) of a given configuration \( \{l_j\} \) of a one-dimensional interface is described by

\[
U(l_0, l_1, \ldots, l_L) = \sum_{j=1}^{L} P(l_j - l_{j-1}) - \mu_0 l_0,
\]

where \( l_0 \) is the linear extent (in units of \( a \)) of the ‘precursor’ film next to the solid substrate, \( \mu_0 \) is a wall contact potential and the function \( P(l_j - l_{j-1}) \) describes the free energy contribution due to the non-planar liquid–vapour interface. Explicitly, this latter contribution corresponds to a discretized version of the length of the one-dimensional interface:

\[
P(l_j - l_{j-1}) = J \sqrt{1 + (l_j - l_{j-1})^2},
\]

where the parameter \( J \) is the surface tension of the one-dimensional interface.

The dynamics of the layers \( \{l_j\} \) has been described in [123–125] by a set of \( L \) coupled Langevin equations (recall that \( l_1 \) is fixed),

\[
\frac{\partial l_k}{\partial t} = -\frac{\partial U(\{l_j\})}{\partial l_k} + f(l_k; t),
\]

where \( \xi \) is a certain phenomenological ‘friction’ coefficient per unit length of the interface, which is supposed to be the same for all layers, and \( f(l_k; t) \) is Gaussian white noise. Note that in this model \( \xi \) has a different meaning as compared to the model by de Gennes and Cazabat [122], where \( \xi \) is the friction coefficient between adjacent layers and varies with the distance from the substrate; here \( \xi \) is associated with the dynamics of the interface only, it does not depend on the distance from the substrate and it does not account for the dissipation processes occurring in the bulk.

Note as well that the Langevin description of the interface dynamics tacitly presumes that \( \{l_j\} \) are continuous variables so that the difference \( l_j - l_{j-1} \) is not necessarily constrained to be an integer. This implies that one may encounter two different types of behaviour depending on whether the difference \( l_j - l_{j-1} \) is small or large, because the free energy contributions due to the non-planar liquid–vapour interface in equation (17) exhibit different asymptotic behaviours. Indeed, in the limit \( l_j - l_{j-1} \ll 1 \) the function in equation (17) is quadratic, i.e. \( P(l_j - l_{j-1}) \approx J[1 + (l_j - l_{j-1})^2]/2 \), while for \( |l_j - l_{j-1}| \gg 1 \) one has \( P(l_j - l_{j-1}) \approx JL_j - l_{j-1}^3 \).

This model allows for an analytical analysis, which does yield the extraction of a precursor film as well as ‘terraced’ forms of the dynamical thickness profiles. It predicts that for \( \mu_0 > J \) and for sufficiently short precursors (such that the dominant contribution to the surface energy is quadratic) the length of the film increases with time as

\[
l_0(t) \sim \sqrt{\frac{(\mu_0 - J) t}{\xi}},
\]

which resembles the experimentally observed behaviour. For sufficiently long precursors, for which the surface energy increases linearly with the length, the layer next to the substrate grows faster:

\[
l_0(t) \sim \frac{(\mu_0 - J) t}{\xi}.
\]

If \( \mu_0 = J \), the precursor film advances as

\[
l_0(t) \sim t \ln(t).
\]
Therefore, this model predicts that at very large times the advancing precursor film attains a constant velocity such that the $\sqrt{t}$-behaviour is only a transient. This inconsistency with the experimental findings can be traced back to the fact that, by focusing on the evolution of the interface and assuming a viscous-type dissipation only at the locus of the interface, the above model neglects the energy dissipation for each molecule within the precursor film as well as dissipation appearing due to viscous flow in the spreading droplet.

To resolve this inconsistency, Burlatsky et al [126–128] proposed a microscopic, stochastic model for the spreading of molecularly thin precursor films. Within their approach the film was considered as a two-dimensional hard-sphere fluid with particle–vacancy exchange dynamics (see figure 8). Attractive interactions among the particles in the precursor film were not included into the model explicitly, but introduced in a mean-field-like way. It was assumed that the film is bounded by a HSOS-type interface [123–125], in which the energy parameter $J$ penalizing non-flat interface configurations was considered as a certain (not yet specified in [126–128]) function of the amplitude of the particle–particle attractions.\footnote{In [129, 130] an attempt has been made to express the parameter $J$ in terms of the parameters of the interaction between the fluid particles.}

The film was taken to be connected to an unlimited reservoir mimicking the bulk liquid (or a macroscopic drop). The rate at which the reservoir releases particles into the film has been related to the local particle density in the film near the nominal contact line and to the strength of the attractive van der Waals interactions between the fluid particles and the substrate, in accordance with the standard Langmuir adsorption theory. In contrast to [122], the model in [126–128] emphasizes compressibility and molecular diffusion at the expense of hydrodynamic flows. The latter model assumes that the reservoir and the film are in mechanical equilibrium with each other, such that there is no hydrodynamic pressure difference to drive a flow of particles from the reservoir and to push the particles along the substrate and thus away from the droplet. This approach predicted the $\sqrt{t}$-law (equation (15)) for the late time stages of the growth of the molecularly thin film. This law was obtained for the capillary rise geometry and it was found that the density in the film varies strongly with the distance from the reservoir.

Moreover, in [126–128] the conditions were established under which spreading of the precursor film takes place. It was also suggested that the physical mechanism underlying the $\sqrt{t}$-law is provided by the diffusive-type transport of vacancies from the edge of the advancing film to the contact line, where they perturb the equilibrium between the macroscopic drop and the film and become filled with fluid particles from the drop.

An extension of the lattice gas model developed in [126–130] which includes an attractive contribution to the pair interaction between fluid particles, resembling a Lennard-Jones (LJ) potential, has been proposed and analysed in [131]. The spreading of the monolayer from a reservoir covering a half-plane has been studied as a function of the strength of the attractive pair interaction $U_0 = W_0k_BT$ among the particles. The study used both continuous time kinetic Monte Carlo (KMC) simulations and a non-linear diffusion equation for the local coverage $c = c(r,t)$ of the monolayer, which is the probability to find at time $t$ a fluid particle in a small area centred at $r$:

$$\frac{\partial c}{\partial t} = \nabla [D(c)\nabla c].$$

(22)

This equation has been derived, within a mean-field approximation, from the microscopic dynamics in the corresponding continuum limit. $G$ is a numerical factor which depends on the lattice structure and on the detailed form of the pair interaction, while $D_0 = D(c = 0)$ denotes the one-particle diffusion coefficient on the bare substrate. We note that equation (22) has the same mathematical structure as equation (12), which describes spreading of mesoscopically thin films such that the former can be formally thought of as being the microscopic analogue of the latter one. However, they differ in their physical origin. In equation (22) the coverage dependence of diffusivity arises from the fluid–fluid interactions and the functional form of $D(c)$ encodes the competition between the normal diffusion due to concentration gradients and a local ‘drift’ induced by the mean-field potential due to the particle–particle interactions. In contrast, the diffusivity in equation (12) reflects the driving force of the gradients in disjoining pressure, which encodes the effective interaction between the liquid–vapour interface and the substrate.
The model confirms the time dependence \( t_\ell = \sqrt{D_1(W_0, c_0)} t \) of the spreading with a prefactor depending on the strength of the inter-particle attraction and on the fluid coverage \( c_0 \) at the reservoir. The behaviour of \( D_1(W_0, c_0) \) agrees with the existence of a covering–noncovering transition separatrix \( W_0(c_0) \) in the \((c_0, W_0)\) plane [129, 130] below which a macroscopic film is extracted from the reservoir and spreads over the substrate, while above it is not extracted. This refers only to the formation of a liquid-like monolayer but does not exclude the formation of a very dilute two-dimensional gas covering the substrate. The coverage of the expanding film as a function of time and distance from the edge of the particle reservoir exhibits a scaling behaviour as function of the scaling variable \( \lambda = x/\sqrt{D_0} t \). These scaled density profiles exhibit qualitatively different structures above and below a threshold value of the inter-particle attraction; in particular, above the threshold interaction sharp interfaces form inside the extracted monolayer (see figure 9). Such coverage profiles with sharp interfaces are very similar to the experimentally observed ones for the spreading of Bi on Cu(111) (section 4.2), but the cause for their formation is seemingly different. In the former case, they occur because the tendency for clustering becomes dominant for strong inter-particle attraction, which manifests itself as an instability (i.e., a negative diffusion coefficient for a certain range of density values) in the non-linear diffusion equation describing the spreading, while in the latter case a similar instability occurs due to surface alloying of the spreading film.

