

Wetting on soft gels Menghua Zhao

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To my parents

To this wonderful world

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Résumé

Dans cette thèse, nous nous sommes intéressés à la statique et la dynamique du mouillage de gouttes d'eau sur des substrats mous tels que des gels, encore connu sous le nom d'élastomouillage. Pour ce faire, nous avons d'abord développé une méthode quantitative de visualisation par strioscopie permettant de mesurer la déformation de la surface d'un film de gel transparent avec une précision élevée quelque soit l'épaisseur du substrat et sur de grandes distances. Nous montrons que la déformation superficielle de films mous de silicone (PDMS) dépend de la taille des gouttelettes déposées ainsi que de l'épaisseur et de l'élasticité de ces films. Nous avons construit un modèle basé sur la théorie de l'élasticité linéaire tenant compte de la tension superficielle des gels qui prédit bien la forme et l'amplitude de la déformation de surface. Nous apportons aussi la preuve expérimentale et l'analyse théorique de l'importance de l'hystérèse de l'angle de contact dans la description de la déformation en démontrant que la force tangentielle due à la tension superficielle entre liquide et vapeur à la ligne de contact, souvent négligé, contrôle la déformation de la surface. La dynamique de mouillage est étudiée en dégonflant des gouttelettes sur des films de PDMS avec une épaisseur bien contrôlée. Il est démontré que la dissipation d'énergie dans le gel dépend fortement de l'épaisseur lorsque cette dernière est inférieure à 100 μm . L'effet de freinage viscoélastique et l'effet d'épaisseur sont bien rationalisés avec un modèle basé sur la viscoélasticité linéaire et une simple loi l'échelle qui tient compte de l'effet d'épaisseur capture très bien nos expériences. Enfin, nous démontrons que nous pouvons dériver et guider les gouttelettes en mouvement avec la conception de surfaces couvertes de couches de gels ayant des gradients d'épaisseur.

Mots-clés – Elastomouillage, optique de Schlieren, déformation de surface, élasticité linéaire, dissipation, viscoélasticité.

Abstract

In this thesis, we aim at obtaining a better understanding of the statics and dynamics of the wetting of liquids on soft gels, otherwise known as elastowetting. First, we develop a quantitative Schlieren set-up to measure the surface deformation of a transparent gel film with a high precision over large areas and for all thicknesses in real time. The long-range surface deformation of soft PDMS films is found to be dependent on the sessile droplet size, and the thickness and elasticity of soft films. We build a model based on linear elasticity theory that accounts for the surface tension of soft materials. It predicts the long-range surface deformation in excellent agreement with the experimental data. We also bring the experimental proof and theoretical analysis of the importance of contact angle hysteresis in the description of the deformation of the surface of the gel. We demonstrate that the tangential component of the liquid-vapor surface tension at the contact line, whose contribution are often neglected, significantly affects the surface deformation. Wetting dynamics is investigated by deflating droplets on PDMS films with well-controlled thickness. It is shown that energy dissipation in the soft gel depends on the thickness when the latter is smaller than 100 μm . The viscoelastic braking effect and the thickness effect are both well rationalized with a model based on the theory of linear viscoelasticity and a simple scaling law accounting for the thickness effect captures very well our experiments. Finally, we demonstrate that we are able to guide moving droplets with coatings having a gradient of their thickness.

Keywords - Elastowetting, Schlieren optics, surface deformation, linear elasticity, dissipation, viscoelasticity.

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Chapter 1 State of the ART

1.1 Introduction

The spreading of liquids on solid substrates and more generally any motion of a liquid with a dry/wet front is called wetting^{1–5}. The quest for a thorough physical understanding of this topic started two centuries ago^{1,6,7}. However, the description and use of wetting precedes by a long time its academic understanding. Around 1300 years ago, a Chinese poet, named Xin LI⁸, portraited in Figure <u>1.1(a)</u>, wrote in a temple after he quitted his official position:

粲公院各赋一物得初荷	For the nascent lotus of CanGong Temple
微风和众草,大叶长圆阴。	Across grasses flows breeze, grand and round are the leaves.
晴露珠共合,夕阳花映深。	Blinking dewdrops merge, through flowers the setting sunshine goes deep.
从来个者水,清净本因心。	Water it never touches, purity it is for its own nature.

In this poem, he makes a precise observation of water droplets on lotus leaves: in the second line, he states that the dewdrops blink like sunshine, meaning much of the light is reflected back by the bottom of the drop where a liquid-gas interface actually dominates the cross section between the liquid and solid according to the modern observations^{9,10}; in the third line, he tells us that the droplet does not stick to the lotus leaf. This observation is a testimony of the superhydrophobicity of lotus leaves - high apparent contact angle and very low contact angle hysteresis^{11–13}. Li and his contemporaries did not provide an understanding of the underlying mechanism. Nonetheless, people still took advantage of this peculiar phenomenon. For example, tea experts discussed the choice of water for making tea at length, and they compared water collected from rainfalls, snow and dewdrops¹⁴ as soon as the eighth century of our era, during the Tang Dynasty. Dewdrop water, Figure 1.1(b), was believed to be one of the best because Yin nature of them brings faint scent to tea^{15,16}, according to Taoism. Dewdrop water was collected by shaking plant leaves over a bamboo vessel after overnight condensation. Ancient artisans were thus taking advantage of the low contact angle hysteresis of water droplets on plant leaves even without noticing it. Nevertheless, how to understand and increase dew collection efficiency remained an unsolved issue until almost 1000 years later^{1,6,7,17}.



FIGURE 1.1: (a) Poet, Xin LI (690 ?-751 ?), Tang Dynasty. (b) Dew collection for tea-making.

The previous story from ancient China is only one case where human beings took advantage of wetting for their well-being without noticing. In fact, wetting is everywhere. Plants and animals have developed special biological organs with hydrophilicity features to intake water to maintain their livings^{18,19}. Mosquito's eyes are superhydrophobic in order to keep eyes clean and dry in moist conditions²⁰. Feathers of many insects and animals, such duck, butterflies and

water striders, are of hierarchy structures to ensure the hydrophobicity/superhydrophobicity to prevent the water intruding into their body and to keep the body from dessication^{21,22}. When a stone is thrown into the water, splashes are created depending on the surface wettability²³. When we take a shower, water flows down our body in the form of rivulets and droplets because of the high contact angle of water on the skins²⁴. In contrast, lipidic materials will tend to wet our skin and form thin films. In the coating industry, engineers want to insulate the surface from the surface for the specific wettability (superhydrophilicity and superhydrophobicity). Thus, they coat surfaces with adhesive layers, from molecular up to macroscopic thickness, from the liquid phase. The performance of the intersection line among liquid-gas-solid phases is crucial to the coating quality^{25–27}.

Many applications rely on wetting. For instance, to attain high conversion and achieve better heat transfer, petroleum industry use trickle-bed reactors, the efficiency of which is controlled by the catalyst wettability²⁸. In living bodies, cells and tissues assemble themselves together in certain spatial organization to gain their functions. Wettability between cell wall and tissue boundary is critical to those structure formations, which now can be manipulated by biologists^{29–31}. Surface hydrophobicity promotes the cell-cell adhesion and cell-substratum adhesion is dominated on hydrophilic surfaces which leads to new approaches to the development of biomaterials. Besides, scientists and engineers now are able to make use of the wetting on deformable materials. For example, running droplets can slow down due to the viscoelasticity of substrates^{32–42}; an elastic sheet can fold into an origami because of capillary forces^{43,44}; micro-rheometer and surface tension/stress tester can be achieved with very low price^{45–61}; micro-vessels and micro-lenses could be fabricated from polymers by solvent drops⁶²; surface patterns can be created by spreading droplets or dipping technique^{63–69}; droplets and cells can be distributed by rigidity^{70–72}.

The ubiquity of wetting has generated a tremendous interest in the fundamental understanding of its statics and dynamics, both on rigid and deformable substrates. In this thesis, we will cast our eyes on the wetting of soft materials, which is coined "elastowetting"^{56–58,73,74}. The aim of the present chapter is to introduce the basics of elastowetting and interface science. First, how the contact between a liquid droplet and a substrate is described, for substrates that are liquid, rigid and compliant solids (section 1.2). Then, the state of the art of the statics of wetting on soft materials, including static contact angle, contact angle hysteresis and surface deformation, is summed up (section 1.3). Section 1.4 deals with the dynamics of wetting and spreading on soft substrates, with a comparison to spreading on rigid surfaces. Finally, section 1.5 exposes questions we are going to deal with in this thesis and the structure of the manuscript.

1.2 Wetting fundamentals: from Young to Neumann

When a liquid is deposited on a surface, a geometrical angle, measured from the liquid-vapor interface to the liquid-solid interface, is usually observed when the drop reaches its equilibrium. This angle is defined as the static contact angle^{2,3,5,21,75,76}, θ_e . The intersection line where liquid, solid and vapor meet is called the triple line, the contact line, or the wetting line^{2,3,5,21,75,76}, as is illustrated in Figure 1.2(a). Wetting can be characterized as the complete or total wetting ($\theta_e = 0^\circ$), partial wetting ($0^\circ < \theta_e < 180^\circ$), and non-wetting ($\theta_e = 180^\circ$). For elastowetting in this thesis, we are always in the regime of partial wetting. For most of cases, the static contact angle is hardly found to be a single value. There are in general two observed bounds for it^{2,3,5,21,75,76}: one is a maximum, advancing contact angle, above which the contact line starts to move out; another one is a minimum, receding contact angle, below which the contact line will retract back. This non-uniqueness of static contact angle is known as the contact angle

hysteresis^{2,3,5,21,75,76}. When the contact line is in motion, the angle from the liquid-vapor interface to the liquid-solid interface is named as dynamic contact angle^{2,3,5,21,75,76}, θ_d , while the contact line is known as the moving contact line or the dynamic contact line^{2,3,5,21,75,76}.



FIGURE 1.2: (a) A resting droplet on a rigid, smooth surface. (b) Drop of liquid 1 floats on another immiscible liquid 2.

1.2.1 Rigid wetting: Young's equation

The static contact angle characterizing a droplet sitting on a perfectly rigid, flat, smooth, chemically homogeneous substrate adopts a single unique value, known as Young's contact angle^{1–3,5,21,75,76}. A simple way to understand comes from the force balance at the contact line:

$$\overline{\gamma_{SL}} + \overline{\gamma_{SV}} + \overline{\gamma_{LV}} = 0 \tag{1.1}$$

 γ_{SL} , γ_{SV} and γ_{LV} are the solid-liquid, solid-vapor, and liquid-vapor surface tension, respectively. Since the solid is perfectly rigid, the vertical force balance is dropped and only the balance in the horizontal direction is kept:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_Y \tag{1.2}$$

This equation is also known as Young equation, which can be equivalently recovered from theomodynamics^{5,21,77}. Note that the vertical equilibrium cannot be satisfied from Equation (1.2), with a vertical traction, $\gamma_{LV} \sin \theta_Y$, pulling the solid normally on its surface, which is essential in the elastowetting shown below.

1.2.2 Wetting of a liquid on another immiscible liquid: Neumann's triangle

When a liquid drop is floating on another immiscible liquid, a liquid meniscus appears at the three-phase junction (Figure <u>1.2(b)</u>). The force balance at the contact line is similar to Equation (<u>1.1</u>):

$$\overline{\gamma_{V1}} + \overline{\gamma_{V2}} + \overline{\gamma_{12}} = 0 \tag{1.3}$$

here γ_{V1} , γ_{V2} , and γ_{12} are the liquid 1-vapor, liquid 2-vapor and liquid 1-liquid 2 surface tension, respectively. This equation leads to the following relation:

$$\frac{\gamma_{V1}}{\sin(\theta_2)} = \frac{\gamma_{V2}}{\sin(\theta_1)} = \frac{\gamma_{12}}{\sin(\theta_3)}$$
(1.4)

That defines what is known as Neumann's triangle.

1.2.3 Wetting of a liquid on a compliant substrate: elastowetting

In the elastowetting case, as mentioned above, the surface tension of the liquid-vapor interface exerts a pulling force to the substrate. Because of the deformability of the material, part of the substrate will be drawn up, leading to the growth of a bump at the wetting line, the "wetting ridge"^{35,36,53,56,57,78–80}. This ridge has been directly observed by micro-X ray techniques as is shown in Figure $1.3(a)^{80}$, in which the elastomer has a Young modulus of 3 kPa. Once a traction is applied to the surface of a soft slab, the gel in the vicinity of the contact is deformed. The surface area increases, and the associated energy does so too, and the mechanical response in the bulk results into an increase of the elasticity energy. How the surface phenomenon is related to the two channels of gathering energy will be simply considered as follows.



FIGURE 1.3: (a) Image of a wetting ridge of a PDMS gel acquired by the X ray microscopy⁸⁰. The scale bar is 5 μ m. (b) An initially flat slab under a sinusoidal surface deformation. L is the wavelength, and γ_s is the surface tension of the slab.

Suppose an initially flat slab of surface tension γ_s , and of Young modulus *E*, having a sinusoidal surface deformation with a wavelength *L* (Figure <u>1.3(b)</u>). The elastic restoring stress is estimated as: Eh/L, and the capillary restoring stress is scaled as: $\gamma_s h/L^2$. The ratio of the two gives out a length:

$$l_s = \gamma_s / E \tag{1.5}$$

It is one kind of what is called as elastocapillary length^{52,55–57,72}, the other kind being related to the bending mode of an unbounded compliant sheet⁴⁴. This relation compares the magnitude of surface tension with elastic stresses. When the length scale of the deformation is smaller than l_s , solid surface tension γ_s dominates while elasticity dominates at larger length scales. Coming back to the elastowetting, it has been shown that a wetting ridge develops at the three-phase junction, and the length scale of the tip of this ridge is smaller than l_s . Its geometry configuration among the three phases will be a Neumann-like one, decided by the surface tensions^{48,52,53,57,58}.

1.3 Statics in elastowetting

This section will review progresses on three issues in elastowetting: static contact angle, its hysteresis and soft material deformation. One difficulty of such a review is that the domain has been known with a major change recently. Researchers realize that the vertical action of substrate surface tension was forgotten by ancient theoretical works, or at least treated in a questionable way via very complex minimization calculations. A possible reason for this is that: qualitatively, Young horizontal equilibrium is supposed to balance exactly what happens in the

horizontal direction, with the unbalanced vertical contribution only being to be considered within additional deformation calculations performed on the nondeformed reference state of a "flat" solid. Now, when the substrate distortion becomes large, this assumption is no longer valid, the substrate surface tension having a nonnegligible effect even vertically. As a result, if one except a few precursor works (Long et al among others), most papers published before 2010 are of questionable applicability to real situations. Inversely, the complexity introduced by the substrate surface tension is such that only the case of "symmetrical" surface tensions on each side of the contact line is exactly solved, i.e. the case of a "natural" contact angle of 90°. Again, there is possibly one exception with a very recent paper from Bostwick et al⁸¹, trying to solve the asymmetrical, in a more general case, but via integral equations whose solutions are of questionable validity [J. Dervaux and L. Limat, private comunication]. It is also important to say that the 2000's were also the beginning of a new period for experiments, in which more and more accurate techniques emerged, which has greatly catalyzed in turn the theoretical efforts.

1.3.1 Static contact angle and its hysteresis

Static contact angle is taken as the equilibrium contact angle, θ_e , measured from the liquidvapor interface to the horizontal planar and contact angle hysteresis, θ_h , is referred as the difference between the advancing contact angle, θ_a , and receding contact angle, θ_r , from a macroscopic view. Both are illustrated in Figure <u>1.4</u>.



FIGURE 1.4: A resting droplet on a soft substrate.

Static contact angle

A resting droplet on a perfectly rigid, smooth and chemically homogeneous material attains the Young's relation at the contact line as has been demonstrated in section <u>1.2.1</u>. However, when the underlying material is soft, there is a vertical unbalanced component of surface tension that pulls the solid, which can become highly deformed: "The resultant of these tensions is $\gamma_{12}sin\theta$. As long as this force is not balanced, no equilibrium can exist.", as was firstly pointed out by J. J. Bikerman⁷⁷ in 1959, who even directly denied the validity of Young's relation on soft materials. However, no models in describing how this unbalanced force is acting at the contact line are proposed by him. Two years later, G. R. Lester⁷⁸ solved the case of a drop sitting on a deformable substrate with infinite thickness analytically using linear elasticity theory. The static contact angle was found from the surface deformation. And according to Lester, it was neither Young's angle nor Neumann's angle because of the incoherence between the elastic deformation condition and surface tension balance. Later on, another contribution comes from A. I. Rusanov⁸² who introduced a concept of "linear tension", incorporating the elastic deformation energy of soft materials, into the minimization of the global energy. Rusanov found

that the equilibrium contact angle is Young's angle plus a correction originating from the elastic deformation and it goes to Young's value when the substrate is rigid, which was experimentally confirmed by Yuk et al⁸³. In addition, compared to the research of his precursors, Rusanov's work might be the first one addressing the real case in that both the normal and tangential components of the traction imposed by the surface tension on the deformable slab are considered. In the following, Shanahan et al^{36,79}, used a similar approach as A. Rusanov, variation method to minimize the system free energy and unveiled a mesoscopic solution for the static contact angle consisting of a Young's angle with a deviation due to elasticity and Laplace pressure (droplet volume confinement). M. Fortes⁸⁴ came up with a similar result later for a drop deposition on a membrane.

However, as has been stated above, all those researches missed a very subtle point that is as follows. Usually the substrate surface tension affects mainly the tangent situation, in particular by a Young condition that will still hold for very small deformations. Now, when the substrate deformation becomes large, one can no longer neglect the slope of the solid near the contact line, that introduces substrate surface tension effects in the "vertical" equilibrium of the surface. This can be understood in two ways: (1) as the solid surface inclines itself, the tangent force $\gamma_s t$ develops a component normal to the solid surface of order $\gamma_s \partial \zeta / \partial x$ where $\zeta(x)$ is the profile of the deformed solid surface, supposed here in 1D; (2) as the solid becomes highly curved too, there is a Laplace pressure that appears between both side of the solid surface of intensity $\gamma_s \partial^2 \zeta / \partial x^2$ that also "pulls" or "pushes" this surface normally to itself. Both arguments are in fact the same, one being the derivative of the other upon x. As a result, a new term is hatched in the surface equilibrium equations: the direct coupling of the surface effect (surface tension/energy/stress)^{40-42,53,56-58} into elastic deformation equations for the surface deformation. This idea is in fact implicit in precursors' model developed by G. Fredrickson, D. Long et al⁴⁰⁻⁴², who investigated the wetting of liquids on polymer brushes, polymer layer and thin rubber films while accounting for the surface effect into deformations. However, how the static contact angle of soft materials is defined by the elastowetting system is not discussed by them and they rather focus on scaling laws developed for the elastowetting dynamics. However, as we shall see these precursor woks will be extremely important for understanding the dynamics. The decisive idea of incorporating the unexpected substrate surface effect (surface tension/energy/stress) spreads throughout the following researches up to now. Several groups^{48,56,57,85} (Style and Dufresne in Yale, Snoeijer and Andreotti in Twente and PMMH/ESPCI, Limat and Dervaux in MSC lab, among others) develop theoretical calculations including this effect, and simultaneously discover that contact angles stick to the Neumann's triangle at the tip of the ridge and Young's angle in the far field for compliant solids (at least for macroscopic drops on an infinitely deep substrate). Besides, droplet size and thickness of soft film comes into play for the static contact angle as well. Style et al^{72} , reported a strong dependence of θ_e on the droplet size and soft film thickness (Figure 1.5) due to the surface effect. Those results are strengthened further from theoretical calculations from Lubbers et al⁸⁶, and Dervaux et al⁵⁷.



FIGURE 1.5: Droplets deform soft substrates, causing Young's law to fail. (a) X-ray image of the contact line of a water droplet on a soft, silicone gel substrate. The ridge is pulled up by the droplet surface tension. E =3 kPa, and the substrate is 22 µm thick. The droplet radius is ~ 1 mm. (b) The equilibrium of a sessile droplet on a soft surface with $R \gg \gamma_{VL}/E$. (c) A resting droplet on a soft surface with $R \ll \gamma_{VL}/E$. (d) Symbols show measured contact angles of glycerol droplets on a silicone gel as a function of droplet radius. Data are shown for thin silicone gel layers of $h = 3 \mu m$ (red) and thicker layers of $h = 35,38 \mu m$ (blue). Filled/open points were measured by laser scanning (LS)/white-light optical profilometry (WLP). (e) Schematic profile of a droplet on a soft surface of varying thickness, h. (f) Droplets deposited by condensation onto soft, flat surface.

Contact angle hysteresis

Contact angle hysteresis results from the pinning of the contact line^{2,5,76}, because of surface roughness, chemical heterogeneities and solutes. They may arise from reorientation of surface groups, machining, surface deformation, absorption and so on^{87,88}. Many researchers have been focusing on the hysteresis of wetting on rigid surfaces while very few tried to tackle the elastowetting hysteresis^{56,88–90}. To the best of our knowledge, there is only one model⁸⁹, by Extrand et al, and another refined one⁵⁶, by L. Limat, to account for it, which will be briefly reviewed.



FIGURE 1.6: (a) Schematic of the elastomer deformation, pinning post, at the contact line. (b) Hysteresis of water droplets on cis-polybutadiene elastomer as a function of rigidity.

