Dynamics of Soft Wetting

Mathijs van Gorcum

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Front cover - A drop of water wetting a soft, deformable gel; the edge of the drop shows a deformation of the solid due to the liquid surface tension. Vertically on the left an image of a wetting ridge is shown.

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DYNAMICS OF SOFT WETTING

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1

Introduction

1.1 Wetting, from rigid to soft surfaces

The interaction of liquids with solids is an interesting aspect of nature and technology. At small scales, say of millimeter-sized drops or smaller, these interactions are dominated by surface effect[2], figure 1.1 shows a quasi-random assortment of liquid-solid interactions that are governed by capillary phenomena: dew drops on a spider web (a), a soft contact lens (b), and drops deforming the fibers of a feather (c). Clearly, the wetting of surfaces by liquid drops are a part of everyday life, varying from teardrops on your skin when crying to technological applications such as contact lenses, inkjet printing, painting and the food industry. It is also a source of many fundamental questions, as we will

Figure 1.1: (a) Dew drops on a spider web (image by Ivicabrlc, CC-BY-SA 4.0). (b) A soft contact lens (image by Etan J. Tal, CC-BY 3.0). (c) Drops interacting with fibers of a feather (image ©Duprat *et al.* [1])

Figure 1.2: (a) Equilibrium contact angle θ_{eq} of a liquid on a rigid surface calculated using Young's law. (b) A static drop on a rigid hydrophobic (left) and hydrophilic (right) surface. (c) a moving drop on an inclined solid surface, showing a deviation from the static angles.

see throughout this thesis. In order to gain a deep understanding we will focus on a single drop or even on a single contact line. This allows us to abstractly study the dynamics, allowing for extrapolation of the results to larger physical systems.

Traditionally, the study of wetting assumes the solid surfaces to be perfectly rigid. This goes back to 1805, when Young [3] observed that the equilibrium shape of a liquid on a solid is determined by the relative cohesive and adhesive forces of the liquid, solid and surrounding medium. At equilibrium, these forces lead to a well-defined contact angle θ_{eq} that the liquid makes with respect to the solid. For a rigid solid, the angle satisfies the famous Young's law

$$\gamma_{SV} = \gamma_{SL} + \gamma \cos(\theta_{eq}), \quad (1.1)$$

where θ_{eq} is the equilibrium contact angle, γ_{SV} is the surface tension of the solid-vapour interface, γ_{SL} is the surface tension of the solid-liquid interface and γ is the surface tension of the liquid-vapour interface. This relation can be understood as a balance of the horizontal components of the surface tension forces as sketched in figure 1.1 a. The relative values of γ_{SV} , γ_{SL} , and γ determine whether the substrate is hydrophilic or hydrophobic: On hydrophobic substrates the contact angle θ_{eq} is large, while for hydrophilic surfaces the contact angle is small, see figure 1.2 b. If gravity can be neglected both drops form a spherical cap, the shape of which is determined by the contact angle.

If we were to tilt the substrate, the droplet would start moving due to gravity, as shown in figure 1.2 c. From a macroscopic perspective the contact angles then deviate from the equilibrium angle θ_{eq} , resulting in a net force in the horizontal direction. This causes the motion of the contact line, and as a result the drop will slide down the surface (figure 1.2 c). During this motion the shear stress of the liquid at the contact line diverges, causing an apparent singularity in the viscous dissipation, the precise details at the contact line are still a subject of study. [4–8]

One of the reasons the dynamics of wetting has received so much attention is that a deep understanding of moving contact lines is critical to achieve

Figure 1.3: Examples of wetting on soft surfaces. (a) Condensation on a soft surface vs condensation on a rigid surface (image ©Sokuler *et al.* [13]). (b) Durotaxis, droplets move to the softer region of the solid (image ©Style *et al.* [14]), (c) Contact lenses are an example of interaction between liquids and soft surfaces d a single drop of water on a soft surface, showing a deformation at the contact line.

control, design and manipulation of liquids in technologically relevant contexts. After a lot of work focused on the mechanics of the liquid, a recent trend is to manipulate the surface; by using 'smart surfaces' in order to have detailed control over the shape and motion of liquid drops. Examples of this are superhydrophobic surfaces that use both hydrophobicity and surface roughness to reach very high contact angles [9, 10] and Lubiss (lubricant impregnated slippery surfaces) surfaces that use porous surfaces impregnated with lubricant [11, 12]. The lubricant removes any contact angle hysteresis causing any droplets on these surfaces to roll off under very small forcing. In this thesis we focus on another parameter of the solid, namely the stiffness, characterized by its elastic (shear) modulus G . These generically consist of soft crosslinked polymer networks, and offer a new degree of freedom in the design of surfaces.

Figure 1.3 shows a number of examples of wetting on soft surfaces. Panel a shows images of condensation patterns on soft and stiff solids [13]. It was found that a softer surface increases the condensation speed and causes a higher surface coverage. Figure 1.3 b shows a durotaxis effect, where the drop migrates autonomously to the deeper, and thus softer regions of the substrate (appearing as the darker lines in the image) [14]. This allows active control over the motion of droplets and resembles the migration of cells through durotaxis. Figure 1.3 c shows a sessile drop on a surface and is an example of the system this thesis will examine in detail: at the contact line of the drop a clear deformation is visible, known as the *wetting ridge*. By gaining more insight in the fundamental underpinnings of the statics and dynamics of these systems we can gain better control of wetting behaviour on soft solids.

Interestingly, many of the principles that govern 'rigid wetting' are no longer applicable for 'soft wetting.' For example: as seen in figure 1.2 a and equation 1.1, Young's law only involves the horizontal force balance. The vertical force

Figure 1.4: Wetting ridges as observed over the years. (a) Wetting ridge visualized using white light interferometry with a theoretical curve (image ©Carré *et al.* [15]). (b) image ©Pericet-Camara *et al.* [16]. the authors measured the wetting ridge both outside and under the liquid in 2008. (c) Measurement of the wetting ridge using confocal microscopy (image ©Jerison *et al.* [17]). (d) Wetting ridge visualized using X-ray microscopy, showing a sharp ridge tip at the three phase contact line (image ©Park *et al.* [18]).

balance is generally ignored, as the solid that is wetted is assumed to be rigid and any deformation due to this force can be neglected. For soft surfaces, this assumption is no longer valid, as can already be seen in figure 1.3 c, where a vertical deformation at the contact line is visible. This vertical force balance is the source of many interesting phenomena, and as will be the central topic of this thesis, it will be shown to dramatically affect the spreading dynamics as well.

1.2 The wetting ridge

In the 1960-1980s Rusanov, Lester, Shanahan and de Gennes [19–23] first addressed the problem of the vertical force balance on deformable solids. They calculated that elastic solids will deform in to a ridge shape when probed by a line force such as surface tension. Using this Carré *et al.* [15] derived an equation to describe the shape of the wetting ridge h as a function of horizontal position x :

$$h(x) \sim \frac{\gamma \sin(\theta)}{G} \ln\left(\frac{1}{x}\right) \quad (1.2)$$

Here G is the shear modulus of the solid, θ is the liquid contact angle and $\gamma \sin(\theta)$ is the vertical component of the contact line force (figure 1.2 a). We can already see the elastocapillary length $\frac{\gamma}{G}$ appear, which is a length scale that characterizes the size of the wetting ridge. Clearly the result for $x = 0$ is singular, but at an intermediate range this gives a good fit with the shape of the wetting ridge experimentally measured using interferometry, as can be seen in figure 1.4 a. This singularity at $x = 0$, the position of the contact line, is caused by the fact that elastic solids cannot sustain a perfectly localized vertical contact line force. Traditionally, the approach to resolve this issue is to assign a finite width a to compensate for that, allowing the solution to be regularized, predicting that the wetting ridge has a rounded tip. This a represents the width of the contact line force of the liquid surface tension, and is therefore typically 10^{-9}m . This regularization results in a curvature of the solid around the contact line of the order of the size of a .

The proposed microscopical cut-off becomes problematic for very soft gels. Namely, the pressure exerted by the contact line over the width a can become large compared to the shear modulus of the gel. Estimating the capillary stress as $\sigma \sim \gamma/a$ we find a typical value for water of $\sim 70\text{MPa}$. For glass with a modulus of $\sim 70\text{GPa}$ this is not an issue, softer materials can have much lower Young's moduli; such as human skin which has a Young's modulus of $\sim 100\text{KPa}$ [24] and gels that can have a Young's modulus down to the order of 1KPa .

What is happening at the contact line for very soft materials was thus unknown and required experimental examination. In 2008 Pericet-Cámara *et al.* [16] used confocal microscopy to visualize the wetting ridge both outside and under the liquid drop, as can be seen in figure 1.4 b. While these measurements clearly showed the presence of wetting ridge, they still lacked the resolution at a small scale to investigate what happens at the contact line. This changed with the measurement by Jerison *et al.* [17] as shown in figure 1.4 c, who used a confocal microscope to image beads placed at the surface of the gel. This allowed them to obtain an accurate measurement of the static wetting ridge. They observed a sharp tip at the contact line with a finite angle. Park *et al.* [18] later used x-ray microscopy to get a high resolution image of the static wetting ridge, as seen in 1.4 d. This image shows a sharp ridge tip at the contact line, which is evidence of a force balance that is similar to a Neumann balance for liquid liquid interfaces [25]. This points to the possibility that the solid surface of the gel has a surface tension similar to liquids.

In 1996 Long *et al.* [26] already proposed using a solid surface energy penalty to the deformation of the solid. Following this approach, Jerison *et al.* [17] used this added solid surface tension to make a prediction of the wetting ridge shape and compared that to their experiments, as shown with the solid line

in figure 1.4 c. They found that the wetting ridge shape at the contact line is no longer singular using this approach, but exhibits a sharp angle. Later it was demonstrated that the shape of the wetting ridge indeed follows a Neumann balance [27–31]. This leads to the conclusion that the tip of the ridge is governed by a balance of interfacial surface forces, not just in the horizontal direction, but also in the vertical direction.

1.3 Wetting ridge dynamics

While many aspects of the statics of wetting on soft surfaces are starting to be understood, the dynamics of these wetting systems are still barely explored. In the 1980s Shanahan *et al.* [32] already observed that the softer surfaces resulted in slower dynamics. They provided an empirical fit related to the dissipation in the solid, and coined the term ‘viscoelastic braking’ for the slow droplet motion. [14, 33, 34] However, it was still unknown how the rheology of the substrate affects the dynamics, nor what the presence of the wetting ridge meant for any motion of contact lines on deformable surfaces. The dynamics of soft wetting in fact turn out to be very diverse; where the contact line motion can be very slow due to the large dissipation in the solid, or display an irregular stick-slip like motion, as can be seen in figure 1.5 a. Here Kajiya *et al.* [33] showed that the contact line of a drop on a soft surface can make jumps while spreading, leaving behind a static wetting ridge. The image shows the surface immediately after a drop was placed, rapidly inflated – inducing stick-slip – and subsequently removed. The concentric circles visible are remainders of the wetting ridges after the contact line depinned from them, and will disappear over time. By using dip-coating Kajiya *et al.* [35] later were able to use the speed of the contact line as a control parameter. They observed a stick-slip regime where the contact angle makes regular jumps when the contact line slips, as can be seen in figure 1.5 b [35]. While this was correlated with the rheology of the solid, the reasons why the contact line depins from its own wetting ridge remains unknown.

1.4 A guide through this thesis

This thesis will answer key questions about the dynamics of soft wetting, by for the first time looking in detail to the mechanics at the scale of the wetting ridge. Initially we will look at the slow steady state regime, where we will show the intimate relation between the rheology of the solid and the dissipation in contact line dynamics, allowing us to predict the liquid contact angle as a function of contact line speed. In chapter 2 we develop a theoretical prediction

Figure 1.5: Stick-slip dynamics on soft surfaces: (a) Concentric circles showing the remainder of the wetting ridges created by the liquid contact line of a rapidly spreading drop which it subsequently depinned from (image ©Kajiya *et al.* [33]) (b) using dipcoating to impose a constant contact line speed a stick-slip regime is visualized by plotting the contact angle versus time showing regular jumps. (image ©Kajiya *et al.* [35]).

of the shape of the dynamic wetting ridge. This wetting ridge shape allows us to predict the change of liquid contact angle as a function of contact line speed, and validate this prediction experimentally.

In chapter 3 we present a novel experimental setup that allows direct dynamic visualisation of the wetting ridge and uses this to extract wetting ridge shapes as a function of speed. This will validate the predictions made in chapter 2, but also shows a surprising change of the wetting ridge shape at higher contact line speeds. This ridge shape change is characterized by an increase of the solid opening angle, suggesting that the surface tension of the solid is not a constant.

In chapter 4 we further investigate this high speed regime and uncover that this change of shape of the wetting ridge is the key to understanding why the contact line can depin from the wetting ridge it created, explaining the stick-slip regime that was illustrated in figure 1.5.

Finally, we actively manipulate the forces near the contact line by the use of electrowetting in chapter 5. By applying a voltage to the liquid drop a Maxwell stress is exerted near the contact line, deforming both the liquid-vapour and liquid-solid interface. We demonstrate how the softness of the substrate affects the statics and dynamics of electrowetting.

2

Droplets move over viscoelastic substrates by surfing a ridge *

Liquid drops on soft solids generate strong deformations below the contact line, resulting from a balance of capillary and elastic forces. The movement of these drops may cause strong, potentially singular dissipation in the soft solid. Here we show that a drop on a soft substrate moves by surfing a ridge: the initially flat solid surface is deformed into a sharp ridge whose orientation angle depends on the contact line velocity. We measure this angle for water on a silicone gel and develop a theory based on the substrate rheology. We quantitatively recover the dynamic contact angle and provide a mechanism for stick-slip motion when a drop is forced strongly: the contact line depins and slides down the wetting ridge, forming a new one after a transient. We anticipate that our theory will have implications in problems such as self-organization of cell tissues or the design of capillarity-based microrheometers.

2.1 Introduction

Capillary interactions of soft materials are ubiquitous to nature and play a major role in the self-organization of cell tissues [36], e.g. in embryotic development [37, 38], wound healing [39], or spreading of cancer cells [40, 41].

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Not least motivated by this, “soft wetting” [16, 42, 43] recently came to the attention of both, physicists and biologists. Despite its potential for applications, e.g. in the patterning of cells [44] or droplets [14] onto soft surfaces, or the optimization of condensation processes [13], our fundamental understanding especially of the dynamics of soft wetting lags behind by far of what is known about rigid surfaces [6].

Partial wetting of a liquid on a rigid (smooth) substrate is controlled by intermolecular interactions, whose strength is characterized by surface energies [6]. The motion of the three-phase contact line is governed by the viscous dissipation in the liquid. A dissipation singularity arises at the moving contact line [45] and its regularization on the nanoscopic scale can result from various processes [6, 8]. When the substrate is deformable, a sharp ridge forms below the contact line at the edge of the droplet [16, 42, 43]. The ridge geometry (Fig. 2.1a) originates from the coupling between elasticity and surface energy [34, 46–49]. The problem is inherently multi-scale and non-local, even at equilibrium, due to the long-range of elastic interactions [29, 50, 51].

Pioneering experiments have shown that the softness drastically slows down the wetting dynamics [32, 52] as compared to rigid solids. This “viscous braking” has been attributed to a viscoelastic force, as discussed in several recent experimental articles [14, 33]. The theoretical description of moving contact lines over soft solids is so far limited to global dissipation arguments [34], which, at least for wetting of rigid solids, are known not to capture the entire physics behind the process.

In this chapter, the physical mechanism that governs soft wetting dynamics is revealed. We measure the dynamical wetting of small water droplets on a rheologically characterized silicone gel and discover a saturation of the dynamical contact angle for large speeds, associated with a maximum friction force. Driving the contact line motion beyond this maximal force eventually leads to a dynamical depinning where the contact line surfs down the wetting ridge, providing a mechanism for recently observed stick-slip motion [33]. We develop a theoretical framework for dynamical soft wetting, suitable for any substrate rheology. The dynamic wetting angle is calculated from the velocity dependent shape of the deformed solid (Fig. 2.1c). The experimental results are matched quantitatively, including saturation/dynamical depinning. The latter arises from an upper limit of the viscoelastic braking effect, which, by exploring different rheologies, is found to be a robust, universal feature of soft wetting and should thus be relevant far beyond droplets on silicone gels. In addition, the analysis captures recent x-ray measurements on the slow growth of wetting ridges when a drop is deposited on a substrate [18] (Fig. 2.1b).

Figure 2.1: Dynamics of wetting ridges. (a) Equilibrium deformation by a three-phase contact line, inducing a solid contact angle θ_s . The liquid contact angle is denoted θ . (b) Growth of the “wetting ridge” after a drop is deposited. (c) Contact line moving at a velocity V . The motion induces a rotation φ of the wetting ridge and the liquid contact angle, while θ_s remains constant. (d) Dynamical depinning occurs at a critical angle φ_{crit} .

2.2 Results

2.2.1 Experiments.

Experiments were performed using water drops on a silicone gel (cf. methods section for details). This system was previously used in static [28] and transient [18] experiments. Fig. 2.2(a) shows the rheology of this gel; similar data were reported in [53]. The storage G' and loss G'' moduli are related by Kramers-Kronig relation: they originate from the same relaxation function $\Psi(t)$. More precisely, the complex shear modulus obey the relation $\mu(\omega) \equiv G' + iG'' = i\omega \int_0^\infty dt \Psi(t) \exp(-i\omega t)$. A silicone gel is a reticulated polymer formed by polymerizing small multifunctional prepolymers: contrarily to other types of gels, there is no liquid phase trapped inside. Such cross-linked polymer networks exhibit scale-invariance that yields power-law response of the form [23, 34, 54]:

$$\Psi(t) = G \left[1 + \Gamma(1-n)^{-1} \left(\frac{\tau}{t} \right)^n \right], \quad (2.1)$$

where G is a static shear modulus and Γ is the gamma function. The associated complex modulus reads $\mu = G' + iG'' = G[1 + (i\tau\omega)^n]$. The value of n is not universal but depends on the stoichiometric ratio r between reticulant and prepolymer, with n typically between $2/3$ and $1/2$ [55]. The best fit

Figure 2.2: Rheology of the substrate and dynamic contact angle. (a) Storage modulus $G'(\omega)$ (open symbols) and loss modulus $G''(\omega)$ (closed symbols) of the silicone gel. Lines are best fit of $\mu = G[1 + (i\tau\omega)^n]$, giving $n=0.55$, $G=1.2\text{ kPa}$, and $\tau=0.13\text{ s}$. (b) Dynamic angle $\varphi = \theta - \theta_{eq}$ for water on the silicone gel (symbols). Data are averaged over 10 independent experiments, error bars represent the standard deviation. The small v behavior exhibits the same power-law as G'' . Dashed line is the best fit of the asymptote (2.8). Solid line corresponds to (3.18), describing the full range of velocities. The critical angle of depinning $\varphi_{crit} = 39^\circ \pm 3^\circ$, measured separately, is plotted at an arbitrary velocity.

in Fig. 2.2(a) gives an exponent $n = 0.55$. Note that the associated effective viscosity $G''/\omega \sim G(\tau/\omega)^n$ is very large, beyond $10\text{ Pa}\cdot\text{s}$ over the entire frequency domain. This will imply that dissipation mainly occurs in the solid, not in the liquid.

Figure 2.2(b) shows the dynamical angle φ as a function of velocity, both of which are measured while the droplet slowly relaxes over time towards its equilibrium shape (after the injection phase). The resulting φ versus v is not sensitive to the history of the relaxation process, and the dynamics can thus be considered “quasi-steady”. The log-log plot reveals a power-law relation between φ and v at small velocities, with an exponent equal to the rheological

value of $n = 0.55$, within error bars. Such a power-law dependence is similar to previously obtained results [32, 52]. For large velocities, we report a striking saturation of the dynamical contact angle. Neither the small- v power law, nor the saturation, can be explained by dissipation mechanisms in the liquid, and one needs to account for the dissipation within the solid. Long et al. [34] addressed this using a global dissipation argument, based on the solid rheology, but this fails to capture key features such as the saturation.

When the drop is kept inflating with a large over-pressure, we observe a “depinning” of the wetting front, with a sudden increase of its velocity, as the dynamical angle reaches a value $\varphi_{\text{crit}} \approx 39^\circ \pm 3^\circ$. This compares well to the saturation of 37° observed during relaxation (after injection), as indicated in Fig. 2.2. When forcing the contact angle beyond this angle, the contact line dynamically depins from the wetting ridge, surfing it, until a new ridge forms. Note that such a depinning, leading to stick-slip motions, had already been reported in [33, 35]. Our current measurements show that this is a direct consequence of the saturation of the dynamic contact angle.

2.2.2 Theoretical framework.

A liquid drop deposited on a substrate exerts a capillary traction on the surface [42, 56–59]. While the resulting elastic deformation has been computed and measured for static situations [16, 28, 29, 43, 47, 49], the traction becomes time-dependent in the case of dynamical wetting. Here we consider a single straight contact line, for which the elastic problem is two-dimensional. Our goal is to find the deformation of the solid, $h(x, t)$, resulting from the time-dependent capillary traction, $T(x, t)$. For simplicity, we consider the same surface energy γ_s for the wet and the dry parts of the substrate, and assume that there is no Shuttleworth effect: γ_s does not depend on strain [46, 48]. The resulting traction on the solid is then purely normal, and reads $T(x, t) + \gamma_s \partial_{xx} h$, the latter term being the solid Laplace pressure [29, 43, 60, 61]. The theory is rigorous for small slopes $(\partial_x h)^2 \ll 1$, but can be extended in a semi-quantitative way to finite slopes.