An interesting lattice gas model for the spreading of ultrathin precursor films, which can be considered as a microscopic version of the continuum model of permeation layers of de Gennes and Cazabat [122], is the one proposed in [132, 133]. This is an Ising model with nearest-neighbour interactions in an external field, provided by the substrate potential, on a cubic lattice of infinite extent along the \( x-\) and \( y-\)directions and finite extent along the positive \( z-\)direction (in [133], in units of the lattice spacing \( z \in \{1, 2\} \)), with local coverage \( c(x, y, z) = 0, 1 \) if the site is empty (‘vacancy’) or occupied by a ‘particle’, respectively. (The sites \( z \leq 0 \) are attributed to a continuum substrate and cannot be occupied by the fluid.) The model is defined by a configuration-dependent energy at time \( t \) given by \( H = -U_0 \sum_{\mathbf{r}-\mathbf{s}=1} c(\mathbf{r}, t) c(\mathbf{s}, t) + A \sum_{z=1, 2} c(\mathbf{r}, t) / z^2 \). \( A < 0 \). The first term corresponds to a strong nearest-neighbour attraction \((U_0/(k_B T) \gg 1)\) in order to ensure low volatility) and the second one corresponds to a van der Waals attraction by the substrate. The dynamics is defined through particle–vacancy exchange rates corresponding to a Kawasaki dynamics augmented by an instantaneous vacancy–particle exchange process for a particle which would come to be located in the upper layer \( z = 2 \) exactly above a vacancy in the lower layer \( z = 1 \). The simulation of the spreading of a precursor, e.g., along the \( y-\)direction, employs as initial state a lattice which is half-occupied by fluid, \( c(x, y \leq 0, z, t = 0) = 1 \), with a fixed coverage \( c(x, y = 0, z, t) = 1 \) mimicking a fast relaxation of the liquid reservoir at the edge connected to the film. The particles move away from the line \( y = 0 \) into the initially empty area solely due to the concentration gradients; there is no forcing by the macroscopic film occupying the half-space \( y < 0 \). The advancing edge \( \ell_2 \) is defined in the \( z = 1 \) plane as the largest \( y \) position among the rightmost particles in the maximal connected the cluster, i.e., the percolating one in contact with the reservoir. Based on kinetic Monte Carlo simulations it was concluded that the model predicts a compact, first layer precursor spreading which follows \( \ell_2 \sim \sqrt{t} \) and the emergence of a second layer with a much slower spreading. The mechanism of spreading is the diffusion in the lower layer of a low concentration of vacancies, from the advancing edge towards the ‘reservoir’. This is coupled to the diffusion in the upper layer of a low concentration of particles in the opposite direction, as well as to the vacancy–particle exchange between the two layers. Therefore, this model points towards a promising direction for studying terraced spreading, which requires us simply to relax the constraint \( z \leq 2 \). However, it is difficult to estimate the ensuing impact on the computational cost (see also [132]). Moreover, it is unclear whether a non-uniform structure of the first layer, which would involve particle concentration variations along...
the spreading direction (see, e.g., [114]), is compatible with the rules defining the model. This issue arises because the diffusion of vacancies through the high coverage lower layer is much slower than that of particles in the very low coverage upper layer. Thus with increasing extent $\ell_x$ of the precursor (i.e. the first layer) it is likely that the vacancy–particle exchange mechanism becomes very effective, leading to a vanishing density of vacancies in the first layer.

6. Numerical studies of ultrathin precursors

Computer simulations of various models for liquid droplets spreading on solid substrates have been a very valuable tool in the quest for understanding the mechanisms behind the emergence of terraced spreading and the dynamics of ultrathin precursor films. The methods which are usually employed encompass Monte Carlo (MC), kinetic Monte Carlo (KMC), and molecular dynamics (MD). They are discussed in detail in many textbooks (see, e.g., [134, 135]). Therefore, here we focus strictly on their use for studies of precursor film spreading.

6.1. Monte Carlo simulations

Monte Carlo simulations have been employed to elucidate the emergence of a precursor film (first layer) with a growth behaviour $\ell_x \sim t$ (which disagrees with the experimental observations) within the so-called horizontal solid-on-solid (HSOS) model of non-volatile liquid droplet spreading (see section 5). As discussed above, this model can be solved exactly in certain limiting cases. However, although it captures qualitative features of the available experimental results, such as terraced spreading, it predicts a too fast dynamics for the first layer acting as the precursor film. The question arises whether this situation is generic for all the values of the surface tension $\mathcal{J}$ and of the parameters characterizing the interaction with the substrate (see equation (16)). If true, this would rule out this model. Otherwise, the too fast dynamics could be a consequence of the approximations made in order to obtain analytic solutions. Monte Carlo simulations of the HSOS model for a liquid wedge have been performed both in two and in three dimensions (i.e. considering a straight edge or allowing for a fluctuating edge for each molecular layer, respectively) for various values of the surface tension and for various cut-off ranges of a van der Waals type substrate potential which decays as $1/z^3$ with the distance $z$ above the planar continuum substrate [136–138]. Except for special values of the parameters (e.g., above, but very near, to the wetting transition line, i.e. close to the temperature at which complete wetting occurs) for which the results are not conclusive due to the very slow dynamics, the simulations provided strong evidence that the first layer indeed spreads with a linear time dependence. This demonstrates that the model is indeed too simplistic. Nonetheless, the time dependence should be interpreted with some caution because these MC simulations have followed the dynamics in ‘computer time’. This means that each trial move is assumed to take the same average time in order for the timescale of MC steps per lattice site to acquire a physical meaning. This differs from the real time provided by the use of transition rates for various processes, as required by a rigorous KMC method [134]. Later it was argued that the most likely cause for this discrepancy with the experimental observation is that the model does not account for the energy dissipation associated with the necessary transport of mass from the edge of the drop to the advancing tip of the precursor [133].

A three-dimensional Ising model for a droplet spreading upon contact with a planar substrate was proposed by Abraham et al [139]. In this cubic lattice model, the flat substrate occupies the half-space $z \leq 0$, while the sites with $z > 0$ can be occupied by either a fluid particle ($c_i = 1$) or a void ($c_i = 0$), where $c_i \in \{0, 1\}$ denotes the occupation of site $i$. The model employed a fixed size of the simulation cell (therefore there is a fixed volume available to the fluid) and a fixed number of fluid particles. (These constraints do not play a major role in the case in which three-dimensional evaporation is negligible, as was the case for the simulations in [139]; see below.) The initial state is that of a lattice approximation of a semi-cylindrical drop spanning the whole simulation box along the $y$-direction, for which periodic boundary conditions have been imposed. The spreading takes place along the $x$-direction, and the spreading is studied at times for which the advancing edge of the drop or of the precursor (see below) remains far from the boundaries of the simulation box along the $x$-direction. There is an attractive interaction of strength $W_0$ between nearest-neighbour fluid particles, and the substrate interacts with the fluid via a van der Waals type potential. Therefore the corresponding Hamiltonian

$$\mathcal{H} = -\frac{U_0}{2} \sum_{\langle i,j \rangle} c_i c_j + A \sum_i c_i z_i, \quad U_0 > 0, \quad A < 0,$$

(23)

where $\langle i, j \rangle$ denotes nearest-neighbour sites $i$ and $j$ and $z_i > 0$ is the distance of site $i$ from the substrate at $z = 0$ in units of the lattice spacing. The MC simulations of this model employed a dynamics specified to be a particle–void exchange with Kawasaki rates (see, e.g., [134]). By varying the ratio $U_0/A$ of the strength of the particle–particle and of the particle–substrate interactions, while keeping the thermal energy sufficiently low in comparison with the particle–particle interaction strength $(k_B T/U_0 = 1/W_0 \leq 2)$, such that three-dimensional evaporation was negligible, it was shown that the model exhibits the emergence of terraced spreading. The number of steps and their rate of spreading turned out to be practically independent of the strength of the substrate potential. After a transient time, which can be rather long if the substrate potential is not strong, the spreading of each layer obeyed the $\sqrt{t}$ dependence on the ‘time’ measured in MC steps per lattice site. In this case, the mechanism of mass transport to the film was shown to be a flux of particles along the terraced surface of the drop. This is the microscopic equivalent of the permeation layer in the continuum model proposed in [122]. However, the maximum lateral extents of the precursor films observed in these simulations are still
relatively small (no more than 60–80 lattice sites, according to figures 1 and 2 in [139], compared with an initial footprint of the drop of about 30–40 sites and a height of about 10 sites). Therefore, it is difficult to assess if they can indeed be associated with the macroscopically large molecular films observed experimentally. By varying the ratio $k_B T / U_0$ the role of evaporation could be studied. The conclusion was that the qualitative features of the formation and dynamics of the precursor remain the same even if significant evaporation occurs. By varying the number of particles in the drop between 500 and 24,000, the effects of the drop size on the dynamics have also been investigated. It was found that there is no significant difference in the behaviour as long as the drop is far from being emptied by the spreading precursors.

A coarse grained description, which emphasizes the mass transfer along the surface of the drop, has been proposed by De Coninck et al [140, 141]. This is a restricted solid-on-solid (RSOS) model in which the drop and the film (phase A) in contact with the flat substrate (W) and a gas phase (B) are described by a set of columns with height values $h_i = \{l_0, l_1, \ldots \}$ at discrete positions $(x_i, y_i)$ on a planar regular lattice, assuming that there are no overhangs. The free energy of a configuration comprises contributions proportional to the areas (or, in a two-dimensional version, the perimeter) of the liquid–vapour, liquid–wall and vapour–wall contacts multiplied by the corresponding surface tensions, as well as an additional term $\mu(l)$ modelling a long-ranged effective interaction of the liquid–vapour interface with the substrate; $d\mu / dl$ is the so-called disjoining pressure. The dynamics is introduced as transfers of at most one unit height (thus the name ‘restricted’ SOS model) between neighbouring columns with Kawasaki type rates. Due to the coarse grained nature of the model, the MC simulations span much larger time and length scales than the ones for the microscopic Ising model discussed above. The results show that the model captures the emergence of terraced spreading [141] as well as spreading of a single layer ahead of the drop [140]. The thickness of these layers depends on the range and the strength of the effective interface potential $\mu(l)$. In all cases, the dependence on time (measured in units of MC steps per site) of the spreading of the precursor is reported to be in agreement with the expected $\sqrt{t}$-law.