A series of Extrand and Kumagai's experiments showed that static contact angle hysteresis, θ_h , was affected by the elasticity of soft materials once the height, of the wetting ridge, *h* depicted in Figure <u>1.6(a)</u>, exceeds the surface roughness^{88–90}. Liquids such as acetophenone, ethylene glycol, methylene iodide, formamide, distilled water were spread on polymers of poly(tetrafluoroethylene) (PTFE), poly(chlorotrifluoroethylene) (PCTFE), poly(styrene) (PS),

poly(ethylene terephthalate) (PET), natural rubber (NR), cis-poly(butadiene) (BR) with controlled elastic modulus. Surfaces of those materials were characterized and handled with great care. All those polymers gave a similar result on the contact angle hysteresis as is shown in Figure <u>1.6(b)</u>: the hysteresis increases with a decrease of the elasticity modulus. The illustration for this is that the surface tension of the liquid pulls up a local deformation of the soft surface, forming a bump, wetting ridge, at the contact line, which acts as a pinning post for the contact line. Hysteresis is related to the height of this pinning post by:

$$\theta_a \approx \overline{\theta_a} + \frac{6\gamma \sin\theta_a}{bE}$$

$$\theta_r \approx \overline{\theta_r} + \frac{6\gamma \sin\theta_r}{bE}$$
(1.6)

 θ_a , θ_r , and $\overline{\theta_a}$, $\overline{\theta_r}$ are the observed advancing, recending contact angle on soft substrates, and the true advancing, receding contact angle on polymers without the surface deformation, respectively. γ , *E* and *b* are the surface tension of liquid, elastic modulus and a typical length scale of micron order that remained unspecified. This set of equations is approximated from the linear elastic theory. L. Limat⁵⁶ pushed it forwards with a more physical description of the surface deformation by taking account into the surface effect, arriving at a relation similar to Equation (1.6), in which *b* should be given by some elastocapillary lengh. However, both models are inherently problematic because the hysteresis was deduced from pure elasticity theory, which never predicts an energy barrier to the spreading of liquids⁸⁴. As is stated by L. Limat⁵⁶: some plasticity is essential to explain why the ridge could remain static while the liquid explores its sides; The influence of yield and plasticity in Extrand and Kumagai's description is certainly the first missing link to this theory. This claim was also supported by M. Fortes and Lee R.White⁹¹. No further convincing models have been made since L. Limat⁵⁶. How the viscoelasticity, poroelasticity and plasticity affect the hysteresis remains to be elucidated.

1.3.2 Deformation at the contact line

All throughout the following discussions on both experiments and models, we assume that the soft material is incompressible, the deformation of it can be accounted by the linear elasticity theory, and gravity is not important and will be neglected if it is not specially specified. This section will first present a qualitative description of the deformation and then it gives a review on both experiments and models. Finally, we elaborate on a recent model by L. Limat, that allows us to establish some link between "modern" elastowetting approaches and previous approaches, of which a typical one is developed by Shanahan et al^{32,35,38,92}.

A qualitative description

A qualitative description of the problem which we will be faced with in our experiments, is suggested in Figure <u>1.7</u>. We will have to investigate the surface deformation induced by a contact line of a droplet on a soft substrate with finite thickness *h*: First, surface tension, γ_{LV} , from the liquid-vapor interface exerts a pull-up traction on the soft substrate, resulting into a local bump, wetting ridge, at the contact line; The easiest way to estimate the height of this ridge is^{35,56,58}: $\gamma_{LV} sin\theta/E$, in which *E* is the elastic modulus. For instance, in Figure <u>1.3(a)</u>, the surface tension of water is 72 *mN/m* and the elastic modulus of the soft gel is 3 kPa and the contact angle is around 105°. Then the height of the ridge is estimated to be 23 μm , which falls into the mesoscopic region of a rigid wetting case^{3,4,76}. The ridge could then have a non-negligible impact on liquid spreading. The growth of the ridge leads also to the pulling-up of the substrate. Incompressibility imposes that the volume of the substrate displaced due to the ridge growth must be compensated by the motion of an identical volume. Hence, a surface

depression is expected around the contact line (Figure <u>1.7</u>). Third, Laplace pressure, due to the liquid interface curvature, is pushing down the liquid-solid interface inside the drop. Visually, it seems that the droplet sinks into the soft substrate^{57,72,86}, as is drawn in Figure <u>1.4</u> and Figure <u>1.5</u>.



FIGURE 1.7: A 2D schematic of surface deformation at the contact line.

Review on both experiments and models

It will be difficult to compare quantitatively our experiments with existing models, though we will succeed in this, using a generalization of the one developed by Dervaux and Limat⁵⁷. As explained above, there were two successive periods for modeling, separated by the discovery that substrate surface tension plays an essential role, even in the vertical displacement of the deformed surface. In addition to this parameter, i.e. substrate surface tension, there are other more geometrical issues that must be considered, as depicted in Figure <u>1.8</u>. First, if there is a horizontal pinning of the contact line, the tangent component of the force applied at contact line by the liquid must be taken into account, as in Figure <u>1.8(b)</u>, in contrary to the initial guess of Figure <u>1.8(a)</u> (postulated long ago by Lester⁷⁸). Then, in addition to the substrate surface tension effect suggested in Figure <u>1.8(c)</u>, there is the finite depth of the substrate that will matter as in Figure <u>1.8(d)</u>. And finally, the best would be also to add a possible difference between the substrate surface tensions in the "dry" and "wet" regions of the solid (Figure <u>1.8(e)</u>). We now comment what is available in the literature and what could hold or not in our case.

Prior to the model by G. Fredrickson, D. Long et al^{40–42}, the surface deformation had always and solely been described as the balance between the liquid surface tension and substrate elasticity (Figure <u>1.8(a-b)</u>). Figure <u>1.8(a)</u> shows the elastic deformation induced by a resting droplet on a half-infinite slab with a contribution from the Laplace pressure on the solid-liquid interface^{32–38,61,78,79,91,92}. In most theories, this Laplace pressure is missing but can be treated by using the response to the vertical pulling as a Green function for the pressure distribution. The traction force on the soft slab was taken as the vertical component of the liquid-vapor surface tension. G. Lester⁷⁸ simplified the problem into a 2D problem and assumed that the divergent surface tension spread on a ring within a finite width (divergent resolved, being like the Laplace pressure), and finally arrived at an explicit solution for the surface deformation which originated from the elastic solution for a constant pressure spreading on a circle applied on a half infinite solid. Shanahan et al^{38,79,92}, considered an even simpler case: 2D elastic solution for a vertical traction on an elastic solid with infinite thickness. In his model, the horizontal component of liquid-vapor surface tension was dropped and the Laplace pressure on the liquidsolid interface was neglected as well. An analytical solution for the surface deformation, a logarithmic profile, on both sides of the ridge was recovered based on the linear solution for a concentrated force acting vertically on a flat surface of an infinitely large thin plate. L. White⁹¹ found the surface deformation similar to that by Shanahan et al^{38,79,92}. A further understanding of the geometrical effect on the elastowetting is studied by Yu et al⁶¹, they found a finite thickness effect from numerical modelling with an integral transform method and dimples on both sides of the ridge were identified. However, in all those models, solutions for stress/strain/displacement diverge at the contact line. Shanahan et al^{34,38,79,92}, removed this singularity by introducing a cut-off at the contact line by saying "local behavior is of some other type, either non-linearly elastic, or plastic.". However, the singularity still exists in the model. In the next stage, Figure 1.8(b) indicates the surface deformation by a resting droplet on a halfinfinite elastic solid with the Laplace pressure contribution considered and the traction is taken from the surface tension, of which both the normal and tangential components are taken into account^{82,93}. Like G. Lester⁷⁸, A. Rusanov^{82,93} took the liquid-vapor surface tension as constant "pressure" spreading on an annulus over which the liquid-vapor interface is defined. All those models try to find the surface deformation from the linear elastic theory without taking the surface effect (surface tension/energy/stress) into account, and the same singularity was recovered in the outlet. Besides, it is questionable to derive the local contact angle at the wetting line from the surface tension balance or from minimizing the global energy since the surface deformation is already defined by a balance between the liquid-vapor surface tension (sometime with the Laplace pressure) and the elasticity^{32,78,84,91-93}. We will thus avoid any use of those models in the interpretation of our experiments.

When it comes to the new period, surface effect (surface tension/energy/stress) is directly coupled into the solution of surface deformation^{40-42,48,51,53,55-57,81,85,94-100}. Figure 1.8(c) demonstrates the surface deformation on a soft material with infinite thickness is caused by the surface tension of liquid-vapor interface, γ_{LV} , and the Laplace pressure, P, on the liquid-solid interface with another contribution from the liquid-solid and solid-vapor surface tension, γ_s . Figure 1.8(d) denotes the same conditions for surface deformation as Figure 1.8(c) except that the soft material has a finite thickness and is bounded on a rigid solid surface. Figure 1.8(e) illustrates the asymmetry of surface tension between the solid-liquid and solid-vapor interfaces is modeled as an advancement of the model from Figure 1.8(d). Fredrickson et al⁴⁰, firstly derived the energy contribution from increasing surface area, strained bulk by imposing a sinusoid deformation on a thin polymer brush from polymer physics and found the kernel of the first order for the deformation. Then this solution was applied to thin rubber film with finite thickness where the surface tension was the same on the wet and dry side of the ridge. The traction was taken as the vertical component of the γ_{LV} , and the Laplace pressure was neglected. Later, Long et al^{41,42}, reported two results from this model: the singularity at the contact line is automatically removed and the solution converges to the linear elastic solution at the limit of long wavelength. A further advance was made by coupling the surface effect and horizontal traction component of the liquid-vapor surface tension into the linear elastic model^{56,57}. Limat et al^{56,57}, assumed a symmetry of surface energies in the plane of the substrate surface with respect to the contact line. They arrived at an analytical solution of full orders from mechanics while the very first one^{40–42} is a first order approximation. Jerison et al⁹⁴, and Style et al^{53,85}, took the surface effect into the generalized spring constant and hided it in their linear elastic equations. Later on, they discovered and verified from models and experiments that a cusp is determined by surface stresses at the ridge tip. In the frame work of Marchand et al^{95–97}, and C.

Hui⁴⁸, how the force at the ridge tip is balanced and transmitted was discussed. C. Hui⁴⁸ found the liquid surface tension is balanced by the elastic stress and solid interface tensions, and Neumann's triangle holds only for very compliant materials. To break the limit of symmetry surface tension condition, very recently, Bostwich et al¹⁰¹, and Bardall et al¹⁰⁰, developed an integral method to solve this complicated situation and found good agreement when one compares to the situation with very low asymmetry. However, there are problems in their solution of the "Fredholm equation involved" and their model must be taken with caution for large asymmetries [Dervaux and Limat, private communication].



FIGURE 1.8: Models for elastowetting statics. Dashed line indicates infinite thickness of the soft substrates; P, small arrows, represents the Laplace pressure pushing on the soft substrate surface inside the liquid. L, V and S read as the liquid, vapor and solid phase. Parameters of models are categized into five groups: (a)⁷⁸ Thickness: infinite; surface traction: only the vertical component of surface tension is considered; surface tension of solids: no. (b)^{35,79,82,84,92} Thickness: infinite; surface traction: both the vertical and horizontal components of surface tension are considered; surface tension of solids: no. (c)^{40–42,56} Thickness: infinite; surface traction: both the vertical and horizontal components of surface tension are considered; surface tension of solids: ves. (d) ^{53,85}Thickness: finite; surface traction: both the vertical components of surface tension of solids: yes, and symmetry. (e) Thickness: finite; surface traction: both the vertical components of surface tension of solids: yes, and asymmetry.

Experiments went on slowly before the year 2000 due to the high requirement for experimental techniques. There is only one result on the shape of the deformation by Carré et al³⁵, which confirms the logarithmic profile on the dry side as they predicted from their model. After 2000, the first notable results on the surface deformation come from Pericet-Cámara et al^{59,60}. They used laser scanning confocal microscopy and a white-light confocal profilometer with fluorescence dying of droplets to identify the location of the liquid-solid and solid-vapor interfaces of small droplets, with a radius of tens of microns, on thin soft films. Depletion under the liquid was found to be increasing with an increment of the film thickness to a saturation predicted by Rusanov's model on a half infinite solid. Microtrough ouside the droplet moves further away from the triple line as the film becomes thicker and it scales as the film thickness. Pu et al^{63–66}, reported a detailed shape of the dynamic ridge on thermally stripped acrylic polymer films which are highly viscoelastic. In his experiment, he found a stick-break behavior of the moving contact line, from which the shape of the "stick ridge" is detected as two orders

of magnitude taller than elastic predictions and depends on the wetting line speed. The significant point is the high stress at the contact line induces a viscoelastic or plastic growth of the wetting ridge which had never been reported before and this growth causes the contact angle hysteresis. A similar growth of the ridge was also discovered by Kajiya et al⁶⁸, who performed droplet advancing experiments on viscoelastic SBS-paraffin gels. Besides, the diffusion effect of liquids, on the local deformation of soft PAMPS-PAAM hydrogels, at the contact line was also investigated by Kajiya et al^{67} : when the hydrogel substrate is in contact with water, water starts to diffuse into the polymer network and the gel becomes swollen at the contact line until the surface slope measured from the gel phase is the same with that measured from the liquid phase. In parallel to those experiments, the micro-scale surface deformation at the wetting cusp by water droplets on the highly elastic silicone gels was measured by Jerison et al⁹⁴, and Style et al^{53,85} with a fluorescence confocal microscopy. A universal opening angle selected by the surface stress balance at the tip was observed. Although those techniques are highly sensitive and of high precision, they are still non-direct observation. The first direct view of the wetting tip was performed with the X-ray technique by Park et al⁸⁰, as has already been put in the Figure 1.3(a) and 1.5(a). Not only the shape of the ridge was measured, but also the growth of the deformation was tracked. Their measurement also revealed a rotated wetting cusp due to Laplace pressure and allowed a discussion of various models between models and experiments.

An analytical model by L. Limat⁵⁶: Green function solution for a single contact line

To address the 3D problem of a resting droplet on a soft film with finite thickness, the first step is to consider a single contact line on a half-infinite elastic solid for a 2D case. The solution will be taken as a Green function for the real 3D problem and it lays out the theoretical foundation for our current studies. The schematic of this single contact line problem corresponds to the Figure 1.8(c) once its Laplace pressure is neglected.

The assumptions of the model are: 1. $\gamma_{SL} = \gamma_{SV}$, and both will be denoted as γ_S ; 2. The surface slope is everywhere smaller than 1; 3. Surface tension is transmitted to the soft material both horizontally and vertically.

The displacement field of an elastic slab can be described in analogy with the Stokes equation when the trace of the stress tensor is mathematically substituted with a pressure P to avoid the complex infinity of the Lamé coefficients:

$$\nabla \cdot \vec{u} = 0 \tag{1.7}$$

$$G'\Delta \vec{u} - \vec{\nabla} P = 0 \tag{1.8}$$

where \vec{u} , G' are the displacement field and elastic shear modulus. Equation (1.7) describes the impressibility of the material. Equation (1.8) denotes the equilibrium of forces. This set of equations is completed by the condition of stress continuity at the surface:

$$\sigma \cdot \vec{n} = \vec{t} \tag{1.9}$$

in which σ , \vec{n} and \vec{t} are the stress tensor, surface normal vector and traction, respectively.

If a line force $\vec{f}(f_x \delta(x)\delta(y), f_y \delta(x)\delta(y), 0)$ is applied to the free surface of an elastic slab, the boundary condition, Equation (<u>1.9</u>), will take the following form in the small surface slope limit:

$$\sigma_{yy} = 2G' \frac{\partial u_y}{\partial y} - P = f_y \delta(x) + \gamma_s \frac{d^2 \zeta}{dx^2}$$
(1.10)

$$\sigma_{xy} = G'(\frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y}) = f_x \delta(x)$$
(1.11)

By introducing a potential function, ψ , the incompressibility condition will be automatically satisfied:

$$u_x = -\frac{\partial \psi}{\partial y}, \quad u_y = \frac{\partial \psi}{\partial x}$$
 (1.12)

Using a Fourier transform to solve this set of equations, Limat et al^{56,57}, found the following solutions for the interface deformation:

$$u_{y}(interface) = \varsigma_{x} = \frac{\partial \psi}{\partial x} = \frac{f_{y}}{2\pi G'} \int_{1/\Delta}^{\infty} \frac{\cos kx}{k + \frac{\gamma_{S}}{2G'}k^{2}} dk$$

$$u_{x}(interface) = -\frac{\partial \psi}{\partial y} = \frac{f_{x}}{2\pi G'} \int_{1/\Delta}^{\infty} \frac{\cos kx}{k} dk$$
(1.13)

where Δ is a macroscopic cut-off length.

To seek for an analytical expression, Equation (1.13) can be equivalently read as follows:

$$\zeta_{x} = \frac{f_{y}}{2\pi G'} \left\{ -C_{i} \frac{|x|}{\Delta} + \cos \frac{|x|}{l_{s}} C_{i} \left(\frac{|x|}{\Delta} + \frac{|x|}{l_{s}} \right) + \sin \frac{|x|}{l_{s}} (S_{i} \left(\frac{|x|}{\Delta} + \frac{|x|}{l_{s}} \right) - \frac{\pi}{2}) \right\},$$

$$u_{x}(interface) = \frac{f_{x}}{2\pi G'} \left\{ -C_{i} \frac{|x|}{\Delta} \right\}$$

$$(1.14)$$

here, $l_s = \gamma_S/2G'$ is defined as a solid elastocapillary length, and ζ_x , u_x (*interface*) indicate the vertical and the horizontal surface deformation on the surface. C_i and S_i are the Sine integral and Cosine integral functions, defined as follows:

$$S_{i}(x) = \int_{0}^{x} \frac{\sin t}{t} dt, \quad C_{i}(x) = -\int_{x}^{+\infty} \frac{\cos t}{t} dt$$
(1.15)

As explained in Limat's paper, these complex expressions are very close to a simpler expression that reads:

$$\zeta(x) \approx \frac{f_y}{2\pi G'} \log \frac{\Delta}{|x| + l_s}$$
(1.16)

and it reduces to Shanahan Green function in the limit $l_s \rightarrow 0$. In the limit $x \rightarrow 0$, one finds a Neumann equilibrium of the vertical components of surface tension that reads:

$$f_{y} = \gamma_{LV} \sin\theta = 2\gamma_{S} \sin\theta_{S} \tag{1.17}$$

where f_y is the slope of the substrate and θ the contact angle. As one can see, it is essential to not miss the $\gamma_s \zeta_{xx}$ term in the local model, to recover correctly Neumann

equilibrium at small scale, as the limit $l_s = 0$ leads to a logarithmic divergence of the profile for x = 0, for which Shanahan had to invoke contestable cut-offs. In our case, we will develop a finte depth variant of this approach for the substrate thickness that will be sufficient to interpret our data. The above model is, however, important as an intermediate step into this direction.

1.4 Dynamics in elastowetting

Spreading of liquids on soft materials is distinguished from the spreading on rigid substrates, as have been demonstrated by Carré et $al^{35,38}$, shown in Figure <u>1.9</u>. When a formamide liquid, with γ of 45.9 mN/s and η of 3.2cP, is deposited on a silica surface which is almost perfectly rigid, it takes around 20 seconds to reach its equilibrium state. In sharp contrast to this, the equilibrium state is attained 1 hour later when the silica surface is replaced with an aexpoxidized natural rubber with a shear elastic modulus of 0.37 MPa. Reflecting on what is going on in the two cases, one may find: for the spreading on silica surface, liquid-vapor surface tension causes no deformation on the substrate. It is only the liquid inside the drop that is active in the system. There is only one channel that is dissipating energy in the system. However, for the spreading on the ENR 50 surface, a wetting ridge is formed at the triple line. As a result, not only the liquid is sheared, but also the small ridge propagates with the advancing contact line. As a consequence, there will be two dissipation channels, one in the liquid and one in the viscoelastic material. In the end, dissipation during the spreading of liquids on rubber is larger compared to that on the silica surface and it looks as if the motion of spreading is slowed down by a higher friction. This phenomena is known as viscoelastic braking^{34,35,37,39,45,79}. In the following, the two dissipation mechanisms will be reviewed and discussed.



FIGURE 1.9: Spreading of a drop of formamide liquid, 2 µL, on a flat, smooth, horizontal exposidized natural rubber (ENR 50) after deposition. Insert is a cartoon showing the spreading process.

1.4.1 Dissipation in rigid wetting

Huh and Scriven's paradox¹⁰²

If we assume the liquid is incompressible and Newtonian and the solid is perfectly smooth, rigid and flat, the flow at the contact line can be described as a corner flow. In a simplified 2D case, a biharmonic equation, $\nabla \psi^4 = 0$, is used to characterize the shearing of the liquid. ψ is a stream function under the polar coordinate system (r, θ) . With the no-slip boundary condition,

the viscous stress near the contact line is:

$$\tau_{r,\theta} = \frac{2\mu}{r}(\cos\theta - d\sin\theta), \qquad \tau_{\theta,\theta} = \tau_{r,r} = 0$$
(1.18)

 μ is the viscosity of the liquid, *c* and *d* are pre-factor determined from boundary conditions. It can be easily seen the stress has a singularity at the contact line when $r \rightarrow 0$. In this situation, "not even Herakles could sink a solid", as is put by Huh and Scriven¹⁰².

Besides, De Gennes² and Bonn et al³, calculated the energy dissipation for the unit length of the contact line, on a scale from r to r + dr, it is estimated as:

$$d\dot{E} \sim \mu U^2 \frac{dr}{r} \tag{1.19}$$

where U is the wetting velocity of the contact line. It indicates the overall energy dissipation diverges both at $r \rightarrow 0$ and $r \rightarrow \infty$ and each order contributes equally to the energy dissipation. In order to cancel the divergence, cut-off needs to be introduced for both macroscopic and microscope scales^{3,4,102,103}. In general, the macroscopic is on the scale of capillary length $(10^{-3}m)$ and the microscopic one is on the scale of molecules $(10^{-9}m)$. The mechanisms in eliminating the singularities are the presence of precursor films², hydrodynamic slip¹⁰², non-linear slip¹⁰⁴, surface roughness¹⁰⁵, diffuse interface¹⁰⁶, shearing thinning¹⁰⁷, etc. Eyes will only be casted onto the hydrodynamic one concerning of complexity of the problem.

Hydrodynamic model with a cut-off

Hydrodynamic models can properly capture the liquid flow on another surface with the presence of a third phase. However, the singularity at the three-phase line prohibits a correct prediction of the viscous stress at the wetting line. To resolve it, one way is to impose a cut-off at molecule scale at the hydrodynamic solution. For example, boundary slip is allowed by Huh et $al^{102,108}$, Dussan^{103,109}, and Oliver et al^{108} , By adding a cutoff to the Equation (1.16) and Equation (1.17), the stress goes to a finite value. In general, the hydrodynamic models hold at small capillary number and the liquid-vapor interface will adopt a static solution when it is far away from the contact line and dynamic contact angle can be acquired by the asymptotic solution. Hence, the bending of liquid-vapor interface in the mesoscopic region is crucial in connecting the microscopic condition with the macroscopic observation, as is shown in Figure 1.10.