The shape of the deformed substrate $h(x, t)$ follows from the normal substrate displacements. Inside a purely elastic material, the displacements adapt instantaneously to changes in the capillary traction; the problem is therefore essentially static. For realistic soft materials, however, the displacements are delayed with respect to the imposed forcing. For small deformations, this is captured by a linear stress-strain rate relation

$$\sigma_{ij}(\mathbf{x}, t) = \int_{-\infty}^t dt' \Psi(t - t') \partial_{t'} \epsilon_{ij}(\mathbf{x}, t') - p(\mathbf{x}, t) \delta_{ij}, \quad (2.2)$$

where Ψ is the relaxation function previously introduced and p is the pressure. Like [34], we apply a Fourier transform with respect to time (noted by “ $\hat{}$ ”):

$$\hat{\sigma}_{ij}(\mathbf{x}, \omega) = \mu(\omega) \hat{\epsilon}_{ij}(\mathbf{x}, \omega) - \hat{p}(\mathbf{x}, \omega) \delta_{ij}, \quad (2.3)$$

The mathematical problem defined by mechanical equilibrium, $\nabla \cdot \hat{\sigma} = 0$, the constitutive relation (2.3) and the traction at the free surface is identical to the static problem, but features dependences on the frequency ω . The time-dependent traction can therefore be solved analogously to [29, 43, 51], by an additional spatial Fourier transformation (noted by “ $\sim$ ”):

$$\hat{h}(q, \omega) = \frac{\hat{\hat{\mathcal{G}}}(q, \omega) \hat{T}(q, \omega)}{1 + \gamma_s q^2 \hat{\hat{\mathcal{G}}}(q, \omega)}, \quad (2.4)$$

where q is the wavenumber. The Green’s function $\hat{\hat{\mathcal{G}}}(q, \omega)$ is the product of the time kernel $\mu(\omega)^{-1}$ by the space kernel $K(q)$. For an incompressible layer of thickness h_0 [62] it is

$$K(q) = \left[\frac{\sinh(2qh_0) - 2qh_0}{\cosh(2qh_0) + 2(qh_0)^2 + 1} \right] \frac{1}{2q} \quad (2.5)$$

Left-right symmetry and volume conservation are reflected by $K(q) = K(-q)$ and $K(0) = 0$. Sharp features in the solid profile, like the solid contact angle, are found in the large q asymptotics for which $K(q) \simeq (2|q|)^{-1}$.

2.2.3 The moving contact line.

We now apply our theory to a contact line moving at a constant velocity v , which induces a traction

$$T(x, t) = \gamma \sin \theta \delta(x - vt). \quad (2.6)$$

This reflects the normal force per unit contact line that is exerted by the liquid on the solid, while θ is the liquid angle at the location of the cusp. For simplicity we consider that the drop size is much larger than the substrate thickness, in which case the Laplace pressure inside the liquid can be neglected [28]. We indeed verified that the finite drop size has a negligible influence on the resulting motion: the relevant scale for the dynamics is the size of the ridge γ_s/G , which is much smaller than the drop size. This also justifies a two-dimensional model. Another important simplification comes from the quasi-steady nature of the droplet relaxation: temporal changes of contact angle and contact line velocity are small in our experiments ($d\theta/dt \ll \tau^{-1}$), so that the process can be modeled by a constant velocity.

According to (2.4), the capillary traction induces a wetting ridge moving at a velocity v (cf. methods section):

$$\tilde{h}(q) = \frac{\gamma \sin \theta}{\gamma_s} \left[q^2 + \frac{\mu(qv)/\gamma_s}{K(q)} \right]^{-1}, \quad (2.7)$$

in the comoving frame. In real-space this gives profiles such as shown in Fig. 2.1(c). The motion induces a left-right symmetry breaking: the asymmetric deformation of the solid results in a tilt angle $\varphi(v)$ of the cusp. Since the liquid is close to equilibrium, because the dominant dissipation takes place inside the solid, the change in the solid angle φ directly yields a change in the liquid angle θ (Fig. 2.1d). Hence $\theta = \theta_{\text{eq}} + \varphi$, where θ_{eq} is the equilibrium liquid angle by Neumann's law. The liquid contact angle θ gets deviated away from θ_{eq} due to the viscoelastic forces in the substrate.

Fig. 2.2(b) shows the calculated tilt curve for the gel used in experiments. It predicts not only the power-law behavior at low velocity, but also presents a saturation of the tilt angle. The tilt angle quantifies the velocity-dependent viscoelastic force between the solid and liquid phases. For a well-established moving ridge, it behaves as a resistive force increasing with the velocity. When the drop is forced to inflate with a driving force larger than the maximal braking force, the contact line can no longer remain “pinned” to the steadily moving solid ridge and surfs the gel wave. To investigate further the relation between the tilt φ and the substrate constitutive relation, we use the gel-rheology (3.30), and expand (3.18) in the small v asymptotics (and hence small φ i.e., $\sin \theta \approx \sin \theta_{\text{eq}}$), which gives (cf. methods section):

$$\varphi = \frac{2^{n-1}n}{\cos(n\pi/2)} \frac{\gamma \sin \theta}{\gamma_s} \left(\frac{v}{v^*} \right)^n, \quad (2.8)$$

where the characteristic velocity scale emerges as $v^* = \gamma_s/(G\tau)$. Note that the outer length scale (thickness of substrate) does not appear. This expression can be simply interpreted. At vanishing response time τ , a deformation matching the static ridge would propagate at a velocity v , pushing the substrate material up and down at a characteristic frequency ω equal to the velocity v divided by the characteristic width of the ridge $\sim \gamma_s/G$. The perturbation introduced by a finite τ is encoded by the loss modulus $G''(\omega)$. As the characteristic strain is set by the slope of the ridge $\sim \gamma \sin \theta / \gamma_s$, one obtains dimensionally Eq. (2.8). The scaling law $\varphi \propto (v/v^*)^n$ thus simply carries over the low frequency behavior $G''(\omega) \propto \omega^n$, which is a robust mechanism valid beyond the small slope approximation of our theory. At small v (small ω), dissipation will dominantly occur in the solid because $n < 1$, while the loss modulus of a newtonian liquid $G''_{\text{liq}} \propto \omega$.

In contrast to the tilt angle φ , we find that the solid angle θ_s does not depend on v . This result can be derived analytically from the large- q asymptotics of (3.18), $\tilde{h} \simeq \frac{\gamma \sin \theta}{\gamma_s} q^{-2}$, valid for all v and arbitrary $\mu(\omega)$. In real space, this implies a slope discontinuity

$$\theta_s \simeq \pi - \gamma \sin \theta / \gamma_s, \quad (2.9)$$

which is the small-slope limit ($\gamma/\gamma_s \ll 1$) of Neumann's contact angle law. Physically, (2.9) reflects that θ_s is determined by surface tensions only [43, 47, 63]: bulk viscoelastic stresses are not singular enough to contribute to the contact angle selection. This feature remains true for arbitrary angles [29]. In order to match Neumann's law quantitatively, our theory must be corrected at large slopes to take geometric nonlinearities into account. This can be achieved phenomenologically in (2.4) by replacing $\gamma_s \rightarrow \sqrt{\gamma_s^2 - \gamma^2/4}$. Indeed, the Neumann condition for $\theta = 90^\circ$ reads $2\gamma_s \sin \alpha = \gamma$, where α is the angle of the solid interface with the horizontal. Small-slope theory gives $2|h'| = 2 \tan \alpha = \frac{\gamma}{\gamma_s}$, and hence lacks a factor $\cos \alpha = \sqrt{1 - (\gamma/2\gamma_s)^2}$.

For the first time, we reveal that the exponent of the dynamical contact angle directly originates from the gel rheology. The rheological parameters being calibrated independently, the dynamic contact angle can be fitted to the model to extract the solid surface tension. Using Eq. (2.8), which is valid for small slopes, we find $\gamma_s = 16 \text{ mN/m}$. This is a reasonable value, though a bit lower than the value previously derived from Neumann's law [28]. We think this difference can be attributed to the small-slope nature of our theory: condering the phenomenological correction for large slopes gives a value $\gamma_s = 39 \text{ mN/m}$, in close agreement with [28]. The solid line in Fig. 2.2(b) shows the prediction from (3.18), providing an excellent description over the full range of velocities. The model captures also the saturation, though the value for φ_{crit} is slightly overestimated.

2.2.4 Depinning and growth of a new wetting ridge.

How can the contact line escape pinning, without dragging the capillary wedge along with it? To answer this question, let us consider the recent experiments investigating the growth of a wetting ridge after depositing a droplet on a silicone gel [18]. The substrate was observed to only very slowly establish the final shape of the wetting ridge – such a delay in growth (or decay) of wetting ridges would explain how a sufficiently rapid contact line could escape from the ridge. However, the solid angle θ_s (cf. Fig. 2.1a) appeared very quickly and remained constant during the entire growth of the ridge [18].

These features of ridge growth can all be explained by considering our theory for a traction that is suddenly imposed at the time of deposition ($t = 0$),

Figure 2.3: Relaxation of the central height of the wetting ridge after drop deposition. The curves show the approach to equilibrium height, $h_\infty - h$ at $x = 0$, for two rheologies: (a) Power-law rheology ((3.30) with $n = 1/2$) and (b) standard linear model, $\beta = 300$ ((2.11), see inset). The dimensionless substrate thickness for these plots was $\gamma_s/(Gh_0) = 0.5$.

so that

$$T(x, t) = \gamma \sin \theta \delta(x) \Theta(t) \quad (2.10)$$

where θ is the liquid contact angle and $\Theta(t)$ is the Heaviside step function. Combining this traction with (2.4), one can compute the resulting $h(x, t)$ for any rheology $\mu(\omega)$. An example of the evolution of the wetting ridge is shown in Fig. 2.1(b). A movie is given in the Supplementary material (Supplementary Movie 1).

First, the theory recovers the experimental finding that θ_s is constant at all times. As for the moving contact line, this result can be derived analytically from the large- q asymptotics of (2.4), which again results in Eq. (2.9): the asymptotics are independent of the rheology and the history of the traction, but entirely governed by the surface tensions.

Second, the theory explains why, contrarily to the rapid appearance of θ_s , the global shape of the ridge evolves much more slowly. Figure 2.3 shows the evolution of the central height of the ridge, $h(x = 0)$, towards its static value h_∞ , for the two idealized rheological models. The relaxation towards the equilibrium height is algebraic for the gel model, with an exponent directly following that of rheological relaxations (Fig. 2.3(a), as $t^{-1/2}$ for $n = 1/2$). This clarifies the complex evolution of the wetting ridge of the silicone gel in [18]: small-scale characteristics like θ_s are dominated by surface tension and relax quickly, while large scale features inherit the relaxation dynamics from the bulk rheology. This means that immediately after depinning, where the contact line exhibits a rapid motion, the solid cusp cannot adapt quickly. The liquid will slide down the wetting ridge, which appears “frozen” on the timescale of the depinning. During this phase it is clear that the liquid dynamics will be important – still, the onset of the depinning can be explained quantitatively

Figure 2.4: Cusp tilt for standard linear model. Solid lines: numerical results; dashed lines: analytical approximation (2.14). The upper bound for the viscous braking force is robust with respect to the details of the rheology.

without invoking the fluid dynamics inside the liquid, because the saturation angle $\varphi_{\max}$ coincides with the observed depinning angle φ_{crit} [Fig. 2.2(b)].

2.2.5 Robustness and interpretation.

The theory can be applied to any viscoelastic substrate, assuming that it is probed in the linear regime. Generic reticulated polymer networks possess a long time entropic elasticity [64, 65], that is characterized by a static shear modulus G . Such networks become viscoelastic when excited over time-scales shorter than a certain response time τ . In order to investigate the robustness of the phenomenology that was observed experimentally and reproduced quantitatively by our model, we will consider a different rheological limit. When cross-linking long polymer chains, one forms an elastomer rather than a gel. Assuming a single (Rouse) timescale τ to characterize the onset of entanglements, the rheology can be idealized as [23, 34, 65]:

$$\Psi(t) = G(1 + \beta e^{-t/\tau}). \quad (2.11)$$

This single timescale response is also referred to as standard linear model and has frequently been used to describe the transition from rubber to glass behaviors. In general, several relaxation times must be introduced to capture quantitatively the rheology of actual elastomers.

The wetting ridge relaxation, which follows the rheological relaxation, becomes exponential for the standard linear model (Fig. 2.3b). The case of a moving contact line with the rheology (2.11) is given by the solid lines in figure 2.4, showing the tilt curves for various parameters β . As for the gel

case, the tilt has an upper bound and this therefore appears a robust feature of soft wetting. Note that the maximum depends on γ/γ_s and β (or n for the gel case), illustrating that the value of $\varphi_{\max}$ will in general depend on the details of the rheology (e.g. $\varphi_{\max}$ in [33] is much smaller than in the presented experiments). The dynamic contact angle for a standard linear solid can actually be captured in a simple analytical form. For this we consider the limit $\beta \rightarrow \infty$ while keeping $\tau' \equiv \beta\tau$ constant – this corresponds to the Kelvin-Voigt model with a frequency-independent effective viscosity $\eta = G\tau'$. Intriguingly, this limit turns out to be singular: the high-frequency behaviour of (2.11) becomes purely viscous and gives a non-integrable singularity of the dissipation. This singularity could already be anticipated from (2.8), since the Kelvin-Voigt rheology has $G'' \sim \omega^1$, while (2.8) presents a divergence for $n = 1$.

In fact, this viscoelastic singularity is the soft-solid analogue of the classical Huh & Scriven-paradox for viscous contact line motion [45]. This is demonstrated from the large- q asymptotics of (3.18) in the Kelvin-Voigt limit, giving a slope close to the contact line (cf. Supplementary Note 1):

$$\partial_x h \simeq -\frac{\gamma \sin \theta}{2\pi\gamma_s} \left(\frac{|x|/x - 4(\gamma E + \ln|x|/h_0) v/v^*}{1 + 4(v/v^*)^2} \right), \quad (2.12)$$

with $\gamma E = \text{Euler's constant}$ and $v^* = \gamma_s/(G\tau')$. This expression reveals a logarithmic divergence of the slope, in perfect analogy to the Cox-Voinov result for liquid contact lines [66, 67].

Contrarily to the viscous-liquid singularity, the presence of an instantaneous elastic response, i.e. a finite value of β , is sufficient to regularize the divergence. This is illustrated in Fig. 2.5, which shows the slope ahead of the moving contact line as a function of the distance to the contact line. The dashed line corresponds to the Kelvin-Voigt limit (2.12), showing the logarithmic steepening of the slope. For finite β , the slope saturates upon approaching the moving contact line. The saturation wavenumber is found $q' \sim (v\tau)^{-1}$, which corresponds to a length

$$\ell = \tau v. \quad (2.13)$$

ℓ is a dynamical regularization length that depends linearly on the velocity of the contact line; for $v \sim \mathcal{O}(1)$ this scale is still much smaller than the substrate thickness, by a factor β^{-1} . The physical origin of the regularization lies in the instantaneous elasticity in the high-frequency limit, which applies at frequencies beyond $\sim \beta\tau$.

Inserting the regularization length into the Kelvin-Voigt limit (2.12), we identify the tilt and get an analytical expression of the dynamic liquid contact angle (the strict validity of the analysis requires small slopes, i.e. small φ ; we

Figure 2.5: Logarithmic variation of the profile slope. $\partial_x h$ is plotted as a function of the distance to the contact line. Different curves correspond to different instantaneous relaxation moduli βE , for identical dimensionless velocity $v = 1$. In the limit $\beta \rightarrow \infty$ (the Kelvin-Voigt solid), the slope diverges logarithmically at the contact line. For finite β , the slope saturates at a regularization length given by (2.13).

therefore replaced $\sin \theta = \sin(\pi/2 + \varphi) \simeq 1$):

$$\theta = \theta_{\text{eq}} + \frac{2}{\pi} \text{Ca}_s \ln \left(\frac{h_0}{e\gamma^E \ell} \right). \quad (2.14)$$

This result is analogous to the Cox-Voinov law [66, 67] in partial wetting of viscous fluids. In that case a similar logarithmic factor linking microscopic and macroscopic scales appears, for arbitrary contact angles [67], and the resulting expression for small Ca is of the form (2.14). Interestingly, the analysis reveals that the relevant dimensionless velocity for soft wetting is not the classical liquid capillary number $\text{Ca} = v\eta_\ell/\gamma$, based on the liquid viscosity η_ℓ , but the “solid capillary number”

$$\text{Ca}_s = \frac{vG\beta\tau\gamma}{\gamma_s^2}. \quad (2.15)$$

Equation (2.14) closely follows the numerical results (Fig. 2.4(d), dashed and solid lines, respectively). The moving contact line singularity is avoided altogether when G'' has an exponent $n < 1$, as was the case for the power-law gel, in perfect analogy to shear-thinning fluids moving on a rigid substrate.

2.3 Discussion

We have shown how contact lines can surf on a wetting ridge, and that this governs the remarkable spreading of drops on viscoelastic substrates. We have quantified this dynamics by measuring the dynamic contact angle of water on

a PDMS gel for a wide range of velocities and described, for the first time, a saturation of the dynamical angle for large velocities. This saturation is in harsh contrast to wetting dynamics of rigid solids and leads to depinning, where the contact line slides down the ridge until a new wetting ridge has had time to grow and sustain a steady motion – hence, explaining the remarkable stick-slip motion [33] found recently on soft solids. We develop a theory that identifies a robust maximum in viscous braking force that correctly predicts the onset of dynamical depinning. In addition, our theory captures the unsteady growth of a wetting ridge [18]. This work provides a framework for viscoelasto-capillary dynamics valid beyond droplets, and should be applicable e.g. within a biological context. It also opens a new perspective where droplets can be used droplets as Microrheometers, since I) the length scales probed by the droplets is given by the elastocapillary length i.e., a few microns, and II) the tilt saturation occurs at velocities that are directly related to the relaxation timescale.

2.4 Appendix: Methods

2.4.1 Wetting experiments.

The silicone gels (Dow Corning CY52-276) are prepared by curing the mixed components onto glass slides, yielding 0.8 mm thick substrates. The rheology was determined using a MCR 501 rheometer (Anton Paar). Dynamic contact angles were measured using droplets of MilliQ water dispensed from a clean Hamilton syringe. First, a small droplet ($\approx 2...20\mu\text{l}$) was placed onto the substrate, leaving the syringe needle attached to the droplet. Then, the contact angle of the droplet was increased by quickly injecting water ($\approx 3...20\mu\text{l}$ with $\approx 2...8\mu\text{s}^{-1}$) to it. After the injection phase the drop relaxes quasi-statically, causing the contact line velocity to decay slowly. The advancing motion of the contact line and the relaxation of the contact angle were imaged at 50 Hz with a long distance video microscope. The droplet contour was extracted with sub-pixel resolution, and velocities down to nm/s could be detected. The measured contact angles were translated to tilt angles φ by subtracting $\theta_{\text{eq}} \approx 106^\circ \pm 1^\circ$.

2.4.2 The moving contact line

Fourier transforming (2.6) from x to q and from t to ω preserves the δ -shape of the traction:

$$\hat{\hat{T}}(q, \omega) = 2\pi \gamma \sin \theta \delta(\omega - vq). \quad (2.16)$$

Inserting the above into Eq. (2.4), the inverse transform to the time domain yields

$$\tilde{h}(q, t) = \frac{\gamma \sin \theta}{\gamma_s} \left[q^2 + \frac{\mu(vq)}{K(q)} \right]^{-1} e^{iqvt}. \quad (2.17)$$

The only explicit time dependence appears in the phase factor that shifts the profile in x -direction linearly with time. The transformation to the co-moving frame is done by multiplication with e^{-iqvt} , which cancels the only explicit time dependence, and one obtains Eq. (3.18).

The slopes are evaluated by multiplication with $-iq$ prior to the inverse transform (in the co-moving frame):

$$h'(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} (-iq\tilde{h}(q)) e^{-iqx} dq. \quad (2.18)$$

$h'(x)$ is a real function because $\Re[-iq\tilde{h}(q)] = \Re[iq\tilde{h}(-q)]$ and $\Im[-iq\tilde{h}(q)] = -\Im[iq\tilde{h}(-q)]$. $h'(x)$ can be split into a symmetric and an antisymmetric part, where the symmetric part is given by the inverse transform of the real part of $iq\tilde{h}(q)$:

$$\frac{1}{2} (h'(x) + h'(-x)) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \Re[-iq\tilde{h}(q)] e^{-iqx} dq, \quad (2.19)$$

The antisymmetric part is obtained from the imaginary part:

$$\frac{1}{2} (h'(x) - h'(-x)) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \Im[-iq\tilde{h}(q)] e^{-iqx} dq. \quad (2.20)$$

The solid angle θ_s is given by the (antisymmetric) slope discontinuity at $x = 0$ and is thus encoded in the backward transform of the imaginary part. The discontinuity is caused by the large- q asymptotics alone. If $\mathcal{O}(\mu(vq)) < \mathcal{O}(q)$, which is the case for the exponential- and power law ($n < 1$) relaxation (but not for the Kelvin-Voigt model), it is independent of rheology:

$$\begin{aligned} & \lim_{x \rightarrow 0^+} h'(x) - \lim_{x \rightarrow 0^-} h'(x) \\ &= \frac{1}{\pi} \left(\lim_{x \rightarrow 0^+} \int_{-\infty}^{\infty} \frac{-i\gamma \sin \theta}{\gamma_s q} e^{-iqx} dq \right) = -\frac{\gamma \sin \theta}{\gamma_s}. \end{aligned} \quad (2.21)$$

The rotation of the wetting ridge is given by the symmetric part of $h'(x)$ and thus obtained by the backward transform of the real part, evaluated at $x = 0$:

$$\begin{aligned} \tan \varphi &= \lim_{x \rightarrow 0} \frac{1}{2} (h'(x) + h'(-x)) \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} \Re[-iq\tilde{h}(q)] dq \end{aligned} \quad (2.22)$$

With the symmetry property $K(q) = K(-q)$, and small, positive v , Eq. (3.20) simplifies to (primes omitted):

$$\varphi = \frac{\gamma \sin \theta}{G} \frac{\sin^{n\pi/2}}{\pi} \int_0^\infty \frac{q(qv\tau)^n K(q)}{((\gamma_s/G)q^2 K(q) + 1)^2} dq. \quad (2.23)$$

In the limit of thick elastic layers, $K(q) = (2|q|)^{-1}$. After non-dimensionalizing the integration variable as $q' = \frac{\gamma_s}{G}q$, one obtains (primes omitted):

$$\begin{aligned} \varphi &= \frac{\gamma \sin \theta}{\gamma_s} \left(\frac{v}{\gamma_s/(G\tau)} \right)^n \frac{\sin^{n\pi/2}}{2\pi} \int_0^\infty \frac{q^n}{(q/2 + 1)^2} dq \\ &= \frac{2^{n-1}n}{\cos^{n\pi/2}} \frac{\gamma \sin \theta}{\gamma_s} \left(\frac{v}{v^*} \right)^n, \end{aligned} \quad (2.24)$$

where $v^* = \gamma_s/(G\tau)$ is the characteristic velocity.