As discussed in section 5, in [131, 142] a lattice gas model for the spreading of a monolayer precursor in contact with a reservoir of particles mimicking a drop [127, 130, 131] was studied using continuum time KMC. Due to the focus on the dynamics of the precursor, the computer simulations could explore the dynamics on relatively long time (seconds) and large spatial (more than a hundred times the molecular size) scales. They confirmed that the model predicts that the linear extent of the spreading monolayer (provided it does occur) grows in time as $\sqrt{t}$. These simulations revealed a complex structure of the concentration profiles as a function of the distance from the reservoir, including the emergence of sharp interfaces within the expanding monolayer. A similar model, but one in which the constraint of single occupancy of a site was relaxed, has been proposed for studying the spreading of a mesoscopically thick precursor films [143]. Numerical simulations of this model in a one-dimensional geometry predict a spreading dynamics of the emerging precursor film which also follows a $\sqrt{t}$ dependence on time.

Finally, we note that in [144] MC simulations have been reported for the spreading of a polymer droplet of chain-like molecules. They consist of 32 particles with a finitely extendible, non-linear and elastic potential between the components of each chain, with a Morse potential as the pair interaction between the components of distinct chains, and with an attractive van der Waals particle–substrate potential. While macroscopic drop spreading (i.e. Tanner’s law) and the early stages of precursor formation have been successfully captured by the simulations, the spreading of the precursor film could not be studied in detail because due to computational limitations the drop size of 128 chains with 32 particles each was too small. Such numerical limitations are expected to become severe if the number of conformational degrees of freedom per molecule is large, in particular as the complexity and the range of the pair potentials are increased.

6.2. Molecular dynamics simulations for simple or polymeric liquids

A molecular description is provided by MD simulations, in which the particle–particle interactions are specified and the dynamics follows from direct integration of Newton’s equation of motion. In the context of droplet spreading and the formation of precursor films, MD simulations have been a very useful tool in obtaining direct insight into the molecular details of the physical mechanisms driving the spreading (see [145–148] and references therein). Before embarking on a summary of the main corresponding developments, a word of caution is yet in order. While the MD method has the advantage of eliminating from the modelling part the numerous assumptions needed as input for the rates which define a MC or KMC dynamics, the method suffers from being computationally extensive and therefore requiring extremely large computer resources (both in terms of memory and CPU time) even for simulating relatively small systems (100,000 particles) over real timescales of less than one nanosecond. In addition, the actual interaction potentials are rarely well known. The results of MD simulations of droplet spreading should thus be considered as capturing qualitative features, rather than providing a bona fide quantitative description. Moreover, they should be carefully scrutinized with respect to finite-size effects and timescales which are intrinsically small, in particular if an interpretation for the asymptotic long time behaviour is sought (for an illuminating discussion see, e.g., [135, 147]).

The first MD studies successfully captured the occurrence of terraced spreading but led to contradictory results for the dynamics of precursors [149–152]. In [149, 150] fully atomistic MD simulations have been performed, in that both the drop and the substrate were represented as atoms with corresponding inter-particle interactions of an LJ form with a cut-off range of the order of the atomic diameter. The various potential parameters characterize the fluid–fluid, fluid–solid, and solid–solid pair interactions, and they are chosen such
that at the temperature of the simulations most of the fluid is in the liquid state and that the solid maintains its initial crystalline fcc structure with a (100) plane exposed to the liquid. Due to the aforementioned computational constraints, the size of the system was very small: 4000 particles for the fluid and 9000 particles for the solid, which corresponds to five atomic planes. By varying the strength of the liquid–solid interactions, while keeping the fluid–fluid ones fixed, the simulation explored various wetting regimes. In [150] an additional strong bonding was introduced between pairs of fluid particles, mimicking diatomic molecules; this sheds light on the influence of the size of the fluid particles on terraced spreading. The results provide clear evidence for the occurrence of terraced spreading as well as for layering inside the core of the drop but still within the liquid state. As intuitively expected, the number of distinct layers increases with increasing strength of the solid–fluid interactions. In these MD simulations the atomic liquid was fairly volatile, whereas the diatomic molecules were practically non-volatile. The simulations revealed that for very strong substrate–fluid interactions the vapour played some role in the formation of the precursor, but by comparing with the case of diatomic molecules it turned out that this evaporation–condensation process is a sub-dominant effect. However, in all cases studied the precursor film associated with the liquid layer next to the substrate showed a much slower spreading, i.e. $t_s \sim \sqrt{\ln(t)}$, than the one observed experimentally and predicted theoretically. This result was puzzling, as it apparently was not a finite-size effect; simulations with twice as many fluid particles reproduced the same behaviour [150].

The MD studies in [151, 152] considered the case of an atomic fluid as well as that of a binary mixture of single particles, acting as a solvent, and chain molecules. The latter consist of two, four, or eight single particles interconnected by a stiff, isotropic harmonic oscillator potential. All particles are taken to interact via LJ potentials and they are in contact with a homogeneous impenetrable substrate, which additionally interacts with the particles at a distance $z$ from the substrate via a van der Waals type potential $A/z^6$, $A < 0$. In [152] the impenetrability condition is implemented by a strongly repulsive term in the substrate–particle interaction $A/z^3 + B/z^5$, $A < 0$, $B > 0$. This substrate potential follows from integrating over a half-space the pair potentials between substrate and fluid particles. Concerning the leading term this is equivalent to carrying out the corresponding discrete sum of pair potentials as used in [149, 150].

The simulations, performed at temperatures at which evaporation is negligible, have shown that for atomic or diatomic molecules a precursor film occurs in most of the cases, while for longer molecules with orientational degrees of freedom layering and terraced spreading occur only if the strength of the attractive part of the substrate potential is above a threshold value, which depends on the chain length. In contrast to the results reported before [149, 150], in all cases in which a precursor film occurred its dynamics did show a $\sqrt{t}$ spreading behaviour after a transient due to the precursor formation. This was followed by a slower expansion once the reservoir drop began to empty. (In [151] it is pointed out explicitly that the initial spreading with nearly constant speed later crosses over to diffusive spreading, in turn followed by a slower regime once the macroscopic drop has emptied into the film.) Concerning the studies in [149, 150], the discrete structure of the substrate consisting of particles of the same size as the fluid particles, the strong substrate–fluid pair interactions, and the moisture of the substrate due to significant evaporation–condensation processes have been surmised [151] to be the most likely sources for the significant difference between the results of [149–152].

The issue of the dynamics of the precursor spreading has been further investigated with MD simulations in [153, 154]. These studies employed the same atomistic representation of the substrate as in [149, 150], with a cut-off for all LJ pair potentials at a distance equal to 2.5 times the fluid core size, but with an additional $A/z^3$ contribution to the resulting substrate potential. However, these studies used chain molecules consisting of eight or 16 atoms, bond together by a confining pair potential. This led to negligible evaporation and eliminated the similarity in size between the species forming the solid and the fluid, respectively. The simulations revealed the formation of a well defined first layer precursor film, as well as up to three additional layers spreading much more slowly than the first one. The dynamics of the first layer shows a clear $\sqrt{t}$ behaviour, which therefore indicates that the behaviour $t_s \sim \sqrt{\ln(t)}$ reported previously must be related to the size of the fluid particles used there. It was speculated that due to the compatibility in size the fluid particles in the previous MD simulations are trapped for long times in the local minima of the corrugated substrate potential, which leads to a slow motion along the surface and a correspondingly slow spreading, whereas the chain molecules are incommensurate with the distribution of mimina in the corrugated substrate potential and therefore can move easily along the surface [145, 153, 154].

The reason for the slow $\sqrt{\ln(t)}$ spreading behaviour has been finally clearly identified by the MD study in [155]. It revealed the substrate as being porous, which occurs for specific choices of the lattice constant of the substrate and of the core size of the fluid particles; they are both implicitly fixed by the choice of the parameters in the LJ pair potentials of the substrate and the fluid particles, respectively. The study employed an atomic fluid and a discrete representation of the substrate as atoms forming a lattice. By varying the parameters in the various LJ pair potentials, the size of the initial drop, the structure of the substrate lattice (fcc or (sc) lattices), and the type of thermostat employed in the simulations (see [135]), the authors convincingly showed that in all situations when the precursor film occurs (i.e. for a sufficiently attractive substrate potential and for a sufficiently large drop) its spreading dynamics follows the $\sqrt{t}$ time dependence if the substrate is impenetrable (see figure 10(a)) and if the drop acts as a reservoir. All the other parameters (including the evaporation–condensation processes) influence only the prefactor in this dependence (see equation (15)). In contrast, for parameters similar to those used in the studies in [149, 150], the fluid penetrates into the solid (see figure 10(b)) and this indeed gives rise to a much
square root dynamics is observed in all cases because one component, i.e. the 16-atom chains, is in the complete wetting regime. The spreading speed lies between those of the pure components. As expected, the monolayer precursor is enriched by and the next layer depleted of the 16-atom chains as long as the interaction of the eight-atom chains with the substrate maintains a strength leading to partial wetting. Similar conclusions have been drawn from recent [158] much larger scale MD simulations (300 000 atoms, interacting according to LJ potentials) of hemi-cylindrical droplets consisting of either pure 10-, 40-, or 100-atom chains, or mixtures of them.