FIGURE 1.10: (a) Interface bending of the hydrodynamic model, reproduced from T.D.Blake⁷⁶. (b) Schematic

of liquid spreading at different scales, reproduced from D. Bonn et al³.

Three regions are usually defined in hydrodynamic models: the microscopic region, the mesoscopic region and the macroscopic region. In the microscopic region, the liquid meets with the solid and a microscopic contact angle, θ_m , is found to account the liquid-solid interactions. This angle can be either a constant, like an intensive parameter of the system which assumes the molecule jump is much faster than the moving of the contact line, or a variable, like an extensive parameter, which considers the moving contact line is comparable to the rearrangement of local molecules at surface sites. In the mesoscopic region, the liquid-vapor interface is strongly curved to accompany the microscopic and the macroscopic region. For the macroscopic region, the apparent contact angle is observed and used to characterize the dynamic behavior of the system.

To have a good estimation of the dissipation for the liquid spreading on a rigid surface and at the same to be simple, we stick to Voinov's solution¹¹⁰:

$$\chi(\theta_d) - \chi(\theta_m) = \operatorname{Caln}\left(\frac{L}{L_m}\right)$$

$$\chi(\theta) = \frac{1}{2} \int_0^{\theta} \left[\frac{\hat{\theta}}{\sin\hat{\theta}} - \cos\hat{\theta}\right] d\hat{\theta}$$
(1.20)

Here Ca, L and L_m are the capillary number defined as $Ca = \mu U/\gamma$, macroscopic and microscopic cut off to remove the singularity of the integrand. As has been stated before, the macroscopic cut-off, L, is on the scale of capillary length $(10^{-3}m)$ and the microscopic one, L_m , is on the scale of molecules $(10^{-9}m)$. By using the Taylor expansion, the integrand is approximated as $2\theta^2/3$ when $\theta_d < 3\pi/4$. Then the Equation (1.18) takes the form:

$$\theta_d^3 - \theta_m^3 = 9Caln\left(\frac{L}{L_m}\right), \qquad \theta_d < 3\pi/4$$
(1.21)

1.4.2 Dissipation in elastowetting

For soft materials, a small ridge, shown in Figure <u>1.4</u>, forms at the wetting line. When the liquid spreads, this ridge will accompany the motion of the contact line, inducing a cycling motion of soft material^{32,34,79}. Usually, hysteresis occurs on the loading-unloading curves of materials, meaning that at the same strain, stress response of the material is different according to its loading history. The area difference between two curves, stress versus strain, is the energy dissipation in the process. This principle is applied to elastowetting materials as well. As a consequence, certain amount of energy is dissipated as the contact line is moving. In general, there are mainly two ways to predict energy dissipation: one is initiated and refined by M. Shanahan et al^{32–38,79,92}. It is also used by the other researchers, including Voué et al³⁹; the other one is developed by G. Fredrickson, D. Long et al^{40–42}. The latter one is not widely used because of its complicated calculations. Details of the two will be summarized in the following.



FIGURE 1.11: (a) Surface deformation at the moving contact line³². (b) Polymer brush of thickness h_0 under a sinusoidal surface deformation⁴⁰.

Dissipation from "elastic" model

Calculation for the surface deformation of an elastic solid by Shanahan et al, has been briefly introduced in section <u>1.3.2</u>. The elastic deformation is not assumed to be modified by the moving of the contact line but is simply decided by the vertical component of the traction force, $\gamma_{LV} sin\theta$. The ridge accompanying the spreading of liquid is shown in Figure <u>1.11(a)</u>: the radius of the non-linear region at the wetting tip is ε ; the vertical surface deformation outside the droplet is denoted by ζ and the horizontal displacement is σ ; spreading velocity is indicated as *V*. The main results are presented in the following. The surface deformation at the moving contact line is:

$$\zeta = \frac{2\gamma_{LV}(1-\nu^2)}{\pi E} \left[\sin\theta \ln\left(\frac{\Delta}{x-x_0}\right) - \frac{\sin\theta}{2(1-\nu)} + \frac{(1-2\nu)\theta\cos\theta}{2(1-\nu)} \right]$$

$$\sigma = \frac{2\gamma_{LV}(1-\nu^2)}{\pi E} \left[\frac{(1-2\nu)\theta\sin\theta}{2(1-\nu)} - \cos\theta \ln\left(\frac{\Delta}{x-x_0}\right) \right]$$
(1.22)

where *E* and *v* are the Young elastic modulus and Poisson ratio of the elastic solid. Δ is a macroscopic cut-off, beyond which zero surface deformation is assumed. Then the work done per second per unit length of the contact line is:

$$W = \gamma_{LV} V(\frac{d\sigma}{dx}|_{x_0 + \varepsilon} \cos\theta - \frac{d\zeta}{dx}|_{x_0 + \varepsilon} \sin\theta)$$
(1.23)

At small contact angle, Equation (1.21) goes to:

$$W \approx \frac{2\gamma_{LV}^2(1-\nu^2)V}{\pi E} \left\{ \frac{1}{\varepsilon} + \frac{6\theta}{r} \sin\theta \cos\theta \ln\left(\frac{d}{\varepsilon}\right) - \frac{3\theta}{2(1-\nu)r} \left[\theta(1-2\nu) + \sin\theta \cos\theta\right] \right\}$$
(1.24)

For the straining cycling of elastomers, Ω fraction of the input energy is dissipated and $1 - \Omega$ fraction is conserved as the elastic energy in the material. Thus, for the elastowetting dynamics, the energy dissipated into heat is similar to the straining cycling result when high orders are dropped:

$$W\Omega \simeq \frac{2\Omega\gamma_{LV}^2(1-\nu^2)V}{\pi E} \left\{ \frac{1}{\varepsilon} + \frac{3\theta^2}{r} \left[2\ln\left(\frac{d}{\varepsilon}\right) - 1 \right] \right\}$$
(1.25)

In fact, Ω is frequency dependent thus should also be velocity dependent. To keep simple, for a certain system, Ω is normally taken as $(V/V_0)^n$, where V_0 and n are material constants which characterize the damping properties of solids.

Dissipation from viscoelastic model

Although relative good agreements between experiments and the "elastic" dissipation have been observed, there are still several intrinsic flaws in this "elastic" dissipation: 1. The surface deformation is deduced from linear elastic theory and the surface effect is discarded. 2. Only the vertical component of the surface tension is taken as the traction on the elastic slab. 3. The thickness of the elastic slab is assumed to be infinite. 4. Rigidity of the soft material is constantly taken as Young's modulus. Moreover, dissipation is included in an ad-hoc fashion, with no clear origin. However, it is not true for a viscoelastic material. Difficulties are how to take the surface effect into the model for the surface deformation, and how to correctly predict the surface deformation and dissipation by obeying the viscoelastic nature of the material. Those concerns are partly addressed in the framework of the viscoelastic model developed by G. Fredrickson, D. Long et al⁴⁰⁻⁴², as will be stated in the following.

(A) Dynamic deformation^{40–42}

When a molten polymer brush of thickness, h_0 , is forced with a surface sinusoidal deformation: $h(x) = h_0 + \epsilon \cos(qx)$, as is demonstrated in Figure 1.11(b), the free energy in x and z directions was calculated. Then for an arbitrary perturbation on the surface, the elastic free energy of the first order in the limit of long wavelength is given by: $f_{long} \approx 3G\epsilon^2/4q^2h_0^3$; in the limit of short wavelength: $f_{short} \approx G\epsilon^2 q/2$. The free energy for increasing the surface area: $f_{area} \approx \gamma(q\epsilon)^2/4$; G is the instantaneous shear modulus felt by the traction. Then the free energy in causing an arbitrary distortion, δh , is:

$$F(\delta h) = \frac{1}{4\pi} \int_{-\infty}^{+\infty} \chi^{-1}(q) \hat{h}(q) \hat{h}(-q) dq$$
(1.26)

where, $\chi^{-1}(q) = \gamma q^2 + 3Gq^{-2}h_0^{-3} + 2qG$; The surface deformation, δh , due to a traction f can be obtained by minimizing $F(\delta h) - f\delta h(0)$ and it yields:

$$\delta h(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \chi(q) fexp(-iqx) dq \qquad (1.27)$$

The picture of liquid spreading on gels can be simplified as the following in a 2D picture: Laplace pressure will be neglected; A point traction force which has an angle of θ_d to the horizontal direction, is propagating at a constant velocity V on a viscoelastic substrate with the thickness of h_0 ; The material will be considered to be incompressible. Surface deformation follows a similar result as the above expression except the surface traction f is substituted by $\gamma_{LV} \sin \theta$.

(B) Energy dissipation from the Chasset-Thirion model (Figure 1.12)



FIGURE 1.12: Dynamic surface deformation of a viscoelastic material with a moving contact line at speed V. $f_0 = \gamma_{LV} \sin \theta_d.$

The energy dissipation in a viscoelastic material is⁴⁰⁻⁴²:

$$P_{film} = \iint_B \sigma: \dot{\varepsilon} \, d^2 x \tag{1.28}$$

This integration is for the overall body of the material. The above equation can be rewritten in temporal Fourier space:

$$P_{film} = \iint_{B} \sigma_{ij}(x,t)\partial_{i}\partial_{t}u_{j}(x,t) d^{2}x$$

$$= \frac{1}{2\pi^{2}} \int_{B} d^{2}x \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} d\omega'$$

$$\times (i\omega')e^{i(\omega+\omega')t}G(\omega)u_{ij}(x,\omega)u_{ij}(x,\omega')$$
(1.29)

If the viscoelasticity of the gel can be described by the Chasset-Thirion model, $G(\omega) = G_0 + isign(\omega)G_0|\omega\tau_m|^m\beta$, one would arrive at the following for the dissipation at low speed:

$$P_{film} \cong \frac{1}{\pi} \int_{0}^{h_{0}} dx_{2} \int_{-\infty}^{+\infty} d\omega G_{0} \frac{|\omega| |\omega \tau_{m}|^{m}}{V} \hat{u}_{ij}^{s}(\frac{\omega}{V}, x_{2}) \, \hat{u}_{ij}^{s}(\frac{-\omega}{V}, x_{2}) \tag{1.30}$$

 $\hat{u}_{ij}^{s}(q, x_2)$ is the spatial Fourier of the static deformation at the wavenumber q. There are four terms associated with the summation of \hat{u}_{ij}^{s} and the contribution of each is equal. Dropping the prefactor and using the result for the surface deformation from Equation (1.25) with a temporal Fourier transform from G(t) to $G(\omega)$, one gets an estimation of dissipation in the soft material phase:

$$P_{film} \cong G_0 V(V\tau_m)^m \left(\frac{\gamma_{LV} \sin\theta_d}{\gamma_s}\right)^2 \int_{q_1}^{q_2} |q|^m dq$$
(1.31)

q1 and q2 are two cut-offs between which the deformation penetrates to a depth q^{-1} , and $q1 = h_0^{-1}$, $q2 = G'/\gamma_s$. In the end, the dissipation power is:

$$P_{film} \cong \frac{(\gamma_{LV} \sin\theta_d)^2}{\gamma_s^{m+1}} (\tau_m G_0)^m V^{m+1}$$
(1.32)

Here, the viscoelastic model, developed by G. Fredrickson, D. Long et al^{40–42}, adheres closer to the real in that the viscoelasticity is directly injected into the model. However, it lacks a true and full order prediction for the viscoelastic surface deformation for its over simplified conditions: first order approximation; horizontal force transmission neglected, symmetry surface tension, etc. No further model responsible for viscoelastic dissipation on elastowetting dynamics appears after this "dissipation" one though there is one phenomenological model which forces a local stress balance at the wetting tip⁴⁵.

1.5 Open questions and the structure

Open questions are categorized in the order of elastowetting statics and spreading dynamics.

Elastowetting statics

(A). Static contact angle hysteresis

Very few reports on contact angle hysteresis in an elastowetting case can be seen up to now. On the one hand, very good knowledge of the elastowetting surface deformation was lacking until the very last decade. This impedes a further understanding of the connection between the deformation and the contact angle hysteresis. For example, singularity and surface effect at the contact line has confused scientists for decades and developing proper models^{53,55,56,85} for deformation only happens recently; on the other hand, hysteresis itself is a very difficult topic because of its complex origins⁸⁷. In general, it is believed that certain degree of plasticity is responsible for it^{56,84,91}. With the micro-X ray technique, it has been directly observed that the wetting ridge grows with time⁸⁰. However, no discussion has been made in relating this growth with the contact angle hysteresis. As to the precise mechanism, nothing has been experimentally and theoretically proposed.

(B). Static surface deformation

Experimentally, a full description of the deformation both at small scale and large scale is lacking, though there are a set of measurements in the microscopic scale^{53,80,85} and one measurement on a large scale^{59,60}. Those measurements are either on very thin layer^{53,80} or with very small droplets^{59,60}. How the thickness of the film, the droplet size and elasticity systematically affect the static deformation is still missing from an experimental point of view.

Theoretically, models including the surface effect appear recently and it is usually assumed the thickness of the soft substrate is infinite and a full comparison between new models and experiments of the long-range deformation is in demand. Besides, how to model a 3D droplet and how each component of applied stresses contributes to the overall surface deformation remain to be solved.

Spreading dynamics

Very rare models have been built to account the elastowetting spreading. To name all of them: the "elastic" model by Shanahan et al^{32–35,38,39,79}; the viscoelastic model by G. Fredrickson, D. Long et al^{40–42}, the phenomenological model by Karpitschka et al⁴⁵. For the "elastic" model, it is a very primitive one: 1. The surface deformation is calculated from linear elasticity theory. 2. The surface effect is missing. 3. The horizontal component of the liquid-vapor surface tension is neglected. 4. Dissipation is over simplified for certain types of polymers. For the viscoelastic

model, the dynamic surface deformation is a first-order solution and still the horizontal component of the liquid-vapor surface tension is dropped. As to the phenomenological model, a local surface tension/stress balance is forced at the wetting tip and the liquid-vapor interface has to bend to accompany the rotation of wetting ridge at spreading, which is in debate. How to correctly predict the spreading is to be addressed.

To address all the above concerns, the thesis will consist three main parts: the first part is about the experimental techniques (Chapter 2), in which materials' fabrication (polydimethylsiloxane gel, PVA hydrogel, and SBS-paraffin gel) and their rheology, techniques of measuring surface deformation (home-made quantitative Schlieren optics), controlling thickness of soft films, detecting contact angle/contact line velocity will be discussed. The second part is on elastowetting statics (Chapter $\underline{3}$), where we will focus on elastic substrates (PDMS): measurement of surface deformation as a function of droplet size, thickness of the soft layer and elasticity; modeling for the surface deformation from the theory of linear elasticity; how the tangential component of the liquid-vapor surface tension affects the long-range surface deformation; contact angle hysteresis. The third part is on elastowetting dynamics (Chapter 4 and 5). Chapter 4 elaborates on effects of the thickness of soft gels, droplet size, and flux rate on the spreading dynamics, which will be experimentally and theoretically explored. Energy dissipation from the soft gel phase will be calculated based on the theory of linear viscoelasticity. Two scaling laws for the spreading dynamics at small velocity limit and at small thickness limit will be derived and verified. Chapter 5 uses the main results from a fundamental understanding of elastowetting dynamics from Chapter 4 to applications: sliding and drifting of droplets, in which droplet size effect and thickness effect will be experimentally investigated. Chapter $\underline{6}$ will draw a general conclusion of this thesis and present perspectives on elastowetting on complex gels.

Chapter 2 Experimental techniques and materials

2.1 General review of experiments

In this thesis, several main experiments are conducted to investigate the statics and dynamics of elastowetting:

- Measurement of the contact angle and surface deformation. The monitoring of both the static and dynamic contact angle is usually accomplished by side view cameras, from which the contact line velocity can also be deduced; for the surface deformation, a detection platform, called the quantitative Schlieren optics, is developed to enable the direct observation of surface deformation in real time. By combining the two, a system, being able to detect the contact angle, wetting velocity and the surface deformation at the same time, is built and used to study elastowetting.

- Preparation of soft materials and substrates with well-defined thickness. In this thesis, we will use three types of soft materials: PDMS gel, SBS-paraffin gel and the PVA_SbQ/GA hydrogel. The fabrication and precise control of the mechanical properties of those materials are important ingredients in this study. How the properties of these materials affect wetting will be explored. Besides, thickness effect on elastowetting is investigated, which demands excellent control of the thickness of soft substrates.

Experimental techniques and materials relating to the two general experiments (measurements of the elastowetting and material preparation) will be broken up into pieces and each of them will be discussed in the following.

2.2 Quantitative Schlieren optics

Ordinary experimental techniques have difficulties in observing surface deformations in elastowetting. As elastic interactions are long-ranged, the deformation induced by a resting droplet on a soft substrate can extend to several millimeters away from the contact line while there is a sharp cusp at the contact line^{53,58,111}. The elastowetting deformation needs to be tracked in real time because most materials are viscoelastic in dynamics, in which case the dynamic deformation is different from a static one. The two require an experimental technique which is sensitive to both the short-range and long-range surface deformation in real time. Confocal microscopy is frequently used to study the wetting ridge^{53,59,85,94}. This technique offers excellent vertical precision and it is clearly able to detect the 3D topology of materials. However, it takes time to do a full 3D scanning of the object. The higher the resolution is, the longer it takes. Hence, it is not applicable to the dynamic case. In static cases, deformation on viscoelastic materials may grow with time^{58,63–66}, and it might be questionable whether the deformation from time-averaged surface scanning techniques, such as confocal microscopy, is the real surface deformation or not. Bearing the two requirements of great lateral extent and vertical precision in mind and with the fact that all the soft materials in this thesis are transparent, we propose to use Schlieren optics, which is sensitive to the light deflection induced by the change in the surface slope of the sample^{112–117}.

2.2.1 Principle and setup

Before setting out all the details of our quantitative Schlieren optics set-up, we will start with a
simple description of the principle of the Schlieren technique.

When a camera is targeting at a transparent object with the surface deformation with a uniform surface slope at certain region under the natural illumination (Figure 2.1(a)), a picture with homogeneous light intensity will be acquired. Equivalently, nothing will be observed on the acquired picture. The amount of light received by the CCD or CMOS sensors inside the camera from the deformed part and flat part is the same because the natural light is of all directions thus the overall sum of light beams that go to the camera from any point on the surface is almost the same. However, if the illumination light beam is collimated (Figure 2.1(b)), there are two changes compared to the case under the natural illumination: first, only a small part of the object is visible to the camera because the light beam, after passing through the part outside the yellow region (Figure 2.1(b)), is out of the camera, as is drawn in red line, can be sensed. However, the deformed region deflects light beams, leading them with a new path into the camera's range, blue line in Figure 2.1(b). With the parallel light beam, the surface slope of the deformed part can be calculated through Snell's law once the distance between the camera and the object, and the size of the camera lens are known.



FIGURE 2.1: (a) How a camera takes a picture in the natural illumination. The size of the arrow stands for the light intensity. (b) Shadowgraphy under the collimated light. (c) Snell's law when a light beam travels through a titled surface

The advantage of parallel light beam illumination is obvious in determining the surface slope compared to the natural light illumination. However, the proposed mean in Figure 2.1(b) is only able to detect a constant surface slope while the real surface slope is varying spatially. It is not possible to directly apply this method to the elastowetting case. One step to move forwards is to address how to let the camera be sensitive to the different surface slope continuously. By using the dependence of light bending on the surface slope, one strategy is shown in Figure 2.2. A convex lens and a knife cut-off are added to the previous solution: all the collimated light beams will go through the focal plane of the convex lens with the focal length f_0 before they arrive at the camera, and the deviation from the focal point is: $\Delta a = \varepsilon f_0$ at the small angle approximation^{112,114}(see Appendix A), where ε is the deflection angle when the light beam passes through the object. All light sources have a certain size, leading to that the conjugated

image of the light source on the focal plane has a finite size, $h \times b$, as is shown in the insert of Figure 2.2. On the focal plane, a knife cut-off is applied and Δa can be tuned so that different light intensity sensed by the camera, $I = I_0 \frac{a + \Delta a}{h}$, is ensured according to different light beam deflection Δa , where I_0 is the background light intensity. In this way, different surface slope will finally induce different light intensity on the camera sensors, granting this design an ability to detect a continuous change of the surface slope, which can be deduced from the following equations:

$$\Delta a = \varepsilon f_0$$

$$\varepsilon = \theta_2 - \theta_1$$

$$n = \frac{\sin \theta_2}{\sin \theta_1}$$
(2.1)

in which n is the refractive index of the material.



FIGURE 2.2: Optical set that is sensitive to the surface slope. The insert one is to show how the light deflection is related to the light intensity, reprinted from G. S. SETTLES¹¹².

Based on the core idea from Figure 2.2, a full set of solutions is proposed by improving the light source and path design as is sketched in Figure 2.3(a) and this system is called quantitative Schlieren optics based on the lens-type Schlieren¹¹².



FIGURE 2.3: (a) Schematics of the quantitative Schlieren optical platform. (b) Surface deformation detected by

the Schlieren. The shear elastic modulus is 1.2 kPa; thickness of the soft substrate is 228 μ m; and the diameter of the droplet is 1.51 mm.

This setup consists of four parts: I, SLC (slit light source), indicated as the dotted rectangle; II, the Schlieren field, including CL (collimating lens), TGC (transparent glass chamber to control the humidity) and DL (de-collimating lens); III, knife cut-off, i.e., KC (knife cut-off); IV, camera and post-computing. A white LED light source (LUXEON, LUMILEDS, USA) is used and refocused on a mechanical slit (VA100/M, THORLABS, USA) by a condenser. Thus, we obtain a slit light source (1 $mm \times 13.6 mm$) that is conjugated at the focal plane of a second Schlieren lens (DL). Afterwards, the light beam goes to part II and is collimated by CL ($\Phi = 25.4 mm$, $f_0 = 101.6 mm$; MPD149-P01, THORLABS, USA). This parallel light beam traverses the TGC (transparent glass chamber) and the sample. It is later collected by DL (LB1374-B, THORLABS, USA) and reimaged on the KC plane. Finally, all the light beam falls onto CCD sensors of the camera (DFK 23UX174, IMAGING SOURCE, Germany) with a lens (AVENIR TV ZOOM LENS F1.8, JAPAN), which exactly focuses on the sample plane. The size of the camera sensor is 1280×960 pixel², resulting in a lateral resolution of $10.2 \mu m/pixel$.