2.4.3 Growth of a wetting ridge.

Here we give the full derivation of the time-dependent wetting ridge shape after the deposition of a droplet. We only discuss the result for the exponential relaxation model. An analogous calculation can be performed for the power-law relaxation.

In the following, we non-dimensionalize x with h_0 , q with h_0^{-1} , t with $\beta\tau$, ω with $(\beta\tau)^{-1}$, and h with $\gamma \sin \theta / G$. With this scaling, the Fourier transform of the time-kernel for exponential relaxation (2.11) reads

$$\mu(\omega) = G \left(1 + \frac{\omega}{\omega/\beta - i} \right). \quad (2.25)$$

The space kernel in scaled variables is

$$\kappa(q) = \frac{K(q)}{h_0} = \left[\frac{\sinh(2q) - 2q}{\cosh(2q) + 2q^2 + 1} \right] \frac{1}{2q}. \quad (2.26)$$

The traction Eq. (2.10) is transformed to

$$\hat{T}(q, \omega) = \frac{\gamma \sin \theta}{h_0} \left(\frac{i}{\omega} + \pi \delta(\omega) \right). \quad (2.27)$$

Equations (2.16), (2.17), and (2.18) are inserted into the general expression Eq. (2.3), which yields:

$$\hat{h}(q, \omega) = \frac{\left(\frac{i}{\omega} + \pi \delta(\omega) \right)}{\left(1 + \frac{\omega}{\omega/\beta - i} \right) \kappa(q)^{-1} + \alpha_s q^2}, \quad (2.28)$$

with the dimensionless parameter $\alpha_s = \gamma_s/(Gh_0)$. α_s compares the elastocapillary length for the solid surface tension to the layer thickness h_0 . The inverse Fourier transform to the time-domain yields

$$\tilde{h}(q, t) = \frac{1 - \frac{\beta \exp\left[-\frac{1 + \alpha_s q^2 \kappa(q)}{1 + \beta + \alpha_s q^2 \kappa(q)} \beta t\right]}{1 + \beta + \alpha_s q^2 \kappa(q)}}{\kappa(q)^{-1} + \alpha_s q^2}. \quad (2.29)$$

Fourier transformation to real space is performed numerically.

Spreading on viscoelastic solids: Selection of contact angles *

The spreading of liquid drops on soft substrates is extremely slow, owing to strong viscoelastic dissipation inside the solid. A detailed understanding of the spreading dynamics has remained elusive, partly owing to the difficulty to assess the strong viscoelastic deformations below the contact line. Here we present direct experimental visualisations of the dynamic wetting ridge, as the contact line moves over a soft viscoelastic gel. The experiments reveal that the wetting ridge exhibits a rotation that increases with the contact line speed. It is shown that this ridge rotation angle is responsible for the change in liquid contact angle of the liquid with velocity – as was hypothesized in chapter 2 and here corroborated further by a dissipation analysis. However, we identify several experimental features that are not captured by current models. Based on this we provide a critical overview of the commonly used approximations, and point out the steps needed towards a more complete description for spreading on viscoelastic solids.

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3.1 Introduction

The mechanical properties liquids and polymeric solids near an interface are fundamental to nanometer scale devices, with applications in tribology and lubrication, transport across membranes, nanofluidic devices, and biological systems. However, it has remained a challenge to characterise the interfacial mechanics of soft solids [68, 69]. It has been proposed recently that liquid drops can serve as an effective tool to quantify the interfacial mechanics [28, 70, 71]. Namely, droplets act on the solid with an extremely localised traction, probing the nanoscale, since molecular interactions are localised over the thickness of the interface. The droplets deform the soft solid into a “wetting ridge” that moves along with the contact line, and thus also probe the viscoelastic response of the polymer [21, 26]. It has been shown that the response of nanometer scale polymers grafted or adsorbed at a surface presents a scaling law consistent with the picture emerging from statistical physics [72]. However, in order for droplets to be fully useful as a rheological tool, one must have a perfect theoretical understanding of the processes at work.

Spreading drops and contact line motion have been extensively studied on rigid surfaces [2, 6, 8]. Detailed hydrodynamic analysis has demonstrated how the liquid interface is affected by contact line motion [66, 73, 74]. This leads to dynamic (macroscopic) contact angles, which differ from the equilibrium angles and which depend on the contact line velocity. This intricate mechanics has been compactly summarized via a dissipation analysis [2, 75], balancing the power injected by capillary forces with the dissipation in the vicinity of the contact line. These mechanical and dissipation approaches were shown to be strictly equivalent [6], though the expressions for the dynamic contact angle can appear slightly different due to different levels of mathematical approximations. The spreading of drops over soft surfaces was first addressed in a series of papers by Carré & Shanahan [15, 32, 76], and by Long, Ajdari & Leibler [26]. The main observation is that contact line motion is slowed down dramatically as compared to spreading over rigid surfaces. This slowing down can be attributed to the strong dissipation in the polymer layer, and was termed “viscoelastic breaking”. From a modeling perspective, the dynamic contact angles were estimated using a dissipation approach [15, 26].

In recent years there have been major advances on the wetting of soft substrates [77, 78]. A variety of experimental methods have provided detailed information on the wetting ridge below the contact line [15, 16, 18, 70, 79], complemented by theoretical developments [15, 17, 19–23, 26–31]. The typical size of the wetting ridge is given by the ratio of surface tension of the drop γ and the substrate’s shear modulus G , which defines the elastocapillary length γ/G . A striking feature is that, at equilibrium, the ridge satisfies the Neumann

Figure 3.1: (ab) Soft wetting at equilibrium. (a) Zoom of the wetting ridge near the contact line on the scale of the elastocapillary length γ/G . The profile is computed from linear response theory, where we define the liquid angle θ and the solid angle θ_s . (b) Experimental side view image of a static drop. (cd) Soft wetting dynamics. (c) When the contact line is moving, the viscoelasticity of the substrate leads to a rotation of the wetting ridge by an angle φ (again computed from linear response). (d) Experimental side view image of a spreading drop, which exhibits a dynamic contact angle θ .

law: similar to liquid interfaces, the surface tension of the solid balances the traction imposed by drop. This gives rise to a well-defined solid angle, defined as θ_S in figure 3.1(a). While at equilibrium Neumann's law can be derived from energy minimisation [29, 80], there is no consensus as to whether it is valid for wetting dynamics [81, 82]. In a previous chapter 2 we hypothesised that the dynamic liquid angle is selected by a rotation of the wetting ridge, while maintaining the Neumann angles for the geometry of the wetting ridge. This mechanism is sketched in figure 3.1(c), where the liquid angle θ follows the ridge rotation over an angle φ . However, this point of view was challenged by Zhao *et al.* [83], claiming that the dissipation-based theory implies that Neumann's law is not valid in dynamical situations.

An additional complexity to the problem, which arises even under static conditions, is that the surface tension of a solid interface is not constant. Owing to the so-called Shuttleworth effect [77, 78, 84], the surface energy depends on the amount of surface strain. At equilibrium this strain dependence was recently confirmed [70, 71, 80], giving rise to variations of the solid angle θ_S . Similar variations of the ridge geometry have been reported in dynamical experiments in chapter 4 and [49], though a systematic analysis of all the contact angles is still lacking.

With this chapter we aim to address a series of unresolved issues, which naturally emerge from these recent experimental and theoretical developments. These are centred around question on how the contact angles are selected during the spreading of drops over viscoelastic substrates. Is Neumann's law still applicable in dynamical conditions? Is the change of the liquid angle directly associated with a rotation of the wetting ridge? To what extent can these relations be derived from a power balance or from a stress balance, and are these approaches equivalent? Finally, how is the dynamics affected by the Shuttleworth effect? The chapter starts off with detailed experiments, where we quantify the dynamic contact angles from direct visualisation of the wetting ridge. The experimental method is described in Sec. 3.2, while the results are presented in Sec. 3.3. After summarising our findings, Sec. 3.4 provides a critically review of the state of the art modelling approaches, and point out the steps needed towards a more complete description for spreading on viscoelastic solids. The chapter closes with a discussion in Sec. 3.5.

3.2 Experimental set-up

We experimentally investigate the dynamical behavior of wetting ridges formed by moving contact lines. Our specific aim here is to determine the angles that describe the local geometry of the three-phase region: the liquid angle

θ , the solid angle θ_S , and rotation of the ridge φ (see Fig. 3.1). Due to the topography of the wetting ridge it is challenging to resolve the solid angles with sufficient accuracy. Here we design an experimental setup that allows for a direct visualisation of the wetting ridge with unprecedented spatio-temporal resolution (see Sec. 3.2.1). The liquid angle is measured in a separate experiment using a classical drop-on-planar-substrate geometry (Sec. 3.2.2).

3.2.1 Visualizing the wetting ridge

The visualization of the wetting ridge is performed with the setup sketched in figure 3.2a. The idea is to create a nearly cylindrical cavity inside a square block of a soft viscoelastic substrate material. The cavity can then be filled partially with water, creating a single moving contact line that exerts an inward-pointing capillary traction onto the substrate. This deforms the cavity surface into an axisymmetric wetting ridge with a cross-section that is virtually identical to a wetting ridge on a planar surface as long as the radius of the cavity is much larger than the ridge. In this configuration the wetting ridge can be imaged shadowgraphically through the planar faces of the square block, thus minimizing any optical distortions.

The liquid used in the experiments is deionized water. For the polymer gel we have chosen two different reticulated polymer networks: a polydimethylsiloxane (PDMS) gel (Dow Corning CY52-276 mixed at a 1.3:1 (A:B) ratio), and a polyvinyl siloxane (PVS) gel (Esprit Composite RTV EC00 mixed at 1:2.5 (base:catalyst) ratio). Both are referred to as gels, in the sense that they cross a gelation transition during the curing, at which the system presents a vanishing shear modulus and a diverging viscosity at low frequencies. Both gels are prepared such that their static shear modulus after curing is around $G = 400$ Pa. For details on the viscoelastic rheology we refer to Appendix 3.6.1. The elastocapillary length is then around $\gamma/G = 180 \mu\text{m}$, and leads to relatively large wetting ridges that are comfortably measurable.

The cylindrical cavity is created by the following procedure. We first fill a standard spectroscopy cuvette (with inner dimensions of $1 \times 1 \times 4.5$ cm) with uncured but mixed and degassed liquid components of the gel, leaving enough air volume for a cylindrical cavity to form, and seal the open end of the cuvette. The cuvette is then spun at ≈ 100 RPS about its long axis, such that the centrifugal forces turn the air volume into nearly cylindrical cavity extending to the bottom of the cuvette. We verify that the radius of the cavity (typically 4 mm) is constant within the measurement section (~ 2 mm). The diameter of the cavity and the gel thickness are much larger than the elastocapillary length (γ/G), while the Bond number ($\Delta\rho GL^2/\gamma$) remains low to keep the effect of gravity negligible. The gel is cured while spinning at room

Figure 3.2: (a) A rectangular cuvette filled with transparent gel with a cylindrical cavity is observed perpendicular to the sidewall as the cavity is filled with water from the bottom. A backlight illuminates the cuvette through a diffuser plate. (b) Logarithmic fits of the gel shape on either sides of the contact line are used to find the ridge tip and the contact angles. (c) Example of a static wetting ridge (left), and a dynamic ridge from which we determine the rotation angle φ (right). In the latter case, the contact angle moves to the right.

temperature for ~ 14 hours. For the PDMS gel, the cuvette is additionally heat cured afterwards in an oven at 80 degrees for two hours.

The gel surface is observed shadowgraphically using a long distance video microscope perpendicular to the cuvette wall, focused on the diametral plane of the cavity. The cuvette is illuminated with diffuse light from the back (figure 3.2). The cavity reflects and refracts light while the bulk gel is transparent. Thus the gel appears bright, and the cavity dark. Then the cavity is partly filled with MilliQ water. The capillary deformation caused by the water meniscus can be directly observed, with a spatiotemporal resolution limited only by the optical properties of the shadowgraphy setup. In these experiments a 2-4x lens is used, leading to a pixel scale of $\approx 2\mu\text{m}$ per pixel and a field of view of about 2.2×1.6 mm. The images were recorded with a CMOS camera at rates of 2 to 52 frames per second.

The gel interface profile is detected with sub-pixel accuracy by fitting the greyscale profile in the vertical direction by an error function, locating the interface at its inflection point. The tip of the wetting ridge is rounded in our measurement due to the diffraction limit of the shadowgraphy setup. The typical radius of curvature detected for the blurred image of the ridge tip is about $2 - 3 \mu\text{m}$, independent of the imaging scale. The ridge is found to be sharp on the order of the width of the contact line with a well defined opening angle θ_s , as observed previously by X-ray microscopy [18, 79].

To extract the relevant angles we extrapolate the surface profiles both sides into the diffraction limited region at the ridge tip. Because the elastic response to a point force is known to be logarithmic at large distance, we use a least squares fit of a generic logarithm function $f = a + b\log(c + x)$ to the left and right of the contact line, as shown in figure 3.2b. The intersection of the extrapolated logarithmic fits is used to measure the solid opening angle (θ_s) and the relative rotation angle (φ). The latter is defined as the angle between the horizontal and the bisector of the two profile fits (figure 3.2c). As long as the change in solid opening angle is small, or the change in θ_s is symmetric for the liquid and vapor-sides of the gel, this gives an accurate measurement of the ridge rotation φ . A linear regression on the horizontal position of the intersection is used to measure the contact line speed.

The experiments using 2 fps allow us to measure very slow dynamics, where the experiments were run for approximately 10 minutes. The gradual deceleration of the contact line allowed us to resolve velocities down to ~ 1 nm/s. While the PDMS gel is optically clear, the PVS gel is slightly opaque, resulting in a reduced contrast of the wetting ridge. Within our subpixel resolution scheme, this can be partially corrected for, yet the measurements on the PVS gel have a slightly lower precision.

3.2.2 Liquid contact angle

The liquid contact angle measurements are performed with a DataPhysics OCA 15 apparatus. A $\sim 10 \mu\text{L}$ drop is deposited on a 12 mm thick gel layer and the droplet volume is quickly increased to $\sim 20 \mu\text{L}$. After this increase, the droplet relaxes toward its equilibrium wetting configuration. All measurements presented here are performed during this overdamped relaxation phase, governed by the dissipation in the viscoelastic substrate. The liquid contact angle θ and contact line speed are determined from the recorded video by using a sub-pixel resolution edge detection in MATLAB. The edge detection scheme uses a threshold value for the pixel scale edge detection and a linear interpolation around the edge to find the sub-pixel position. The speed is deduced from the variation of the contact line position, with a resolution down to $\sim 1 \text{ nm/s}$. To obtain the relative rotation angle $\theta - \theta_{eq}$, the contact angle θ_{eq} was determined at vanishing speed.

3.3 Experimental results

3.3.1 Phenomenology

Before coming to detailed measurements of the contact angles, let us first describe the types of wetting dynamics that are observed in our system, and relate this to previous observations in the literature.

In figure 3.3a we show a typical experimental result in the “slow” regime, where the water is injected into the cavity at a constant, moderate flow rate. The image is obtained by stacking the gel profiles at different times, so that one can track the evolution of the wetting ridge. In the case of figure 3.3a, the contact line moves at a constant velocity v such that the ridge tip location imprints a straight line to the space-time plot. For this steady motion, the liquid contact angle and the shape of the moving liquid meniscus are stationary. Thus mass conservation dictates that the contact line velocity $v = Q/A$ where Q is the imposed flow rate and A is the cross-sectional area of the cavity. The contact angle θ takes on a value larger than θ_{eq} and depends on the (imposed) contact line velocity.

Then, at some time we suddenly stop the injection of fluid ($Q = 0$) so that the contact line will eventually come to rest. This relaxation dynamics is shown in figure 3.3b. The wetting ridge does not stop instantaneously but relaxes over about 50-100 seconds since the contact angle $\theta > \theta_{eq}$. However, at the end of the sequence shown in figure 3.3b, the contact line velocity is still $\sim 10^{-3} \text{ mm/s}$, and it takes on the order of 5 minutes to reach an equilibrium position as far as is detectable within the measurement precision.

Figure 3.3: Space-time diagrams for slow dynamics. (a) Wetting ridge moving at a constant velocity, for $v < v_c$. (b) Relaxation of the wetting ridge towards a static equilibrium, after stopping the injection of water into the cavity. The size of the wetting ridge is indicated by the scale bars; the static ridge being significantly larger than the dynamic ridge.

Figure 3.4: Experimental ridge shapes, for gradually increasing contact line speeds (0 , 6.3×10^{-3} , 3.2×10^{-2} , 1.0×10^{-1} mm/s). The contact line motion is towards the right.

This very slow relaxation is due to the strong viscoelastic dissipation associated to the contact line motion, an effect that was established already by Carré & Shanahan [15, 32, 76, 85] and Long, Ajdari & Leibler [34] who termed it “viscoelastic braking”. As can be seen in figure 3.3b, the wetting ridge also increases in amplitude during the relaxation. This is due to the fact that moving wetting ridges are smaller in amplitude than static ridges – a fact that can be attributed to a “dynamical elastocapillary length” that is decreasing with velocity. Note the scale bars indicated in both figure 3.3ab, showing that the wetting ridge is indeed relatively large in the static regime. More detailed zooms of dynamical profiles are given in figure 3.4. Importantly, the dynamics in this relaxation regime is “quasi-steady”: we have verified that the contact angle θ depends on the instantaneous velocity v in the same way as in the steady-state regime. As is commonly done in wetting dynamics, this means that the entire curve $\theta(v)$ can be obtained from a single relaxation experiment. The quantitative analysis of the next section will indeed be based on this principle.

The same setup can be also be used to quantify stick-slip motion of the contact line, which recently gained much attention [33, 35, 79] and is studied in this thesis in chapter 4. Again, we first consider the situation where we impose a constant flow rate Q , but now at a sufficiently large value that $v = Q/A$ exceeds a critical velocity $v_c \sim 1$ mm/s for the PDMS gel. The system then undergoes a transition to stick-slip dynamics, a cycle of which is shown in figure 3.5a.

Figure 3.5: Space-time diagrams for rapid dynamics, leading to stick-slip motion. (a) Wetting ridge moving at high velocity, with $v > v_c$. Even though the imposed volume flux of water Q into the cavity is constant, the contact line undergoes a stick-slip motion where it periodically “depins” from its own wetting ridge. Here one cycle is shown. (b) Initial contact line motion, after starting the injection of liquid from an equilibrium state. The contact line first depins from a large static wetting ridge (which very slowly decays over time), leading to subsequent stick-slip motion. The size of the wetting ridge is indicated by the scale bars; the static ridge being significantly larger than the dynamic ridge.

We characterize this transition in detail in chapter 4, and identified the criterion for spontaneous depinning of the contact line from its own wetting ridge. It turns out that the depinning occurs due to a violation of the classical Gibbs inequality for sharp edges – but in the case of soft, dynamic ridges, the angles of the ridge are intricate functions of the velocity. For details we refer to chapter 4. After depinning, the rapid contact line motion slows down over the timescale of about 5 ms, which is due to the growth of a new wetting ridge. After deceleration, the cycle is repeated. The typical velocities during the rapid slip are between 10^2 and 10^3 mm/s, which are comparable to contact line velocities on rigid surfaces [6, 8]. The stick-slip dynamics was also revealed by X-ray measurements [79], who referred to this regime as “stick-slipping by a medium sized ridge”.

Finally we also visualize the onset of contact line motion, starting from an equilibrium wetting configuration and then suddenly imposing a finite Q . The dynamics is shown in figure 3.5b. Since we start from rest, the initial wetting ridge is relatively large and the contact line does not immediately leave the wetting ridge. Instead, this initially causes a slow transient response of the ridge. However, as soon as the Gibb’s inequality is violated, the contact line is able to depin from the initial ridge. This regime was referred to by [79] as “stick-breaking by a fully grown ridge”. After depinning, this fully developed static ridge is observed to decay very slowly. At the same time, the rapid contact line motion subsequently undergoes a series of stick-slip cycles, similar to those reported in figure 3.5a.