The role of the particle size and of the substrate potential was further explored with MD simulations of binary mixtures with an equal number of chain-like molecules consisting of eight and 16 atoms, respectively, for which the interactions with the substrate atoms are chosen such that the 16-atom molecules are completely wetting the substrate, while the eight-atom molecules’ interaction with the substrate is tuned from a partial to a complete wetting behaviour [157]. A precursor film with the expected \( \sqrt{t} \) dynamics is observed in all cases because one component, i.e. the 16-atom chains, is in the complete wetting regime. The spreading speed lies between those of the pure components. As expected, the monolayer precursor is enriched by and the next layer depleted of the 16-atom chains as long as the interaction of the eight-atom chains with the substrate maintains a strength leading to partial wetting. Similar conclusions have been drawn from recent [158] much larger scale MD simulations (300 000 atoms, interacting according to LJ potentials) of hemi-cylindrical droplets consisting of either pure 10-, 40-, or 100-atom chains, or mixtures of them.

Large scale and long time MD simulations, which allow a simultaneous study of both droplet spreading and precursor film formation and spreading, have been performed in order to investigate the role played by various details, such as the atomic versus a homogeneous structure of the substrate, the type of thermostat algorithm used, the initial shape of the drop, or the size of the substrate [147]. The conclusion is that the computationally most effective method is to use a continuum representation of the substrate, if the porosity of the substrate (see, e.g., [155]) or substrate alloying (see, e.g., [159, 160]) are expected to be irrelevant, and to use a thermostat algorithm which decays rapidly with the distance from the substrate. The study in [147] reports the formation of precursor films only for parameters of the LJ pair potentials which ensure complete wetting of the substrate by the liquid of chain-like molecules. This is in agreement with similar observations made in [146, 158], but it leaves open the question of why such films do not occur in partial wetting situations, which is in contrast to the experimental observations (see section 4.2) and to the MD simulation results for metal-on-metal systems (see, cf. section 6.3). Whenever the precursor occurs, its spreading dynamics at sufficiently long times is clearly compatible with a \( \sqrt{t} \) time dependence for as long as the drop acts as a reservoir and the advancing edge of the film is far from the edges of the substrate. The speed of spreading decreases with the length of the chain-like molecules. Similar conclusions have been reached in MD simulations of a nano-sized droplet with LJ pair potentials spreading on a substrate in the complete wetting case [161]. Additionally, this latter study emphasizes a comparison with the case of strongly forced wetting occurring when a drop with a non-zero vertical velocity hits a flat impenetrable substrate. In this case, inertial terms are actually dominant: the drop spreads and retracts several times before reaching the equilibrium state. Precursor films do not occur because their kinetics is too slow at the timescales imposed by the external driving.

The question of the influence of substrate corrugation, i.e. the periodic lateral variation of the substrate potential due to the crystalline structure of the top layer of the substrate, on the dynamics of the precursor remains basically open. If one investigated the spreading of a colloidal...
obviously is at odds with the experimental evidence (see it cannot be generalized to other fluid–solid models as it hold for LJ fluids and van der Waals substrate potentials, from partial to complete wetting. While this claim seems to emergence of precursor films is an indication of a transition i.e. a few atomic diameters—it has been claimed that the over the timescale of the simulation is microscopic in size, unjustified, because in that region the linear extent of the film with a√ time dependence, with a prefactor depending on the speed of the spreading precursor film on the volume of the drop. It remains to be seen if such a dependence turns out to be a finite-size effect due to the intrinsically small spatial scales explored by MD simulations. This is a new challenge for theoretical analyses, which so far have been focused on the case of a large reservoir-like drop and a spreading speed which is independent of the drop volume. It remains as an open question why in these MD simulations the precursor film occurs even under partial wetting conditions, whereas in other MD simulations it does not.

6.3. Molecular dynamics simulations for metal-on-metal systems

The experimental results which have provided evidence for precursor films in metal-on-metal systems (see section 4.2) have stimulated the interest in MD simulations for such systems.

Moon et al. [163] studied the formation and spreading of precursor films of Ag on Ni(100). The choice of Ag and Ni was motivated by the fact that the inter-atomic interactions suspension, corrugation could indeed be completely switched off, because for the large colloids the substrate is de facto not corrugated; however, for MD simulations of molecular liquids or metal-on-metal systems, this is not the case. The studies in [155] and [147] clearly show two limiting cases: one in which the influence of the substrate corrugation is very significant [155], the other in which it plays a minor role [147]. We are not aware of any systematic MD studies of the dynamics of the precursor as a function of the lattice structure of the substrate, e.g., concerning the crossover between porous and non-porous substrates. The studies in [147] indicate that as long as the substrate is not porous the spreading follows the√t-behaviour. However, for the case of non-porous substrates, systematic MD studies of the effects of the lattice geometry and of the lattice spacing on the value of the prefactor have not yet been carried out.

An interesting approach for resolving the issue of volatility in MD simulations was proposed recently in [162], where the authors use a quarter of a cylindrical liquid drop confined by a rectangular wedge formed by two atomistic semi-infinite fcc walls (minus their overlap). This quarter of a cylindrical liquid drop is covered by an immiscible fluid of equal density and viscosity, and the confinement is completed by two additional homogeneous walls enclosing the covering fluid; periodic boundary conditions apply in the longitudinal direction. By studying the spreading of the first liquid covered by a second, immiscible one, the issue of volatility is bypassed. Both fluids are modelled as atoms interacting with LJ pair potentials. The interaction with the atomistic walls is described by LJ pair potentials, too, whereas the interaction of any liquid atom with the other two homogeneous walls is described by a van der Waals type substrate potential corresponding to a wedge formed by two semi-infinite walls (minus their overlap). The spreading of the drop away from the corner of the atomistic wedge is initiated by ‘turning on’ an additional attractive van der Waals substrate potential between the droplet atoms and the bottom, horizontal and atomistic wall, along which the spreading takes place. By varying the strength of this latter substrate potential, the liquid–liquid–substrate system is driven from a partial to a complete wetting state. In agreement with the previous results of MD simulations for LJ fluids (composed of atoms or chain-like molecules) [146, 147, 157, 158], for the complete wetting case only, a thin precursor film extending in front of the ‘macroscopic’ edge of the drop has been observed. The extension of this film was shown to be in agreement with a√t time dependence, with a prefactor depending on the strength of the substrate potential. By fitting ad hoc a power law to the extent of this precursor film close to the partial to complete wetting transition point—which is a priori unjustified, because in that region the linear extent of the film over the timescale of the simulation is microscopic in size, i.e. a few atomic diameters—it has been claimed that the emergence of precursor films is an indication of a transition from partial to complete wetting. While this claim seems to hold for LJ fluids and van der Waals substrate potentials, it cannot be generalized to other fluid–solid models as it obviously is at odds with the experimental evidence (see section 4.2). As we shall discuss below, this is also at odds with the results of MD simulations for other pair potentials, such as for metal-on-metal systems. In these systems ultrathin precursor films, expanding proportional to√t, emerge also in partial wetting situations. This is intuitively expected in view of the equilibrium picture of partial wetting corresponding to drops being in spatial contact with microscopically thin films (see section 1).