In principle, the slit light source is perfectly refocused on the KC plane as marked by the red solid arrow in insert of Figure 2.3(a), as long as no light beam is disturbed. If there is any disturbance on the focal plane of the camera (sample surface), such as the light beam deflection induced by interface undulation and density variation, etc., the conjugated image will be shifted by a distance Δa at the KC plane. At the small angle approximation: $\Delta a = \varepsilon f_0$ where f_0 is the focal length of the second lens. Δa can be acquired either from a standard calibration lens in the presence of Schlieren object^{112,116,117} or from a pre-calibration process as will be discussed in the next section. In our studies here, the deflection will be considered to be only due to the surface slope. With Snell's law, the local surface slope will be recovered from ε .

Our system is sensitive to a deflection angle of 0.0007 rad, with the total range of 0.05 rad with the pre-mentioned configuration. Sensitivity is extracted from our camera and the range is computed by applying a 50% cut-off because surface slope of the substrate could be positive and negative: h/2f. An example of a visualization obtained with our Schlieren set-up is showed in Figure 2.3(b), where a droplet of diameter 1.51 mm, sits on a PDMS layer of thickness 228µm. Light intensity around the contact line varies regarding to the distance from the contact line, which indicates a changing surface slope. Vertical displacement of the soft material is reached by the integration from the surface slope. It is plotted as the blue solid line in Figure 2.3(b).



FIGURE 2.4: Reflection, refraction, deflection and shading of light beams passing through a liquid drop on a soft substrate.

Three factors restrict our measurement scope (Figure 2.4):

(1) The high refraction of the liquid drop. The different refractive index among liquid, air and soft substrate not only dims the light intensity, but also deflects light beam by an angle, θ_{out} . To evaluate the light intensity decrease, we assume that the incident light is unpolarized. Consider the liquid to be water with a refraction index of 1.33 and soft substrate to be PDMS with a refraction index of 1.4, the intensity of the light beam after passing through the drop is $0.95I_0$ from Fresnel equations where I_0 is the intensity of the incident light beam. Hence, it is a small effect. However, the parallel light beam, which passes through the wetted part, is strongly deflected away. The incident light beam is related to its outgoing by:

$$\frac{\sin\theta_{in}}{\sin(\theta_{in} - \theta_{out})} = n \tag{2.2}$$

where *n* is the refractive index of the liquid. At the limit of the Schlieren optics' sensitivy (0.05 rad), the maximum θ_{in} that can be sensed is around 10° for water. As a result, most part of the drop is invisible because those light beams are deflected too much to be out of the range of the Schlieren.

(2) The shading of the liquid drop. When the static contact angle is larger than 90°, the parallel light beam is partly shaded by the droplet, shown in dotted black line of Figure 2.4. For all the water drops on PDMS and SBS-paraffin substrates we will use, the static contact angle, θ_e , is larger than 90°, meaning that shading is always present in the vicinity of the contact point. This region is unreachable to our set-up.

(3) The systematic capacity of Schlieren optics because of the finite lens dimension¹¹². Only the surface slope smaller than 0.124 rad can be captured if the refraction index of PDMS is taken as 1.4 (Guidance book, Dow Corning, US).

As we are only interested in the region, outside the droplet, typically larger than the elastocapillary length, where the surface slope is smaller than that in the inner region ($< l_s$), the experimental results in chapter <u>3</u> tell us the capacity of technique is enough for our research.

2.2.2 Calibration and validation

For quantifying purposes, Δa must be detected. However, the only data we can directly get from the Schlieren optics is the picture taken by the camera. The question becomes how to deduce Δa the from those pictures. A simple strategy is to put a standard lens with known surface slope with the presence of the Schlieren object^{112,116,117} and surface deformation can be deduced from a comparison between grayscale values of object surface and those from the calibration lens. However, it is not practical to always follow this routine in our measurement in that the presence of the calibration lens on soft materials would induce long range deformation and the size of this thin lens is comparable to our camera observation window. To resolve this, an alternative way for calibration is proposed based on the unequivocal relation between the local grayscale value of pictures (light intensity received by the camera) and the cut-off $(\Delta a + L_c)$ (Figure 2.5). If the background light intensity is I_0 and the length of the slit light source is h, the light intensity, I_c , sensed by the camera is $(h - \overline{L_c})I_0/h$ with a total cutoff $\overline{L_c}$ at the focal plane (insert of Figure 2.5); This relation always holds regardless the origin of the cut-off¹¹², which could come either from the blocking of the knife edge, L_c , or from the shifting of the light beam in addition to the knife edge cut-off, $\Delta a + L_c$. If the surface of the Schlieren object is flat, light beams collectively focus onto the conjugation image of the slit light source (solid black line in Figure 2.5) and $I_c = (h - L_c)I_0/h$. Nevertheless, light beams going through a tilted surface would be deflected by a distance, Δa , at KC and $I_c =$ $(h - L_c - \Delta a)I_0/h$ (solid red line in Figure 2.5). By comparing the relation of $I_c =$ $(h - \overline{L_c})I_0/h$ and $I_c = (h - L_c - \Delta a)I_0/h$, Δa can be determined when L_c is known which can be easily defined experimentally.



FIGURE 2.5: Diagram of the deflection and cut-off

Hence, a three-step measurement is carried out: First, a sequence of pictures is recorded by applying different cut-off positions at the KC and a map relating the pixel grayscale value (light intensity) to the deflection by the knife cut-off will be built. During this step, object of interest

is absent; second, all the camera parameters are kept the same, pictures are taken after the drop is deposited; third, the grayscale value of the Schlieren picture is compared to the calibration map and the deflection, Δa , is obtained. Further, by employing the deflection relation and Snell's law (Equation (2.1)), the surface slope can be recovered and the vertical surface deformation is obtained by integrating it from the far to the near. Additionally, one side benefit of this calibration is that the background noise, including the uneven illumination, dust shadows, etc., is removed as well because the local dependence of light intensity (grayscale value of each pixel) is determined in the first step.

This method is validated by a plano-concave lens (#45-376, Edmund) which is placed on the Schlieren object plane. The lens is of diameter 3 mm and has an effective focal lens of 9 mm. Its deflection, ε defined in Figure 2.2 and Figure 2.3, can be conveniently acquired from its geometry. And ε acquired from the calibration method and its comparison with the standard lens is as follows:

- A plano-concave lens is placed on the Schlieren object plane. Then different cut-offs are applied and the corresponding images are recorded. A representative picture from the Schlieren camera at one blade cut-off is shown in Figure 2.6(a). The yellow spot is the lens' geometrical center from a circle fitting. Outside of the lens is the homogenous background because the same amount of light beams is blocked at the blade cut-off plane. In the middle of the lens, a region of the white can be found, which is due to the small deflection of light beams (part of light beams still can reach the camera sensor). However, this white region is not a circular in that blade blocks all the light beams that are deflected by a distance to the blade side longer than $h - L_c$.

- The light intensity (grayscale value) profiles on both the lens and the background (red line in Figure 2.6(a)) are plotted at different cut-off length as is shown in Figure 2.6(b). The profile is plotted from one end I to the other end II (red line with two red stars at each end). When the cut-off distance, L_c , is increasing, the background light intensity in the end of I and II is equally decreasing, as is shown in Figure 2.6(b) that the grayscale of two ends of a single grayscale profile for any cut-off is dropping and of the same value. At the center of the lens, the surface slope is zero so that the light intensity at this point is expected to be changing identically with the background light intensity. Hence, the point on the light intensity profile that is simultaneously changing with the background light intensity is tracked for all the cut-off. Those points are indicated as red points in the region 1.5 mm < X < 2 mm on Figure 2.6(b) and the position of the lens geometrical center is displayed as the yellow solid line in Figure 2.6(b). Good agreement between the location of center points detected from the grayscale profile and that from the geometrical fitting is recovered. This is the first evidence that the designed Schlieren method can be validated.



FIGURE 2.6: Validation of the quantitative Schlieren optics. (a) A standard plano-concave lens is placed on the objective plane and various cut-offs from the knife edge are applied. (b) The light intensity (grayscale value) variation along the selected line (red solid line in (a)) at different cut-offs. The profile of it is plotted from the I (red star in (a-b)) to II (red star in (a-b)). (c) The background light intensity (grayscale value) at different blade cut-offs. (d) Comparison of the light deflection calculated from the knife edge cur-off and that from the calibration lens.

- The background light intensity from the red points (Figure 2.6(b)) at X = 0.026 mm is drawn in Figure 2.6(c) at different blade displacement, D_k . However, it has to be pointed out that D_k in Figure 2.6(c) is not L_c in Figure 2.5. It simply indicates the displacement of the knife edge. The true relation between them is $L_c = D_k + c$, where c is a constant. A good linear relation between L_c or D_k and light intensity (grayscale value) is uncovered, as is expected by the geometrical optics from Figure 2.2, Figure 2.3 and Figure 2.5. This is the second evidence that the proposed method is valid.

- Deflection, ε , is independently calculated from the geometry of the lens, and from the relation of the light intensity and the cut-off (proposed method). ε , based on the geometry of the lens, is drawn as blue dot in Figure 2.6(d) with the known distance from the lens center. For ε from the proposed method, the lens center, X_c , is detected from the comparison of the light intensity profile with the background light intensity in the first place. Then, the light intensity around this center is compared with the relation (calibration map) from Figure 2.6(c), and the corresponding displacement of the knife edge, D_k , can be found. The reference displacement of the knife edge, D_r , can also be recovered where $L_c = h/2$ in Figure 2.5 (equivalently at the point $X = X_c$). Afterwards, the deflection distance of light beam at the blade plane is $\Delta a =$ $D_k - D_r$. Then the deflection, $\varepsilon = \Delta a/f_0$, is obtained (blue circles in Figure 2.6(d)) and compared with its counterpart from the geometry of the lens (black solid line in Figure 2.6(d)). The ultimate step for the validation is shown in Figure 2.6(d) in which a good collapse between the proposed method and the standard lens is revealed.

The surface deformation of a droplet standing on a thick PDMS soft substrate, shown in Figure 2.7(a), is detected by the two methods, respectively. The light intensity along the orange solid line around the contact line is varying, which indicates a changing of the surface slope of the soft substrate. Surface deformation from the standard lens is shown as black solid curve in Figure 2.7(b) and the other by the proposed method is drawn as green solid line in Figure 2.7(b). There is no difference between the two methods. As a result, all throughout this thesis, measurements of the surface deformation in the following will adopt our proposed method without presence of the standard lens.



FIGURE 2.7: (a) A water droplet sits on a PDMS substrate which is attached to a rigid glass slide. The thickness of the substrate is around 1 mm. (b) Comparison of the surface deformation detected by the two methods.

2.3 Contact angle detection

Both for elastowetting statics and dynamics, how the contact between liquid and the soft materials needs to be experimentally characterized. From a thermodynamic point of view, the contact angle measured from the current experiments is conveniently referred to as the macroscopic contact angle, because this angle is associated to the capillary energy release in dynamics for the system^{12,21,118}. Thus, all throughout this thesis, when the experimental contact angle is referred, we always mean the macroscopic contact angle unless it is specifically defined.



FIGURE 2.8: Contact angle detection. (a) Water droplet sitting on a soft PDMS substrate with Young's modulus of 3.6 kPa. The thickness of the soft film is 242 μ m and the droplet diameter is 1.52 mm. The edge of the liquid-vapor interface in the white square around the contact line is fitted into a circle and the contact angle is taken as the intersection angle between the fitted circle and the substrate surface. (b) Schematic of how the experimental contact angle is detected. As can be seen from both (a) and (b), A small ridge forms at the contact line, the apparent contact angle, θ , is defined as the angle measured from the imaginary flat soft substrate interface to the extrapolated liquid-vapor interface into the soft substrate.

Figure 2.8 (a) is a typical picture from experiments showing the contact between the liquid (water) and soft substrate (PDMS, E = 3.6 kPa). A small ridge can be observed with naked eye at the contact line. Its details have been reviewed in section 1.2.3 and 1.3.2. A manifestation of this contact is sketched in Figure 2.8(b). The liquid not only induces a short-range ridge and a long-range deformation around the contact line, but also penetrates into the soft material^{57,59,86}. Close to the contact line, the soft material rises. There are several contact angles defined at this cusp (Figure 2.9). Right at the tip, the contact angle between each neighbor interface is selected by the surface tension/stress^{53,80}. However, these several angles are not relevant to this thesis in that: 1. We are not able to directly visualize those angles from our experimental setup. 2. The overall interfacial energy release is not strongly affected by those angle relations for large droplets. As a result, we only detect the macroscopic contact angle experimentally and use this angle to quantify the elastowetting statics and spreading dynamics.

To measure this macroscopic angle, we first define a region around the contact line to find the liquid-vapor interface, as is the white rectangular shown in Figure 2.8(a); then liquid-vapor interface, red cross marked in Figure 2.8(a), is detected by Canny edge detection technique and those edge pixels are fitted into a circle with the least square algorithm, with the fact that the droplet size is in general smaller than the capillary length, $\sqrt{\gamma_{LV}/\rho g} \approx 2.7mm$; finally, the experimental contact angle is measured from the flat surface to the tangential line at the point where the fitted circle meets the flat surface.



FIGURE 2.9: Contact angle relations at the small scale of a water droplet on a PDMS film from the micro-X ray techinique⁸⁰. (a)-(b) Zoom-in of the wetting ridge. (c) Surface stress balance at the cusp tip.

Figure 2.10 shows a water droplet evaporation and the corresponding contact angle is measured with this local circle fitting technique. Contact angle decreases fast initially because of the strong non-equilibrium of the contact angle, equivalently large capillary driving force for the system. After 300 seconds, the droplet dynamics is slowed down and determined by the liquid evaporation (a small driving force proportional to the surface area).



FIGURE 2.10: Evaporation of a water droplet in an open chamber at the ambient temperature (~25°C). (a), superimposition of image sequence of droplet after its deposition by a micropipette. The initial volume is 3 μL. (b), time evolution of the contact angle measured with the proposed method.

2.4 Wetting velocity measurement

As part of this thesis is to investigate the spreading dynamics of liquids on soft materials, two sets of elastowetting dynamics are designed: droplet deflation, and droplet sliding and drifting on a titled substrate. We describe now how the contact line velocity is extracted with a subpixel precision.

Droplet deflation

The experimental setup for droplet deflation, Figure 2.11(a), is part of the quantitative Schlieren system (Figure 2.3(a)) so that not only the contact line velocity/angle can be measured by a side view camera, which is equivalently shown as SC in Figure 2.3(a) and the camera in Figure 2.11(a), but also the simultaneous surface deformation is monitored by the Schlieren camera.

Liquid spreads on a horizontal, flat soft layer that is coated on the rigid glass slide. The side view camera is mounted in perpendicular to the parallel light beam plane and is on the same altitude to the soft substrate surface. The spreading velocity is tuned by the flux rate of a pump.



FIGURE 2.11: (a) Experimental setup for droplet inflation and deflation. (b) Superimposition of water droplet images at receding where the flow rate is $120 \,\mu$ L/min. The black pipe in the middle is the needle for sucking liquid. The start-up diameter of the droplet is 4.2 mm. The time interval between each image is 24.25 s, 14.5 s, 3.65 s, 1.55 s.

Figure 2.11(b) is the superimposition of images of a deflating droplet by the side view camera. White dotted line stands for the initially flat surface. The contact line velocity is determined by a three-step procedure:

- Following the circle fitting technique in the contact angle detection, a rough location which comes from the intersection of the fitting circle (red line in Figure 2.12(a-b)) and the substrate surface is calculated, as is marked as the green cross in Figure 2.12(a-b);

- As the position found in the first step is not the real location where the contact line lies, shown in Figure 2.8(b) and sub-pixel technique is difficult to implement at the green cross because of the shading of wetting ridge and its sensitivity to the light illumination, it needs to find the real three phase line or at least a location where the wetting velocity can be the best approximated. An estimation for the height of the wetting ridge is $\gamma_{LV} \sin\theta/E^{35,56,58,79}$, thus a profile, white solid line in Figure 2.12(b), in parallel to the substrate interface above white dotted line shifted by a distance $\gamma_{LV} \sin\theta/P_r E$ (yellow arrow in Figure 2.12(b)), is selected so that the edge on it is taken as the position of the contact line. Here, P_r is the spatial resolution of each pixel.

- Sub-pixel technique is applied on the selected line. For the edge of an object, it can be represented by an Erf function because of the defocusing and blurring due to the integration of the image sensors (CCD and COMOS) and the point spreading function of the optical element^{119–121}:

$$I(x) = \frac{\Delta I}{2} \left\{ Erf\left(\frac{x - X_e}{\sqrt{2}\sigma}\right) + 1 \right\} + I_0$$
(2.3)

$$Erf(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-t^2} dt$$

here, I(x) is the light intensity (grayscale value) across the edge of each pixel; ΔI is the edge contrast; X_e is the real edge location; I_0 is the background light intensity (background scale value). It is described in Figure 2.12(c) which is a plot of the light intensity (grayscale value) along the selected white solid line from Figure 2.12 (b). As this function's first derivative is a Gaussian function, we fit the difference of the grayscale value of pixels with a Gaussian, as can be observed in the Figure 2.12(d). The scatted dotted data is the difference of the grayscale value between each neighbor pixels and the solid blue line is the Gaussian fitting. The peak of the fitted Gaussian curve corresponds to X_e from Equation (2.3) and is taken as the location of the wetting contact line. This method has been validated elsewhere by the author with a sinusoidal motion of a spherical head on a Fatigue Testing Machine (FTM)¹²². This technique gives us a precision of 0.1-0.3 pixel for the position depending on the quality of the illumination though higher precision is reported elsewhere¹²³⁻¹²⁵.



FIGURE 2.12: Contact line position detection with the sub-pixel detection technique. (a) A macroscopic view of a droplet on a soft material. White dotted line denotes the surface of the substrate. The red curved line indicates the fitting of a circle close to the contact line and the green cross marks the position where the fitted circle meets with the substrate surface. (b) Zoom-in at the contact line. White dotted line represents the surface of the soft material and the white solid line cuts across the tip of the wetting ridge and the grayscale value on this profile will be detected for the sub-pixel technique. (c) Plot of the light intensity of the selected white solid line and a demonstration of the edge model (Erf function). (d) The first derivative distribution of the light intensity and its fitting with a Gaussian function.

The deflation dynamics of droplet in Figure 2.12 is proceeded with proposed sub-pixel location detection technique and the corresponding result and its comparison with the direct edge detection technique from the circle fitting are shown in Figure 2.13. For the displacement, there is a small deviation between the two methods. This might be due to the existence of the ridge which makes one or two pixels' shifting from the soft substrate surface to the real contact in Figure 2.12(b); later when the contact line moves and the dynamic contact angle decreases so that the shifting distance, $\gamma_{LV} \sin\theta/E$, becomes small, the substrate interface line and the selected solid white line collapse together. As a result, the difference between the two methods

is smaller than one pixel. However, for the contact line velocity which is the first derivative of the location, the difference is very pronounced: red solid line from the direct edge detection algorithm in Figure 2.13(b) is very noisy, 0.13 mm/s, while small fluctuation, 0.015 mm/s, is observed for the velocity from the sub-pixel method. This significant improve of the signal falls in our expectation: 3-10 times.



FIGURE 2.13: Receding dynamics of a water droplet. (a) Comparison of the contact line position from the direct edge detection method and that from the sub-pixel edge detection method. (b) Comparison of the contact line velocity from the direct edge detection method and that from the sub-pixel edge detection method.

Sliding and drifting

Figure 2.14 is the experimental apparatus for sliding and drifting experiments. Humidity and illumination are well controlled (details in section 5.1). A LED array is used to provide homogenous illumination. Droplet slides down the soft film layer which is coated on a rigid glass slide along the gravity direction. A front view camera is placed in perpendicular to the droplet sliding plane. A video is recorded when the droplet is in motion.



FIGURE 2.14: Experimental setup for sliding and drifting experiments.

Representative pictures of the sliding are shown in Figure 2.15. The volume of those droplets changes from $1 \mu L$ to $20 \mu L$. The shape of all those droplets is found to be the same because each droplet finds its steady state during the sliding. Assuming that those droplets are all in steady sliding state, the shape of each droplet and the velocity will be the same during its sliding. To detect the velocity, a possible solution is to use the unchanging front of each droplet and fit it into any defined shape with the least square method. The displacement of this defined shape

is taken as the displacement of the droplet and its first derivative will be the velocity of the droplet, that we are interested in.



FIGURE 2.15: Sliding of water droplets on a vertically titled soft substrate of thickness 117 μm with Young's modulus of 3.6 kPa. The red arrow indicates the motions of droplets that follow the gravity. (a)
Superimposition of two images with the time interval of 10 mins; The droplet volume ranges from 1 μL to 4 μL (b) Superimposition f two images with the time interval of 19 seconds; droplet volume is 18 and 20 μL.

It is reasonable to take the defined shape, to be fitted into a circle from the shape of the sliding droplet for the following reasons:

(1). This defined shape doesn't matter as long as the fitting gives a single solution, $F(\tilde{x}, y, t)$, from the drop shape, I(x, y, t), at any moment t. When there is a displacement Vdt, the new drop will be fitted into F(x, y, t + dt) which is simply a combination of $F(\tilde{x}, y, t)$ and its translation Vdt in the following form:

$$I(x, y, t) \xrightarrow{\text{yields}} F(\widetilde{x, y}, t)$$

$$I(x, y, t) + Vdt \xrightarrow{\text{yields}} F(x, \widetilde{y, t} + dt) = F(\widetilde{x, y}, t) + Vdt$$
(2.4)

Equation (2.4) tells that the displacement and the velocity can be acquired from the new fitting at the moment t + dt and the old fitting at the moment t.