3.3.2 Contact angles

We now turn to the main experimental results of this chapter, where we quantify the contact angles of dynamical wetting ridges. These are extracted from the profiles at different velocities such as in figure 3.4 – details of how the contact angles are determined are given in Sec. 3.2. We restrict ourselves to the quasi-steady dynamics, for which the contact line does not depin from its own ridge.

Low velocity.

We first report contact angles in the regime where the contact line velocity is relatively low. This is quantified by $v \ll v^*$, where the characteristic speed $v^* \sim \gamma/(G\tau)$ compares the elastocapillary length and the timescale τ of the gel (see Appendix 3.6.1 for the rheology of the gel). For the PDMS and PVS substrates, we find v^* of the order of 1 mm/s. In figure 3.6 the measurements of the ridge rotation angle φ are reported as grey diamonds. On the same

figure, we superimpose the change of the liquid angle $\theta - \theta_{eq}$. At small velocities $v \ll v^*$, the two measurements perfectly overlap, for both the PDMS substrate (main figure) and the PVS substrate (inset). This is a central experimental result of the chapter: It provides a direct evidence that the dynamic contact angle θ is passively following the rotation of the ridge φ . In other words, all dynamical effects take place inside the viscoelastic gel, while the liquid drop statically adapts to the change of solid. The equality of the angles implies that the angles satisfy the Neumann's law, dictated by surface tensions as in the static case. This point will be further elaborated in Sec. 3.4.

These observations are in line with the theoretical prediction in chapter 2, based on small deformations of the substrate. For small velocity, the theory simplifies to a power law form chapter 2,

$$\varphi = \frac{2^{n-1}n}{\cos(n\pi/2)} \frac{\gamma \sin \theta_{eq}}{\Upsilon_s} \left(\frac{v}{v^*} \right)^n. \quad (3.1)$$

In this expression γ is the liquid-vapor surface tension, Υ_s is the solid surface tension, n is the exponent of the gel's loss modulus $G'' \sim \omega^n$, while we now more precisely define the characteristic velocity $v^* = \Upsilon_s/(G\tau)$ using the solid surface tension. The predicted power law dependence (3.1), with n and v^* obtained from independent rheological measurements, is in excellent agreement with experimental observations. Importantly, however, the agreement is not fully quantitative. In the model, the solid surface tensions are assumed to be equal, $\Upsilon_s = \Upsilon_{SV} = \Upsilon_{SV}$. Its value is here used as an adjustable parameter, giving $\Upsilon_s = 27\text{mN/m}$ for the PDMS gel ($\Upsilon_s = 15\text{mN/m}$ for PVS). This fitted value is in fact too small to be able to create a Neumann balance with the surface tension of water, which requires that Υ_s is at least $\gamma/2$. A similar lack of quantitative agreement was discussed in experiments of drops sliding down on thin elastic layers [83].

Large velocity.

Clearly, the experimental data in figure 3.6 show that a new regime appears when approaching $v^* \sim 1$ mm/s. First, the power-law regime is no longer followed but gives way to a saturation of φ and $\theta - \theta_{eq}$. More strikingly, however, the angles no longer take on the same value. To interpret these findings, we present the measurement of θ_S versus instantaneous contact line velocity U , shown in figure 3.7. The main panel shows the result on PDMS substrates, while the inset reports very similar trends observed on PVS. As can be observed, θ_S is approximately constant at low velocities ($< 10^{-3}$ mm/s). This is in line with the expectation, since the solid angle is determined by the surface tensions according to Neumann's law. At larger velocities, however, θ_S

Figure 3.6: Equality of the dynamic contact angle of the liquid and the ridge rotation angle. The main panel reports data on the PDMS substrate. The white circles show the change in macroscopic contact angle $\theta - \theta_{eq}$, with $\theta_{eq} = 105 \pm 2^\circ$. The grey diamonds show the ridge rotation φ . The errorbars represent 2 times the standard deviation of the corresponding data. The red line shows the prediction by (3.21). Inset: Same data obtained for wetting on the PVS substrate.

is found to increase with U . This effect is reported in chapter 4, where the shallower angle was shown to be the origin of the depinning transition.

The intriguing change in θ_S has important consequences. Firstly, it implies a change of ridge geometry and by consequence, one can no longer unambiguously define a rotation angle φ . In particular, our choice of using the bisector of the tangent vectors becomes arbitrary, and there is no reason why the determined φ would coincide with $\theta - \theta_{eq}$. Secondly, and more importantly, the change in θ_S points to a dynamical increase of the solid surface tension. This assertion is based on the hypothesis that the Neumann's law still holds in the dynamical case; this hypothesis will be motivated in more detail below. Given that the liquid-vapor surface tension is known, we can in fact estimate the solid surface tensions using the Neumann balance, see also [70]. For the PDMS gel, this gives $\Upsilon_{SV} = 42 \pm 2$ mN/m and $\Upsilon_{SL} = 58 \pm 4$ mN/m at vanishing velocity. The values change to $\Upsilon_{SV} = 37 \pm 4$ mN/m and $\Upsilon_{SL} = 82 \pm 7$ mN/m for a relatively large velocity (0.07 mm/s).

3.3.3 Summary and open issues

From these experimental observations, we draw the following conclusions:

- At low velocity, the liquid angle θ exactly follows the rotation of the ridge

Figure 3.7: Solid opening angle θ_S as function of contact line speed V for wetting on the PDMS gel. Inset: Same data obtained for wetting on the PVS gel. Inset: Same data obtained for wetting on the PVS substrate.

φ .

- Both angles exhibit a power law dependence $\theta - \theta_{eq} = \phi \sim v^n$, with the exponent n directly given by the scaling of the loss modulus $G'' \sim \omega^n$.
- The ridge rotation φ is qualitatively described by a theory based on linear viscoelastic response (i.e. small deformations) and constant solid surface tension.
- This linear theory (3.1) does not quantitatively describe the experiment, i.e. the value of the fitted solid surface tension Υ_s is off roughly by a factor 2.
- At large velocity, the solid angle θ_S increases with velocity; this points to a variable solid surface tension.

Interestingly, a similar quantitative issue with (3.1) was found by Zhao *et al.*[83], for drops sliding down thin viscoelastic layers. As the thickness was reduced, the linear theory based on ridge rotation leads to an overestimation of the sliding velocity. Zhao *et al.*[83] proposed an alternative approach to the problem, based on a dissipation analysis in the small-velocity regime. Their conclusion, however, is that the liquid angle does not follow the ridge rotation, even at small velocity, which is at odds with the presented experiments.

Another important set of recent experiments revealed variations of static contact angles upon stretching the substrate [70, 71]. While the experiments

were performed at equilibrium, the solid angle θ_S was found to increase with surface strain, in a way similar to the θ_S dependence on velocity reported here. This points to the need to introduce a variable surface tension Υ_s in the theoretical description of soft wetting, both for statics and for dynamics.

3.4 Theoretical approaches

In the remainder of the chapter, we critically review the theoretical approaches followed in the literature. We start out by a general formulation for a two-dimensional contact line moving over a viscoelastic substrate, where we pose the mechanical problem beyond the limitations linear viscoelastic response and constant solid surface tension. Subsequently, we systematically introduce the various approximations made in order to make analytical progress, and establish the connections between the existing modelling approaches.

3.4.1 Mechanical equilibrium and the Shuttleworth effect

We consider the dynamics of both the liquid and the solid to be overdamped, such that inertial effects can be neglected. In that case, the Cauchy stress inside the elastic solid ($\boldsymbol{\sigma}$) and inside the liquid ($\mathbf{T}$) are both divergence-free

$$\nabla \cdot \boldsymbol{\sigma} = 0, \quad \nabla \cdot \mathbf{T} = 0. \quad (3.2)$$

These equations represent the mechanical equilibrium of volume elements, respectively, inside the solid and the liquid. The solid-liquid interaction takes place at the interface, by the boundary condition on the stress. In a two-dimensional description, the interface condition can be written as [80]

$$\boldsymbol{\sigma} \cdot \vec{n} - \mathbf{T} \cdot \vec{n} = \frac{\partial}{\partial s} (\Upsilon_s \vec{t}), \quad (3.3)$$

where we introduced the surface normal $\vec{n}$ and tangential $\vec{t}$ unit vectors, and the curvilinear coordinate s running along the interface (cf. figure 3.8). The right hand side of (3.3) represents the discontinuity of stress due to the solid's surface tension Υ_s . Using the connection $d\vec{t}/ds = \kappa \vec{n}$, where κ is the interface curvature, the discontinuity of the normal stress gives the Laplace pressure $\Upsilon_s \kappa$. In the tangential direction, one recognises a Marangoni-like stress $\partial \Upsilon_s / \partial s$ whenever the surface tension is not uniform along the interface.

Let us elaborate on the physics of solid capillary effects. In case the interfacial mechanics is non-dissipative, it can be fully captured by a surface free energy γ_s . While for simple liquids the surface energy takes on a constant value, this is not necessarily the case for (visco)elastic interfaces, owing

Figure 3.8: Curvilinear coordinate s along the deformed interface, using the tangential unit vector $\vec{t}$ and normal unit vector $\vec{n}$. The curvilinear coordinate in the reference state is denoted S , from which we define the displacement field $\vec{u}$.

to the Shuttleworth effect [77, 78, 84]. Namely, the surface energy $\gamma_s(\epsilon)$ is in general expected to be a function of the surface strain ϵ , a fact that was verified explicitly for polymeric interfaces [70, 71, 80]. Then, surface tension Υ_s is not equal to the surface energy γ_s , but follows from the Shuttleworth equation [84],

$$\Upsilon_s = \gamma_s + (1 + \epsilon) \frac{d\gamma_s}{d\epsilon}. \quad (3.4)$$

In general, one thus cannot assume a priori that surface tension takes on a constant value. This also implies that the Marangoni stress in (3.3) need to be taken into account.

3.4.2 When is Neumann's law valid?

Let us now consider the case of wetting, where the material in contact with the solid substrate consists of two phases, say liquid and vapor. This creates a three phase contact line at the location $s = s_{cl}$. From a theoretical point of view, we can now proceed along two distinct routes, that lead to the same result. In the first route, we represent the capillary action of the liquid-vapor interface as a highly localised traction, pulling with a tension γ along the direction $\vec{t}_{LV}$ of the liquid-vapor interface. Treating this liquid traction as a perfectly localised Dirac δ -function at $s = s_{cl}$,

$$\mathbf{T} \cdot \vec{n} = \gamma \delta(s - s_{cl}) \vec{t}_{LV}, \quad (3.5)$$

equation (3.3) can be written as

$$\vec{\sigma} = \gamma \delta(s - s_{cl}) \vec{t}_{LV} + \frac{\partial}{\partial s} (\Upsilon_s \vec{t}). \quad (3.6)$$

Here we further introduced the traction vector $\vec{\sigma} = \boldsymbol{\sigma} \cdot \vec{n}$ on the viscoelastic medium. Equation (3.6) provides a way to derive the Neumann law for the contact angle, by integrating over an arbitrarily small distance across the contact line, from s_{cl}^- to s_{cl}^+ . This gives

$$\begin{aligned} \int_{s_{cl}^-}^{s_{cl}^+} ds \vec{\sigma} &= \gamma \vec{t}_{LV} + (\Upsilon_s \vec{t})^+ - (\Upsilon_s \vec{t})^- \\ &= \gamma \vec{t}_{LV} + \Upsilon_{SV} \vec{t}_{SV} + \Upsilon_{SL} \vec{t}_{SL}, \end{aligned} \quad (3.7)$$

where in the last line we expressed the values on either sides of the contact line, by respectively using the indices for the solid-vapor (SV) and solid-liquid (SL) interfaces. Importantly, the bulk viscoelastic traction is integrated over an infinitesimally small distance that crosses the contact line. As long as the traction exhibits a divergence that is weaker than $1/(s - s_{cl})$, the integrated contribution $\int ds \vec{\sigma} \rightarrow 0$ and can thus be omitted. In that case (3.7) indeed reduces to a vectorial balance of the three surface tensions, which is the Neumann law.

A more rigorous route to (3.7) is based on variational principles [80]. In that case, one does not represent the liquid-vapor interface by the traction δ -function. Instead, one provides symmetric treatment of the three interfaces and explores the work done by a virtual displacement of the Eulerian contact line position. Kinematically, this contact line displacement is coupled to virtual displacements of material points at the interface, which probes the virtual work done by $\vec{\sigma}$. Application of the virtual work principle then indeed leads to (3.7) as a *boundary condition* that needs to be imposed at the contact line [80].

Importantly, we conclude that the validity of Neumann's law, based on (3.7), crucially hinges on the nature of the viscoelastic traction $\vec{\sigma}$ in the vicinity of the contact line. As an interesting example of a non-integrable traction, we quote the case of Newtonian liquids. In that case, the viscous stress $\boldsymbol{\sigma} \sim \eta v / (s - s_{cl})$, where η is the liquid viscosity and v the contact line speed. This non-integrable stress gives rise to the famous "moving contact line singularity" [4], which is also expected for motion over a Kelvin-Voigt viscoelastic solid see chapter 2. In that case, contact angles cannot be defined without the explicit introduction of a regularisation of the stress [6, 8]. By contrast, for a purely elastic substrate the formation of a solid angle θ_S leads to a weakly, logarithmic singularity of the $\vec{\sigma}$ – both in linear elasticity [29, 86] and at large deformation [87]. This renders the elastic stress in (3.7) integrable, and justifies the validity of Neumann's law for elastic media. Below we assess this criterion in the context of contact lines moving over viscoelastic media.

3.4.3 The ridge shape

With the basic mechanic relations in place, the next step is to express the constitutive law of the viscoelastic layer, and proceed by computing the shape of the wetting ridge. This has been done analytically in chapter 2 and [83], under the assumptions of (i) constant velocity, (ii) linear viscoelastic response, i.e. small substrate deformations, (iii) constant solid surface tension, with identical values on the wet and dry state $\Upsilon_{SV} = \Upsilon_{SL} = \Upsilon_s$. Below we will systematically discuss all approximations behind these analytical predictions.

From finite to small deformations.

Given that the material exhibits a reference state, i.e. $G'(\omega = 0)$ takes a finite value, it is natural to express the constitutive law using materials coordinates in the reference state. We therefore introduce the reference curvilinear coordinate of the interface S in its undeformed state. The current and reference curvilinear coordinates are related as $ds = (1 + \epsilon)dS$, where ϵ is the surface strain. Our prime interest is to find the (Eulerian) shape of the dynamical wetting ridge $h(x, t)$, as measured in experiment. Upon introducing the horizontal and vertical surface displacements u_x and u_y , the ridge shape $h(x, t)$ can be computed as

$$x = S + u_x(S, t), \quad h = u_y(S, t). \quad (3.8)$$

Using $ds^2 = dx^2 + dh^2$, we can express the surface strain as

$$1 + \epsilon = \left[\left(1 + \frac{\partial u_x}{\partial S} \right)^2 + \left(\frac{\partial u_y}{\partial S} \right)^2 \right]^{1/2}. \quad (3.9)$$

When we restrict ourselves to small deformations, we find

$$x \simeq S, \quad h(x, t) \simeq u_y(x, t), \quad \epsilon \simeq \frac{\partial u_x}{\partial x} + \frac{1}{2} \left(\frac{\partial h}{\partial x} \right)^2. \quad (3.10)$$

In this limit we also find that $\vec{t}$ and $\vec{n}$ tend towards the horizontal and vertical directions, respectively denoted $\vec{e}_x$ and $\vec{e}_y$. Therefore, it is natural to project (3.6) on $\vec{e}_x$ and $\vec{e}_y$. Denoting the liquid angle with respect the horizontal as θ , the projection gives to leading order

$$\vec{\sigma} \cdot \vec{e}_x \simeq \sigma_{xx} = -\gamma \delta(x - x_{cl}) \cos \theta + \frac{\partial \Upsilon_s}{\partial x}, \quad (3.11)$$

$$\vec{\sigma} \cdot \vec{e}_y \simeq \sigma_{yy} = \gamma \delta(x - x_{cl}) \sin \theta + \Upsilon_s \frac{\partial^2 h}{\partial x^2}. \quad (3.12)$$

Even in this limit of small deformations we face an intricate problem. Namely, the left hand side represents the forcing on the elastic medium, based on which we can compute deformations u_x and $u_y = h$ using linear response. However, the right hand side depends itself on the deformation, via $\Upsilon_s(\epsilon)$ and the Laplace pressure term proportional to $\partial^2 h / \partial x^2$.

Green's function approach.

To make analytical progress, the literature has primarily focussed on the case where $\Upsilon_s = \Upsilon_{SL} = \Upsilon_{SV}$ to be constant. In that case the $\theta \approx \pi/2$, all terms in (3.11) are of higher order and one assumes that the vertical displacement $h(x, t)$ can be determined from the vertical balance only, i.e. by (3.12). The latter assumption is even exact for thick incompressible layers [86], where horizontal and vertical directions perfectly decouple.

The problem (3.12) can be solved using a Green's function approach, using a viscoelastic rheology characterised by $\mu(\omega) = G'(\omega) + iG''(\omega)$. For this it is convenient to take the Fourier transform of (3.12) both in space (indicated by "tilde") and in time (indicated by "hat"). Writing the vertical components of the elastic and liquid tractions respectively as $\sigma(x, t) = \sigma_{yy}$ and $T(x, t) = T_{yy}$, we can write (3.12) as

$$\hat{\tilde{\sigma}}(q, \omega) = \hat{\tilde{T}}(q, \omega) - q^2 \Upsilon_s \hat{\tilde{h}}(q, \omega). \quad (3.13)$$

In this expression q and ω respectively are the wavenumber and frequency associated to the spatial and temporal Fourier transforms. Within linear response, the normal traction and normal displacement are related as in chapter 2 and [34]

$$\hat{\tilde{\sigma}}(q, \omega) = \frac{\mu(\omega)}{k(q)} \hat{\tilde{h}}(q, \omega), \quad (3.14)$$

where $\mu(\omega)$ is the material rheology, while $k(q)$ is a spatial Green's function that originates from solving (3.2). For an incompressible layer of thickness h_0 , this is given by

$$k(q) = \left[\frac{\sinh(2qh_0) - 2qh_0}{\cosh(2qh_0) + 2(qh_0)^2 + 1} \right] \frac{1}{2q} \quad (3.15)$$

Finally, we thus arrive at (see also chapter 2)

$$\hat{\tilde{h}}(q, \omega) = \frac{\hat{\tilde{T}}(q, \omega)}{\Upsilon_s q^2 + \frac{\mu(\omega)}{k(q)}}. \quad (3.16)$$

For a contact line moving at a constant velocity v , one can model the traction applied to the gel as a travelling wave

$$T(x, t) = \gamma \sin \theta \delta(x - vt). \quad (3.17)$$

This expression describes the traction induced by the liquid-vapor surface tension γ by a perfectly localised Dirac δ function, while θ is the (dynamic) liquid contact angle. Working this through like in chapter 2, one can compute the shape of the profile $h_c(x)$ in the the co-moving frame:

$$\tilde{h}_c(q) = \frac{\gamma \sin \theta}{\Upsilon_s} \left[q^2 + \frac{\mu(qv)/\Upsilon_s}{k(q)} \right]^{-1}, \quad (3.18)$$

This analytical solution for the ridge shape has two important features. First, there is a discontinuity of the slope at the contact line. This follows from the large- q asymptotics of (3.18). Noting that $k(q) \sim 1/|q|$ and assuming that at large frequency $\mu(\omega) \ll \omega$, we find the dominant behaviour $\tilde{h}_c \sim \gamma/(\Upsilon_s q^2)$. This scaling implies a slope-discontinuity, which gives rise to a solid angle θ_S – that in the limit of small slopes reduces to

$$\theta_S = \pi - \frac{\gamma \sin \theta}{\Upsilon_s}. \quad (3.19)$$

Reminding that the formalism a priori assumed small substrate deformations, i.e. $\gamma/\Upsilon_s \ll 1$, the result for θ_S can be recognised as Neumann’s law. Interestingly, the value of θ_S depends only on the surface tensions, and is totally independent of $\mu(\omega)$ and of the contact line velocity. This reflects that the viscoelastic traction is integrable at small scales, see the discussion of Sec. 3.4.2. From the above it is clear this is satisfied whenever $\mu(\omega) \ll \omega$ at large frequency. This is indeed the case for the experiments presented here, and others available in the literature, for which $\mu \sim \omega^n$ with $n < 1$ at large frequency. These observations are in perfect agreement with the discussion of Neumann’s law in Sec. 3.4.2. Namely, at a typical distance ℓ from the contact line, the material is excited at a frequency v/ℓ and the associated stress $\sigma \sim \mu(v\tau/\ell)^n$ is integrable as long as $n < 1$.

A second important feature of the ridge solution (3.18) is that due to the motion the shape becomes asymmetric, and the ridge tip exhibits a rotation that we describe by an angle φ . The rotation can be calculated by taking the symmetric (real) part of h' :

$$\begin{aligned} \varphi &\approx \tan(\varphi) = \lim_{x \rightarrow 0} \frac{1}{2} (h'(x) + h'(-x)) \\ &= \frac{1}{2\pi} \int \Re[-iq \tilde{h}_c(q)] e^{-iqx} dq. \end{aligned} \quad (3.20)$$

Using the explicit form (3.18), the rotation angle can be written as

$$\varphi = \gamma \sin \theta \int \frac{dq}{2\pi} \frac{qk(q)G''(qv)}{|k(q)\Upsilon_s q^2 + \mu(vq)|^2}. \quad (3.21)$$

This form involves the loss-modulus G'' , showing that the ridge rotation is directly linked to dissipation inside the solid. This is to be contrasted with the solid angle θ_S , which depends on surface tensions and is predicted to remain constant with velocity.