Moreover, the most important recent MD simulation results in this field are those reported in [160]. The dependence of the precursor spreading on the size of the drop, taken to be a semi-cylindrical drop in contact with a homogeneous flat substrate, was studied in both complete and partial wetting regimes. For the former, a polymer (chain-like molecules with 10 particles) fluid was used, in contact with a substrate acting on the fluid with an integrated LJ potential. For the latter, an atomistic representation of Pb on Cu(111) was used; the equilibrium contact angle was found to be 33°, which is very close to the experimental observations in [114]. (We re-emphasize, though, that an extrapolation of MD results to macroscopic scales and predictions of material specific properties deserve caveats.) In both cases the temperature and the parameters defining the potentials have been chosen such that the fluid is in the liquid state and practically non-volatile during the timescales of the simulations. The large scale MD simulations involving up to 78 000 polymer chains and up to 220 000 Pb atoms have provided the following results. (i) In both cases a monolayer precursor film emerges from the drop and spreads ahead of it. The radius of the precursor film, extending to more than 100 times the drop radius, follows a√t time dependence in both cases; for Pb on Cu(111), the total MD simulation time corresponded to approximately 4 ns, which is a very long timescale by MD standards. (ii) In both cases, the prefactor in the√t dependence is directly proportional to the square root of the initial radius R0 of the droplet. Extending this finding to the more common case of a spherical drop, this latter result can be interpreted as a dependence of the speed of the spreading precursor film on the volume of the drop. It remains to be seen if such a dependence turns out to be a finite-size effect due to the intrinsically small spatial scales explored by MD simulations. This is a new challenge for theoretical analyses, which so far have been focused on the case of a large reservoir-like drop and a spreading speed which is independent of the drop volume. It remains as an open question why in these MD simulations the precursor film occurs even under partial wetting conditions, whereas in other MD simulations it does not.
in metallic systems consisting of different atomic species can be calculated by using the semi-empirical embedded atom method (EAM), and that such EAM potentials are well established for Ni–Ni, Ag–Ag, and Ag–Ni pairs. The MD simulation employed a hemi-cylindrical Ag drop on an atomistic representation (ten atomic planes) of the Ni(100) substrate. The formation and spreading of precursor films from the already equilibrated Ag drop was studied at the temperatures \(T = 800, 900\) and \(1000\) K. (At these temperatures the studied Ag drop is actually in a solid state, according to the phase diagrams obtained from numerical simulations [164].) At all temperatures, a film with submonolayer coverage emerged. The coverage \(c\) varied as a function of the position \(x\) from the edge of the drop and of the time \(t\). The centre of the drop maintained a coverage in between three and four monolayers, fulfilling its role as a reservoir of particles. The dynamics of the film is compatible with the \(\sqrt{t}\) time dependence, as shown by the scaling of the coverage profiles when plotted as a function of the scaling variable \(x/\sqrt{D_t}\). No surface alloying or surface ordering in the precursor film were observed. The scaled profiles showed complex shapes, indicating coverage-dependent diffusion coefficients. A Boltzmann–Matano analysis [114, 119] was used to extract the diffusion coefficient as a function of coverage. The results exhibit qualitative features of the diffusion coefficient, such as a minimum at intermediate coverages and a maximum at large coverages. This behaviour shares a certain similarity with corresponding predictions of lattice gas models with particles interacting via simple LJ potentials as proposed in [126, 127, 131].

The study of Ag spreading on Ni substrates has been extended by Webb et al. [165] to include the case of cylindrical liquid Ag droplets brought into contact with and spreading on Ni(111) or Ni(100) surfaces. The MD simulations have been performed at 1200 K and 1500 K, i.e. slightly above and well above the melting point, respectively. The experimental bulk melting temperature of Ag is 1235 K, whereas the MD prediction based on the EAM potentials used in [165] is 1144 K. The numerical results show that spreading on the two surfaces is practically independent of the (111) or (100) surface structure. At 1200 K as a final state incomplete wetting with a contact angle of about \(10^\circ\) has been found. At 1500 K a significant dissolution of the Ni substrate occurred and no precursor film has been observed. This is similar to the results of MD simulations for high temperature Ag drops on a Cu surface [164]. In the simulations at 1200 K no surface alloying and very little substrate dissolution were observed, together with evidence for the formation of a submonolayer precursor film. However, even at—by MD simulation standards long—times of approximately 12 ns the extent of the precursor is extremely small. By analysing the data only up to 4–6 ns one could easily be misled to conclude that no precursor is forming. This further emphasizes the need for extreme care in extrapolating the results of MD simulations towards macroscopic, asymptotic behaviours.

An MD simulation study of precursor films of Pb emanating from liquid Pb droplets in contact with Cu(111) and Cu(100) substrates at 700 K has been reported in [159, 160]. The precursors occur in a state of partial wetting (contact angles of \(33^\circ\) and \(18^\circ\) on Cu(111) and Cu(100), respectively). In both cases the precursor films expand following a \(\sqrt{t}\) time dependence, with a significantly larger prefactor for the Cu(111) substrate. On Cu(100) the precursor is a submonolayer thick and, in agreement with theoretical expectations [112], significant surface alloying is observed. In contrast, on Cu(111) no alloying is observed and the precursor consists of two layers. While the lack of surface alloying seems to contradict the theoretical expectations and the experimental observations [113, 114], the occurrence of films thicker than a monolayer seems to agree with the experimental observation of a thick film in equilibrium with drops at temperatures above the melting point of Pb [115].

The results and studies discussed in section 6.2 have significantly contributed towards the understanding of the microscopic mechanisms of ultrathin precursor film formation and of the structure of these films. They have helped to reveal effects particularly significant for small drops, such as the slowing down of a precursor when the size of the drop becomes too small to act as a reservoir. This also holds for the apparent absence of precursor film formation over timescales which are long by MD standards, yet too short to be asymptotically long. This demonstrates that great care must be exercised concerning the extrapolation of MD data to the large spatial scales and the long timescales typically explored by experimental studies. These observations also show that, after all, it is only the careful comparison with experimental data which validates a numerical simulation. Moreover, even in the case of favourable agreement this holds usually only at a qualitative level, because there is only limited knowledge of the actual form of the force fields governing drop–substrate systems.

Therefore, the recent report in [166] of an ultrathin precursor film extending in time by following a power law with exponents varying between \(\approx 1/7\) and \(1/4\) is surprising. This claim is based on MD simulations of a water drop spreading on an (eventually charged) gold substrate. However, direct inspection of the data reveals that they actually correspond to the spreading of the drop, which consists of a quasi-spherical cap and a foot region (see figure 1), and not that of a film. (For a macroscopic drop it is indeed well documented that the base radius expands more slowly than the precursor film (see sections 2 and 3).) What the authors observe is, at most, the formation of the foot of the drop and not, as claimed, a precursor film. This assessment stems from the following observations. (i) The film in figure 2(a) in [166] has an extent from the edge of the drop of only three molecules, which renders a power-law fitting meaningless. (ii) In the case of the reported ‘complete wetting’, a layered film, with no evidence for a precursor, is formed (see figures 1(c) and 2(c) in [166], for electric field \(E > E_c\)), while nevertheless figure 2(c) therein features an exponent \(n(E)\) stemming from a power-law fitting of the extent of a non-existent precursor. (iii) The droplet is too small to act as a particle reservoir for the film. The transverse cross section of the initial droplet contains roughly 120 molecules, so a film even with a very small lateral extent (e.g., of 15 molecules measured from
the edge of the droplet) would already consume 25% of the initial droplet mass. A closer look at the data reveals additional issues associated with the simulated system. After what the authors call full spreading, the ‘water’\textsuperscript{17} droplet shown in figure 1(b) in [166] exhibits a non-zero (and rather large) contact angle, which is confirmed by figure 2(c) therein listing a ‘partial wetting’ state for fields $E < E_s$. This is in conflict with the experimental evidence that a smooth and clean gold surface is completely wetted by pure water [167]. Therefore, either the interaction potentials used are not appropriate for capturing the behaviour of the system at macroscopic scales, or the potentials are satisfactory but the wetting behaviour of a nano-scale drop of water is different from that of a macroscopic one in a way which is captured, rather than bypassed, by the MD simulations. In either case, extrapolating the results of these MD simulations towards claims of ‘resolving the Huh–Scriven paradox’ (which occurs only within the framework of macroscopic hydrodynamics)\textsuperscript{18} and of understanding actual electro-wetting experiments is unwarranted.

7. Recent developments

The rapid development of micro- and nano-fluidics devices and the emergence of more accurate and faster methods of surface characterization and analysis has recently led to a renewed interest in the spreading of small droplets and in the formation and structure of precursor films. For example, a new method for studying the precursor dynamics, called epifluorescence, has been proposed. This is a microscopy technique in which the visible light in the microscope eyepieces is that emitted, through fluorescence, by the specimen itself upon being exposed to a light source with a specific wavelength. It has been applied for a silicone oil (PDMS) drop spreading on a glass substrate [168]. The advantages of this method are a lateral resolution of about 0.2 $\mu$m, which is significantly better than that of ellipsometry, and a fast response allowing for a temporal resolution of about 200 ms. In principle, such a temporal resolution allows one to study the microscopic details of spreading even of low viscosity liquids, which so far has not been possible. A potential drawback of this method is the need to enrich the liquid drop with a fluorescent dye. This may restrict the choice of liquids, and it may even affect the spreading, if for any reason the dye behaves as a surfactant at the liquid–solid or the liquid–gas interfaces of interest. However, these are technical challenges rather than basic drawbacks and it seems reasonable to expect that an adequate choice of dyes can be found for a variety of liquids.

\textsuperscript{17}The quotation marks serve as a reminder that in the MD simulations assumptions have to be made about the interaction potentials and about the structure of the liquid, e.g., the formation and the strength of hydrogen bonds characteristic for actual water.

\textsuperscript{18}The Huh–Scriven paradox is that imposing the no-slip boundary condition at the solid–liquid interface in the case of a three-phase contact line moving over a flat and smooth solid leads to a logarithmic divergence of the rate of viscous dissipation in the fluid as function of, e.g., the vanishing slip length (see [16]).