(2). The camera targets at a front view (plane \vec{C}). Along the gravity direction (\vec{G}), the droplet experiences a force balance between friction from the soft material and the gravity, which stretches the droplet, as can be observed from a side view (plane $\vec{C} \times \vec{G}$). Thus, the drop shape adapts to the pressure gradient which drives the sliding, in balancing with the friction from the solid-liquid wall. Since the droplet is sliding only along the gravity on a uniform thick film, there should not be a net force in the plane \vec{G} , which ensures the symmetry of the interfacial shape in the plane \vec{G} . What's more, no direct force is exerted on the droplet in plane \vec{C} except there are some confinements from the plane $\vec{C} \times \vec{G}$. It is expected that the droplet will keep a local circle shape in plane \vec{C} to minimize the capillary interfacial energy in a steady sliding. Those can be observed in the head of droplets shown in Figure 2.15.

Therefore, our strategy to detect the motion of a sliding droplet from the camera is the following: first, the edge of the sliding droplet is found by the Canny edge detection algorithm; then a group of pixels in the front of the sliding droplet edge are used for the circle fitting to quantitatively locate the droplet (red dotted line in Figure 2.16(a)) and the center of the fitted circle (red cross in Figure 2.16(a)) is taken as the position, P(x, y, t) of the droplet (Figure 2.16(b)); next, the difference of P(x, y, t) with respect to time t is regarded as the sliding velocity (Figure 2.16(c-d)).



FIGURE 2.16: Detection of the location and the velocity of a sliding droplet. The volume is 4 μ L. The thickness of the soft substrate is 117 μ m with Young's modulus of 3.6 kPa. (a) Edge detection and fitting of the front of the droplet; Red dotted line is the front edge that is used to fit a circle; The red cross is the center of the fitted circle, and it is taken as the position of the droplet. Gravity direction is along the -X. (b) The trajectory of the sliding droplet in 12 minutes. (c) Sliding velocity along the gravity direction in respect to the sliding time. (d) Sliding velocity in perpendicular to the gravity direction.

2.5 Thickness control of soft films

Liquid droplets sit or spread on soft films and the thickness of those films needs to be well controlled. In this thesis, we deal with three types of soft materials: polydimethylsiloxane (PDMS) gel, PVA hydrogel and SBS-paraffin gel. All those gels are prepared and crosslinked on the surface of glass slide. The preparation of those gels is very different and their thickness control should also be different. However, to investigate the elastowetting properties of soft materials, we pay most of our attention to the PDMS gel. For the PVA hydrogel and SBS-paraffin gel, we only look at their contact angle hysteresis and spreading of liquid on very thick film. Consequently, thickness control technique concerns only the PDMS gel if it is not specifically specified. For the PDMS soft film, its thickness ranges from several microns to several millimeters. Two techniques are employed for the thin and thick film, respectively. The thickness is measured with a 3D profiler (Microsurf 3D, Fogal Nanotech, France) at a precision of nanometers with the white light scanning mode. For drifting experiments of sliding droplets, a soft film with thickness gradient is needed. Its preparation will be described in the third part and the thickness measurement is performed by a side view microscopic camera with a precision of $3.3 \,\mu m$.

Thin film (< 100 μ *m*): spin coating

To obtain soft film with small thickness, we adopt the spin coating technique. The procedure and the setup are demonstrated in Figure 2.17. A glass slide is fixed onto the horizontal rotational plate of a home-made spin coater. The polymer melt, Sylgard 527, is deposited onto the glass slide as is shown in Figure 2.17(a). The angular speed, ω , of the spin coater can be tuned from 0 *RPM* to 3640 *RPM*. After a spinning time *T*, a homogeneous liquid film forms and its thickness *h* is predicted from the centrifugal force and the viscous force as^{126,127}: $h = k\omega^{\alpha}$, where *k* and α are determined from experiments.



FIGURE 2.17: Preparation of thin soft films. (a) Deposition of Sylgard liquid onto a glass slide which is fixed on the coating plate of spin coater. (b) After certain time T, a homogeneous soft film with a thickness h is obtained on the surface of the glass slide.

Figure 2.18(a) shows our experimental setup: I (yellow square), the rotational plate with a closed wall to avoid spilling of liquid during spinning; II (red square), motor to drive the spinning; III (purple square), controller for adjusting the spinning speed. The thickness of soft PDMS layer after crosslinking is plotted with respect to the angular speed in Figure 2.18(b) with a good prediction of $h = 2993\omega^{-1.069}$ at fixed spinning time T = 180 s.



FIGURE 2.18: Picture of the setup(a) and relation of the rotational speed and thickness (b)

Thick film (> 100 μm)

For the preparation of PDMS thick film, a pre-layer needs to be coated so that the Sylgard will have a complete wetting condition and is able to spread all over the glass surface to form a flat interface. This pre-layer is obtained with the angular speed 350 *rad/s* for 2 *mins* and is of several microns thick. Then the volume of the Sylgard, V, is carefully controlled and the thickness, h, is roughly regulated as: h = V/S, where S is the surface area.



FIGURE 2.19: Preparation of thick soft films by controlling the liquid volume. (a) Deposition of polymer solutions. (b) After a period, liquid spontaneously spreads out and forms a liquid film.

For the thick films for paraffin gel and hydrogel, their thickness is not strictly controlled as the PDMS films. Their polymer solutions before the crosslinking are poured directly on clean glass slides and those solutions spread all over the glass slide surface. When the liquid reaches the glass slide edge, it stops spreading because of the edge pinning effect^{2,21}. Then the thickness is determined similarly as the PDMS film except that it is not possible to have thin flat film because of the partial wetting conditions.

Film with thickness gradient

Principle of preparing soft films with thickness gradient is shown in Figure 2.20: in the first step, a glass slide is tilted by an angle α from one side; next, liquid solution for crosslinking gels is deposited onto the titled glass slide from the side with a lower height as is sketched in Figure 2.20(a); in the following, the tilted glass slide with the liquid solution is enclosed with a clean chamber to avoid the surrounding contaminations and around 20 minutes is needed to wait for the liquid spreading to the case of Figure 2.20(b) in which static wetting condition and gravity are the driving force. After the liquid solution fully spreads, two edges are obtained: one is the edge on a higher altitude on the left and the other one is the edge of the glass slide of a lower altitude as can be seen in Figure 2.20(b); finally, this glass slide with the wedge-like liquid covered on is moved into the oven for the liquid solution to crosslink.



FIGURE 2.20: Preparation of soft films with thickness gradient. (a) Deposition of Sylgard liquid onto a tilted glass slide. (b) Sylgard liquid spreading due to the gravity and the edge pinning.

PDMS films form after 24 hours baking in the oven and they are of the same shape as the liquid wedge from Figure 2.20(b). When the glass slide is placed horizontally, the thickness profile of this soft film (Figure 2.21(a)) on the glass slide looks like the cross-section of the film shown in Figure 2.21(b). The side view of the thickness profile in Figure 2.21(b) comes from a slice of the soft film in its waist and is taken by a horizontally continuously translating camera. The pictures by this translating camera are superimposed and the full side view of the whole film on which a thickness gradient is designed can only be visualized. When the titled angle α is tuned, the corresponding thickness profile and gradient is consequently regulated as is demonstrated in Figure 2.21(b). Sample I and II in Figure 2.21(b) correspond to the black solid curve and red solid curve in Figure 2.21(a), respectively.



FIGURE 2.21: Thickness of soft films. (a) Profile of the soft films with different thickness gradient. (b) Side view of the cross-section of soft films from experiments.

2.6 Materials

2.6.1 PDMS fabrication and its rheology

In order to prepare chemically crosslinked soft PDMS gel samples having controlled mechanical properties, we use two commercially available silicone elastomer kits (Sylgard 184 and Sylgard 527 from Dow Corning company). Their mechanical properties are tuned by controlling the mass ratio of the two Sylgard¹²⁸, $\alpha = m_{S184}/(m_{S184} + m_{S527})$, where m_{S184} and m_{S527} are the mass of the Sylgard 184 and Sylgard 527, respectively. The two Sylgards are prepared according to the manufacturer's guide: Sylgard 184 is obtained from mixing the base and curing agent with a mass ratio of 10:1; Sylgard 527 is achieved by mixing part A and part B at a mass ratio of 11:1. As a result, the stoichiometry of each is always kept the same even when the proportion of them is different for different stiffness.



FIGURE 2.22: Synthesis of PDMS gel. (a) Formulation of Sylgard blend. (b) Mixing of the blend. (c) Gas removing with the vacuum. (d) Liquid layer preparation. (e) Crosslinking in the oven. (f) PDMS gel after crosslinking.

The preparation process of the PDMS gel is shown in Figure 2.22. First, Sylgard 527 and Sylgard 184 are separately prepared at stoichiometric rates and they are poured together into a beaker (Figure 2.22(a)). Second, the Sylgard blend is stirred with a magnetic stirrer (DC 180, Froilabo, France) for around 30 *minutes* at a rotation speed 100 *RPM* to ensure the complete mixing (Figure 2.22(b)). Third, the fully mixed blend is degassed in a vacuum of 50 *mbar* for 1 hour (Figure 2.22(c)). The degassed blend is then deposited onto glass slides which have already been treated in a UV Ozone cleaner (PSD Pro Series, Digital UV Ozone System with an OES-1000D Ozone Elimination System, Novscan Technologies, Inc, USA) for 15 *minutes* (Figure 2.22(d)) and the required coating technique has been put in Section 2.5 in line with the desired thickness. The glass slides coated with the blend is transferred to the oven reserved for PDMS to avoid contamination of the surface at a constant temperature 65°C for 24 hours (Figure 2.22(e)). Finally, the transparent crosslinked PDMS is obtained with the crosslinking network shown in Figure 2.22(f).

The mechanical properties of the PDMS gels are characterized by small amplitude oscillatory shear measurements by using a strain-controlled rheometer (Physica MCR 500; Anton Paar, Austria) with a parallel plate geometry (PP20-MRD) at controlled temperature, $25 \pm 0.2^{\circ}C$. The gap was set at 0.6 mm and the strain was fixed as 1%. The gel sample is directly prepared in the geometry. The viscoelastic moduli of the PDMS of different α are plotted as a function of frequency in Figure 2.23(a). For all the gels studied, the storage modulus G' is found independent of the frequency, while the loss modulus G'' shows a weak frequency dependence $G'' \sim \omega^m$. The power m ranges from 0.615 for the softest one to 0.323 for the most rigid one. In Figure 2.23(b) the value of G' at the elastic plateau was plotted as a function of α . The color of each point corresponds to the color in Figure 2.23(a). The value of G' increases with the fraction of Sylgard 184 from 1 to 600 kPa, indicating that we are able to tune the elastic modulus of PDMS gel by 3 orders' magnitude. One can conclude from the rheological measurements that the chemically crosslinked PDMS is elastic at low frequency (elastowetting statics) because of the large ratio of G'/G'' while it is viscoelastic in the full spectrum (elastowetting dynamics). What's more, those types of gel contain certain amount of free chains, which can be extracted by a paper tissue covering on the gel surface.



FIGURE 2.23: Mechanical properties of the PDMS. (a) Rheology of PDMS at different formulation of Sylgard 184 and Sylgard 527. Solid line with a triangle stands for the storage modulus, G', and solid line with a circle represents the loss modulus, G''. Different color means the PDMS of different α . (b) Storage modulus when the oscillating frequency f = 1 Hz as a function of the mass ratio of Sylgard 184 in the Sylgard blend.

2.6.2 SBS-paraffin gel fabrication and its rheology

SBS-paraffin gel is developed from mixing the commercial SBS powder (Styrene Butadiene Styrene; G1682, Kraton Polymers, USA) with paraffin liquid (Norpar15, ExxonMobil, USA) at different concentrations. SBS powder is dissolved into the paraffin oil under stirring at 90°C for 2 hours. After the full mixing of the two, the solution is poured onto a glass slide at ambient temperature ($\sim 25^{\circ}C$) in a fashion as described in section <u>2.5</u>.

The rheological properties of SBS-paraffin gels are measured by T. Kajiya at fixed temperature of $25^{\circ}C$ by a strain-controlled rheometer (Physica MCR 500; Anton Paar, Austria)^{68,69}. The rheological response is that of entangled polymer solution: the loss modulus dominates at very low frequency thus the gel flows at a long-time scale, while at high frequency the storage modulus dominates and the system is elastic due to the entanglement of the chain.

2.6.3 Hydrogel fabrication and its rheology

Hydrogels are synthesized from a commercially available photocrosslinkable polymer (PVA_SbQ, Poly (vinyl alcohol), N-methyl-4 (4'-formylstyryl) pyridinium methosulfate acetal, Polysciences, Inc, USA) and a crosslinker GA (Glutaraldehyde solution, Grade II, 25% in H₂O, Sigma-Aldrich Co, USA). The preparation procedures are in the following: Firstly, the PVA SbQ solution, GA, distilled water (Milli-Q Integral; Millipore, USA) and acid HCl are mixed with the designed stoichiometry at the ambient temperature. HCl is used as catalyst of the PVA-GA crosslinking reaction. The reaction rate depends on the HCl concentration: we use 0.03 mol/L for gelation time about several hours. The mixture solution is placed under the UV light (VL-206.BLB, $2 \times 6 W$ - 365 nm Tube, France) at a distance of 9 cm for 18 hours to ensure the completion of the gelation. The sample is enclosed with a specifically designed chamber saturated with water to avoid drying during the crosslinking reactions. Figure 2.24 shows the crosslinking reactions during the UV light exposure. Not only is the PVA_SbQ polymer itself crosslinked (reaction in Figure 2.24(a)), but also they are crosslinked by the GA crosslinker through the hydroxyl group (reaction in Figure 2.24(b)).



FIGURE 2.24: Crosslinking of PVA SbQ polymer. (a) Network crosslinking due to UV light. (b) Network crosslinking due to GA.

The mechanical property can be tuned by varying the concentration of PVA SbQ and GA, as is shown in the Figure 2.25. The small amplitude oscillatory shear measurements were performed by a stress-controlled rheometer (DHR3, TA Instruments, USA) with a parallel plate geometry (108060, TA Instruments, UK) at fixed strain 1%. PVA hydrogel disc prepared on a plate is immediately tested after the crosslinking reaction under UV. It is insulated from surroundings and saturated with water inside to avoid the drying during the rheology test. As is seen in Figure 2.25(a), an elastic plateau is observed for all the gels tested. The values of G'' are very low compared to those of G', indicating that these hydrogels are practically purely elastic. In Figure 2.25(b), the value of G' at the plateau are plotted as a function of the GA concentration. Though the data are rather dispersed, we see that the crosslinker, GA, hardens the polymer network by inducing extra crosslinks from the reaction shown in Figure 2.24(b). A magnitude of 2 for G' can be tuned by manipulating GA concentration.



FIGURE 2.25: (a) Viscoelastic moduli of PVA hydrogel of different GA concentration (mol/L) at fixed mass concentration 4.4% of PVA SbQ. Different color stands for different GA concentration. Circle and triangle represent the shear storage modulus G' and loss modulus G'', respectively. (b) Storage modulus at plateau as a function of GA concentration when f = 1 Hz. Scattered circles are from experiments and the blue solid line is the linear fit of them. Circle color corresponds to the color in (a).

Chapter 3 Statics: surface deformation and contact angle on elastic materials

3.1 Introduction

Elastowetting on soft materials has been studied for many years. Various models have been proposed to rationalize the surface deformation induced by capillary forces on soft materials^{35,40-42,53,57,79,81,85,93,96,129-131}. However, the play of the surface effect into the elastocapillary problem is only a recent event^{42,45,53,56,57}. There is still a gap in the understanding of the long-range surface deformation⁵³ and the short-scale surface deformation⁵³: Different values of surface tension/stress have to be used to predict the shape of a gel depending on the chosen system. Besides, surfaces tensions deduced from a study of the shape of the surfaces over long distances are of order of several hundred mN/m and are usually considered to be unphysical⁹⁴. Moreover, many studies on elastowetting are conducted either with small droplets (~ 100 μ m) or with thin layers^{53,59,80} (< 100 μ m). Finally, the wetting ridge (< l_s) has received most of attention in the past few decades. The deformation outside of this area has never been systematically investigated and well characterized.

In this chapter, we will cast our attention on the surface deformation on elastic gels, and the observation of the contact angle hysteresis of resting droplets on soft gels will be briefly summarized in the end. Rheology tests in the previous chapter show us that the chemically crosslinked PDMS gel can be regarded as elastic in statics (very small $\tan \delta = G''/G'$ in the low frequency). All throughout this chapter, we solely use PDMS gel as the soft gel to study the elastowetting except when specified, and distilled water (Milli-Q Integral; Millipore, USA) is the single liquid employed in all the following experiments. We are going to address several questions in the following:

- What is the long-range surface deformation induced by resting droplets on soft substrates? How is it determined by the mechanics of the gel, including elasticity and surface tension, and geometry of the system, such as the droplet size, and the thickness of soft films? Can we develop a thorough model to predict the surface deformation? As is shown in Figure 3.1 and section 1.3, the surface deformation (black dotted rectangle in Figure 3.1(a)) can be divided in two regions, between which a cross-over is described by the elastocapillary length, l_s . The first region, whose size is smaller than l_s , is located around the wetting ridge induced by the pulling of the liquid-vapor surface tension^{35,53,58,79}. It is characterized by a universal cusp at the ridge tip whose shape is believed to be dictated by the Neumann's law^{53,80}. This region is dominated by the surface tension. The second region encompasses the gel surface beyond l_s (red solid curve on the gel interface), dominated by the elasticity of the gel. Here we will focus on the latter one. For this purpose, we will use a home-developed quantitative Schlieren optics set-up to visualize and quantify this deformation. Its cut-off, where the Schlieren setup loses sensitivity for the surface deformation, is drawn at the intersection point between the black interface and the red interface in Figure 3.1(b). The distance of this stop-point from the contact line will be discussed later. In addition, we are going to rationalize our experiments with a model based on the linear elasticity theory that accounts for surface tension. Besides, we will analyze more about the exact contribution from each component of stresses in the system to the surface deformation, including the Laplace pressure, traction from nearby contact line and that from the far away contact line, vertical and tangential/translational components of the surface tension traction (γ_{LV}) . This part will be a combined study including experiments and theoretical calculations.

- We will also show that many of our experimental observations demonstrate that the contact angle hysteresis (translation force at the contact line), in fact, plays a pronounced role. Hence, we will study the static contact angle and its hysteresis for water on the soft PDMS substrate. How is the growth of the local deformation induced by a sessile drop at the contact line related to the contact angle hysteresis or the pinning of the contact line? The corresponding contact angle measurement technique has been detailed in section 2.3. The definition of both is shown in Figure 3.1(a) and they are defined in the same way as in Figure 1.4. This part will be demonstrated from the experimental point of view.



FIGURE 3.1: Surface deformation detection of a resting droplet on a soft layer of thickness h_0 . (a) Macroscopic view of an elastowetting drop. D is the diameter of the droplet, which is experimentally approximated as the diameter of the liquid-gel interface area. Contact angles are of the same definition as in Figure 1.4. θ_e is the static contact angle at $V_d < 4 \mu m/s$, where V_d is the wetting velocity of the contact line. (b) Magnification of the dotted square from (a). Surface deformation in the vicinity of the contact line can be classified into two regimes by the elastocapillay length, l_s , according to the prevalence of stresses: elastic stress and surface tension/stress. A dimple is usually observed close to the contact line because of the incompressibility of the PDMS gel. The depth of it is called dimple depth, D_p . ζ is the out of plane surface deformation. (c) Camera view of the resting droplet. The contact angle θ_e is identically defined as (a). (d) Schlieren camera view of the surface deformation. The black is water droplet and the light intensity varies with respect to the distance to the contact line along the blue line, which is a direct indication of the changing surface slope. (e) Out of plane surface deformation acquired from the quantitative Schlieren optics along the blue line in (d).

3.2 Measurements of the surface deformation

We will use the home-made Schlieren optics to study the static elastowetting surface deformation (details in section 2.2 and in Figure 2.3). As a short summary, it is able to measure the surface slope up to $\sim 7^{\circ}$ (deflection angle 0.05 *rad*) for PDMS (refractive index 1.4) with a sensitivity of $\sim 0.1^{\circ}$ (deflection angle sensitivity 0.0007 *rad*). For the following experiments, the Schlieren camera resolution is $10.2 \,\mu m/pixel$, which gives a spatial sensitivity of the vertical displacement as $\tan(0.0007) \times 10.2 \,\mu m \approx 7.1 \,nm$. As the current study mainly targets

statics, the moving of contact line, solely due to the evaporation in our experiments, should be strongly avoided. Hence a transparent glass chamber ($75mm \times 50mm \times 8mm$) is assembled so as to control the humidity. The cover of it can be removed when droplets are to be deposited. Extra water is deposited around glass slide-supported PDMS films, which will be embedded in the chamber before sealing the vessel with the top cover. All the measurements are performed around 5 mins after the deposition. A side view camera (DMK23UV024 IMAGING SOURCE, Germany) with a lens (TV LENS-50mm-1:2.8, RICOH, Japan) is also employed to monitor the contact line motion at a speed of 1 *fps* and the equilibrium contact angle θ_e . The resolution of the camera is 13.9 $\mu m/pixel$, thus granting us a sensitivity of the wetting velocity around 4 $\mu m/s$ with the sub-pixel technique. This limit of wetting velocity is applied to all the following static deformation measurements at $V_d < 4 \mu m/s$ if it is specifically pointed out.

In the following, we will first experimentally investigate the effects of the thickness of a soft layer h_0 , the shear storage modulus G' of a soft layer, and the droplet diameter D on the static elastowetting surface deformation. The definitions are also drawn in Figure 3.1. Figure 3.1(c) is the experimental view of the Figure 3.1(a). Figures 3.1(d-e) correspond to Figure 3.1(b).