Let us reiterate the importance of the large- ω behaviour of $\mu(\omega)$ for the above considerations. We already noted that the appearance of a solid angle θ_S , and hence the validity of Neumann's law, for a moving wetting ridge hinges on the sublinear behaviour of $\mu(\omega)$. The same condition arises for the appearance of a well-defined rotation angle. Namely, for $\mu \sim G'' \sim \omega^n$ with $n < 1$, the integrand in (3.21) scales as q^{n-2} . Then, the expression for φ is integrable at large q if, and only if, $n < 1$. For the limiting case $n = 1$, there is a logarithmic singularity and the contact angle cannot be defined – in direct analogy to the viscous moving contact lines. In the experiments on soft wetting available in the literature, and for the experiments presented here, the rheological condition $n < 1$ is usually satisfied. Hence, the assumptions underlying Neumann's law should be valid, and the prediction φ according to (3.21) is well-defined.

3.4.4 Selection of the liquid contact angle

Dissipation approach.

The price to pay for omitting the horizontal force balance from the analysis is that we do not have an explicit equation to solve for θ , as a function of the imposed velocity v . In chapter 2, we argued that when dissipative forces inside the liquid drops are small compared to those in the bulk solid, the liquid angle θ rotates along with the ridge, in order to maintain the Neumann balance. Hence, the liquid angle $\theta(v) = \theta_{eq} + \varphi(v)$; in perfect agreement with the experimental results of Fig. 3.6 at small velocity.

However, this notion was recently challenged by Zhao *et al.* [83], who estimated the liquid angle based on a dissipation approach – as originally proposed by Long, Ajdari & Leibler [26]. The analysis builds on a balance of the work per unit time performed by the capillary force and the dissipation inside the layer, i.e.

$$P = \gamma v (\cos \theta_{eq} - \cos \theta), \quad (3.22)$$

where P is the total dissipation (per unit contact line length)

$$P = \int d^2x \, \boldsymbol{\sigma} : \nabla \dot{\mathbf{u}}. \quad (3.23)$$

Here we will demonstrate by explicit calculation that, within the current theoretical framework, the dissipation approach (3.22) indeed leads to the same contact angle as that predicted by $\theta(v) = \theta_{eq} + \varphi(v)$.

The integral of (3.23) can be brought to the free surface using Gauss's divergence theorem

$$P = \int d^2x \, \boldsymbol{\sigma} : \nabla \dot{\mathbf{u}} = \oint ds \, \vec{n} \cdot \boldsymbol{\sigma} \cdot \dot{\mathbf{u}}. \quad (3.24)$$

Given that the displacement vanishes at the bottom of the substrate, the only contribution comes from the integral over the free surface, where for small deformations the normal displacement reads $h(x, t)$. For constant surface tensions, the elastic stress at the free surface only has a normal component, so that, for small deformations, we can further simplify:

$$P = \int_{-\infty}^{\infty} dx \, \sigma(x, t) \dot{h}(x, t), \quad (3.25)$$

where σ denotes the normal component of the stress. In the frame comoving with the moving contact line, the elastic stress at the free surface follow from (3.14),

$$\tilde{\sigma}_c(q) = \frac{\mu(qv)}{k(q)} \tilde{h}_c(q). \quad (3.26)$$

Then, (3.25) can be written as

$$\begin{aligned} P &= \int dx \left\{ \int \frac{dq}{2\pi} \tilde{\sigma}_c(q) e^{iq(x-vt)} \right\} \left\{ \int \frac{dq}{2\pi} (iq'v) \tilde{h}_c(q') e^{iq'(x-vt)} \right\} \\ &= \int d\bar{x} \int \frac{dq}{2\pi} \int \frac{dq'}{2\pi} \frac{(iq'v)\mu(qv)}{k(q)} \tilde{h}_c(q) \tilde{h}_c(q') e^{i(q+q')\bar{x}}, \end{aligned}$$

where in the last line we introduced the change of variables $\bar{x} = x - vt$. Using the identity $\int d\bar{x} e^{i(q'+q)\bar{x}} = 2\pi\delta(q+q')$, we finally obtain

$$\begin{aligned} P &= -v \int \frac{dq}{2\pi} \frac{\mu(qv)}{k(q)} (iq) |\tilde{h}_c(q)|^2 \\ &= v \int \frac{dq}{2\pi} \frac{qG'''(qv)}{k(q)} |\tilde{h}_c(q)|^2. \end{aligned} \quad (3.27)$$

This expression provides the dissipation for any travelling wave of shape $h_c(x)$, regardless of the traction that generates it. Naturally, the dissipation is strictly positive and only involves the loss modulus G'' . The final step is to impose the specific shape generated by (3.18), for which the dissipation becomes

$$P = v(\gamma \sin \theta)^2 \int \frac{dq}{2\pi} \frac{qk(q)G''(qv)}{|k(q)\Upsilon_s q^2 + \mu(vq)|^2}. \quad (3.28)$$

For small changes in the contact angle, $\Delta\theta = \theta - \theta_{eq} \ll 1$, the dynamic contact angle selection (3.22) then gives the final result

$$\theta - \theta_{eq} = \gamma \sin \theta \int \frac{dq}{2\pi} \frac{qk(q)G''(qv)}{|k(q)\Upsilon_s q^2 + \mu(vq)|^2}. \quad (3.29)$$

It provides a closed form expression for the dynamic contact angle, for arbitrary rheology and arbitrary layer thickness (encoded via the Green's function $k(q)$).

Mechanism of ridge rotation.

We are now in a position to compare the dynamical variation of the contact angle $\theta - \theta_{eq}$, computed from a dissipation analysis (3.29), to the ridge rotation φ as derived from (3.21). Indeed, the two expressions are strictly equivalent, and thereby confirm that the liquid angle θ is selected by passively following the rotation of the ridge. This provides a direct demonstration that, within this small-deformation linear viscoelastic framework, the Neumann condition remains valid for arbitrary speed, and for arbitrary layer thickness.

As mentioned above, however, there is a strict condition for the expressions to be valid – namely, the large- ω limit of $\mu \sim \omega^n$ must have $n < 1$, in order for φ and the dissipation (3.28) to remain integrable. Another point of possible concern, raised in [82], is the use of the divergence theorem (3.24). Namely, the solution exhibits a discontinuity of the strain field at the contact line, reflected by the discontinuity of interface slope, and care must be taken when applying the divergence theorem. In App. 3.6.2 we demonstrate that the use of the divergence theorem in the present problem is valid as long as the dissipation P is integrable, i.e. whenever $n < 1$, as is usually the case. Hence, contrarily to the claim in [82, 83], the dissipation route in linear viscoelastic theory thus predicts that the liquid angle θ is selected via the ridge rotation φ .

3.5 Conclusion

In summary, we presented a new method for direct visualisation of the dynamics of a wetting ridge. We have provided detailed insight in the various regimes of soft wetting dynamics, from rapid stick-slip motion to very slow relaxation

towards equilibrium. However, the focus of the manuscript was on a quantitative measurement of the dynamic contact angles, and a short overview of the results and open issues is given in Sec. 3.3.3.

A key result pertains to the low velocity regime, for which we provide a direct experimental confirmation that liquid contact angle changes by a rotation of the wetting ridge, while the ridge geometry maintains a Neumann balance. Within the context of a linear theory, this mechanism of contact angle selection mechanism is further confirmed by a dissipation analysis in Sec. 3.4.4. As such, there is now ample evidence that the spreading of liquid drops is governed by ridge rotation, which settles the debate in [81, 82].

At larger velocities, however, the “linear response” modelling framework breaks down due to an observed increase in the solid angle. Under the assumption that the Neumann balance at the contact line is still applicable for dynamic wetting, this points to a variable solid surface tension – and requires the inclusion of the Shuttleworth effect. We derived the conditions for which the Neumann law is expected to hold, beyond the restrictions of small deformations, and showed that these are indeed satisfied in our dynamical experiments. The variable surface tension dramatically changes the modelling approach – it involves large deformations and invokes new phenomena such as Marangoni-stresses due to surface tension gradients. Fully quantitative agreement calls for a self-consistent solution of the viscoelasto-capillary problem, e.g. by numerical solutions.

From a more general perspective, the experiments presented here may serve as a rheological tool – both for bulk rheology and surface rheology. This is of relevance for the functionality of extremely soft materials emerges from a combination of bulk elasticity and surface effects. These potential applications further underline the importance of developing a fully quantitative modelling.

3.6 Appendix

3.6.1 Gel rheology

The gel rheology is measured using an Anton Paar MCR 502 rheometer, in a parallel plate geometry, using a frequency sweep at 1% strain (both elastomers show a linear response up to 100% strain). The gel, prepared by mixing the prepolymers, is cured inside the rheometer using the same batch and following the same procedure as the gel used for the experiments. The PVS gel is cured at room temperature for approximately 10 hours. The PDMS requires an additional step to be fully reticulated: the temperature is increased to 80°C for 200 minutes.

The measured rheology for both gels are shown in figure 3.9, where we can

Figure 3.9: Measured PDMS gel rheology. The diamonds show the storage modulus, the circles show the loss modulus. The fit for equation 3.30 is shown in the lines resulting in: $n = 0.58$, $G = 390Pa$, $\tau = 0.54s$. The inset shows the measured rheology for the PVS gel, with the following fit parameters: $n = 0.61$, $G = 415Pa$, $\tau = 0.08s$

see that both gels behave similarly. The storage modulus, $G'(\omega)$, approaches a finite value at vanishing frequency ω , which defines the shear modulus according to $G \equiv G'(0)$. This means that the gels are elastic in the long time limit, and hence can be classified as viscoelastic solids. The loss modulus, $G''(\omega)$, exhibit a power-law behaviour over nearly the entire frequency range. The rheology of the gels can in fact be accurately fitted by a complex modulus

$$\mu(\omega) = G' + iG'' = G[1 + (i\omega\tau)^n], \quad (3.30)$$

which in terms of storage and loss modulus reads

$$\begin{aligned} G'(\omega) &= G \left[1 + (\omega\tau)^n \cos\left(\frac{n\pi}{2}\right) \right] \\ G''(\omega) &= G \sin\left(\frac{n\pi}{2}\right) (\omega\tau)^n. \end{aligned} \quad (3.31)$$

These satisfy the Kramers-Kronig relations, since the complex modulus derives from a stress relaxation function

$$\Psi(t) = G \left[1 + \Gamma(1-n)^{-1} \left(\frac{\tau}{t} \right)^n \right]. \quad (3.32)$$

Here, G is the static shear modulus, τ is the response time of the gel and ω is the excitation frequency. These constants were determined by fitting equation

(3.30) to the measured rheology. The fit was done by finding n from the loss modulus G'' , which for (3.31) is a pure power-law, and using a least squares fit to find G and τ from G' . The PDMS has the following properties: $n = 0.58$, $G = 390Pa$, $\tau = 0.54s$, while for the PVS gel we find $n = 0.61$, $G = 415Pa$, $\tau = 0.08s$.

3.6.2 On the validity of using the divergence theorem to estimate dissipation

Here we investigate the validity of using the divergence theorem (3.24) in the case where the interface slope exhibits a discontinuity at the contact line. To this end, we replace the Dirac δ -function in (3.17) by a smooth function of width a , i.e.

$$T(x, t) = \gamma \sin \theta \frac{1}{a} f\left(\frac{x - vt}{a}\right). \quad (3.33)$$

For example, one consider f to be a Gaussian, which in the limit of $a \rightarrow 0$ gives a representation of the Dirac δ function – in fact, the true capillary traction is not infinitely sharp, but has a of the order of the nanometric width of the interface [27, 29, 48, 88]. Carrying through this modification, one ends up with smooth, differentiable stress and displacement fields, regularising the slope discontinuity at the contact line. Hence, with (3.33) there is no uncertainty in the use of Gauss's divergence theorem. It gives

$$\theta - \theta_{eq} = \gamma \sin \theta \int \frac{dq}{2\pi} \frac{q k(q) G''(qv) |\tilde{f}(qa)|^2}{|k(q) \Upsilon_s q^2 + \mu(vq)|^2}. \quad (3.34)$$

The factor $\tilde{f} \rightarrow 1$ in the limit of $|qa| \ll 1$, so that the integrand of (3.34) approaches the result (3.29) as $a \rightarrow 0$. To ensure that this limit is not singular, we also evaluate the integral at finite a , and consider the limit of vanishing a after integration. Clearly, $\tilde{f}(qa)$ acts as a cutoff of the integral beyond wavenumbers $q \sim a^{-1}$. Since the integrand scales as $\sim q^{n-2}$, the integral for small but finite a will scale as $\sim (a^{-1})^{n-1} \sim a^{1-n}$, which is convergent in the limit $a \rightarrow 0$ as long as $n < 1$.

In summary, our calculation clearly demonstrates that $\theta - \theta_{eq}$ for a "smoothened" contact line shape will converge to φ as computed in (3.21). The only requirement for the analysis to be valid is that the dissipation P is integrable in the sharp-interface limit where $a \rightarrow 0$.

Dynamic solid surface tension causes droplet pinning and depinning *

The contact line of a liquid drop on a solid exerts a nanometrically sharp surface traction. This provides an unprecedented tool to study highly localised and dynamic surface deformations of soft polymer networks. One of the outstanding problems in this context is the stick-slip instability, observed above a critical velocity, during which the contact line periodically depins from its own wetting ridge. Time-resolved measurements of the solid deformation are challenging, and the mechanism of dynamical depinning has remained elusive. Here we present direct visualisations of the dynamic wetting ridge formed by water spreading on a PDMS gel. Unexpectedly, it is found that the opening angle of the wetting ridge increases with speed, which cannot be attributed to bulk rheology, but points to a dynamical increase of the solid's surface tensions. From this we derive the criterion for depinning that is confirmed experimentally. Our findings reveal a deep connection between stick-slip processes and newly identified dynamical surface effects.

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4.1 Introduction

Liquid drops on vertical glass windows frequently get stuck due to sub-micrometric heterogeneities of the surface. Indeed, while a drop on a perfectly flat homogeneous surface will slide down under its own weight, surface defects result into pinning of the contact line and can give rise to a characteristic stick-slip motion. Different aspects of the depinning transition on rigid surfaces have been studied experimentally and theoretically [6], revealing critical phenomena [89] that are blurred by thermal activation at the nanoscale [90]. From an engineering perspective, there is a continued effort in designing surfaces with low contact angle hysteresis for purposes of hydrophobicity, self-cleaning, or anti-fouling coatings [91, 92].

Recently, wetting of soft surfaces has generated a large interest: The liquid-like surface properties of reticulated polymer networks and brushes can offer nearly hysteresis-free substrates [72, 80]. However, despite the absence of hysteresis, drops on these soft surfaces *do* exhibit a stick-slip motion when forced to spread beyond a threshold velocity as observed in chapter 2 and [33, 35, 79]. This stick-slip behaviour is highly unexpected, since the steadily moving contact line is not pinned to a material point of the solid, but “surfs” a wetting ridge created by the capillary forces located at the contact line. This suggests a rather intriguing scenario of self-pinning, and subsequent depinning of the contact line from its own wetting ridge. While stick-slip motion was qualitatively correlated to the viscoelastic rheology of the substrate [33, 35], or weakening of the wetting ridge [79], the current models predict a stable steady-state motion even at large velocities see chapter 2. As such, there is no explanation why the contact line would depin from its own ridge and start a stick-slip cycle.

In this chapter we identify the origin of the stick-slip transition using a direct high-speed visualisation of the full wetting ridge during self-pinning and depinning. The experiments reveal an increase of the solid angle at the ridge tip with contact line velocity, which is interpreted as a dynamical increase of solid surface tensions. We identify the criterion for the instability and as such reveal the origin of the stick-slip motion: the increased solid angle enables the contact line to depin from its ridge and rapidly slide down its own wetting ridge.

4.2 Wetting ridge visualisation

It is notoriously difficult to image the wetting ridge below the contact line. Techniques such as confocal [70] or X-ray microscopy [18, 79] have provided excellent spatial resolution, but the rapid dynamics during stick-slip motion

Figure 4.1: (a) Schematic of the experimental setup. A cylindrical cavity of gel is partially filled with water, with an imposed velocity $\bar{U}$. (b) The shape of the gel can be accessed optically from the side. The image was taken just after the contact line depinned from the old ridge (left), forming a new ridge (right). The liquid-vapor interface is indicated by the dashed line. (c) Space-time diagram showing the dynamics of the wetting ridge in steady state (left) and in the stick-slip regime, which is reached above a critical velocity U_c (right).

constitute a challenge. To overcome this, we present the setup shown in Fig. 4.1(a) consisting of a square block of transparent gel with a cylindrical cavity. The block has a width of 10 mm, the cavity diameter is 4 mm, leaving about 3 mm of gel thickness. These dimensions ensure a separation of length-scales where the elastocapillary length is small compared to the thickness and the meniscus, while the effect of gravity is still negligible. The cavity is partially filled with MilliQ water. The contact line pulls the gel inwards, creating an axisymmetric wetting ridge. This setup allows to accurately trace the edge of the gel when observing from the side [dashed rectangle in Fig. 4.1(a)] without the otherwise unavoidable optical distortions. Using a high speed camera (3200 frames per second) and a long working distance microscope (giving a spatial resolution of $1.0 - 2.2\mu m/\text{pixel}$) we image the wetting ridge, and the stick-slip motion with the necessary spatio-temporal resolution. A sample image is shown

in Fig. 4.1(b), which was taken during a rapid “slip” event after the contact line depinned from the ridge. The image reveals both the new wetting ridge (right) and the decaying old wetting ridge (left).

The reticulated polymer used is a PDMS gel (Dow Corning CY52-276, mixed at a 1.3:1 (A:B) ratio). The dynamic modulus is accurately described by $G'(\omega) + iG''(\omega) = G[1 + (i\omega\tau)^n]$, where the static shear modulus $G = 265$ Pa, $\tau = 0.48$ s and the exponent $n = 0.61$ (cf. appendix 4.5.) With the surface tension of MilliQ water $\gamma = 72$ mN/m, this gives rise to the elastocapillary length $\gamma/G = 0.27$ mm, which makes the wetting ridge easily accessible for optical microscopy. We verified that the experimental aspects such as the surface tension of the water and the wetting ridge dynamics remain consistent over extended periods of time (days), even when leaving the water in contact with the PDMS. The motion of the contact line is imposed by filling the cavity at a constant volumetric rate using a syringe pump; control parameter is the imposed averaged contact line speed $\bar{U}$. The opening angle of the solid ridge was measured at the micron scale within $\pm 3^\circ$ by fitting the gel profile on both sides of the ridge (cf. appendix 4.5). The contact angle of the liquid was measured in a separate experiment using a sessile drop on a flat surface of the same gel of sufficiently large thickness.

4.3 Results

4.3.1 From steady motion to stick-slip cycles

At small velocity $\bar{U}$, the contact line moves in a steady state, as can be seen by the left space-time diagram in Fig. 4.1(c). This steady regime has been studied in chapter 2 and previous works [15, 26, 32, 83, 93], which have shown that the motion is governed primarily by the viscoelastic dissipation inside the solid. The speed at which a drop can spread thus depends on the rheology of the solid, as well as on the size of the wetting ridge where most of the dissipation occurs.

Our prime interest lies in the high velocity regime, where wetting is forced beyond a critical speed U_c . The contact line motion then turns unstable, and results into a stick-slip behaviour that we resolve in detail at the scale of the wetting ridge. The space-time plot of a stick-slip cycle is shown in Fig. 4.1(c), with the corresponding dynamic wetting ridges presented in detail in Fig. 4.2.

At the start of a cycle, the contact line depins from the wetting ridge and suddenly moves with a much higher velocity over the substrate (slip phase). The first data in Fig. 4.2 (red) shows the profile just after depinning, where we observe both the abandoned wetting ridge (rounded tip, left) and the newly formed wetting ridge (sharp tip, right). The old ridge is no longer pulled by

Figure 4.2: Dynamical ridge shapes at different times during a stick-slip cycle. The coloured asterisks on the inset space-time diagram denote the point in time the snapshot was taken (time interval between snapshots ≈ 0.04 s).

the contact line and will decay over time. The evolution of the new ridge can be followed by the subsequent profiles in Fig. 4.2 (from dark blue to light blue). The wetting ridge initially grows, while also moving along the surface. In contrast to the sudden depinning, the transition to the stick phase is characterized by a continuous deceleration of the ridge. The growing ridge causes more viscoelastic dissipation, slowing down its motion. At a later stage, the wetting ridge becomes markedly asymmetric, with a large rotation of the ridge tip (light blue). Finally, the contact line depins and the stick-slip cycle is repeated.

The speed during the slip phase is two to three orders of magnitude faster than during the stick phase (Fig. 4.1c). Slip velocities, between 10^2 and 10^3 mm/s, are actually comparable to those measured during the wetting of a rigid surface [6, 8]. In this phase of rapid motion there is essentially no wetting ridge, and hence negligible viscoelastic dissipation inside the solid. During the slow phase, the velocity typically remains larger than $\approx 30\%$ of the critical speed $U_c = 1.0 \pm 0.1$ mm/s. Therefore, the contact line never really “sticks” to a material point of the substrate, but rather creeps, as for the stick-slip associated with solid friction [94].