Tapping mode atomic force microscopy (AFM) has also been employed in recent studies of precursor films [169]. This technique, which provides a lateral resolution down to a few nanometres while preserving a vertical spatial resolution of less than 1 nm, had been used previously to study the spreading of drops [170, 171]. By employing a well suited setup, with the AFM repeatedly scanning a region at a certain distance from the macroscopic edge of a quasi-stationary drop, Xu et al have been able to detect and monitor a precursor film of a complex polymer (poly( tert-butyl acrylate) brush molecules) spreading on a planar highly oriented pyrolytic graphite substrate (which is graphite with an angular spread between the graphite sheets of less than 1$^{\circ}$). The observed dynamic behaviour obeys the generic $\sqrt{t}$ dependence [169]. In contrast, the report based on tapping mode AFM of what is called in [172] a ‘precursor’ film of nanometre extent at the periphery of a small drop consisting of star-shaped polymers, in contact with a silicon oxide substrate has to be treated with caution. The setup of this experiment is that of a dewetting situation and, as the authors acknowledge, the actual film observed was the one remaining on the surface during dewetting, rather than one emerging from the drops. Therefore, it is probably an equilibrium film instead of a precursor.

The ever increasing computing power and storage capabilities of computers combined with the development of new, efficient methods and algorithms for numerical simulations allow one to explore new types of computer experiment as well as to significantly improve the accuracy of previous results. For example, [173] employed both MD and lattice–Boltzmann (LB) simulations in order to study the capillary imbibition and precursor film formation in nanotubes. It has been reported that both types of simulation agree in that a molecularly thin precursor film forms ahead of the advancing meniscus, and the lateral extension of this film grows in time as $\sqrt{t}$, similarly to the observations for other geometries. This is particularly interesting as in this setup the position of the meniscus moves with a similar time dependence (i.e. following Washburn’s law), but with a smaller prefactor. Therefore, this is a more complex situation, in which the dynamics of the precursor film is more connected to that of the meniscus rather than being independent of it. Moreover, excellent quantitative agreement has been reported between the results of MD and LB simulations. This opens the perspective of using LB simulations, which allow the exploration of time and length scales inaccessible by other numerical methods, for a variety of other systems.

Finally, we note a recently reported [174, 175] surprising example of the formation of a ‘ultrathin’ (i.e. monolayer) precursor film, with a spreading dynamics described well by a $\sqrt{t}$ behaviour. The system is a spheroidal aggregate of cells, the surface of each cell containing a certain level of a cell–cell adhesion agent (E-cadherin molecules), in contact with a glass substrate decorated with a mixture of a cell-adhesion agent (fibronectin) and a non-adhesive component (PEG–poly-L-lysine, PEG–PLL). The behaviour of such cellular aggregates bears strong similarities with that of a viscoelastic liquid drop. Accordingly, a spreading
coefficient $S_0 = W_{CC} - W_{CS}$, given by the difference between the cell–cell ($W_{CC}$) and cell–substrate ($W_{CS}$) adhesion energies per unit area, can be defined analogously to that of a liquid. By varying the amounts of E-cadherin on the cell surface and fibronectin on the glass substrate, it was possible to change $S$ from negative to positive values. This is the equivalent of a transition from incomplete wetting to complete wetting for a liquid-on-solid system. This was confirmed by the corresponding ‘wetting’ behaviour of the cell aggregates. In the complete wetting regime, in which the glass substrate was fully covered by fibronectin, a precursor film, with a thickness equal to one layer of cells, was observed to spread on the substrate ahead of the cell aggregate. The structure of the film is more compact, i.e., liquid-like for stronger cell–cell adhesion; it turns into a sparse, two-dimensional gas-like configuration as the cell–cell adhesion is weakened. The analogy with the liquid-on-solid systems is completed by the observation of an expansion of the liquid-like precursor film showing good agreement with a $\sqrt{t}$ time dependence.

8. Summary and outlook

It can be easily inferred that the combination of experiment, theoretical analysis, and numerical simulations has led to a good understanding of the mechanisms of formation and the dynamics of precursor films on homogeneous, planar, smooth substrates. However, in our view even for this most basic case several important questions still await answers.

- What are the necessary and sufficient conditions for a precursor film to emerge during the spontaneous spreading of a (quasi)-non-volatile drop? Are these the same for a solid-on-solid system such as the metal-on-metal one discussed in section 4.2?
- A good understanding of the dynamics of mesoscopically thick precursor films is available, and theoretical lattice gas models seem to capture well the dynamics of ultrathin films. A comprehensive theory, which would deal with all length scales and recover the behaviour of thick and ultrathin films as particular limiting cases, remains to be developed.
- The early experiments, and so far the only systematic studies of ultrathin precursors, focused on the case of complete wetting. Apart from [110, 111], we are not aware of a similar systematic experimental study of the partial wetting case. Such results are needed to elucidate the importance of the detailed shape of inter-particle pair potentials as revealed by the MD simulations. As we discussed in sections 6.2 and 6.3, the choice of the interaction potentials leads to conflicting results on whether or not a ultrathin precursor film emerges in partial wetting situations.

By using KMC simulations of lattice gas models a few studies have addressed the issue of ultrathin precursor films spreading on chemically inhomogeneous substrates [105, 106, 176] or upon encountering chemical patterns [177]. However, questions such as how precursor films form and spread on chemically inhomogeneous or patterned substrate are yet to be explored systematically. Millimetre-sized drops which are set in motion upon contact with a chemically patterned substrate have been recently studied experimentally [178]. However, the question of formation and dynamics of precursor films, as well as that of their influence on the emerging motion of the drop, has not yet been addressed. In thermal equilibrium, partially wetting nanodrops coexist with a microscopic film. When placed near topographic or chemical heterogeneities on the substrate surface, they interact with them via this film and therefore they are set into motion [179–183]. This naturally leads to the question of how these dynamic phenomena translate to the case in which a ultrathin precursor film, which spreads ahead of a nanodrop, will interact with such geometrical or chemical structures. For example, one can consider the encounter of a precursor with a small chemical patch, which was addressed briefly in [184], and how in turn this interaction has an influence on the drop. We note here a recently reported elegant example of such precursor film mediated interactions, applied to achieve thermocapillary actuation even at microscopic scales [25]. By applying a thermal gradient to a parylene-coated silicon substrate, an ultrathin precursor film emerges out of a heptanol drop. This film mediates both the driving of this oil drop towards a water drop sitting nearby and the encapsulation of the water drop by the heptanol. Once the encapsulation is complete, the composite starts moving along the temperature gradient, and thermocapillary actuation is achieved.

The complexity increases by considering whether or not precursor films occur and, if so, how they spread in situations in which the substrate is responsive. Examples are soft substrates such as the case of a liquid lens at the interface between two immiscible liquids, or at flexible, hairlike substrate structures. Spreading on curved substrates, such as for a sessile drop on a cylindrical or conical rod [185], as well as on substrates with other types of complex geometry, are issues of significant interest which have barely been studied. For example, the very interesting question of spreading of a drop and the formation of precursor films inside a wedge (corner) have been recently approached using MD simulations [186]. These preliminary results (although suffering from a premature interpretation in terms of a heuristic model presumably applicable to the motion of a three-phase contact line but not to the dynamics of ultrathin precursor films [63]) hint at a wealth of qualitatively new phenomena, such as the coexistence of two-dimensional and one-dimensional precursor films spreading ahead of the ‘macroscopic’ contact line. The occurrence and dynamics of precursor films in situations where a volatile or non-volatile colloidal suspension spreads on a substrate [187] provide further important challenges for theory and for applications of wetting.

Acknowledgments

MNP and SD acknowledge financial support from the Australian Research Council (grant DP1094337). AMC wishes to thank Professor John Ralston for many helpful discussions.
References