3.2.1 Thickness effect

Interface profiles of the dry part of the surface of PDMS gels (red solid line on the interface from Figure 3.1(b)) with various thickness are plotted in Figure 3.2, for similar droplet size. The extent of the profiles is limited by both the hydrophobic shading ($\theta_e > 90^\circ$) and by the Schlieren cut-off (surface slope is sensible up to 7°),). As our results show, the surface slope is typically smaller than the Schlieren capacity (7°), meaning that those profiles are mainly cut by the shading (Figure 2.4).



FIGURE 3.2: Surface deformation on substrates with different thickness. G' for all the samples is the same, i.e, 1.2 kPa. The dotted line corresponds to the flat surface. These curves are horizontally translated in order to be well separated and compared. The x-axis simply marks the scale of the deformation.

To know how far away those profiles acquired from the Schlieren optics are from the contact line, a simple geometry estimation is done as follows: since the representative droplet radius, $R \sim 1.4 \text{ mm}$, is smaller than the capillary length, $l_c \sim \sqrt{\gamma/\rho g} \sim 2.7 \text{ mm}$ in which ρ is the water density and g is the gravitational acceleration, all the drops are supposed to have a spherical cap and the gravity doesn't play much role here. Hence the gapping, l_q , from the measured

profile to the tip of the deformed ridge can be written as $R(1 - sin\theta_e)$. If we take θ_e as 100° and R as 1.4 mm, l_g is about 21 μ m. Morever, as the solid elastocapillary length is^{56,57}: $l_s \sim \gamma_s/2G' \sim 17 \mu$ m if we take γ_s as 40 mN/m. The interface profiles, that we are able to extract, fall very close to the elastocapillary regime. l_g should coincide with l_s in Figure 3.1(b) and the detectable surface deformation in red line from 3.1(b) stops close to the surface tension dominated region where a universal tip exists^{45,53,80}, which will be seen in Figure 3.3.

Figure 3.2 shows the finite thickness effect on the interface deformation. The gel used here is chemically the same. Its wettability and mechanical property can be taken identical on the whole. Nevertheless, a dimple forms on the thin layer when $h_0 < 380 \ \mu m$, and it disappears on the thick layer when $h_0 > 530 \,\mu m$. The response of gel is different due to this geometrical confinement. The depth of the dimple, D_p , is decreasing from 0.57 μm to ~ 0 μm as the thickness is increasing from 170 μm to 2970 μm . A transition for the disappearance of the dimple can be found at 380 $\mu m < h_0 < 530 \mu m$. Qualitatively, the existence of the dimple can be rationalized as follows: because of the incompressibility of the PDMS gel, the pulling-up of the ridge (Figure 3.1(b)) must be compensated by the motion of the same amount of volume around it; hence, a dimple appears for thin soft layers: however, for the very thick layer, the pulled-up volume maybe compensated by the gel from beneath the droplet and surface undulation can be so small that it is not detectable with our Schlieren technique. The dimple extends over several hundreds of microns, which is large compared to the "universal tip", that extends over tens of microns^{45,53,80}. Additionally, for the interface with the presence of dimple, the surface slope gently changes when it is still away from the contact line. Once it approaches the elastocapillary length scale regime, it increases logarithmically as will be shown in Figure <u>3.3(b)</u>.

3.2.2 Droplet size effect

On each PDMS layer, droplets of various size are deposited. The surface deformation after the full relaxation of droplets is shown in Figure 3.3. For each gel layer, the interface profiles are horizontally translated and superimposed in Figure 3.3(a). We checked the distribution of the deformation for droplet diameter ranging from 0.42 mm to 2.95 mm. Each 0.5 mm is clustered and indicated as the same color and symbol.



FIGURE 3.3: (a) Droplet size effect on the surface deformation. The curves are horizontally translated and superimposed. The dotted line is the unaffected surface. (b) Logarithmic surface profile in the capillarity dominated region for the soft layer of 343 μ m thick. $x = 0 \mu$ m is the location of the tip of the wetting ridge. It is estimated from the static contact angle and the size of the droplet.

For the gel layer with the same thickness, droplet size modifies the shape of the ridge in several ways: For thin layers, the dimple depth and its longitudinal size increases with the size of the droplets; From $h_0 = 670 \,\mu m$, the profile is almost independent of droplet size and the dimple is hardly observed; For very thick layer, $h_0 = 1840 \,\mu m$, the whole interface seems to be continuously pulled up and the lateral scale of the disturbed interface increases from hundreds microns to millimeters, as the droplet size increases. In this case, no dimple is detected.

Furthermore, when all the curves for the same thickness are superimposed, a well aligned profile is found in the near region of contact line (Figure 3.3(a)). This points to the universal cusp at the wetting tip that has been demonstrated by Style, etc.⁵³. And the deformation in the close region of the contact line is logarithmic^{35,56}, as is shown in Figure 3.3(b).

3.2.3 Rigidity effect

By fixing the droplet size and controlling the PDMS layer thickness, we investigate the effect of substrate rigidity on the deformation. We performed three runs on three PDMS layers with different shear elastic modulus, i.e., 1.2 kPa, 7.0 kPa and 15.7 kPa. Details of the rheology of those three PDMS gels is shown in Figure 3.4(a). The experimental result is demonstrated as scattered symbols in Figure 3.4(b). It is observed that both the scale and the amplitude of the dimple decrease with an increase of the rigidity. For all the three gel layers, the interface slope changes slowly when it is far from the contact line and once it approaches the elastocapillarity length, it increases sharply. D_p decreases by a factor of 3 and the scale of the deformation (from the profile cut-off to the non-perturbated interface) changes from around 250 μm to 150 μm when G' increases from 1.2 kPa to 7.0 kPa. However, when G' increases further, the surface deformation doesn't change significantly. This is due to the fact that the static contact angle decreases from 102° to 93°. The gel outside of drops experiences not only the pulling in the out of plane direction but also a squeezing or stretching in the in-plane direction depending on the static contact angle. The pulling can be expressed as $\gamma_{LV} \sin \theta_e$ and the in-plane stretching or squeezing will be read as $\gamma_{LV} cos \theta_e$, where the negative indicates squeezing and positive is stretching. Larger G' tends to make a smaller dimple while the in-plane stretching and out-ofplane pulling-up make a larger dimple because of gel incompressibility. As a result, when G'increases from 7.0 kPa to 15.7 kPa, no apparent growth of the dimple is observed. How the static contact angle modifies the surface deformation will be discussed in the following.



FIGURE 3.4: Rigidity effect on the surface deformation. (a) Rheology of the three types of PDMS gel. The number is the mass ratio of Sylgard 184 in the formulation. The G' of them is 1.2 kPa, 7.0 kPa and 15.7 kPa at f = 1 Hz, respectively. (b) Surface deformation for three soft layers with different G'. Drop size, D, for PDMS layers with G' of 1.2 kPa, 7.0 kPa and 15.7 kPa is 0.75 mm, 0.76 mm and 0.76 mm, respectively. Scattered dot, triangle and square are experimental results and solid lines are the calculation results when γ_s is

taken as 40 mN/m. The contact angles are 100°, 102°, and 93° for G' of 1.2 kPa, 7.0 kPa and 15.7 kPa, respectively.

3.3 Model from the linear elastic theory

To rationalize the observations reported in the previous section, we have developed a model based on an extension to the finite thickness of a model built by Dervaux and Limat^{56,57}. In the limit of small strain, the displacement, $u_i(x_j)$, of an elastic material can be described by an expression of Newton's second law:

$$\rho \frac{\partial^2 u_i}{\partial t^2} = \frac{\partial \sigma_{ij}}{\partial x_i} \tag{3.1}$$

here ρ is the density of the elastic material and σ_{ij} is the stress tensor. It can be decomposed into normal and shear component:

$$\sigma_{ij} = \lambda \varepsilon_{kk} \delta_{ij} + 2G' \varepsilon_{ij}$$

$$\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$
(3.2)

where ε is the strain tensor and δ_{ij} is the Kronecker delta symbol. In general, λ and G' are referred to as Lamé's first parameter and Lamé's second parameter, respectively. In the context of elasticity, G' is called shear modulus. By substituting Equation (3.2) to Equation (3.1), one gets:

$$\rho \frac{\partial^2 \vec{u}}{\partial t^2} = G' \Delta \vec{u} + (\lambda + G') \nabla (\nabla \cdot \vec{u})$$
(3.3)

In statics, the above equation equals 0. We assume that the material is incompressible, thus the Poisson ratio ν should be 0.5. However, Lamé's first parameter, $\lambda = \nu G'/(0.5 - \nu)$, goes to an infinite in this case. For the Equation (3.3), the second term $(\lambda + G')\nabla(\nabla \cdot \vec{u})$ now becomes cumbersome in that $(\lambda + G')$ is an infinity while $\nabla \cdot \vec{u} = 0$ as a result of incompressibility. To seek a simple solution, we introduce an effective pressure with the trace component:

$$P = -\frac{1}{3}\sigma_{kk} = -(\lambda + 2G')(\nabla \cdot \vec{u})$$
(3.4)

Hence,

$$\nabla \cdot \vec{u} = 0 \tag{3.5}$$

$$G'\Delta \vec{u} - \nabla P = 0 \tag{3.6}$$

Equation (3.5) stands for the incompressibility of the soft gel. Equation (3.6) represents the static condition and it can be solved in analogy to the Stokes equation in fluid mechanics. This set of equations is completed by the condition of stress continuity at the boundary:

$$\sigma \cdot \vec{n} = \vec{t} + \gamma_s \vec{n} (\nabla \cdot \vec{n}) \tag{3.7}$$

in which σ , \vec{n} and \vec{t} are stress tensor, surface normal vector and traction force exerted at the substrate boundary, respectively. γ_s is the surface tension of the elastic gel and we

assume the surface tension between liquid-solid and that between solid-vapor to be the same and equal to a constant γ_s . We will not try to differentiate the concept of surface tension, surface energy and surface stress in our context either and they will be always referred to as the surface tension.

In addition, the elastic layer is bounded on the rigid glass slide, thus at the bottom of this soft layer:

$$\vec{u}(x, -h_0) = 0 \tag{3.8}$$

Let us denote the surface profile of the soft gel to be $\zeta(x)$. If a line force $\vec{f}(f_x\delta(x)\delta(y), f_y\delta(x)\delta(y), 0)$ is applied to free surface of the elastic slab, the boundary condition, Equation (3.7) and (3.8), will take the following form within the small surface slope limit, i.e $\zeta'(x) \ll 1$:

$$\sigma_{yy} = 2G' \frac{\partial u_y}{\partial y} - P = f_y \delta(x) + \gamma_s \frac{d^2 \zeta}{dx^2}$$
(3.9)

$$\sigma_{xy} = G'(\frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y}) = f_x \delta(x)$$
(3.10)

$$u_x(x, -h_0) = 0 (3.11) (3.12)$$

$$u_{y}(x, -h_{0}) = 0 \tag{3.12}$$

The above equation set can be solved by using a potential function ϕ for the displacement field defined as:

$$u_x = -\frac{\partial \phi}{\partial y}$$

$$u_y = -\frac{\partial \phi}{\partial x}$$
(3.13)

Zero divergence or the incompressibility condition of the elastic gel at deformation is assumed. Equation (3.5) is hence automatically satisfied. By combined Equation (3.13) and the equilibrium condition of the Equation (3.6), one gets the biharmonic equation:

$$\Delta^2 \phi = 0 \tag{3.14}$$

It will be solved by the Fourier transform. Hence, ϕ is defined in Fourier form as:

$$\phi(x,z) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{\phi}(k,z) e^{ikx} dk$$
(3.15)

Inserting this Fourier definition of ϕ into the biharmonic equation yields a fourth order linear differential equation:

$$\frac{\partial^4 \tilde{\phi}}{\partial z^4} - 2k^2 \frac{\partial^2 \tilde{\phi}}{\partial z^2} + k^4 \tilde{\phi} = 0$$
(3.16)

The general solution for this linear differential equation is:

$$\tilde{\phi}(k,y) = Ae^{ky} + Be^{-ky} + Cye^{ky} + Dye^{-ky}$$
(3.17)

With the boundary condition from Equation (3.9) to Equation (3.12), four unknown parameters, A, B, C, D can be determined. The sets of boundary conditions can be expressed in Fourier form:

$$2G'ik\frac{\partial\tilde{\phi}}{\partial y} - \frac{\mu i}{k}\left(\frac{\partial^{3}\tilde{\phi}}{\partial y^{3}} - k^{2}\frac{\partial\tilde{\phi}}{\partial y}\right) = f_{y} - \gamma_{s}ik^{3}\phi, \qquad y = 0$$
(3.18)

$$G'\left(-k^2\tilde{\phi}+\frac{\partial\phi}{\partial x}\right) = f_x, \qquad y = 0 \tag{3.19}$$

$$\frac{\partial \phi}{\partial y} = 0, \qquad y = -h_0 \tag{3.20}$$

$$\tilde{\phi}(\mathbf{x}) = 0, \qquad y = -h_0$$
 (3.21)

This system of equation leads to the following expression for the Fourier transform $\tilde{\zeta}$ of the surface displacement field ζ :

$$\tilde{\zeta}(k) = \frac{f_y \sinh(2h_0 k) - 2Hk(f_y + if_x h_0 k)}{k\{2[h_0 k^2(2h_0 G' - \gamma_s) + G'] + \gamma_s k \sinh(2h_0 k) + 2G' \cosh(2h_0 k)\}}$$
(3.22)

or in a more compact form:

$$\tilde{\zeta}(k) = \frac{1}{\gamma_s} \left[k^2 + \frac{\mu}{\gamma_s K(k)} \right]^{-1} \left[\tilde{f}_y - i \tilde{f}_x \frac{2h_0^2 k^2}{\sinh(2h_0 k) - 2h_0 k} \right]$$
(3.23)

here,

$$K(k) = \frac{1}{2k} \left[\frac{\sinh(2h_0k) - 2h_0k}{2h_0^2k^2 + \cosh(2h_0k) + 1} \right]$$
(3.24)

Finally, the interface deformation of the elastic gel is:

$$\zeta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{\zeta}(k) e^{ikx} dk$$
(3.25)

Single contact line on an elastic layer with finite thickness

As is drawn in Figure 3.5(a), a single contact line with infinite extension into the thirddimension acts on an elastic slab with finite thickness h_0 at an angle of θ_e . The traction will be as follows if the surface tension is γ_{LV} :

$$f_x = \gamma_{LV} \cos \theta_e$$

$$f_y = \gamma_{LV} \sin \theta_e$$
(3.26)

As a result, the interface deformation of the elastic slab is:

$$\zeta(x) = \frac{\gamma_{LV} \sin \theta_e}{2\pi\gamma_s} \int_{-\infty}^{+\infty} \left[k^2 + \frac{\mu}{\gamma_s K(k)} \right]^{-1} \cos(kx) \, dk$$
$$+ \frac{\gamma_{LV} \cos \theta_e}{2\pi\gamma_s} \int_{-\infty}^{+\infty} \frac{2h_0^2 k^2}{\sinh(2h_0 k) - 2h_0 k} \left[k^2 + \frac{\mu}{\gamma_s K(k)} \right]^{-1} \sin(kx) \, dk$$
(3.27)



FIGURE 3.5: Theoretical models. (a) A single contact line on a soft layer of finite thickness h_0 . (b) A 2D resting droplet on soft gel with the 3D correction for the Laplace pressure f_p .

Solution for a 3D droplet

When an infinite long 2D rivulet sits on an elastic gel layer at equilibrium (Figure 3.5(b)), the force experienced by the layer can be classified into two: the liquid-vapor surface tension, γ_{LV} , which is pulling the gel interface outwards, and the Laplace pressure that is pushing the gel phase inwards. If we set the centerline of the rivulet as the 0 for *x*, this rivulet will exert two lines of surface tension and an area of Laplace pressure on the elastic gel interface:

$$f_{1} = (\gamma_{LV} \cos\theta_{e} \delta(x - D/2), \gamma_{LV} \sin\theta_{e} \delta(x - D/2), 0)$$

$$f_{2} = (\gamma_{LV} \cos\theta_{e} \delta(x + D/2), \gamma_{LV} \sin\theta_{e} \delta(x + D/2), 0)$$

$$f_{p} = \frac{2\gamma_{LV}}{D} H\left(x + \frac{D}{2}\right) H\left(\frac{D}{2} - x\right)$$
(3.28)

where *H* is the Heaviside step function. However, for a 3D droplet to be resting on a substrate, the Laplace pressure will be twice as large as f_p from Equation (3.28). Hence, when we apply Equation (3.27) as a Green function in the condition of Equation (3.28), we will correct the

Laplace pressure contribution by reducing the droplet diameter by half. Then the explicit solution for a 3D droplet resting on an elastic layer with finite thickness h_0 analytically reads:

$$\begin{aligned} \zeta(x) \\ &= \frac{\gamma_{LV}}{\pi G'} \int_{0}^{+\infty} \frac{e^{ik\left(x - \frac{D}{4}\right)} [2h_0 k(ih_0 k \cos\theta_e - \sin\theta_e) + \sin\theta_e \sinh(2h_0 k)]}{k[2 + 2h_0 k^2 (2h_0 - l_s) + 2\cosh(2h_0 k) + kl_s \sinh(2h_0 k)]} dk \\ &+ \frac{\gamma_{LV}}{\pi G'} \int_{0}^{+\infty} \frac{e^{ik\left(x + \frac{D}{4}\right)} [2h_0 k(-ih_0 k \cos\theta_e - \sin\theta_e) + \sin\theta_e \sinh(2h_0 k)]}{k[2 + 2h_0 k^2 (2h_0 - l_s) + 2\cosh(2h_0 k) + kl_s \sinh(2h_0 k)]} dk \\ &+ \frac{4\gamma_{LV}}{\pi D G'} \int_{0}^{+\infty} \frac{2\cosh(kx)\sin(kD/4)\sin\theta_e(-2h_0 k + \sinh(2h_0 k))}{k^2 [1 + 2h_0 k^2 (h_0 - l_s/2) + \cosh(2h_0 k) + kl_s \sinh(2h_0 k)/2]} dk \end{aligned}$$
(3.29)

here $l_s = \gamma_s/2G'$. The three terms on the right side indicate contributions to the overall surface deformation from the contact line C1, contact line C2 and Laplace pressure.

3.4 Results

The above equation can be integrated once the experimental parameters are all known. However, there is still one undetermined constant, γ_s , which is a tanglesome concept to describe the surface of soft materials^{132–138}. As we are not aiming at a thorough understanding of it, we will take the simplest approach: the surface of the soft material is liquid-like and there will be a Laplace pressure inside the gel when its interface is curved; the liquid-gel surface tension and the gel-vapor surface tension can be equally accounted by a constant γ_s . When we try to find the surface deformation, we will leave it free as a fitting parameter.



FIGURE 3.6: (a) Static contact angle observed for the surface deformation measurements. (b) Comparison of the interface deformation of soft layers from experiments and that from calculations.

Each detection of the static contact angle was recorded and further summarized in Figure <u>3.6(a)</u>. It has to be mentioned that the error bar is not the contact angle hysteresis because we didn't try to inject liquid into those droplets and observe an advancing contact angle. It is the measurement error of the static contact angle, which in the ideal case (perfectly smooth, purely elastic, etc.) should be of a single value. However, in the real case, contact angle hysteresis can be introduced by many factors^{2,3,5,21}, one of which will be discussed later in section <u>3.6</u>. When the experiment starts, a droplet is deposited onto the soft layer in the open environment and then immediately transferred into the closed chamber which is saturated with water vapor. However, there will be more or less liquid loss during its stay (5 *mins*) onto the substrate,

although the contact line velocity is not detectable ($V_d < 0.45 \ \mu m/s$). It is expected that smaller droplets tend to have a smaller contact angle, which is exactly what we see in experiments.



FIGURE 3.7: Comparison of experiment and calculations for a resting water droplet (D = 1.51 mm) on a PDMS layer film (G' = 1.2 kPa) of $h_0 = 228 \mu \text{m}$. (a) Surface tension effect on the surface deformation from calculations at fixed $\theta_e = 98^\circ$. (b) Dimple depth D_p as a function of surface tension from calculations.

When all experimental parameters of a thin layer ($h_0 = 228 \ \mu m$) and a thick layer ($h_0 = 670 \ \mu m$) are injected into Equation (3.29), it is found the experimental deformation can be very well reproduced by calculations when $\gamma_s = 40 \ mN/m$. The good agreement is shown in Figure 3.6(b). To demonstrate how the surface tension γ_s plays a role in the interface deformation, a resting water droplet ($\gamma_{LV} = 72 \ mN/m$) of diameter 1.51 mm on a soft PDMS layer ($G' = 1.2 \ kPa$) of thickness 228 μm is experimentally observed and numerically analyzed. We give the value of γ_s from 10 mN/m to 300 mN/m. As is shown in Figure 3.7(a), the deformation is well predicted by $\gamma_s = 40 \ mN/m$. Besides, we choose one specific parameter, the depth of dimple D_p to evaluate how the surface tension, the less the surface is deformed and the smaller the dimple depth is. This effect is reasonable because the surface tension tends to flatten a curved interface^{98,139}, thus alleviate the dimple.

Next, we will address the thickness effect, rigidity effect and droplet size effect from our calculations. The static contact angle is fitted as a function of thickness and droplet size from the dataset shown in Figure 3.6(a) so that we will have a smooth curve for the droplet size effect in calculations. Equation (3.29) is integrated from 10^{-7} to 10^{6} for k. As is the same in Figure <u>3.7(b)</u>, a specific parameter, the dimple depth D_p , is chosen to assess our calculations. The best fit of our model gives $\gamma_s = 40 \ mN/m$. This value is very close to other values reported in the literature based on visualizations at the ridge scale, i.e., much smaller scale than our observations⁵³. It is in sharp contrast to the model which doesn't take the translation force into account⁹⁴: an unphysically large surface tension/stress of PDMS gel, 514 mN/m, is needed to rationalize the surface deformation when it is measured at more macroscopic scales. Figure 3.8(a) demonstrates that our model successfully captures all our experimental results: smaller is the thickness and larger is the droplet, deeper the dimple depth is. In addition, as has been put in Figure <u>3.4(b)</u>, rigidity effect is also recovered. However, for very big droplet $(D > l_c)$, a considerable deviation is observed in Figure 3.8(a), this is probably due to the gravity effect and the increase of θ_e . Gravity increases the pressure inside the drop and thus can be taken as an extra Laplace pressure. In our model, this is equivalent to the decrease of droplet size. Besides, the increase of θ_e results into a smaller pulling force (normal direction) and a larger squeezing force (tangential direction) in the dry part of gels. The details will be discussed in

section <u>3.5</u>. Both leads to a shallow dimple. Another prominent phenomenon is the disappearing of the dimple in the dry part of gels, we have observed in Figure <u>3.2</u> and Figure <u>3.3</u> that the dimple fades away at large thickness. This is also verified by our calculations as is shown by Figure <u>3.8(b)</u>: increasing thickness decreases the dimple depth. To some critical value, here 420 μm , dimple totally vanishes for fixed droplet size (D = 1.3 mm). Red circles are from experiments and green dotted line is from calculations.