The depinning from the wetting ridge cannot be explained as a simple consequence of the viscoelastic “friction” force. Namely, classical stick-slip in

Figure 4.3: The solid opening angle θ_S versus contact line speed U . The red curve shows θ_S for the steady state regime ($U < U_c$), accurately fitted by $\theta_S - \theta_{S,0} \sim U^{0.31}$ (black line). The blue curve represents a stick-slip cycle ($U > U_c$). The light blue part of the curve represents the decelerating part of the cycle, where the wetting ridge is growing and the solid opening angle θ_s is decreasing. The dark blue part of the curve shows the accelerating part of the cycle, up to the point of ridge detachment (slip, arrow). Inset: zoom on the stick-slip cycle with the arrows denoting the direction of time.

solid friction is due to the sharp decrease of the friction force with velocity, modeled in Coulomb's law by a jump from static to dynamic friction. The decrease of friction causes an overshoot of the speed of the slipping object, which in turn induces the irregular stick-slip regime. However, the gel used in these experiments presents a loss modulus increasing monotonically with frequency, $G'' \sim \omega^n$ with exponent $n = 0.61$, so that the dissipation in each material element, and subsequently the effective friction force, increases with velocity. Indeed, theory based on linear viscoelasticity assuming constant surface tensions, predicts a stable, steady solution for *all* velocities, see chapter 2. This calls for a more detailed investigation, given below, of how the contact line detaches from the wetting ridge.

4.3.2 Dynamic surface tension

The main surprise of the profiles in Fig. 4.2 is that the solid angle θ_S at the tip of the wetting ridge is not constant, but increases with velocity; it will provide the key to the depinning mechanism. Figure 4.3 shows the dynamics of θ_S for both the regime of constant velocity ($\bar{U} < U_c$) and during the stick-slip cycle ($\bar{U} > U_c$). In the steady-state regime (red) we observe a gradual increase with

velocity, from the static value $85 \pm 2^\circ$ at equilibrium to $140 \pm 4^\circ$ at the critical speed $U = U_c$. The data is very accurately described by the fit $\theta_S - \theta_{S,0} \sim U^{0.31}$ (black). A similar trend is observed during the stick-slip cycle (blue), where U denotes the instantaneous contact line velocity. The moment of slip is indicated by the arrow, where the surface is very flat and we set θ_S to 180° . Then, as the contact line velocity decreases, a decrease in θ_S is observed that follows the same trend as in the steady-state, in first approximation. At the minimum velocity, θ_S slightly undershoots the steady-state curve in red. Subsequently the contact line velocity increases, while θ_S follows the steady state curve until depinning occurs and the cycle is repeated.

This unexpected increase of θ_S with velocity can be interpreted as a dynamical increase of the solid surface tensions. Here we follow [70, 95], where θ_S is used to measure surface tensions based on the Neumann condition for the contact angles. This is a balance of forces applied to an elementary material system surrounding the contact line: the liquid surface tension γ is counteracted by the solid surface tensions, respectively Υ_{SV} (solid-vapor) and Υ_{SL} (solid-liquid). By this argument, we assume that the bulk viscoelastic stress cannot contribute on small scales, which is in fact consistent with the shear-thinning nature ($n < 1$) of the gel. This point can be quantified by estimating the bulk stress at a distance ℓ from the contact line. The characteristic frequency at which the material is excited by the moving contact line is $\omega \sim v/\ell$, which for the present rheology implies a bulk stress $\sigma \sim G(\tau\omega)^n \sim G(v\tau/\ell)^n$. When computing the integral of viscoelastic stress from a distance ℓ up to the contact line, we find $\ell\sigma \sim G(v\tau)^n \ell^{1-n}$; for shear-thinning materials with $n < 1$, this integrated stress vanishes in the limit $\ell \rightarrow 0$, so ultimately capillary effects prevail. The cross-over scale from bulk-to-surface is obtained from the balance $\ell\sigma \sim \gamma$, which gives $\ell \sim (\gamma/G)^{1/(1-n)}(v\tau)^{-n/(1-n)}$. For the gel used in our experiment, this gives $\ell \gtrsim 10\mu\text{m}$ for $U \lesssim 5\text{ mm/s}$, ensuring that the measurement of θ_S is indeed not obscured by bulk effects. Importantly the corresponding characteristic frequencies are within the range that is accessible by bulk rheometry (see appendix 4.5).

4.3.3 Depinning mechanism

Finally, we demonstrate how the change in θ_S is indeed responsible for depinning [Fig. 4.4(a)]. First we revisit the classical depinning from a “rigid wedge” [96, 97], used as a model for topographic roughness on stiff solids [panel (i)]. The contact line can slide off the ridge once the liquid angle *with respect to the inclined edge* exceeds the Young’s angle θ_Y that marks the wetting equilibrium. Any (virtual) displacement to the right with a lower angle will result in a restoring force that pushes the contact line back to the tip of the ridge. The

Figure 4.4: (a). Mechanism for ridge detachment in the stick-slip regime. (i) A rigid defect. The contact line depins as soon as the liquid angle with respect to the inclined edge ($\theta - \theta_R$) exceeds the Young angle (θ_Y). (ii) On a soft wetting ridge with constant surface tensions, the ridge rotates along with any change of the liquid angle (θ), in order to maintain a constant θ_S . (iii) Depinning can only occur when θ_S increases as a function of U . (b). Validation of the depinning condition (4.1), verified by plotting θ and $\theta_R + \theta_Y$ versus contact line speed U . The critical speed for depinning occurs when $\theta > \theta_R + \theta_Y$, at which the contact line can detach from the ridge.

depinning criterion thus reads

$$\theta > \theta_R + \theta_Y, \quad (4.1)$$

where θ is the liquid angle with respect to the horizontal, while θ_R is inclination angle on the right of the wedge [panel (i)]. A similar argument applies for depinning to the left, which in the case of a rigid wedge gives rise a range of possible values for θ . This is the source of contact angle hysteresis on rigid topography, for which (4.1) goes by the name of the Gibbs inequality [98]. For *soft* wetting ridges, however, the mechanics is fundamentally different – for example, no contact angle hysteresis is observed [80]. Instead, any change of the liquid angle θ is followed by a rotation of the ridge itself, as is clearly visible in Fig. 4.2. In the absence of changes of surface tensions, there is no depinning, but instead foresees a stable steady motion at all speeds, see chapter 2. In this case of constant surface tensions, the solid angle θ_S takes on a constant value (dictated by the Neumann balance), and θ and θ_R will always rotate by exactly the same amount to maintain a constant θ_S [panel (ii)]. By consequence the depinning criterion (4.1) will never be satisfied. All this changes dramatically, however, when surface tensions allow for an increase of θ_S , and thereby reduce θ_R , enabling the contact line to slide off the wetting ridge [panel (iii)].

This scenario for dynamics-induced depinning is confirmed in Fig. 4.4(b), where we verify the depinning criterion (4.1). The blue data shows the increase of the liquid angle θ with velocity U . This is compared to the angle relative to the right-side of the ridge, $\theta_R + \theta_Y$, shown as the red data. In accordance with recent work [70, 71, 80], we set θ_Y to a constant value measured from equilibrium. The motion leads to a decrease of θ_R that allows for a crossing of the curves that indeed coincides with U_c [Fig. 4.4(b)]. This is direct evidence for the depinning criterion (4.1) as the cause of stick-slip. This mechanism does not involve any sudden failure of the Neumann condition, as was suggested in [79], which is corroborated by the gradual evolution of θ_S .

4.4 Discussion and outlook

In summary, we revealed that the surface tension of a soft solid is a truly dynamical quantity, which has important consequences in contact mechanics. It provides the mechanism responsible for depinning and the rapid stick-slip motion of drops on soft substrates. The change in ridge angle θ_S provides direct evidence for a dynamic coupling between the surface tensions and the mechanical state of the substrate. A similar variability of θ_S , and thus of the solid's surface tensions, was recently observed for *static* drops, when progressively stretching the substrate [70, 95]. This was attributed to the

so-called Shuttleworth effect [77, 84, 99], where the surface tension depends on the elastic surface strain. It is tempting to interpret the results of Fig. 4.3 along the same lines, by considering the strain induced by the droplet motion. Indeed, the motion of the contact line induces a rotation (visible in Fig. 4.2) of the wetting ridge with respect to its more symmetric static shape; this rotation leads to an increase of the stretch on the liquid side and a decrease of the stretch on the vapour side. However, the observed change of θ_S is found to change as $U^{0.31}$, while the rotation angle φ – and its induced strain – exhibits a much weaker dependence $\sim U^n$ dictated by the rheology exponent $n = 0.58$, see also chapter 2. It is thus unlikely that the strain-dependence of surface tension is sufficient to explain our observations in Fig. 4.3.

The above considerations suggest that surface tension of such a polymer gel is a truly dynamic quantity that depends on the *rate* of strain at the surface as the contact line passes by. This opens the exciting perspective of surface rheological effects, as is for example known for interfaces with surfactants [100, 101]. For the present case of cross-linked polymer networks, this will require a detailed understanding of non-equilibrium interfacial effects that find their origin at a scale smaller than the distance between cross-linkers. The observed time-dependent surface tension suggests, as for thixotropy, the possibility that the surface tension actually depends on a micro-state variable that remains yet to be identified. Future work on surface effect in reticulated polymer network will have to focus on the micro-physics of the problem.

4.5 Appendix

In this appendix we provide experimental details on the measurement of the contact angles of the wetting ridge and on the rheology of the gel.

4.5.1 Wetting ridge angle measurement

As a first step, we detect the edge of the gel from images such as shown in Fig. 1 of the main text, using a subpixel measurement scheme. For this, we fit an error function of the grey values of a vertical cut around the edge where the inflection point is set to the subpixel height of the gel. This leads to profiles shown in Fig. 2 of the main text. The imaging scale of our setup is $1.0 \mu\text{m}/\text{pixel}$ or $2.2 \mu\text{m}/\text{pixel}$, depending on the series of experiments, and we estimate the accuracy of the vertical position to be $\approx 0.5 \mu\text{m}$, which is not limited by the imaging scale, but by the optical resolution power and the recording noise.

Unavoidably, however, the tip of the ridge will appear rounded because of the limited optical resolution of such kind of shadowgraphy setup. The

Figure 4.5: a: Unprocessed image from a measurement series b: Fitting method used to measure the relevant angles on the shown image. On the right (air) side of the gel a generic log function is fit, while on the left side a 2nd degree polyfit is used, c: Zoomed in version of the same data and fit.

typical residual radius of curvature at the ridge tip that is extracted from the images is about $2 - 3 \mu\text{m}$, independent of the imaging scale. This indicates that the resolution is limited by the aperture (numerical aperture ~ 0.1) of the shadowgraphy setup and not the imaging scale. This optical limitation blurs the discontinuity of the gel's orientation when crossing the contact line. To accurately determine the solid angle θ_S as reported in Fig. 3 of the main text, we therefore fit both sides of the contact line and subsequently determine the discontinuity from the crossing of the fits (Fig. 4.5). To perform the fit, we first estimate the horizontal position of the contact line from the local maximum around the ridge. We then use phenomenological fit-functions that provide an accurate description of the local profile on either side of the contact line. From the profiles in Fig. 2 in the main text, it is clear that the wetting ridges present a strong asymmetry. We therefore used different fits for the two sides. To the right of the contact line (on the side of the air), the shape is fitted by the form $y = a + b \log(c + x)$. To the left of the contact line (on the side of the liquid), a second order polynomial is used, $y = a + bx + cx^2$. For both fits, the points around the maximum within the limit of optical resolution are discarded to account for the tip rounding (1 pixel on each side for the measurement with imaging scale $2.2 \mu\text{m}$). Fig. 4.5 of this appendix shows a representation of the fitting procedure on a measurement with an imaging scale of $2.2 \mu\text{m}/\text{pixel}$ at $U = 0.45 \text{ mm/s}$ and $\theta_s = 135^\circ$, using 60 datapoints to the left and the right of the detected ridge tip. The fits have a norm of residuals of 5.9×10^{-6} for the blue fit and 1.5×10^{-3} for the red fit, which are typical values. Panel c shows a zoom of the of the same fit.

The intersection of the two fitted curves gives a good estimate of the actual location of the ridge tip, and the slopes at that point then give the relevant angles. Importantly, as described in the main manuscript, the length scale on which the surface curvature could change due to bulk rheological effects is

Figure 4.6: Rheological measurement of the gel, with the fit $\mu(\omega) = G'(\omega) + iG''(\omega) = G(1 + (i\omega\tau)^n)$. The best least-squares fit is obtained with $G = 265$ Pa, $\tau = 0.48$ s, $n = 0.61$.

typically more than a factor 10 larger than the optical resolution limit.

4.5.2 Rheology measurement

The rheological properties were measured with an Anton Paar MCR 502 rheometer in a parallel plate geometry using a frequency sweep at 1% strain, the results are shown in Fig. 4.6 of this appendix. The datapoints are fitted with $\mu(\omega) = G'(\omega) + iG''(\omega) = G(1 + (i\omega\tau)^n)$, where G' is the storage modulus and G'' is the loss modulus. Using a least-squares fit on the three parameters, we found the static shear modulus $G = 265$ Pa, the timescale $\tau = 0.48$ s, and the exponent $n = 0.61$, as reported in the main text. The fits are superimposed in Fig. 4.6.

Soft electrowetting *

Electrowetting is a commonly used tool to manipulate sessile drops on hydrophobic surfaces. By applying an external voltage over a liquid and a dielectric-coated surface, one achieves a reduction of the macroscopic contact angles for increasing voltage. The electrostatic forces all play out near the contact line, on a scale of the order of the thickness of the dielectric layer of the solid. If this dielectric layer were to be made soft, with deformations comparable to the layer thickness, one expects an interplay between elastic and electrostatic effects. This offers a way to probe the mechanics of the soft wetting ridge by an external field. Here we explore the effect of electrowetting on a soft dielectric, by measuring the static and dynamic contact angles as function of voltage. To look into detail at the microscopic effects at the contact angle we present some preliminary results using confocal microscopy, comparing the ridge shape with and without the electrostatic effects.

5.1 Introduction

Drop manipulation using electrowetting has been shown to have many applications, varying from digital microfluidic chips to e-ink screens, controllable lenses, electronic control on lab-on-a-chip, and as a general tool to investigate systems for a range of wettabilities. [102–108] The application of an external electrical voltage to a conducting sessile droplet, resting on a hydrophobic

*To be submitted. M. van Gorcum, R. Dey, F. Mugele, J. H. Snoeijer.

Figure 5.1: Schematic view of electrowetting. (a) Macroscopic picture: An electric potential is created between the drop and the surface causing the macroscopic angle to decrease to the Lippmann angle θ_L . (b) Microscopic picture: The Young's angle θ_Y is recovered at the contact line and the Maxwell stress imposes a curvature of the liquid, deforming the interface to the macroscopic Lippmann angle θ_L . (c) Sketch of electrowetting on a soft dielectric.

5

dielectric film covering an electrode, results in enhanced wetting of the droplet on the dielectric film (see figure 1a). Such electrically controlled partial wetting of a sessile liquid drop on a dielectric film is referred to as ‘electrowetting-on-dielectric’ (EWOD) or simply ‘electrowetting’. The change in the macroscopic contact angle of the sessile drop under the applied electrical voltage can be understood by means of an energy minimization approach [102, 109]. At zero voltage, the free energy of the system is given by the surface energies γ , γ_{SL} , γ_{SV} , respectively and the net electrostatic energy of the system originates from the difference between the energy stored in the dielectric and that stored in the external charging source (or the battery), as shown in figure 5.1 a. Assuming the droplet is a perfect conductor and has a size much larger than the dielectric thickness d , the total electrostatic free energy per unit wetted area reads $-\frac{\epsilon\epsilon_0 V^2}{2d}$, effectively lowering the solid-liquid surface energy. Here ϵ is the relative permittivity of the dielectric, ϵ_0 is the permittivity of free space and V is the applied voltage. When incorporating this in the total free energy of the system, and minimizing, we obtain the Young-Lippmann equation [102, 109]:

$$\cos\theta_L = \frac{\gamma_{SV} - \left(\gamma_{SL} - \frac{\epsilon\epsilon_0 V^2}{2d}\right)}{\gamma} = \cos\theta_Y + \frac{\epsilon\epsilon_0}{2\gamma d} V^2. \quad (5.1)$$

This can be viewed as a modified form of Young's equation. At vanishing voltage we recover Young's angle θ_Y , while at finite V one observes the Lippmann angle θ_L . The dimensionless combination

$$\eta = \frac{\epsilon\epsilon_0 V^2}{2\gamma d} \quad (5.2)$$

is also referred to as the electrowetting number [102].

The Young-Lippmann equation can be also derived from a force balance on a liquid control volume very close to the contact line. On rigid surfaces, it turns out that the true microscopic angle is again given by Young's law [110], i.e. we observe θ_Y , as is sketched in figure 5.1 b. However, the presence of surface charges gives rise to a Maxwell stress, pulling on the liquid-vapor interface. This Maxwell stress must be balanced by the Laplace pressure, which leads to a region of large curvature of the droplet surface near the contact line. The Maxwell stress is distributed over a region having a length scale comparable to the dielectric thickness d . Hence, when the droplet length scale is much larger than d , the increased curvature (bending) of the droplet surface close to the contact line manifests in a lowering of the macroscopic contact angle θ_L as sketched in figure 5.1b. It is the variation of this θ_L with V that is given by Equation (5.1).

It is now of interest to see how this scenario is altered if the dielectric layer is made soft, a sketch of the expected result is shown in figure 5.1 c. Wetting on soft surfaces lead to elastic deformations, altering the geometry near the contact line by creating a ridge on the soft substrate. The size of this wetting ridge can be of the order of the elastocapillary length γ/G , where G is the shear modulus of the dielectric layer. The geometry of the wetting ridge is dictated by a vectorial balance of surface tensions, known as Neumann's law [25], but the liquid contact angle typically remains at θ_Y . Interestingly, for soft PDMS layers, the elastocapillary length can easily be tens of microns. For the physical situations when γ/G is comparable to d , or larger, it is reasonable to expect an interplay between elasticity and electrostatics which may culminate in a change of the electrowetting effect as classically established solely for rigid dielectrics. Conversely, electrowetting provides an active way to probe the mechanics of the elastic wetting ridge, by imposing a highly localised forcing near the contact line.

The combination of the elasticity and electrowetting has been studied recently [111, 112]. These works showed experimentally that at a particular value of the applied voltage the macroscopic contact angle increases with increasing softness of the dielectric film [111, 112], suggesting the possibility of a departure from the classical Young-Lippmann equation. Furthermore, a simplified theoretical prediction for the shape of the wetting ridge as a function

of voltage was also proposed [111]. However, the details of the associated dynamics of the electrowetting process on soft dielectric films, and the resulting shape of the wetting ridge under electrowetting still remain to be better understood. Especially for the latter, no experimental data are available, not even under static conditions. In this Chapter we therefore experimentally investigate the statics and dynamics of Soft Electrowetting. We perform a systematic study of the macroscopic contact angles of the liquid, as a function of voltage V and contact line speed U . This is complemented with preliminary results, where we show the first images of wetting ridges in the presence of strong Maxwell stresses.

5.2 Methods

Electrowetting on soft solids was explored using a sessile drop on an ITO coated glass where we spincoated a thin layer of CY52-276 A/B PDMS gel. The gel has a shear modulus of ~ 1 KPa and exhibits a rheology that is similar to that discussed in the previous chapters. The spincoating is done by first pouring the uncured gel on the substrate, spreading this out to the edges of the glass and subsequently spincoating for 40s at 30rps. The samples were then cured by heating them at 70°C for 30 minutes. This resulted in a dielectric gel layer thickness of $22 \pm 1 \mu\text{m}$, measured using reflectometry with an Ocean Optics HR2000+ spectrometer and a HL-2000-FHSA halogen light source. The ITO surface below the gel coating was connected by scratching off the gel in a small area and using silver paste to glue a wire to the surface. Norland Optical Adhesive was applied on top of the connection and subsequently cured using UV light to fixate wire. We used 1mM KCl in deionised water to create a conductive liquid giving a surface tension of 72 mN/m . This gives an elastocapillary length $\gamma/G \sim 70 \mu\text{m}$, which is even larger than the dielectric thickness d . Hence, we expect a large deformation that is at least similar in magnitude to the layer thickness.

The system is placed in a dataphysics OCA15 to measure the contact angle, and we use a hamilton gas tight $500 \mu\text{l}$ syringe to deposit the drop on the surface. The metal needle is kept inserted inside the drop and connected to a function generator and an amplifier in order to apply a DC voltage between the drop and the ITO surface as shown schematically in figure 5.1. On quickly inflating the drop ($\sim 5 \mu\text{l/s}$), the drop spreads while the contact angle θ relaxes towards its equilibrium value θ_L . This is tracked as shown in figure 5.1 a. Typically the relaxation phase lasts for ~ 10 minutes.

We measured the the contact angle $\theta(t)$ and the corresponding position of the contact line $r(t)$. This was done using a MATLAB code that detects the

edge of the drop for each frame. The edge above the baseline is then fitted with a polyfit, both left and right sides of the drop. The intersection point of the polyfit with the baseline then gives the position of the contact line and the angle between the baseline and the polyfit at the intersection point gives the contact angle. The contact line speed U is subsequently extracted using a linear regression on the measured position of the contact line. The equilibrium angle θ_L is found by extrapolating the θ vs. U data for vanishing velocity, and cross-checked by finding the contact angle when the contact line speed reached 0 from the data recorded using the OCA. This yields the same result because the contact angle hysteresis of the gel is negligible [70, 80].