[1] Padday J F (ed) 1978 Wetting, Spreading, and Adhesion (New York: Academic)
[2] de Gennes P G, Brochard-Wyart F and Quere D 2004 Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves (Berlin: Springer)
[3] Starov V M, Velarde M G and Radke C J 2007 Wetting and spreading dynamics Surf actant Science vol 138 (Boca Raton, FL: CRC Press) (Taylor and Francis: London)
[4] Fuerstenau M C, Jameson G and Yoon R-H (ed) 2004 Froth Flotation: A Century of Innovation (Littleton, CO: Society for Mining, Metallurgy, and Exploration)
[5] von Michaelis H (ed) 1989 Innovations in Gold and Silver Recovery: Phase IV (Golden, CO: Randol International)
[6] Young T 1805 An essay on the cohesion of fluids Phil. Trans. R. Soc. Lond. 95 65–87
[7] Laplace P S 1805 Mécanique Céleste (Paris: Courcier)
[8] Plateau J 1869 Experimental and theoretical researches into the figures of equilibrium of a liquid mass without weight Phil. Mag. 38 445–55
[9] Gibbs J W 1957 The Collected Works of J. Willard Gibbs (London: Yale University Press)
[10] Rowlinson J S and Widom B 1982 Molecular Theory of Capillarity (Oxford: Clarendon)
[11] Hansen J P and McDonald I R 1986 Theory of Simple Liquids (London: Academic)
[12] Evans R 1979 The nature of the liquid–vapour interface and other topics in the statistical mechanics of non-uniform, classical fluids Adv. Phys. 28 143–200
[13] Evans R 1990 Microscopic theories of simple fluids and their interfaces Liquids at Interfaces, Proc. Les Houches Summer School Lectures, Session XLVIII ed J Charvolin, J F Joanny and J Zinn-Justin (Amsterdam: Elsevier) pp 1–98
[14] Napiórkowski M and Dietrich S 1993 Structure of the effective Hamiltonian for liquid–vapor interfaces Phys. Rev. E 47 1836–49
[15] Mecke K R and Dietrich S 1999 Effective Hamiltonian for liquid–vapor interfaces Phys. Rev. E 59 6766–84
[16] de Gennes P G 1985 Wetting: statics and dynamics Rev. Mod. Phys. 57 827–63
[17] Sullivan D E and Telo da Gama M M 1986 Wetting transitions and multilayer adorption at fluid interfaces Fluid Interfacial Phenomena ed C A Croxton (New York: Wiley) pp 45–134
[18] Dietrich S 1988 Wetting phenomena Phase Transitions and Critical Phenomena vol 12, ed C Domb and J L Lebowitz (London: Academic) pp 1–218
[19] Schick M 1990 Microscopic theories of simple fluids and their interfaces Liquids at Interfaces, Proc. Les Houches Summer School Lectures, Session XLVIII ed J Charvolin, J F Joanny and J Zinn-Justin (Amsterdam: Elsevier) pp 415–97
[20] Parry A O and Rascon C 2011 The self-interaction of a fluid interface, the wavevector dependent surface tension and wedge filling J. Phys.: Condens. Matter 23 015004
[21] Bernardino N R, Parry A O, Rascon C and Romero-Enrique J M 2009 Derivation of a non-local interfacial model for 3d wetting in an external field J. Phys.: Condens. Matter 21 465105
[22] Parry A O, Romero-Enrique J M and Lazarides A 2004 Nonlocality and short-range wetting phenomena Phys. Rev. Lett. 93 086104
[23] Pang L, Landau D P and Binder K 2011 Simulation evidence for nonlocal interface models: Two correlation lengths describe complete wetting Phys. Rev. Lett. 106 236102
[24] Zisman W A 1964 Contact angle, wettability and adhesion Advances in Chemistry Series vol 43, ed F M Fowkes (Washington, DC: American Chemical Society) p 1
[25] Zhao Y, Fangjie L and Chen C-H 2011 Thermocapillary actuation of binary drops on solid surfaces Appl. Phys. Lett. 99 104101
[26] Léger L and Joanny J F 1992 Liquid spreading Rep. Prog. Phys. 55 431–86
[27] Heslot F, Cazabat A M and Levinson P 1989 Dynamics of wetting of tiny drops: Ellipsometric study of the late stages of spreading Phys. Rev. Lett. 62 1286–90
[28] Beaglesholec H 1989 Profiles of the precursor of spreading drops of siloxane oil on glass, fused silica, and mica J. Phys. Chem. 93 893–9
[29] Heslot F, Cazabat A M and Fraysse N 1989 Diffusion-controlled wetting films J. Phys.: Condens. Matter 1 5793–8
[30] Heslot F, Fraysse N and Cazabat A M 1989 Molecular layering in the spreading of wetting liquid drops Nature 338 640–2
[31] Bonn D, Eggers J, Indekeu J, Meunier J and Rolley E 2009 Wetting and spreading Rev. Mod. Phys. 81 739–805
[32] Pandit R, Schick M and Wortis M 1983 Systematics of multilayer adorption phenomena on attractive substrates Phys. Rev. B 26 5112–40
[33] Bauer C and Dietrich S 1999 Quantitative study of laterally inhomogeneous wetting films Eur. Phys. J. B 10 767–79
[34] Indekeu J O 1994 Line tension at wetting Int. J. Mod. Phys. B 8 309–45
[35] Getta T and Dietrich S 1998 Line tension between fluid phases and a substrate Phys. Rev. E 57 655–71
[36] Dobbs H 1999 The modified Young’s equation for the contact angle of a small sessile drop from an interface displacement model Int. J. Mod. Phys. B 13 3255–9
[37] Pompe T 2002 Line tension behavior of a first-order wetting system Phys. Rev. Lett. 89 076102
[38] Pompe T and Herminghaus S 2000 Three-phase contact line energetics from nanoscale liquid surface topographies Phys. Rev. Lett. 85 1930–3
[39] White L R 1978 On deviations from Young’s equation J. Chem. Soc. Faraday Trans. 1 83 390–17
[40] Churaev N V, Starov V M and Derjaguin B V 1982 The shape of the transition zone between a thin film and bulk liquid and the line tension J. Colloid Interface Sci. 89 16–24
[41] Schimmel L, Napiórkowski M and Dietrich S 2007 Conceptual aspects of line tensions J. Chem. Phys. 127 164715
[42] Mechkov S, Oshanin G, Rauscher M, Brinkmann M, Cazabat A M and Dietrich S 2007 Contact line stability of ridges and drops Europhys. Lett. 70 66002
[43] Ruckenstein E 1982 Conditions for spreading as single molecules or as a thin planar drop J. Colloid Interface Sci. 86 573–4
[44] Joanny J F and de Gennes P J 1984 Static structure of wetting films and contact lines C. R. Acad. Sci. 299 279–83
[45] Cazabat A M, Fraysse N, Heslot F, Levinson P, Marsch J, Tiberge P and Valignat M P 1994 Pancakes Adv. Colloid Interface Sci. 48 1–17
[46] Cazabat A M 1987 How does a droplet spread? Contemp. Phys. 28 347–64
[47] Cazabat A M 1991 Wetting films Adv. Colloid Interface Sci. 34 73–88
[48] Rauscher M and Dietrich S 2008 Wetting phenomena in nanofluidics Annu. Rev. Mater. Res. 38 143–72
diffusivity on the growth of precuring films of Pb on Cu(111) Surf. Sci. 488 73–82
[115] Moon J, Wynblatt P, Garoff S and Suter R 2004 Pseudopartial wetting and precursor film growth in immiscible metal systems Langmuir 20 402–8
[116] Moon J, Wynblatt P, Garoff S and Suter R 2004 Diffusion kinetics of Bi and Pb–Bi monolayer precursing films on Cu(111) Surf. Sci. 559 149–57
[117] Monchoux J P, Chatain D and Wynblatt P 2005 On Auger microscopy study of the meeting and interdiffusion of pure Pb and Bi adsorbed layers on polycrystalline Cu Surf. Sci. 575 69–74
[118] Monchoux J P, Chatain D and Wynblatt P 2006 Impact of surface phase transitions and structure on surface diffusion profiles of Pb and Bi over Cu(100) Surf. Sci. 600 1265–76
[119] Wynblatt P, Chatain D, Ranguis A, Monchoux J P, Moon J and Garoff S 2007 Factors affecting the coverage dependence of the diffusivity of one metal over the surface of another Int. J. Thermophys. 28 646–60
[120] Bonn D, Meunier J and Indekeu J 2005 Comment on pseudopartial wetting and precursor film growth in immiscible metal systems Langmuir 21 3722–3
[121] Matano C 1933 On the relation between the diffusion-coefficients and concentrations of solid metals (the nickel–copper system) Japan. J. Physiol. 8 109–13
[122] de Gennes P G and Cazabat A M 1990 Spreading of a stratified incompressible droplet C. R. Acad. Sci. Paris II 310 1601–6
[123] Abraham D B, Collet P, De Coninck J and Dunlop F 1990 Langevin dynamics of spreading and wetting Phys. Rev. Lett. 65 195–8
[124] Abraham D B, Collet P, De Coninck J and Dunlop F 1990 Langevin dynamics of an interface near a wall J. Stat. Phys. 61 509–32
[125] De Coninck J, Dunlop F and Menu F 1993 Spreading of a solid-on-solid drop Phys. Rev. E 47 1820–3
[126] Burlatsky S F, Oshanin G, Cazabat A M and Moreau M 1996 Microscopic model of upward creep of an ultrathin wetting film Phys. Rev. Lett. 76 86–9
[127] Burlatsky S F, Oshanin G, Cazabat A M, Moreau M and Reinhardt W P 1996 Spreading of a thin wetting film: microscopic approach Phys. Rev. E 54 3832–45
[128] Burlatsky S F, Cazabat A M, Moreau M, Oshanin G and Villette S 2000 Spreading of molecularly thin wetting films on solid interfaces Nonlinear Phenomena and Complex Systems, Instabilities and Non-Equilibrium Structures VI ed E Tirapegui, J Martinez and R Tiemann (Dordrecht: Kluwer Academic Publishers) pp 233–67
[129] Oshanin G, De Coninck J, Cazabat A M and Moreau M 1998 Dewetting, partial wetting, and spreading of a two-dimensional monolayer on solid surface Phys. Rev. E 58 20–3
[130] Oshanin G, De Coninck J, Cazabat A M and Moreau M 1998 Microscopic model for spreading of a two-dimensional monolayer J. Mol. Liq. 76 195–219
[131] Popescu M N and Dietrich S 2004 Model for spreading of liquid monolayers Phys. Rev. E 69 061602
[132] Lukkarinen E, Kaski K and Abraham D B 1995 Mechanisms of fluid spreading: Ising model simulations Phys. Rev. E 51 2199–202
[133] Abraham D B, Cuerno R and Esteban M 2002 Microscopic model for thin film spreading Phys. Rev. Lett. 88 206101
[134] Binder K and Heermann D W 2010 Monte Carlo Simulation in Statistical Physics: An Introduction (Heidelberg: Springer)
Lukkarinen A, Kaski K and Abraham D B 1995 Mechanisms of fluid spreading: Ising model simulations Phys. Rev. E 51 2199–202