FIGURE 3.8: (a) Comparison of the dimple depth between experiments and calculations. (b) Dimple depth as a function of the thickness of the soft film at fixed droplet size 1.3 mm.

3.5 Discussions

3.5.1 Contributions from two contact lines and the Laplace pressure

Our solution Equation (3.29) consists of three terms: the first term can be interpreted as the contribution to the interface deformation from the contact line on the right side if we refer to the cartesian coordinate in Figure 3.5(b); the second term represents the contribution from the contact line on the left side; the third term refers to the contribution from the Laplace pressure. To understand how those three terms compare with each other and how important they might be to the overall surface deformation, we will study the case depicted in Figure 3.7.

Since the surface deformation around the droplet should be axisymmetric, we will only focus on the left side surface deformation which lies outside the droplet in Figure 3.5(b). The overall deformation from calculation has been compared with the experiment result in Figure 3.6(b). Now the contribution to it will be decomposed into three parts: the one comes from the rightside contact line in Figure 3.5(b), which will be referred to "Contact line-1" or C1 later on; the one originates from the close side (left-side) contact line as is drawn in Figure 3.5(b), which will be called as "Contact line-2" or C2 afterwards; the one roots from the Laplace pressure (LP) inside the droplet. Surface deformation will be the sum of the three. They are shown in Figure 3.9(a). Solid curves are from the calculation and they are 10 μm away from the contact line. We observe that: the contribution from C2 overwhelms the deformation when it is less than 45 μm away (X > -0.8 mm) from the contact line X = -0.755 mm) and it contributes to more than 90% to the surface deformation; the contribution from C2 and LP is close to each other when it is more than 45 μm away from the contact line (X < -0.8 mm). As is shown in Figure 3.9(b) and Figure 3.9(c), the absolute value of C2 and LP are close; the contribution of the C1 is always small over all the range of the deformation as from Figure 3.9(c), the deformation induced by LP and C2 is in general 5 times more than that by C1; in addition, C2 induces a pull-up of the surface in the very close region (< 135 μ m) of the contact line (X > -0.89 mm) and a depletion when it is far away (X < -0.89 mm); C1 always causes a depletion since the deformation we are discussing about is already far from C1; Laplace

pressure always gives rise to the extrusion-up of the surface in that it squeezes the surface; however, the Laplace pressure is not a strong effect when it is very close to the contact line (< 15 μ m) on the scale of the elastocapillary length ($l_s = \gamma_s/2G' \sim 17 \mu$ m) and it starts to cause significant surface deformation when it is out of the elastocapillary regime.



FIGURE 3.9: Comparison of contributions from the two contact lines and Laplace pressure for the surface deformation. Experimental parameters: D = 1.51 mm, G' = 1.2 kPa, $h_0 = 228 \mu \text{m}$, $\theta_e = 98^\circ$. γ_s is chosen from our best fit: 40mN/m. (a) A panorama view of the contribution of each component. (b) Zoom-in of the dimple regime from the black dotted rectangle in (a). (c) The ratio of the contribution from the close contact line and Laplace pressure to that from the far side contact line as a function of the distance.

From the above analysis, it can be concluded that the surface deformation is determined mainly by the traction from the close contact line and the Laplace pressure. When it is far away from the elastocapillary regime (> l_s), the two terms contribute equally to the interface deformation. Nevertheless, inside the elastocapillary length the surface deformation is dominated by the traction from the close contact line and Laplace pressure in this regime is only a small fraction.

3.5.2 Tangential force

We take the tangential force of the traction at the contact line into our model, as is express in Equation (3.26) and Equation (3.28). This component has been neglected by many researchers^{40–42,53,94}. When they try to find the surface deformation with small droplets on soft PDMS surface, they arrive at an unbelievably large value for γ_s^{94} . When it comes to the deformation at the ridge cusp, they find another quite reasonable value for γ_s^{53} with the same

model. There is a gap in a full understanding of the small-scale surface deformation and longrange surface deformation. There could be several possibilities:

- There is something wrong in the measurement. It is not very likely true, because several independent groups report a similar dataset for the wetting ridge^{35,59,80}.

- The theory is wrong. The models we are commenting on are only those taking the surface effect into consideration^{40–42,53,94}. It is likely wrong since they work well for the wetting tip and predicts the deformation quite well in some sense^{81,94}.

- Something is missing in the models. For most models^{41,42,45,94}, scientists assume that the symmetry surface tension, linear elasticity, incompressible condition, etc. And they always neglect the translation force of the traction at the contact line. Models might be oversimplified.

In the following, we will prove that the translation force is in fact important to deform the soft material surface from calculations and experiments. By taking into account this force into our model, we are able to find the surface deformation very well with a reasonable surface tension for the solid.

Calculations

The translation force at the contact line is expressed by $\gamma_{LV} \cos \theta_e$, where θ_e is the static contact angle. Addressing the translation force will be equivalently addressing the effect of θ_e in our solution Equation (3.29). Note that changing θ_e won't modify our symmetry surface tension assumption.

To study the effect of the translation force or θ_e , we keep $\gamma_s = 40 \text{ mN/m}$ and numerically vary θ_e from 90° to 108°. The comparison of the calculation and experiment is drawn in Figure 3.10(a). The surface deformation is very sensitive to the selection of θ_e . Smaller contact angle tends to make a bigger dimple. If we plot the depth of the dimple as a function of θ_e , we find that the dimple depth increases with the decreasing of θ_e . and. And it seems that the dimple depth is linearly related to the static contact angle to some critical value, which will be experimentally attested in Figure 3.12(e-f).

To see how our model compares with the one without the translation force and reinforce the importance of the tangential component of the surface tension traction, we turn it off in our model and try to see how θ_e modifies the surface deformation. It turns out even 20° change of θ_e makes an unperceivable effect, as the results show in Figure <u>3.10(c-d)</u>. With the experimental conditions, it fails to predict the surface deformation with a reasonable surface tension γ_s (40 mN/m). A possible way to fit the experimental data is to increase the value of γ_s to be as high as 350 mN/m to be close to our experimental observation. This high value is only possible for metals. Hence, it is safe to draw a conclusion: the tangential component of the surface tension is very important to induce the surface deformation; its existence in the model seems to be necessary.


FIGURE 3.10: Comparison of experiments and calculations for a resting water droplet (D = 1.51 mm) on a PDMS layer film (G' = 1.2 kPa) of $h_0 = 228 \mu\text{m.}$. (a) Static contact angle θ_e effect on the surface deformation at fixed $\gamma_s = 40 \text{ mN/m}$. (b) Dimple depth D_p as a function of static contact angle θ_e .(c) Static contact angle θ_e effect on the surface deformation at fixed $\gamma_s = 40 \text{ mN/m}$ when the tangential component of the surface traction is removed. (d) Dimple depth D_p as a function of static contact angle θ_e at zero translation traction. (e) The best fit of calculation without the translation force. $\gamma_s = 350 \text{ mN/m}$.

In the next, we aim at understanding how each component of the applied stresses compares with each other and contributes to the surface deformation. In general, those stresses will be sorted into three types: the vertical component of the liquid-vapor surface tension, i.e., $\gamma_{LV} \sin \theta_e$; the

tangential component of the liquid-vapor surface tension, i.e., $\gamma_{LV} \cos \theta_e$; the Laplace pressure. The surface deformation, ζ , from calculations will be sum of the surface deformation induced by each: $\zeta = \zeta_l + \zeta_t + \zeta_v$. For the Laplace pressure's contribution(ζ_l), we turn off the first two terms (contact line traction) from Equation (3.29); for the translation force's contribution (ζ_t), we turn off the third term (Laplace pressure) and force $\sin \theta_e = 0$ in the first two terms from Equation (3.29); for the vertical traction's contribution(ζ_v), we turn off the third term (Laplace pressure) as well and impose $\cos \theta_e = 0$ in the first two terms from Equation (3.29). As a result, we plot the surface deformation ζ induced by each term when the θ_e varies from 90° to 108° in Figure 3.11(a-d). We discover that:

- Both ζ_v and ζ_l barely changes with θ_e , as can be seen in the superimposed curves of them for various θ_e in Figure 3.11(a-c). However, the tangential component (ζ_t) of the liquid-vapor surface tension varies a lot. When we track the displacement at X = -1 mm for various θ_e in Figure 3.11(d), $\zeta_v(X = -1 mm)$ and $\zeta_l(X = -1 mm)$ are not changing. Nevertheless, ζ_t increases from 0 to 0.92 μm which is comparable to the unvarying $\zeta_v(X = -1 mm)$ and $\zeta_l(X = -1 mm)$.

- When it is very close (X > -0.8 mm) to the contact line (-0.75 mm), ζ is dominated by ζ_v , as are demonstrated in Figure 3.11(a) and Figure 3.11(c). A large ratio of ζ_v to the ζ_l is found at X > -0.8 mm, which is demonstrated by the black dotted curve for both $\theta_e = 98^\circ$ and $\theta_e = 108^\circ$. This result justifies the success of the model in predicting the wetting cusp which only takes the vertical component of the surface tension traction^{45,53}. In this region, all the three components tend to pull up the surface.

- When it is further away from the contact line $(> l_s)$, ζ_v is on the same order of ζ_l . Figure 3.11(c) shows a ratio of them close to 1.5. The dominance of ζ_t is becoming more and more obvious when θ_e is increasing, as the ratio of ζ_t to ζ_l is getting bigger in Figure 3.11(a). It seems this observation demonstrates the failure of models in calculating the long-range surface deformation^{59,94}. In this regime, vertical component is likely to cause an interface depletion while both the Laplace pressure and the translation component tend to make a squeezed-up bump.

From our calculation, we find the surface deformation very close to the contact line (< l_s) is dominated by the vertical component of surface tension. Laplace pressure begins to play a role on the surface deformation when it starts to get outside of the elastocapillary regime. However, both of them barely depends on the θ_e . The tangential component will not modify the surface deformation in the elastocapillary regime. However, it will contribute equally as the other two components for the long-range surface deformation. What needs to be pointed out is that ζ_t is sensitive to θ_e . By introducing this long-neglected translation force at the contact line, we are able to predict the over-all surface deformation with a reasonable value of γ_s (40 mN/m). Besides, our additional calculation of this model predicts a Neumann's triangle at the wetting tip⁵⁷. In a short summary, we demonstrate that the gapping in the understanding of the smallscale surface deformation and the long-range surface deformation can be resolved by taking the translation component of the surface tension traction into the model. In the following, we are going to present experimental proof for our findings here.



FIGURE 3.11: Calculations with the translation force. Parameters are the same as those in Figure 3.10. (a) Contributions from the three components for surface deformation when the static contact angle, θ_e , changes from 90° to 108°: normal component of the surface tension, tangential component of the surface tension and the Laplace pressure component. Those three contributions are grouped automatically into three, as are indicated by names in the Figure. (b) Zoom-in of the black dotted rectangle in (a). (c) The ratio (Vertical/LP) of the $\gamma_{LV} \sin \theta_e$ (Vertical) induced surface deformation to the Laplace pressure (LP) induced surface deformation and that (Translation/LP) of the $\gamma_{LV} \cos \theta_e$ (Translation) induced surface deformation to the Laplace pressure (LP) induced surface deformation as a function of the θ_e . (d) Contributions from the normal component of the surface tension, tangential component of the surface tension and the Laplace component to the ultimate surface deformation at X = -1 mm as a function of θ_e .

Experiments: using contact angle hysteresis effect to evidence the effect of tangential component of γ_{LV} on the surface deformation

From above discussion, we know that, if the tangential component of the surface tension traction doesn't play any role on the surface deformation, several degrees' even 10 degrees' change of θ_e will not cause detectable changes for the surface deformation. However, if there is a strong effect of the θ_e on ζ , we shall be qualified to conclude that the tangential component is indeed important in making the elastowetting surface deformation if the other experimental parameters don't change. So, the simplest way to test this is to check the contact angle hysteresis effect on the surface deformation.

Contact angle hysteresis always exists for materials. With the current technique: it ranges from several degrees to tens of degrees depending on many factors. One of them will be discussed in

this chapter later. Here, we only take advantage of the contact angle hysteresis on smooth soft PDMS gel layers that we can manipulate in experiments.

The surface deformation with an evaporating droplet is investigated on a soft PDMS layer. Water would be deposited onto the PDMS soft layer and left in the open surroundings. The volume of the droplet is 2 μL and the thickness of the soft layer is 150 μm . *G'* of the soft gel is 1.2 *kPa*. A side view camera is employed to monitor the wetting velocity V_d and contact angle θ of the evaporating droplet (Figure 3.12(a)). Schlieren camera is also turned on to monitor the surface deformation in real time (Figure 3.12(b)). The two measurements are carried on at the same time and they are well synchronized with an error of 0.1 *second*. Contact line will be considered to be pinned at $V_d < 0.15 \,\mu m/s$ (Figure 3.12(c)).



FIGURE 3.12: Hysteresis effect on the surface deformation. (a) Side view of a 2 µL water droplet on a PDMS gel layer. The shear storage modulus is 1.2 kPa and the thickness of the soft layer is 150 µm. Red dotted line indicates the non-moving contact line after 250 seconds' evaporation. (b) Schlieren view of the surface deformation around the contact line. (c) Wetting velocity measured from the side view camera and it is shown here as a function of time. Red triangles stand for the hysteresis regime (120 seconds to 370 seconds) where the wetting velocity is smaller than 0.15 µm/s. (d) The shape of the surface deformation for the same droplet but with different contact angle. The two profiles correspond to (a-b). (e) The observed contact angle as a function of evaporation time. Red diamonds are taken to be the contact angle hysteresis. (f) Dimple depth evolution with respect to time. Red circles mean the dimple grows with the decrease of the contact angle when the contact line is pinned.

Figure <u>3.12(a)</u> illustrates the droplet is losing volume from 120 seconds to 370 seconds while contact line motion is not detectable within this 250 seconds. However, the surface deformation varies by a factor of 1.5 as is shown in Figure <u>3.12(d)</u>. The shadow (negative surface slope) in the Figure <u>3.12(b)</u> grows after 250 seconds' evaporation, which is the direct proof of the growing of the dimple. During this period, the observed contact angle, θ , decreases from 108° to 98° (Figure <u>3.12(e)</u>) while the depth of the dimple rises from 0.6 to 0.88. The change of stresses that are exerting on the soft layer is estimated as follows:

- Laplace pressure *P*: it can be evaluated from the droplet area change. The area of the droplet *S* is related to the radius of the drop at small droplet size ($< l_c$) by $S \sim R^2$. Hence $P \sim 1/R \sim S^{-0.5}$. From the camera, the ratio of S_1 at 120 seconds to S_2 at 370 seconds is 1.044. As the results, the ratio of Laplace pressure P_1 at 120 seconds to P_2 at 370 seconds is 0.98. The change of Laplace pressure during this 250 seconds is only 2%.

- Normal component of γ_{LV} : at 120 seconds, it is $\gamma_{LV} \sin(108^\circ)$; at 370 seconds, it is $\gamma_{LV} \sin(98^\circ)$. The variation of the normal component is 4%.

- Tangential component of γ_{LV} : at 120 seconds, it is $\gamma_{LV} \cos(108^\circ)$; at 370 seconds, it is $\gamma_{LV} \cos(98^\circ)$. The variation of the normal component is 55%.

Figure 3.13(a) shows how the normal and tangential components of γ_{LV} changes with the observed contact angle θ for any droplet size. We can see that the tangential traction, $\cos \theta \gamma_{LV}$, is more sensitive to θ for 90° < θ < 115°. Based on this fact and our precious calculations in Figure 3.10 and Figure 3.11, we should already be able to claim that the tangential traction of the liquid-vapor surface tension is important in determining the interface deformation. To validate our claim, additional experiments are conducted as well: instead of placing droplet in the open ambient, we place the droplet in a closed chamber which is saturated with water vapor. We monitor the contact angle and the surface deformation in the same way as for the hysteresis effect test. The difference only comes from the evaporation control, and we do not see a detectable contact angle variation during the test. The result is shown in Figure 3.13(b), X axis is the distance from the contact line with a camera unit (pixel) and Y coordinate stands for the surface slope of the interface with a camera unit (gray scale value). Resting time of the sessile drop is indicated by T_r . As we can see, during the 32-minute's resting, no detectable surface deformation is observed. This experimental result further strengthens our claims above: the presence of the tangential force is necessary to capture the full surface deformation, including the short-range one (wetting cusp) and the long-range one (outside of the elastocapillary regime).



FIGURE 3.13: (a)Normal and tangential components of the traction from the liquid-vapor interface as a function of the apparent contact angle θ . The liquid is water. $\gamma_{LV} = 72 \text{ mN/m.}$ (b)Surface deformation measurements at different resting time T_r . Water droplet diameter is 4.03 mm. Thickness of the soft PDMS layer is 124 μ m. G' = 1.2 kPa.

3.6 Modifying contact angle hysteresis with a resting droplet

By following the last section on the hysteresis effect on the surface deformation, we experimentally find that contact angle hysteresis is not a material property per se and the same material can exhibit very different contact angle hysteresis depending on the experimental conditions. Here we will report the resting time effect on the contact angle hysteresis on soft materials that has never been seen in published papers.

Observation

Resting time is defined as the time duration from the moment the contact line is pinned to the moment of the measurement, during which a liquid droplet sits still on the soft film. Since the surface tension spreads across a distance of several nanometers at the contact line^{57,78}, a high stress is present at the liquid-vapor-solid junction and viscoelastic material grows with regards to the applied stress and time^{45,58,99}. Although the PDMS gel from elastomer Sylgard 527 that we use in this study is elastic at low frequency as to its rheology (high ratio of G'/G''), it still carries on a viscous feature. Besides, this type of PDMS might also be poroelastic, which would be another reason for inducing a ridge growth¹⁴⁰.



FIGURE 3.14: Resting time effect on the contact angle.

A specially designed chamber is employed to control the humidity and avoid the evaporation of droplets. Two experiments to control the resting time are performed inside it:

- Short resting time: water droplet is deposited onto a PDMS layer of 20 μm thick, and it is immediately sucked up by a pump (PUMP 33, HARVARD APPARATUS, USA) at fixed flow rate 10 $\mu L/min$. The resting time for the droplet ($|V_d| < 0.45 \,\mu m/s$) is ~20 seconds. The wetting velocity and the dynamic contact angle is recorded and plotted as red dots in Figure 3.14. If we define here the hysteresis at $V_d = 0 \,\mu m/s$, then the hysteresis $\theta_{h1} = 7^\circ$.

- Long resting time: a water droplet is deposited and kept onto the soft gel surface for 30 minutes. Then liquid is withdrawn by the same pump at fix flow rate $10 \,\mu L/min$. The corresponding result for dynamics is shown as green dots in Figure 3.14. Now, hysteresis θ_{h2} increases to 14°.

These two experiments justify that longer resting time can induce a high hysteresis of the contact angle. During the experiments, we notice that traces are left behind by droplets, as is shown in Figure 3.15. Its location is exactly where the contact line lies and its lifetime depends on the resting time of the contact line. Those are the evidences that the wetting ridge actually grows with the presence of the surface tension at the contact line.



FIGURE 3.15: Trace left behind after receding a water droplet. The resting time of the droplet is 30 minutes. The droplet diameter, soft PDMS layer thickness, and the shear storage modulus of PDMS gel are 4.97 mm, $104 \mu m$, and 1.2 kPa, respectively.

Dynamic pinning

To strengthen our results on the pinning effect, an additional experiment focused on receding dynamics is performed: a water drop is kept resting on a soft PDMS layer of 20 μm thick and it is removed after 22 minutes. A trace, that is visible with the naked eye, is left behind as is similarly shown in Figure 3.15. Afterwards, another droplet of a bigger volume is deposited onto the same location of the previous one so that the new resting contact line overruns the trace left behind. And this new droplet is retracted back by the pump at fixed flow rate 10 $\mu L/min$. The contact line dynamics is shown in Figure 3.10. In the early stage (< 119.3 seconds), the contact line propagates to the left smoothly and it is then pinned when it meets the trace at time T = 119.3 seconds. In the next 10.3 seconds, the contact line is released because of the strong capillary force (highly curved interface close to the contact line shown in the last picture from Figure 3.16(a)). This dynamic experiment hence provides another evidence that trace induced by the resting droplets on soft films can pin the contact line and hence modify the contact angle hysteresis.



FIGURE 3.16: Pinning of the contact line by a pre-induced trace from a resting droplet. Flux rate: $10 \,\mu$ L/min. (a) Side view of the moving contact line. Scale bar is 0.2 mm. Before 119.3 seconds, the contact line recedes to the left and it is then pinned until 129.6 seconds when it is released. (b) The dynamic contact angle θ_d as a function of time.

Trace measurement

We know that: the resting time of sessile droplets affects the contact angle hysteresis; there is a trace after the removal of the droplet; and this trace can also pin a dynamic contact line. Now, we will look into the details of the trace. For its timescale, the lifetime of the trace t_t is found to depend on the resting time T_r : t_t is several seconds if T_r is from several seconds to several minutes. By observation, $t_t < 10$ seconds when $T_r = 2$ minutes; t_t goes up to several hours when T_r increases to tens of minutes. $t_t \sim 2$ hours when $T_r = 30$ minutes. This resting time dependence implies that the wetting ridge grows with the applied stress at the contact line. The question now is what is the shape of this contact line, how it grows and how its growth is related to the pinning of the contact line.