In a second set of experiments we focus on the shape of the wetting ridge in close proximity of the contact line. For this we use confocal microscopy. For confocal microscopy we use two fluorescent dyes—DFSB-K175 (Risk Reactor) in the gel and Alexa FluorTM 647 (ThermoFisher SCIENTIFIC) in the drop. The dye DFSB-K175 is mixed with the gel in the volume ratio of 50 μ l per ml. In order to index match the water with the gel, deionized water was mixed with glycerol in a container with fully cured gel until the interface between the liquid and the gel optically disappeared. Alexa Fluor 647 was added with a ratio of 0.2mg per ml and 1 mM of KCl was subsequently added to make the liquid conductive. The maximum emission wavelength for the dye DFSB-K175 corresponding to an excitation wavelength of 488 nm is 540 nm, while the maximum excitation and emission wavelengths for Alexa Fluor 647 is 653 nm and 669 nm respectively. For confocal imaging we use a Nikon A1 inverted line scanning confocal microscope with excitation lasers at 488 nm (for DFSB-K175 in the substrate) and 638 nm (for Alexa Fluor 647 in the drop), and with a 60x water immersion objective with numerical aperture (NA)=1.2. The emissions from the two dyes are collected using band filters in the range 500 nm to 550 nm for DFSB-K175 and in the range of 663 nm to 700 nm for Alexa Fluor 647. 3D confocal scans are performed in the immediate vicinity of the contact line such that surface of the gel wetted by the droplet as well as the dry side are simultaneously visible. The 3D confocal scans are post-processed using ImageJ, and the xz slices are analyzed using an in-house MATLAB code to evaluate the deformation characteristics of the soft gel.

To measure the dielectric constant we performed an independent calibration of ϵ . For this, a glass slide was coated with platinum square of a known area, and placed below a platinum conductive slide, with 0.55 ± 0.01 mm glass spacers between. The gap was filled with the gel and the capacitance was measured using an HP 4194A impedance gain phase analyzer, while wrapped in aluminium foil as a Faraday cage to prevent EM interference. By a capacitive measurement, we determine the dielectric constant as

$$\epsilon = \frac{Cd}{\epsilon_0 A}. \quad (5.3)$$

Here C is the measured capacitance of $23 \pm 1 \text{ pF}$, $d = 0.55 \pm 0.01 \text{ mm}$ is the thickness of the dielectric layer, ϵ_0 is the permittivity of vacuum and $A = 415 \pm 4 \text{ mm}^2$ is the area. This gives a result of $\epsilon = 3.4 \pm 0.3$.

5.3 Macroscopic contact angles

In figure 5.2 we report the dynamic contact angle as a function of the instantaneous contact line speed $U = dr/dt$, where the various curves correspond to different applied voltages V . The plot shows that the contact angle θ increases as the speed U increases, as is expected for advancing contact angles. When considering a certain velocity, we clearly observe that θ decreases upon increasing the voltage V . The equilibrium angle at zero velocity, which we denote by the Lippmann angle θ_L , is seen to decrease with V . The datasets at varying voltage all lie parallel to one another, suggesting that their behaviour is similar.

Figure 5.2: Liquid contact angle θ as a function of contact line speed U for increasing applied voltage. The data are obtained at 0V (blue), 50V (red), 75V (yellow), 100V (purple), 125V (green), 150V (light blue), 175V (maroon), 200V (sky blue), 250V (pink).

We first analyze in more detail whether the electrostatic effects alter the contact line dynamics. For this we report $\theta - \theta_L$ as a function of U , which is

Figure 5.3: Change of liquid contact angle from the equilibrium angle, $\theta - \theta_L$, as a function of contact line speed U . The data for different applied voltages collapse. Only the errorbars for the 0V are shown, and the same color coding as figure 5.2 is used.

presented in figure 5.3. It can be clearly seen that all the curves collapse. The data exhibits a power law dependence, where the dashed line shows a power law fit for $U^{0.55}$. This follows the same behavior as discussed in Chapter 2 and 3, where we investigated the dynamics at zero voltage. It was found that the dynamic contact angle $\theta - \theta_{eq} \sim U^n$ where n is the exponent of the loss modulus. The power law exponent under electrowetting has the same value as that found in Chapter 2, where we used the same gel at the same mixing ratio. This means that the droplet spreading under an applied electrical voltage is still dominated by viscoelastic dissipation in the gel, and that this dissipation is not significantly affected by the additional electrical effects under electrowetting.

Now we turn to the measured value of the static angle θ_L as a function of V . Given the Young-Lippmann equation (5.1), we report $\cos \theta_L$ as a function of V^2 , as shown in figure 5.4. The experimental data are shown as markers. Indeed, the results clearly give a linear relation and from the linear fit (yellow line) we determine the slope as $8.0 \times 10^{-6} V^{-2}$. The value of the slope can be compared to the prediction $\frac{\epsilon \epsilon_0}{2\gamma d}$, as given by (5.1). Using the measured value for d and the manufacturer supplied value, $\epsilon = 2.5$ [113], we obtain a value for the slope of $7.0 \times 10^{-6} V^{-2}$, as denoted by the dashed line in figure 5.4, while using the measured value for ϵ we obtain $9.5 \pm 0.9 \times 10^{-6} V^{-2}$ as denoted by the shaded grey area in the figure. Hence, we conclude that the static contact angle on soft dielectric layers still closely follows the Young-Lippmann equation.

Figure 5.4: Equilibrium angles as a function of the applied voltage squared, the shaded area shows the result of equation 5.1 based on the measured ϵ while the dashed line uses the manufacturers specification, the yellow linear fit has a slope of $8.0 \times 10^{-6} V^{-2}$.

5.4 The wetting ridge

Since both the elastocapillarity and electrostatic effects act in close vicinity of the contact line, we zoom in to the details at the contact line using confocal microscopy. Our first results of the confocal measurements of the wetting ridge are reported in figure 5.5. We show two wetting ridge shapes at equilibrium: Panel (a) corresponds to a case without any electrowetting, while panel (b) corresponds to 125V and hence exhibits a lower liquid contact angle. Both images correspond to an unprocessed slice of the data obtained through the confocal measurement. The extracted profiles are shown side by side in figure 5.5c, respectively given in blue (0V) and red (125V).

In both cases, the height of the wetting ridge is comparable to the thickness of the viscoelastic layer. We observe that both with and without an applied voltage the gel has a dimple to the left and to the right of the wetting ridge. This is a consequence of the incompressibility of the gel – the volume inside the wetting ridge is directly drawn from the adjacent region. The minimum of the dimple is at a distance comparable to the thickness of the gel [93].

When comparing the two shapes, one observes that the dimple on the side of the the droplet (left to the contact line) is deeper when a voltage is applied. This is a result of the added Maxwell stress on the liquid-solid interface near the contact line, as sketched in figure 5.1c. Consequently, the entire wetting ridge

Figure 5.5: (a,b) Confocal microscopy images of the wetting ridge below the contact line of a liquid drop on gel. Taken at 0V (a) and at 125V (b). (c) Profiles extracted from the confocal measurements at 0V (blue) and 125V (red).

appears to be tilted towards the liquid side, as that is the only place where the Maxwell stress directly acts on the substrate. The tip of the wetting ridge shows no measurable change in the solid opening angle. The constant tip angle suggests that the Neumann law is still applicable at the ridge tip, representing a balance of the three involved surface tensions. This nicely illustrates that at the ultimate scale, neither Maxwell stress or bulk elasticity can compete with surface forces – a result that is known for both electrowetting [110] and for soft wetting [77, 80]. On the scale of the wetting ridge, we thus see that the reduction of the macroscopic angle θ_L comes with a rotation of the wetting ridge, while maintaining the Neumann angles. This is in direct analogy to the dynamic effect; in that case the ridge rotation is induced dynamically as we saw in the previous Chapters 2 and 3.

Finally, we comment on the relative strength of the various forces at play. First, we note in figure 5.5c that the wetting ridge height is decreased when the voltage is applied. This can be explained from the reduced vertical forcing by the drop $\gamma \sin \theta$, which is lowered by the application of a voltage. Second, the Maxwell stress itself is pushing on the wetted part of the solid. The relative strength of the “pulling” by the drop and the “pushing” by the Maxwell stress is directly quantified by the electrowetting number η , and hence by the difference $\cos \theta_Y - \cos \theta_L$. For the present case, $\eta = 0.24$ and we expect the relative change of the wetting ridge by Maxwell stress to be of the order of 25%. This indeed gives a reasonable estimate of the difference between the blue and red data in figure 5.5c.

5.5 Discussion

In summary, we have investigated the macroscopic contact angles for electrowetting on a soft dielectric layer, both in static and in dynamic conditions. It is found that electrowetting does not affect the dynamics of the contact line motion which is still governed by the dissipation in the viscoelastic gel: the dynamic contact angles can be collapsed when plotting $\theta - \theta_L$ versus speed, where θ_L is the static “Lippmann” angle at vanishing velocity. Subsequently, we have qualitatively explored the structure of the wetting ridge, comparing shapes with and without an applied voltage.

To explain why Young-Lippmann equation (5.1) still holds for soft dielectrics we now revisit the macroscopic argument and estimate how this is altered by elasticity. The idea behind the macroscopic reasoning is that one can ignore the intricate structure of the three phase contact line, and one only needs to invoke the surface energies at large distances from the contact line. On the dry part there is no Maxwell stress (outside the contact line region) and hence there

is no elastic deformation. Below the drop, however, there is a homogenous Maxwell stress $p_M = \frac{\epsilon\epsilon_0 V^2}{2d^2}$. On a compressible layer of Poisson ratio ν , this leads to a compression Δd of the layer

$$\frac{\Delta d}{d} = \left(\frac{1-2\nu}{1-\nu} \right) \frac{p_M}{2G} = \left(\frac{1-2\nu}{1-\nu} \right) \frac{\epsilon\epsilon_0 V^2}{4d^2 G}. \quad (5.4)$$

The associated elastic energy per unit surface then follows as $\frac{1}{2}p_M\Delta d$, leading to an increase of the effective surface energy per unit wetted area. Hence, the modified Young-Lippmann equation becomes

$$\cos\theta = \frac{\gamma_{SV} - \left(\gamma_{SL} - \frac{\epsilon\epsilon_0 V^2}{2d} + \frac{p_M \Delta d}{2} \right)}{\gamma} = \cos\theta_L - \frac{1}{4} \left(\frac{1-2\nu}{1-\nu} \right) \frac{p_M^2 d}{G\gamma}. \quad (5.5)$$

When applying this result to our gel, which is incompressible with $\nu = 1/2$, one thus expects there is no departure from the Lippmann equation. Namely, the homogeneous Maxwell stress below the drop does not induce any deformation of the incompressible layer; by consequence no elastic energy is stored far away from the contact line and hence we observe no effect on the static contact angle.

Future work should be dedicated to the physics on the scale where the electrostatic and elastic forces are most prominent, i.e. on the scale of the wetting ridge. This could be done in the form of a more extensive experimental study using confocal microscopy, in combination with explicit mechanical calculations that predict the shape of the wetting ridge.

References

References

- [1] C. Duprat, S. Protière, A. Y. Beebe, and H. A. Stone, “Wetting of flexible fibre arrays”, *Nature* **482**, 510–513 (2012).
- [2] P.-G. de Gennes, F. Brochart-Wyart, and D. Quéré, *Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves* (Belin) (2002).
- [3] T. Young, “An essay on the cohesion of fluids”, *Philos. Trans. Royal Soc.* **95**, 65–87 (1805).
- [4] C. Huh and L. E. Scriven, “Hydrodynamic model of steady movement of a solid/liquid/fluid contact line”, *J. Colloid Interface Sci.* **35**, 85 – 101 (1971).
- [5] E. B. Dussan, “On the spreading of liquids on solid surfaces: Static and dynamic contact lines”, *Annu. Rev. Fluid Mech.* **11**, 371–400 (1979).
- [6] D. Bonn, J. Eggers, J. Indekeu, J. Meunier, and E. Rolley, “Wetting and spreading”, *Rev. Mod. Phys.* **81**, 739–805 (2009).
- [7] Y. Shikhmurzaev, “The moving contact line on a smooth solid surface”, *Int. J. Multiph. Flow* **19**, 589–610 (1993).
- [8] J. H. Snoeijer and B. Andreotti, “Moving contact lines: Scales, regimes, and dynamical transitions”, *Annu Rev. Fluid Mech.* **45**, 269–92 (2013).
- [9] B. Bhushan and Y. C. Jung, “Natural and biomimetic artificial surfaces for superhydrophobicity, self-cleaning, low adhesion, and drag reduction”, *Prog. Mater Sci.* **56**, 1 – 108 (2011).
- [10] Y. Y. Yan, N. Gao, and W. Barthlott, “Mimicking natural superhydrophobic surfaces and grasping the wetting process: A review on recent progress in preparing superhydrophobic surfaces”, *Adv. Colloid Interface Sci.* (2011).
- [11] T.-S. Wong, S. H. Kang, S. K. Y. Tang, E. J. Smythe, B. D. Hatton, A. Grinthal, and J. Aizenberg, “Bioinspired self-repairing slippery surfaces with pressure-stable omniphobicity”, *Nature* **477**, 443–447 (2011).
- [12] F. Schellenberger, J. Xie, N. Encinas, A. Hardy, M. Klapper, P. Papadopoulos, H.-J. Butt, and D. Vollmer, “Direct observation of drops on slippery lubricant-infused surfaces”, *Soft Matter* **11**, 7617–7626 (2015).

- [13] M. Sokuler, G. Auernhammer, M. Roth, C. Liu, E. Bonaccorso, and H. Butt, “The softer the better: fast condensation on soft surfaces”, *Langmuir* **26**, 1544–1547 (2010).
- [14] R. W. Style, Y. Che, S. J. Park, B. M. Weon, J. H. Je, C. Hyland, G. K. German, M. P. Power, L. A. Wilen, J. S. Wettlaufer, and E. R. Dufresne, “Patterning droplets with durotaxis”, *Proc. Natl. Acad. Sci. USA* **110**, 12541–12544 (2013).
- [15] A. Carré, J.-C. Gastel, and M. E. R. Shanahan, “Viscoelastic effects in the spreading of liquids”, *Nature* **379**, 432–434 (1996).
- [16] R. Pericet-Camara, A. Best, H. J. Butt, and E. Bonaccorso, “Effect of capillary pressure and surface tension on the deformation of elastic surfaces by sessile liquid microdrops: an experimental investigation”, *Langmuir* **24**, 10565–10568 (2008).
- [17] E. R. Jerison, Y. Xu, L. A. Wilen, and E. R. Dufresne, “Deformation of an Elastic Substrate by a Three-Phase Contact Line”, *Phys. Rev. Lett.* **106**, 186103 (2011).
- [18] S. Park, B. Weon, J. Lee, J. Lee, J. Kim, and J. Je, “Visualization of asymmetric wetting ridges on soft solids with x-ray microscopy”, *Nat. Commun.* **5**, 4369 (2014).
- [19] A. Rusanov, “Theory of wetting of elastically deformed bodies.1. deformation with a finite contact-angle”, *Colloid J. USSR* **37**, 614–622 (1975).
- [20] G. Lester, “Contact angles of liquids at deformable solid surfaces”, *J. Colloid Sci.* **16**, 315–326 (1961).
- [21] M. E. R. Shanahan, “The spreading dynamics of a liquid drop on a viscoelastic solid”, *J. Phys. D-Appl. Phys.* **21** (1988).
- [22] M. E. R. Shanahan and P. G. de Gennes, “Equilibrium of the triple line solid/liquid/fluid of a sessile drop”, in *Adhesion 11*, 71–81 (Springer Netherlands) (1987).
- [23] P. G. de Gennes, “Soft adhesives”, *Langmuir* **12**, 4497–4500 (1996).
- [24] X. Liang and S. Boppart, “Biomechanical properties of in vivo human skin from dynamic optical coherence elastography”, *IEEE Trans. Biomed. Eng.* **57**, 953–959 (2010).
- [25] F. E. Neumann, *Vorlesungen über die Theorie der Capillarität, gehalten an der Universität Königsberg von Franz Neumann*, volume 7 (BG Teubner) (1894).
- [26] D. Long, A. Ajdari, and L. Leibler, “Static and dynamic wetting properties of thin rubber films”, *Langmuir* **12**, 5221–5230 (1996).
- [27] A. Marchand, S. Das, J. H. Snoeijer, and B. Andreotti, “Contact Angles on a Soft Solid: From Young’s Law to Neumann’s Law”, *Phys. Rev. Lett.* **109**, 236101 (2012).

- [28] R. W. Style, R. Boltyanskiy, Y. Che, J. S. Wettlaufer, L. A. Wilen, and E. R. Dufresne, “Universal deformation of soft substrates near a contact line and the direct measurement of solid surface stresses”, *Phys. Rev. Lett.* **110**, 066103 (2013).
- [29] L. A. Lubbers, J. H. Weijs, L. Botto, S. Das, B. Andreotti, and J. H. Snoeijer, “Drops on soft solids: free energy and double transition of contact angles”, *J. Fluid Mech. Rapids* **747**, R1 (2014).
- [30] J. Dervaux and L. Limat, “Contact lines on soft solids with uniform surface tension: analytical solutions and double transition for increasing deformability”, *Proc. Royal Soc. Lond.* **471**, 20140813–20140813 (2015).
- [31] E. H. van Brummelen, M. Shokrpour-Roudbari, and G. J. van Zwieten, “Elasto-capillarity simulations based on the navier–stokes–cahn–hilliard equations”, in *Adv. Colloid Interface Sci.*, 451–462 (Springer International Publishing) (2016).
- [32] M. Shanahan and A. Carre, “Viscoelastic dissipation in wetting and adhesion phenomena”, *Langmuir* **11**, 1396–1402 (1995).
- [33] T. Kajiya, A. Daerr, T. Narita, L. Royon, F. Lequeux, and L. Limat, “Advancing liquid contact line on visco-elastic gel substrates: stick-slip vs. continuous motions”, *Soft Matter* **9**, 454–461 (2013).
- [34] D. Long, A. Ajdari, and L. Leibler, “How do grafted polymer layers alter the dynamics of wetting?”, *Langmuir* **12**, 1675–1680 (1996).
- [35] T. Kajiya, P. Brunet, L. Royon, A. Daerr, M. Receveur, and L. Limat, “A liquid contact line receding on a soft gel surface: dip-coating geometry investigation”, *Soft Matter* (2014).
- [36] M. L. Manning, R. A. Foty, M. S. Steinberg, and E. M. Schoetz, “Coaction of intercellular adhesion and cortical tension specifies tissue surface tension”, *Proc. Natl Acad. Sci. Usa* **107**, 12517–12522 (2010).
- [37] J.-P. Trinkhaus and P. Groves, “Differentiation in cultures of mixed aggregates of dissociated tissue cells”, *Proc. Nat. Acad. Sci.* **41**, 787–795 (1955).
- [38] M. S. Steinberg, “Reconstruction of tissues by dissociated cells”, *Science* **141**, 401–408 (1963).
- [39] M. Armstrong and P. Armstrong, “Mechanisms of epibolic tissue spreading analyzed in a model morphogenetic system - roles for cell-migration and tissue contractility”, *J. Cell. Sci.* **102**, 373–385 (1992).
- [40] S. Douezan, J. Dumond, and F. Brochard-Wyart, “Wetting transitions of cellular aggregates induced by substrate rigidity”, *Soft Matter* **8**, 4578–4583 (2012).
- [41] J. Sabari, D. Lax, D. Connors, I. Brotman, E. Mindrebo, C. Butler, I. Entersz, D. Jia, and R. A. Foty, “Fibronectin matrix assembly suppresses

- dispersal of glioblastoma cells”, PLoS One **6**, e24810 (2011).
- [42] M. Shanahan, “The influence of solid micro-deformation on contact-angle equilibrium”, J. Phys. D-Appl. Phys. **20**, 945–950 (1987).
 - [43] E. R. Jerison, Y. Xu, L. A. Wilen, and E. R. Dufresne, “Deformation of an Elastic Substrate by a Three-Phase Contact Line”, Phys. Rev. Lett. **106**, 186103 (2011).
 - [44] D. Discher, P. Janmey, and Y. Wang, “Tissue cells feel and respond to the stiffness of their substrate”, Science **310**, 1139–1143 (2005).
 - [45] C. Huh and L. E. Scriven, “Hydrodynamic model of steady movement of a solid/liquid/fluid contact line”, J. Coll. Int. Sci. **35**, 85–101 (1971).
 - [46] R. Shuttleworth, “The surface tension of solids”, Proc. Phys. Soc., London Sect. A **63**, 444–457 (1950).
 - [47] L. Limat, “Straight contact lines on a soft, incompressible solid”, Eur. Phys. J. E **35**, 134 (2012).
 - [48] J. H. Weijs, B. Andreotti, and J. H. Snoeijer, “Elasto-capillarity at the nanoscale: on the coupling between elasticity and surface energy in soft solids”, Soft Matter **9**, 8494–8503 (2013).
 - [49] J. Bostwick, M. Shearer, and K. Daniels, “Elastocapillary deformations on partially-wetting substrates: rival contact-line models”, Soft Matter **10**, 7361–7369 (2014).
 - [50] L. White, “The contact angle on an elastic substrate. 1. The role of disjoining pressure in the surface mechanics”, J. Colloid Interface Sci. **258**, 82–96 (2003).
 - [51] R. W. Style and E. R. Dufresne, “Static wetting on deformable substrates, from liquids to soft solids”, Soft Matter **8**, 7177–7184 (2012).
 - [52] A. Carre, J. Gastel, and M. Shanahan, “Viscoelastic effects in the spreading of liquids”, Nature **379**, 432–434 (1996).
 - [53] R. W. Style, R. Boltyskiy, G. K. German, C. Hyland, C. W. MacMinn, A. F. Mertz, L. A. Wilen, Y. Xu, and E. R. Dufresne, “Traction force microscopy in physics and biology”, Soft Matter **10**, 4047–4055 (2014).
 - [54] H. Winter and F. Chambon, “Analysis of linear viscoelasticity of a cross-linking polymer at the gel point”, J. Rheol. **30**, 367–382 (1986).
 - [55] J. C. Scanlan and H. H. Winter, “Composition dependence of the viscoelasticity of end-linked poly(dimethylsiloxane) at the gel point”, Macromolecules **24**, 47–54 (1991).
 - [56] G. Lester, “Contact angles of liquids at deformable solid surfaces”, J. Colloid Sci. **16**, 315–326 (1961).
 - [57] A. Rusanov, “Theory of wetting of elastically deformed bodies .1. Deformation with a finite contact-angle”, Colloid J. USSR **37**, 614–622 (1975).