De Coninck J, Hoorelbeke S, Valignat M P and Heiniö J, Kaski K and Abraham D B 1992 Dynamics of a microscopic droplet on a solid surface: theory and simulation Phys. Rev. B 45 44409–16

Lukkarinen A, Kaski K and Abraham D B 1995 Mechanisms of fluid spreading: Ising model simulations Phys. Rev. E 51 2199–202

De Coninck J, Hoorelbeke S, Valignat M P and Cazabat A-M 1993 Effective microscopic model for the dynamics of spreading Phys. Rev. E 48 4549–55

De Coninck J, Frayssé N, Valignat M P and Cazabat A-M 1993 A microscopic simulation of the spreading of layered droplets Langmuir 9 1906–9

Lucasta A, Sancho J M, Sagues F and Oshanin G 2001 Propagation dynamics of a particle phase in a single-file pore Materials Research Society Symposia Proceedings vol 651, ed J M Drake, J Klafter, P Levitz, R M Overney and M Urbakh (Pittsburgh, PA: Materials Research Society) pp T9.1.1–T9.1.12

Dotti C, Gambassi A, Popescu M N and Diethrich S 2007 Spreading in narrow channels Phys. Rev. E 76 041127

Milchev A and Binder K 2002 Droplet spreading: a Monte Carlo test of Tanner’s law J. Chem. Phys. 116 7691

De Coninck J 1996 Spreading of chain-like liquid droplets on solids Colloids Surf. A 114 155–60

Voué M and De Coninck J 2000 Spreading and wetting at the microscopic scale: recent developments and perspectives Acta Mater. 48 4405–17

Heine D R, Grest G S and Webb E B 2005 Surface wetting of polymer nanodroplets Phys. Rev. E 71 051603

Simsonov V M 2011 On computer simulation of droplet spreading Curr. Opin. Colloid Interface Sci. 16 303–9

Yang X J, Koplik J and Banavar J R 1991 Molecular dynamics of drop spreading on a solid surface Phys. Rev. Lett. 67 3539–42

Yang X J, Koplik J and Banavar J R 1992 Terraced spreading of simple liquids on solid surfaces Phys. Rev. A 46 7738–49

Nieminen J A, Abraham D B, Karttunen M and Kaski J 1992 Molecular dynamics of a microscopic droplet on solid surface Phys. Rev. Lett. 69 124–7

Nieminen J A and Ala-Nissila T 1994 Dynamics of polymer microdroplets: a molecular-dynamics study Phys. Rev. E 49 4228–36

De Coninck J, D’Ortona U, Koplik J and Banavar J R 1995 Terraced spreading of chain molecules via molecular dynamics Phys. Rev. Lett. 74 928–30

D’Ortona U, De Coninck J, Koplik J and Banavar J R 1996 Terraced spreading mechanisms for chain molecules Phys. Rev. E 53 562–9

Bekink S, Karaborni S, Verbist G and Esselink K 1996 Simulating the spreading of a droplet in the terraced wetting regime Phys. Rev. Lett. 76 3766–9

Hataja M, Sancho J M and Ala-Nissila T 1995 Molecular ordering of precursor films during spreading of tiny liquid droplets Phys. Rev. E 52 R2165–7

Voué M, Rovillard S, De Coninck J, Valignat M P and Cazabat A M 2000 Spreading of liquid mixtures at the microscopic scale: a molecular dynamics study of the surface-induced segregation process Langmuir 16 1428–35

Heine D R, Grest G S and Webb E B 2004 Spreading dynamics of polymer nanodroplets in cylindrical geometries Phys. Rev. E 70 011606

Webb E B, Grest G S and Heine D R 2003 Precursor film controlled wetting of Pb on Cu Phys. Rev. Lett. 91 236102

Heine D R, Grest G S and Webb E B 2005 Surface wetting of liquid nanodroplets: droplet-size effects Phys. Rev. Lett. 95 107801

Sedidi N, Murad S and Aggarwal S K 2011 Molecular dynamics simulations of spontaneous spreading of a nanodroplet on solid surfaces Fluid Dyn. Res. 43 015507

Wu C, Qian T and Sheng P 2010 Droplet spreading driven by van der Waals force: a molecular dynamics study J. Phys.: Condens. Matter 22 325101

Moon J, Yoon J, Wynblatt P, Garoff S and Suter R M 2002 Simulation of spreading of precursing Ag films on Ni(100) Comput. Mater. Sci. 25 503–9

Webb E B, Grest G S, Heine D R and Hoyt J J 2005 Dissolutive wetting of Ag on Cu A molecular dynamics simulation study Acta Mater. 53 3163–77

Sun Y and Webb E B 2009 The atomistic mechanism of high temperature contact line advancement: results from molecular dynamics simulations J. Phys.: Condens. Matter 21 464135

Yuan Q and Zhao Y P 2010 Precursor film in dynamic wetting, electrowetting, and electro-elasto-capillarity Phys. Rev. Lett. 104 246101

Smith T 1980 The hydrophilic nature of a clean gold surface J. Colloid Interface Sci. 75 51–5

Hoang A and Kavehpour H P 2011 Dynamics of nanoscale precursor films near a moving contact line of spreading drops Phys. Rev. Lett. 106 254501

Xu H, Shirvanyants D, Beers K, Matyjaszewski K, Rubinstein M and Sheikh S S 2004 Molecular motion in a spreading precursor film Phys. Rev. Lett. 93 206103

Villette S, Valignat M P, Cazabat A-M, Schabet F A and Kalachev A 1997 Ultrathin liquid films. Ellipsometric study and AFM preliminary investigations Physica A 263 123–9

Glick D, Thiansathaporn P and Superfine R 1997 In situ imaging of polymer melt spreading with a high-temperature atomic force microscope Appl. Phys. Lett. 71 206103

Glynos E, Frieberg B and Green P F 2011 Wetting of a multiarm star-shaped molecule Phys. Rev. Lett. 107 118103

Chibbaro S S, Biernaule L, Diotallevi F, Succi S, Binder K, Dimitrov D, Milchev A, Girardo S and Pisignano D 2008 Evidence of thin-film precursors formation in hydrokinetic and atomistic simulations of nano-channel capillary filling Europhys. Lett. 84 44003

Doeuzan S, Guevorkian K, Naour R, Dufour S, Cuvelier D and Brochard-Wyart F 2011 Spreading dynamics and wetting transition of cellular aggregates Proc. Natl. Acad. Sci. USA 108 7315–20

Doeuzan S, Dumond J and Borchmod-Wyart F 2012 Wetting transitions of cellular aggregates induced by substrate rigidity Soft Matter 8 4578–83

Pesheva N and Oshanin G 2002 Monolayer spreading on a chemically heterogeneous substrate Colloids Surf. A 206 349–61

Popescu M N and Diethrich S 2003 Spreading of liquid monolayers: from kinetic Monte Carlo simulations to
continuum limit Interface and Transport Dynamics: Computational Modelling ed H Emmerich, B Nestler and M Schreckenberg (Berlin: Springer) pp 202–7

[178] Bliznyuk O, Jansen H P, Kooij E S, Zandvliet H J W and Poelsema B 2011 Smart design of stripe-patterned gradient surfaces to control droplet motion Langmuir 27 11238–45

[179] Moosavi A, Rauscher M and Dietrich S 2006 Motion of nanodroplets near edges and wedges Phys. Rev. Lett. 97 236101

[180] Moosavi A, Rauscher M and Dietrich S 2008 Motion of nanodroplets near chemical heterogeneities Langmuir 24 734–42

[181] Moosavi A, Rauscher M and Dietrich S 2008 Size dependent motion of nanodroplets on chemical steps J. Chem. Phys. 129 044706

[182] Rauscher M and Dietrich S 2009 Nano-droplets on structured substrates Soft Matter 5 2997–3001

[183] Moosavi A, Rauscher M and Dietrich S 2009 Dynamics of nanodroplets on topographically structured substrates J. Phys.: Condens. Matter 21 464120

[184] Popescu M N, Dietrich S and Oshanin G 2005 Diffusive spreading and mixing of fluid monolayers J. Phys.: Condens. Matter 17 S4189–98

[185] Lv C, Chen C, Chuang Y-C, Tseng F-G, Yin Y, Grey F and Zheng Q 2012 Driving droplets by curvi-propulsion, arXiv:1202.6582v1

[186] Yuan Q Z and Zhao Y P 2012 Topology-dominated dynamic wetting of the precursor chain in a hydrophilic interior corner Proc. R. Soc. Ser. A 468 310–22

[187] Maki K L and Kumar S 2011 Fast evaporation of spreading droplets of colloidal suspensions Langmuir 27 11347–63