- [58] A. Rusanov, “Thermodynamics of deformable solid-surfaces”, *J. Colloid Interface Sci.* **63**, 330–345 (1978).
- [59] P.-G. de Gennes, F. Brochard-Wyart, and D. Quere, *Capillarity and wetting phenomena: drops, bubbles, pearls, waves* (Springer, New York) (2004).
- [60] S. Mora, T. Phou, J.-M. Fromental, L. M. Pismen, and Y. Pomeau, “Capillarity driven instability of a soft solid”, *Phys. Rev. Lett.* **105**, 214301 (2010).
- [61] A. Marchand, S. Das, J. H. Snoeijer, and B. Andreotti, “Capillary pressure and contact line force on a soft solid”, *Phys. Rev. Lett.* **108**, 094301 (2012).
- [62] Y. Xu, C. Engl, E. Jerison, K. Wallenstein, C. Hyland, L. Wilen, and E. Dufresne, “Imaging in-plane and normal stresses near an interface crack using traction force microscopy”, *Proc. Nat. Acad. Sci.* **107**, 14964 (2010).
- [63] A. Marchand, S. Das, J. H. Snoeijer, and B. Andreotti, “Contact Angles on a Soft Solid: From Young’s Law to Neumann’s Law”, *Phys. Rev. Lett.* **109**, 236101 (2012).
- [64] P. Flory and J. Rehner, “Statistical mechanics of cross-linked polymer networks i: Rubberlike elasticity”, *J. Chem. Phys.* **11**, 512–520 (1943).
- [65] S. Rubinstein and M. Panyukov, “Elasticity of polymer networks”, *Macromolecules* **35**, 6670–6686 (2002).
- [66] O. V. Voinov, “Hydrodynamics of wetting [english translation]”, *Fluid Dyn.* **11**, 714–721 (1976).
- [67] R. G. Cox, “The dynamics of the spreading of liquids on a solid surface. part 1. viscous flow”, *J. Fluid Mech.* **168**, 169–194 (1986).
- [68] N. Nadermann, C.-Y. Hui, and A. Jagota, “Solid surface tension measured by a liquid drop under a solid film”, *Proc. Natl. Acad. Sci. U.S.A.* **110**, 10541–10545 (2013).
- [69] S. Mondal, M. Phukan, and A. Ghatak, “Estimation of solid–liquid interfacial tension using curved surface of a soft solid”, *Proc. Natl. Acad. Sci. U.S.A.* **112**, 12563–12568 (2015).
- [70] Q. Xu, K. E. Jensen, R. Boltyskiy, R. Sarfati, R. W. Style, and E. R. Dufresne, “Direct measurement of strain-dependent solid surface stress”, *Nat. Commun.* **8**, 555 (2017).
- [71] R. D. Schulman, M. Trejo, T. Salez, E. Raphaël, and K. Dalnoki-Veress, “Surface energy of strained amorphous solids”, *Nat. Commun.* **9**, 982 (2018).
- [72] R. Lhermerout, H. Perrin, E. Rolley, B. Andreotti, and K. Davitt, “A moving contact line as a rheometer for nanometric interfacial layers”,

- Nat. Commun. **7**, 12545 (2016).
- [73] R. G. Cox, “The dynamics of the spreading of liquids on a solid surface. part1. viscous flow”, J. Fluid Mech. **168**, 169–194 (1986).
 - [74] L. Tanner, “The spreading of silicone oil drops on horizontal surfaces”, J. Phys. D: Appl. Phys. **12**, 1473 (1979).
 - [75] P.-G. de Gennes, “Wetting: statics and dynamics”, Rev. Mod. Phys. **57**, 827–863 (1985).
 - [76] A. Carré and M. E. R. Shanahan, “Direct evidence for viscosity-independent spreading on soft solid”, Langmuir (1995).
 - [77] R. W. Style, A. Jagota, C.-Y. Hui, and E. R. Dufresne, “Elastocapillarity: Surface tension and the mechanics of soft solids”, Annu. Rev. Condens. Matter Phys. **8**, 99–118 (2017).
 - [78] B. Andreotti and J. H. Snoeijer, “Soft wetting and the Shuttleworth effect, at the crossroads between thermodynamics and mechanics”, Europhys. Lett. **113**, 66001 (2016).
 - [79] S. J. Park, J. B. Bostwick, V. De Andrade, and J. H. Je, “Self-spreading of the wetting ridge during stick-slip on a viscoelastic surface”, Soft Matter **13**, 8331–8336 (2017).
 - [80] J. H. Snoeijer, E. Rolley, and B. Andreotti, “Paradox of contact angle selection on stretched soft solids”, Phys. Rev. Lett. **121** (2018).
 - [81] S. Karpitschka, S. Das, M. van Gorcum, H. Perrin, B. Andreotti, and J. H. Snoeijer, “Soft wetting: Models based on energy dissipation or on force balance are equivalent”, Proc. Natl. Acad. Sci. U.S.A. **115**, E7233–E7233 (2018).
 - [82] M. Zhao, J. Dervaux, T. Narita, F. Lequeux, L. Limat, and M. Roché, “Reply to karpitschka et al.: The neumann force balance does not hold in dynamical elastowetting”, Proc. Natl. Acad. Sci. U.S.A. **115**, E7234–E7235 (2018).
 - [83] M. Zhao, J. Dervaux, T. Narita, F. Lequeux, L. Limat, and M. Roché, “Geometrical control of dissipation during the spreading of liquids on soft solids”, Proc. Natl. Acad. Sci. U.S.A. **115**, 1748–1753 (2018).
 - [84] R. Shuttleworth, “The surface tension of solids”, Proc. Phys. Soc. A **63**, 444 (1950).
 - [85] M. E. R. Shanahan and A. Carré, “Spreading and dynamics of liquid drops involving nanometric deformations on soft substrates”, Colloids Surf., A **206**, 115 – 123 (2002).
 - [86] K. L. Johnson, *Contact mechanics* (Cambridge University Press) (1985).
 - [87] M. Singh and A. C. Pipkin, “Note on ericksens problem”, Z. Angew. Math. Phys. **16**, 706–709 (1965).
 - [88] L. White, “The contact angle on an elastic substrate. 1. the role of

- disjoining pressure in the surface mechanics”, *J. Colloid Interface Sci.* **258**, 82–96 (2003).
- [89] A. Rosso and W. Krauth, “Roughness at the depinning threshold for a long-range elastic string”, *Phys. Rev. E* **65**, 025101(R) (2002).
 - [90] H. Perrin, R. Lhermerout, K. Davitt, E. Rolley, and B. Andreotti, “Defects at the nanoscale impact contact line motion at all scales”, *Phys. Rev. Lett.* (2016).
 - [91] B. R. Solomon, S. B. Subramanyam, T. A. Farnham, K. S. Khalil, S. Anand, and K. K. Varanasi, “CHAPTER 10. lubricant-impregnated surfaces”, in *Non-wettable Surfaces*, 285–318 (Royal Society of Chemistry) (2016).
 - [92] D. Quéré, “Wetting and roughness”, *Annu. Rev. Mater. Res.* **38**, 71–99 (2008).
 - [93] S. Karpitschka, A. Pandey, L. A. Lubbers, J. H. Weijs, L. Botto, S. Das, B. Andreotti, and J. H. Snoeijer, “Liquid drops attract or repel by the inverted Cheerios effect”, *Proc. Natl. Acad. Sci. U. S. A.* **113**, 7403 (2016).
 - [94] T. Baumberger and C. Caroli, “Solid friction from stick–slip down to pinning and aging”, *Adv. Phys.* **55**, 279–348 (2006).
 - [95] Q. Xu, R. W. Style, and E. R. Dufresne, “Surface elastic constants of a soft solid”, *Soft Matter* **14**, 916–920 (2018).
 - [96] J. W. Gibbs, “The scientific papers of jw gibbs, vol. 1”, (1961).
 - [97] J. Oliver, C. Huh, and S. Mason, “Resistance to spreading of liquids by sharp edges”, *J. Colloid Interface Sci.* **59**, 568–581 (1977).
 - [98] D. Dyson, “Contact line stability at edges: comments on gibbs’s inequalities”, *Phys. Fluids* **31**, 229–232 (1988).
 - [99] B. Andreotti and J. H. Snoeijer, “Soft wetting and the Shuttleworth effect, at the crossroads between thermodynamics and mechanics”, *Europhys. Lett.* **109**, 66001 (2016).
 - [100] G. G. Fuller and J. Vermant, “Complex fluid-fluid interfaces: rheology and structure”, *Annu. Rev. Chem. Biomol. Eng.* **3**, 519–543 (2012).
 - [101] H. Ritacco, D. Langevin, H. Diamant, and D. Andelman, “Dynamic surface tension of aqueous solutions of ionic surfactants: role of electrostatics”, *Langmuir* **27**, 1009–1014 (2011).
 - [102] F. Mugele and J.-C. Baret, “Electrowetting: from basics to applications”, *J. Phys.: Condens. Matter* **17**, R705–R774 (2005).
 - [103] H. B. Eral, J. de Ruiter, R. de Ruiter, J. M. Oh, C. Semprebon, M. Brinkmann, and F. Mugele, “Drops on functional fibers: from barrels to clamshells and back”, *Soft Matter* **7**, 5138 (2011).
 - [104] C. U. Murade, J. M. Oh, D. van den Ende, and F. Mugele, “Electrowetting driven optical switch and tunable aperture”, *Opt. Express* **19**, 15525

- (2011).
- [105] R. de Ruiter, C. Semperebon, M. van Gorcum, M. H. Duits, M. Brinkmann, and F. Mugele, “Stability limits of capillary bridges: How contact angle hysteresis affects morphology transitions of liquid microstructures”, *Phys. Rev. Lett.* **114** (2015).
 - [106] D. J. Lomax, P. Kant, A. T. Williams, H. V. Patten, Y. Zou, A. Juel, and R. A. W. Dryfe, “Ultra-low voltage electrowetting using graphite surfaces”, *Soft Matter* **12**, 8798–8804 (2016).
 - [107] R. B. Fair, “Digital microfluidics: is a true lab-on-a-chip possible?”, *Microfluid. Nanofluid.* **3**, 245–281 (2007).
 - [108] A. Pit, M. Duits, and F. Mugele, “Droplet manipulations in two phase flow microfluidics”, *Micromachines* **6**, 1768–1793 (2015).
 - [109] B. Bruno, “Electrocapillarité et mouillage de films isolants par l’eau”, *Comptes Rendus Acad. Sci.* **317**, 157–163 (1993).
 - [110] J. Buehrle, S. Herminghaus, and F. Mugele, “Interface profiles near three-phase contact lines in electric fields”, *Phys. Rev. Lett.* **91** (2003).
 - [111] R. Dey, S. DasGupta, and S. Chakraborty, “Electrowetting of sessile drops on soft dielectric elastomer films”, *Microfluid. Nanofluid.* **21** (2017).
 - [112] R. Dey, A. Daga, S. DasGupta, and S. Chakraborty, “Electrically modulated dynamic spreading of drops on soft surfaces”, *Appl. Phys. Lett.* **107**, 034101 (2015).
 - [113] Dow Chemical Company, *DOWSIL CY 52-276 Gel Technical data sheet*, URL <https://consumer.dow.com/en-us/document-viewer.html?docPath=/content/dam/dcc/documents/en-us/productdatasheet/11/11-12/11-1242-01-dowsil-cy-52-276-gel.pdf>.

Summary

Wetting on soft polymeric solids has seen a large increase in interest over the past decade. Surfaces responding to environmental stimuli are of interest for both technological applications and fundamental understanding of solid-liquid interaction. The interplay between the deformable surfaces and the liquid surface tension has been shown to exhibit intriguing behaviour, varying from very slow dynamics due to the dissipation in the solid, negligible contact angle hysteresis, to irregular rapid drop spreading. The presence of a balance of the liquid surface tension with the solid interfacial tension at the microscopic scale causing the creation of a ridge shape at the contact line significantly affects the macroscopic behaviour of partially wetted surfaces. By abstracting the partially wetted systems to a single contact line, we were able to study the dynamics of a contact line on a soft solid in detail, under various different conditions.

We first studied the steady-state motion of the contact line (chapter 2 and 3). The liquid surface tension imposes a traction on the surface, deforming the surface at the contact line in to a wetting ridge. By imposing a solid surface tension to balance the liquid surface tension at the microscopic scale, and using the linear elasticity we were able to predict dynamic ridge shapes for varying rheologies. In chapter 2 this result was used to calculate a rotation of the wetting ridge as a function of contact line speed for dissipative solids. At the low speed regime, the ridge rotation follows a the same power law behaviour as the loss modulus of the gel, while at a larger speed the rotation saturates. This rotation was compared to the change macroscopic in liquid contact angle where we found that the calculated rotation of the wetting ridge matches the change in contact angle as a function of speed over a large regime. In chapter 3 the veracity of the claim in chapter 2 was tested, next to a description of wetting ridge behaviours currently not captured by theory. By zooming in to the wetting ridge using a novel experimental method to visualize the wetting ridge we were able to confirm that the ridge does indeed rotate at the identical rate as the liquid contact angle changes at a low speed regime. However, a deviation between ridge rotation and contact angle change was observed for higher contact line speeds. This deviation happens as the solid opening angle

of the tip of the wetting ridge starts to increase. This change in solid opening angle (θ_s) points to a change in the force balance at the tip of the wetting ridge. The increase of θ_s suggest that the surface tension in the solid increases with increasing contact line speed, which influences the shape of the wetting ridge at higher speeds.

Chapter 4 focuses at this higher speed regime, where the change in solid opening angle becomes significant. The unexplained dynamic increase in surface tension of the solid leading to the change of the wetting ridge shape is shown to be the cause of the stick-slip-like dynamics for contact lines moving at high speed over the solid surface. Particularly, the increasing θ_s changes the relative angles of the liquid with the solid up to the point that Gibbs inequality is violated leading to the depinning of the contact line from the wetting ridge.

In chapter 5 we introduce an electric potential over the soft solid, leading to an added energy term to the classical Young's equation, changing to the Young-Lippmann equation. This effect lowers the macroscopic contact angle of a liquid on a dielectric solid, and is known as electrowetting. We demonstrate that the electrowetting effect on soft solids follows the same laws as for rigid solids. The decrease in contact angle as a function of voltage is given by the electrical properties of the gel, the thickness of the layer and the applied voltage squared. We also observe that the dissipative dynamical behaviour of the wetting ridge remains constant for different applied voltages, still showing the identical powerlaw behaviour given by the rheology of the gel. Some preliminary results are presented of the shape of the wetting ridge under influence of the applied electric field, using confocal microscopy.

Samenvatting

De interesse in de bevochtiging van zachte polymeer vaste stoffen is sterk gegroeid over het afgelopen decennium. Oppervlakken die reageren op externe stimuli zijn interessant voor zowel technologische toepassingen als voor het fundamentele begrip van vloeistof-vaste stof interactie. De wisselwerking tussen vervormbare oppervlakken en de oppervlaktespanning van vloeistoffen laat intrigerende gedragingen zien, variërend van erg trage dynamica door dissipatie in de vaste stof, verwaarloosbaar kleine contacthoek hysteresis, tot onregelmatige snelle druppeluitspreiding. De aanwezigheid van een balans tussen de oppervlaktespanning van de vloeistof met de grensvlakspanning van de vaste stof op de microscopische schaal die een bevochtigingsrichel creëert heeft een significante invloed op de macroscopische gedragingen van een gedeeltelijk bevochtigd oppervlak. Door de gedeeltelijk bevochtigde systemen te abstraheren naar een enkele contactlijn waren wij in staat om de dynamica van een contactlijn op en zachte vaste stop in detail te bestuderen, in verschillende situaties.

Eerst hebben we de steady-state beweging van een contactlijn bestudeerd (hoofdstuk 2 en 3). De oppervlaktespanning van de vloeistof legt een tractie op aan het oppervlak, dat onder de contactlijn vervormd to een bevochtigingsrichel. Door een oppervlaktespanning van de vaste stof te introduceren om de oppervlaktespanning van de vloeistof te balanceren op de microscopische schaal, en met gebruik van lineaire elasticiteit waren wij in staat om een voorspelling te maken van de vorm van dynamische bevochtigingsrichels voor verschillende reologische modellen. In hoofdstuk 2 gebruikten we dit resultaat om een rotatie van de bevochtigingsrichel te berekenen als functie van de contactlijn snelheid voor dissipatieve vaste stoffen. In het lage-snelheidsregime volgt de rotatie van de bevochtigingsrichel dezelfde power-law als de loss modulus van de gel reologie, echter laat de rotatie een verzadiging zien in het hoge-snelheidsregime. Deze rotatie werd vergeleken met de verandering van de macroscopische contacthoek van de vloeistof waar we vonden dat de berekende rotaties van de bevochtigingsrichel overeenkomen met de verandering van de contacthoek als functie van de contactlijnsnelheid over een breed range van snelheden. In hoofdstuk 3 hebben de claims uit hoofdstuk 2 getest, naast een beschrijving

van gedragingen van de bevochtigingsrichel die nog goed beschreven worden door de huidige theorie. Door in te zoomen op de bevochtigingsrichel met een nieuw uitgevonden experimentele methode om de bevochtigingsrichel te visualiseren waren we in staat om vast te stellen dat de richel inderdaad roteert op identieke wijze als de verandering van de contacthoek van de vloeistof in het lage-snelheidsregime. Echter namen we een afwijking tussen de richelrotatie en de verandering van contacthoek weer in het hogere-snelheidsregime. Deze afwijking vindt plaats wanneer de openingshoek van de spits van de bevochtigingsrichel begint toe te nemen. Deze verandering in openingshoek (θ_s) wijst op een verandering in de krachtenbalans bij de spits van de bevochtigingsrichel. De toename van θ_s suggereert dat de oppervlaktespanning van de vaste stof toe neemt met een toenemende snelheid van de contactlijn, dat de vorm van de bevochtigingsrichel op hogere snelheden beïnvloed.

Hoofdstuk 4 focust zich op dit hoge-snelheidsregime, waar de verandering in θ_s significant wordt. De onverklaarde dynamische toename van de oppervlaktespanning van de vaste stof die leidt tot een verandering van de vorm van de bevochtigingsrichel wordt getoond als de oorzaak van de stick-slip dynamica van contactlijnen die zich snel voortbewegen over het zachte oppervlak. Specifiek laten we zien dat de toename in θ_s de relatieve hoeken tussen de vloeistof en vaste stof verandert tot het punt dat de Gibbs ongelijkheid wordt geschonden, wat leidt tot een depinning van de contactlijn van de bevochtigingsrichel.

In hoofdstuk 5 introduceren we een elektrische potentiaal over het zachte oppervlak, dat leidt tot een additionele energiterm in de klassieke Young's vergelijking, die daarmee veranderd in Young-Lippmann vergelijking. Dit effect verlaagt de macroscopische contacthoek van de vloeistof op een diëlectrische vaste stof, en staat bekend als het electrowetting-effect. Wij demonstreren dat het electrowetting effect op zachte oppervlakken dezelfde wetmatigheden volgt als op harde vaste stoffen. De afname in contacthoek als functie van de elektrische spanning wordt gegeven door de diëlectrische eigenschappen van de gel, de dikte van de laag en de opgelegde spanning in het kwadraat. We observeren ook dat het dynamische dissiperende gedrag van de bevochtigingsrichel constant blijft bij verschillende opgelegde voltages, nog steeds de identieke power-law volgend die gegeven wordt door de reologie van de gel. Enkele preliminaire resultaten van de vorm van de bevochtigingsrichel onder invloed van de elektrische potentiaal worden getoond, gemeten met confocal microscopie.

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About the author

Mathijs van Gorcum was born on 23rd June, 1986 in Amersfoort, the Netherlands. As a self-described geek he always had an interest in science and technology. Growing up he enjoyed working on computers and generally liked physics and math education the most. This naturally lead to him choosing to study applied physics at the University of Twente. Following his Bachelors he finished his Masters degree in the Fluid Physics track. This choice was initially made due to the pretty pictures and complex dynamics of single phase flow, but soon lead him to become more interested in wetting phenomena. His master thesis was on the subject of wetting in complex geometries studied using electrowetting. After finishing his Masters degree in 2015, he came to PoF to do a PhD under the supervision of Prof. Jacco Snoeijer.

Mathijs has a great interest in Free Open Source Software, and enjoys playing guitar. He likes playing real time strategy computer games and currently lives with his lovely wife and two beautiful children in Enschede.