In the first step, it is important to know its shape. We measure the surface topology of the PDMS layer, with a 3D profiler (Microsurf 3D, Fogal Nanotech, France) in white light mode, 20 s after the removal of a resting water droplet, as is demonstrated in Figure 3.17(a). The thickness of this soft layer is 20 μ m. The resting time is 2 hours. A trace is observed and it stands for hours to disappear. A red line normal to this trace is selected and its exact shape is shown in Figure 3.17(b). The height of this trace is 700 nm, which is higher than the surface roughness. When a moving contact line surfs over it, it acts like a local pinning post, grasping the contact line from a further moving.

More ever, the growth of the ridge/trace should be possible to be deduced from its relaxation as it is very difficult to directly measure its growth when the contact line is present. As a consequence, we track the relaxation of this trace for one hour and a half. Then we find a nice feature of the poroelasticity relaxation as the height of the trace relaxes in a logarithmic way as is shown in Figure 3.17(c).



FIGURE 3.17: (a)3D topology of the soft film interface ~ 20 seconds after removal of a 2 hours' resting water droplet on PDMS layer of 20 μ m thick. (b) The profile of the red line in (a). (c) The relaxation of the trace.

As a conclusion for the resting time of droplets on contact angle hysteresis, we confirm the resting of the contact line will initiate the growth of the wetting ridge and this grown deformation "freezes" and pins the contact line, both for a static one and for a dynamic one. The relaxation of the trace on soft PDMS gel carries on a feature of poroelasticity, opening the question of the poroelastic behavior of the gel, which might be the exact mechanism for inducing growing and pinning.

3.7 Summaries and conclusions

3.7.1 Surface deformation

We experimentally and theoretically investigate the long-range surface deformation of a gel layer on which a sessile droplet sits by checking effects of geometrical confinements (thickness of soft layer, droplet size), material properties (elasticity, surface tension). This long-range interface deformation falls outside of the elastocapillary regime ($< l_s$) and extends to millimeters away from the contact line for the soft PDMS with G' = 1.2 kPa. Experimentally, we adopt the home-made Schlieren optics to observe the deformation. Theoretically, we develop a model based on linear elasticity theory and the surface tension of soft gel is accounted as well. For the effect of geometrical confinements, we adjust the droplet diameter from 0.42 mm to 2.95 mm and the thickness of soft layers from 44 μ m to 3 mm. We find a dimple at small thickness and large droplet size. The smaller the thickness is and the bigger the droplet is, the deeper the dimple is. Our calculation agrees well with our experimental data and captures all those features. However, there is a considerable deviation for large droplets. This is likely due to the gravity effect.

For the effect of material properties, we first inspect the rigidity effect and detect the interface deformation of soft layers with G' varying from 1.2 kPa to 15.7 kPa at fix droplet size (0.75 mm - 0.76 mm) and fixed thickness $(32 \mu m - 44 \mu m)$. It is found that rigidity hinders the surface deformation and it is successfully reproduced by our calculation.

For the understanding of contributions to the surface deformation from the Laplace pressure, and the close/far contact line, we separately calculate the surface deformation induced by each. We find that: inside the elastocapillary regime ($< l_s$), the surface deformation is totally dominated by the near contact line, and the surface is pulled up by this traction and Laplace pressure and depleted by the far side contact line; outside of this regime, the close contact line and Laplace pressure contribute equally to the overall surface deformation, and the surface is squeezed-up by the Laplace pressure and depleted by the two contact lines; the far contact line is always a small effect to the surface deformation.

For the understanding of the vertical and translational components of the traction at the contact line, we calculate the surface deformations induced by them, individually. We realize that: close to and inside of the domain of typical size smaller than the elastocapillary length ($\leq l_s$), the surface deformation is dictated by the vertical component of the traction, and Laplace pressure and translational components are negligible; when it is out of this regime, the Laplace pressure and vertical components play equally in making the surface deformation; however, both of them are not sensitive to the static contact angle θ_e while the tangential component of the traction at the contact line is on the contrary; outside the elastocaillary regime $(> l_s)$, translation component can contribute as equally to the surface deformation as the vertical component and the Laplace pressure. We verify our findings by conducting water droplet evaporation experiments on a soft layer. We observe that the deformation around the contact line increases with the decrease of the static contact angle and D_p increases more than 40%. Both our experiments and calculations suggest that the translation component is important to understand the surface deformation in elastowetting. By taking it into the model, we are able to resolve the understanding gap between the small-scale surface deformation (wetting cusp) and the largescale surface deformation (overall shape).

3.7.2 Resting time effect on the contact angle hysteresis

We experimentally study the resting time effect on the equilibrium contact angle and its hysteresis on PDMS gel in this chapter.

For the resting time effect, we build a closed chamber and maintain the humidity to avoid the evaporation for water droplets. Soft smooth PDMS gel of 20 μ m thick is deposited with two droplets: one is deflated instantaneously after its spreading (resting time ~20 seconds); the other is left to be resting for 30 minutes and then deflated. The contact angle hysteresis is observed to increase from 7° to 14° at $V_d = 0 \mu m/s$. By comparing the two surfaces after running droplets, we find a trace left at the location of the resting contact line from the 30 minutes-resting droplet with naked eyes and it stands for ~ 2 hours while nothing is found at the location where the short resting event happens. Its existence might be due to the viscoelastic and poroelastic growth of the gel under the high stress at the contact line. Furthermore, we investigate a receding contact line by deflating a droplet and let it meet the

trace left behind by a 30 *minutes*-resting droplet, a strong pinning of the contact line is observed and θ_d decreases from 67.3° to 24.3° until the depinning happens. In addition, the shape of the trace induced by a 2 *hours*-resting contact line is detected by a 3D profiler around 20 *seconds* after the removal of the droplet. The height of it is 700 *nm*, much smaller than the height ($\sim \frac{\gamma_{LV} \sin \theta_e}{E} \sim 19 \ \mu m$) of the wetting ridge⁵⁸ but is larger than the surface roughness(chain length). It is expected that this trace will pin the contact line and result into the increase of the hysteresis. In addition, our observation of the relaxation of the trace implies a poroelastic mechanism responsible for the ridge growth. The short conclusion for this part is resting time is important to the contact angle hysteresis.

3.8 Perspectives

For now, we understand quite well for the elastowetting statics on elastic materials experimentally and theoretically. However, there are still several issues remaining to be addressed:

For our model, we always assume that the surface tension of liquid-solid interface and that of vapor-liquid interface is the same. This is an easy approach to simplify our calculation. However, this is not true^{56,141–143}. Our model in principle is only applicable to the neutral wetting case ($\theta_e = 90^\circ$). How to extend to the non-neutral is to be solved. Moreover, trials for how to properly account for the surface effect (surface tension, surface stress, surface energy) are still going on^{132,135,136,138,144–146}.

How is the growth of the ridge induced by the surface tension related to the material properties? such as the elasticity, wettability, etc. And how is the growth of the ridge connected to the contact angle hysteresis or the pinning of the contact line? When a gel is under a high stress, osmotic pressure is developed inside the polymer network and hence drives the migration of the remaining free liquid in the polymer network to the high stress region. How the time scale and rate of diffusion is related to the polymer mechanics remains to be elucidated. Besides, rheology shows the PDMS gel is viscoelastic in dynamics. We will see in the next chapter that the role of the viscoelasticity in the motion of droplets is very important.

Chapter 4 Dynamics: moving contact line on viscoelastic materials

4.1 Introduction

Liquid spreading on a soft material will be slowed down compared with its spreading on rigid substrates, this phenomenon has been known as "viscoelastic braking"^{32,35,38,39,42,45,79}. From an experimental point of view, only droplet relaxation experiments have been carried out on soft layers with no systematic control of the thickness. Scientists have focused their attention on the viscoelastic nature of the materials and its impact on the wetting. How the system geometry (droplet size, thickness of the soft layer) affects the spreading dynamics has been hardly studied with only one report of the effect of the thickness of the coating on the spreading dynamics of silicone oil on silicone elastomers³⁹, a system in which the permeation of the liquid in the gel and the swell of the latter cannot be neglected. More ever, the viscoelastic properties of soft materials are rarely reported and their account into the estimation of the dissipation is a recent feature^{32,35,37–39,45}. Still, a full study of geometric effects on liquid spreading over soft substrates is lacking. From a theoretical point of view, the exact calculation of the viscoelastic dissipation inside the soft material is still missing though there are several attempts as we have stated in the section 1.4: estimation of dissipation from "elastic" deformation^{35,37,38}, first order approximation to the viscoelastic dissipation^{40–42}, phenomenological model that forces a local stress balance at the wetting tip⁴⁵.

In this chapter, we are going to experimentally and theoretically study the elastowetting dynamics and point out that the thickness of soft layers is important to the spreading dynamics besides their viscoelasticity. In the following, we will briefly define our experimental setup and relevant parameters to characterize the elastowetting dynamics. Then, following our results obtained with sessile drops, we will experimentally investigate how sample geometry effects (droplet size, thickness of soft layers) and experimental parameters (flux rate, resting time) affect the receding dynamics of a contact line on a soft layer. Finally, we will rationalize our observations by developing a model based on the theory of linear viscoelasticity, from which we will extract two scaling laws.

4.2 Experiments and observation

Our experimental setup for studying the elastowetting dynamics and the required techniques to follow the moving contact line and dynamic contact angle have been introduced in sections 2.3 and 2.4. Important parameters depicting the receding dynamics are shown in Figure 4.1(a): glass slides are coated with soft PDMS films of thickness h_0 ; the circle area where the liquid meets the gel is characterized by its diameter D; θ_d and V_d are the dynamic contact angle and wetting velocity, respectively. Figure 4.1(b) is a picture taken by a side view camera in accordance with Figure 4.1(a). A needle puncturing the water droplet at its apex allows us to force the receding of the contact line by sucking up liquid with a pump (PUMP 33, HARVARD APPARATUS, USA) at controlled flow rate. What's more, we use the Schlieren camera (bottom view of the receding droplet) in the same configuration as in Figure 2.3(a) to monitor the overall receding of the contact line (Figure 4.1(c)). This additional observation enables us to ensure that the receding contact line remains axisymmetric.





(b)



(c)

FIGURE 4.1: Definition of parameters for characterizing the receding dynamics. (a) Sketch of a receding droplet on a soft substrate which is bounded onto a glass slide. Receding contact line is forced by a pump which extracts water from the drop. θ_d , V_d , D and h_0 are the dynamic contact angle, contact line velocity, diameter of the drop and thickness of the soft layer, respectively. (b) The corresponding definitions from (a) in real image taken by the side view camera. Three successive images with the time interval of 1 second are superimposed to show the moving of the contact line and the liquid-vapor interface. The edge of the receding droplet is marked by yellow, blue and purple. (c) Bottom view of the receding droplet by the Schlieren camera. Three pictures correspond to the three successive pictures in (b).

With this setup, we will investigate the receding contact line with distilled water on a soft PDMS gel. All the experiments in this chapter are implemented in the open environment at the ambient temperature ~25°C. The PDMS gel is prepared from the commercial Sylgard 527 as has been elaborated in section 2.6.1. The thickness is well controlled over three orders of magnitude, from several microns to ~ 1 mm. As the thickness of the thinnest soft film (~ μ m) we are going to use is much larger than the mesh size of polydimethylsiloxane, which is estimated as ~10 nm from $\sqrt[3]{kT/G'}$ where k, t are the Boltzmann constant and temperature, respectively. The viscoelasticity of all the gel films from the same preparation is assumed to be identical. In the following, we will report observations of liquid spreading on a soft layer in the first place and show that the hydrodynamic model for liquid spreading on rigid surfaces fails in the elastowetting case. Then we will systematically investigate effects of the inject flow rate, droplet size, resting time and thickness on the receding dynamics of the contact line. We will show that the spreading is quasi-steady for the velocity range we study here and the thickness of the soft gel has a marked effect on elastowetting dynamics.

4.2.1 Hydrodynamics fails

We perform receding dynamic by deflating water droplet on a soft PDMS layer with a syringe pump. The suction flux rate for deflation is $120 \,\mu L/min$. The droplet diameter before receding and the soft layer thickness are 4.9 mm and 150 μm , respectively. The receding velocity and dynamic contact angle are plotted in Figure <u>4.2(a-b)</u>. It can be seen that θ_d and V_d changes slowly at the beginning and then both of them evolve faster later at smaller drop size which is

due to the constant volume loss rate. To identify the receding dynamics for the contact line, we further plot the receding velocity as a function of dynamic contact angle (Figure 4.2(c)). It is found that: the larger V_d is, the smaller θ_d is. This is due to the energy balance of the capillary driving and viscous dissipation at the spreading: the higher the velocity, the more dissipation is, in which case more capillarity driving (smaller θ_d at receding) is needed. To be quantitative, the capillary driving energy at the contact line can be estimated as^{2,3}:

$$P_d \sim \gamma_{LV} (\cos \theta_d - \cos \theta_e) V_d \tag{4.1}$$

and the dissipation in the system comes from two channels^{35,41,42}:

$$P = P_{liquid} + P_{film} \tag{4.2}$$

here, P_{liquid} and P_{film} are the energy dissipation in the liquid phase and that in the soft film phase. To estimate how much dissipation comes from the liquid phase, we first drop the second term, i.e., the contribution from the soft material. Hence, by balancing *P* and P_d , O.V. Voinov found the following solution for liquid spreading on rigid substrate¹¹⁰:

$$\theta_d^3 - \theta_m^3 = 9Caln\left(\frac{L}{L_m}\right), \qquad \theta_d < 3\pi/4 \tag{4.3}$$

where θ_m is the microscopic contact angle shown in Figure <u>1.10(a)</u>. L and L_m are the macroscopic cut-off and microscopic cut-off introduced to avoid stress singularity. Usually, L is on the order of droplet size or capillary length $\sim mm$, and L_m is of the order of molecular length, ~*nm*. As a result, $ln \frac{L}{L_m}$ is estimated as 14.7. When we inject this value into Equation (4.3), we find a non-varying dynamic contact angle for the receding velocity we measured from experiments, as is revealed by the red solid curve in Figure 4.2(c). Furthermore, we try to make the prediction of Equation (4.3) close to our experimental data and we discover that $ln \frac{L}{L_m}$ has to be the order of, 3×10^5 , an unphysical value. Even with this value, the hydrodynamic model doesn't even capture the trend of the data, shown as the blue solid line in Figure 4.2(c). The fact above indicates that there must be another energy dissipation source besides Pliquid coming into play and it should be tens of thousands of times higher than P_{liquid} . By looking at Equation (4.2), we find it safe to conclude that P_{film} should dominate in the overall dissipation in the system when liquid spreads on the soft PDMS gel films, at least for those fabricated from Sylgard 527. Before we try to tackle P_{film} , we will first show how the system geometry and experimental conditions affect the elastowetting dynamics and stress on the thickness effect. With the guidance of those experimental hints, we finally build our model for calculating P_{film} .



FIGURE 4.2: (a) Receding velocity as a function of time. It is positive for a receding contact line and negative for an advancing contact line. (b) Dynamic contact angle as a function of time. (c) Comparison of experiments and hydrodynamic prediction for a receding contact line on a soft layer. $h_0 = 150 \ \mu\text{m}$; $D = 4.9 \ \text{mm}$; flux rate $Q = 120 \ \mu\text{L}/\text{min}$. Calculation parameters for Equation (4.3) are: $\theta_m = 106^\circ$, $L = 2.7 \ \text{mm}$, $L_m = 1 \ \text{nm}$, $Ca = \mu V_d / \gamma_{LV}$, $\gamma_{LV} = 72 \ \text{mN}/\text{m}$, $\mu = 1 \ \text{mP} \cdot \text{s}$.

4.2.2 Thickness matters

In the following, we describe a systematic study of effects of the flux rate, needle position, droplet size, resting time and thickness of soft layers on the dynamics of the elastowetting. In the end, we will demonstrate that the receding dynamics in our study is quasi-steady and highlight that thickness can distinctly modify spreading dynamics and further be used as a parameter to control the liquid spreading.

Flux rate effect

To check the steadiness of liquid spreading on soft layers, we change the flux rate from $20 \,\mu L/min$ to $120 \mu L/min$ for a receding contact line. Droplet receding is performed at the same location on the soft gel surface at least three times for the same flux rate. The time interval between each run is around 5 *minutes* to make sure the surface won't be affected by the previous run. To ensure the axisymmetric receding, we will stop our measurements before the droplets get too small (> 2 mm) because of experimental conditions (needle diameter is

~1 mm). The results are shown in Figure 4.3. We observe that flux rate doesn't play any role in the receding dynamics, i.e., the invariable relation between the wetting velocity V_d and dynamics contact angle θ_d , for thickness ranging from 12 μ m to 1011 μ m by three orders' magnitude. This is because the spreading velocity is very low (< 0.1 mm/s) and capillary number, $Ca = \mu V_d / \gamma_{LV} \sim 1.4 \times 10^{-6}$, is very small. Thus the spreading can always be taken to be quasi-steady.



FIGURE 4.3: Flux rate effect on elastowetting dynamics. Flux rates ranging from $20 \ \mu L/min$ to $120 \ \mu L/min$ are tested on soft PDMS gel films and only the two limits are shown here as black dots ($20 \ \mu L/min$) and red dots ($120 \ \mu L/min$). Thickness of soft films is: $12 \ \mu m$ (a), $37 \ \mu m$ (b), $321 \ \mu m$ (c), $434 \ \mu m$ (d), $1011 \ \mu m$ (e).

Needle effect

As can be seen from Figure <u>4.1(b)</u>, there are two contact lines during the droplet receding: one is the receding line at the liquid-needle-vapor junction; the other is at the liquid-gel layer-vapor junction. If we look them separately, the first contact line moves on a rigid surface (the needle is made of stainless steel, a metal with very high rigidity) while the second one moves on a soft gel layer. If they are both in steady motion, the motion of each of both contact lines should be locally governed by the capillary driving and the viscous friction, which could come from the shearing of liquids or cycling motion of soft gels that accompanies the propagation of the moving contact line. As the flux rate is very low and the receding velocity is also small ($V_d < 0.2 \text{ mm/s}$ in general), the steadiness of the two contact lines is analyzed as follows:

- For the moving contact line on the needle, the dissipation of energy during the liquid retraction comes from viscous shearing and the hydrodynamic model shows a non-varying dynamic contact angle for the velocity we are studying here, as has been demonstrated by the calculation in Figure <u>4.2(c)</u>. Thus, its spreading is a steady motion, which is also always verified by our experiments (a constant dynamic contact angle at the liquid-needle-vapor junction).

- For the moving contact line on the soft layer, it is in the quasi-steady state, as has been demonstrated in the "Flux rate effect" section.

In theory, there shouldn't be any effect of the needle state on the receding contact line on the soft gel. we will now experimentally verify it with two extreme experimental conditions (Figure 4.4): (a) the needle is immersed into the water droplet and intrudes very close to the surface of the soft layer; only when the droplet volume is almost running out does the contact line on the needle starts to find the pinning at the end of the needle; we call this experimental configuration as "Penetrating"; (b) the needle touches on top of the water droplet in the beginning of the experiment and the contact line on the needle wall will be instantaneously pinned once the droplet is retracting. This experimental configuration is defined as "Capping". Then under those two conditions, we check how the elastowetting dynamics varies by receding contact line at the same location on the soft layer. Time interval between the successive run is $\sim 5 \text{ minutes}$. Our experimental results show in Figure 4.4(c) that there is no effect: the extreme pinning of the contact line won't affect the spreading and all the data falls onto a single curve.



FIGURE 4.4: Needle effect on elastowetting dynamics. (a) Schematics of the "Penetrating" of a needle into a water droplet. (b) Schematics of the "Capping" of a needle onto a water droplet. (c) Comparison of "Penetrating" dynamics and "Capping" dynamics. Thickness of the soft layer is 162 μm and the flux rate is 120 μL/min.

As a brief summary, the state of the needle and the moving contact line on the needle wall do not affect our observation of the receding contact line on the soft gel layer at all. This further proves that the spreading on soft layers is a quasi-steady motion.

Droplet size effect

Because we are forcing droplet retraction by sucking its liquid with a pump, the wetting velocity is imposed by our flux rate and the droplet volume. Thus, the same receding velocity can happen at different droplet size for different flux rate. Or if we have the pinning of the contact line on the needle, the same receding velocity on the soft gel layer can be found at any droplet size depending on the location of the pinning. Besides, we already know that the elastowetting spreading, the relation of θ_d and V_d , is determined by the dissipation in the soft layer from

Figure 4.2. This dissipation comes from the cycling motion of gel inside the layer which is set by its surface deformation^{35,41,42}. In the previous chapter, we have identified the droplet size effect for the long-range surface deformation. It is possible that the droplet size effect is present here for the receding dynamics. To check whether this is true or not, we perform experiments for different initial droplet size (Figure 4.5) at fixed flux rate ($Q = 120 \,\mu L/min$), and similar droplet size but with very different flux rate (D = 3.9 mm for $Q = 120 \mu L/min$ and D =3.8 mm for $Q = 20 \,\mu L/min$ in Figure 4.3(d)). The receding dynamics is measured at the same location with a time interval $\sim 5 minutes$ between each experiment. We don't see any effect from the droplet size. Those results have already been partly testified by Figure 4.4 because the pinning effect also imposes the same wetting velocity at different droplet size. Those results are surprising at the first glance. However, we must notice that here we are using big droplets (D > D)2 mm) compared to those in static deformation. Furthermore, we see that there is a saturation for the dimple depth for big droplets (D > 3 mm). Under such experimental conditions, there might also be a saturation for the droplet size effect for the dissipation; Furthermore, we also find that the surface deformation in the vicinity of the contact line is mainly determined by the surface tension from the closest contact line, and Laplace pressure (droplet size) barely plays a role in this regime ($< l_s$). These reasons might explain why we don't see a noticeable effect of the droplet size. A more detailed discussion will be section 4.3.2. Here we should include some gravity effect, which we have not taken into account for the moment. To take a simpler approach, we consider that droplet size doesn't play much role in the spreading dynamics at least for big droplets.



FIGURE 4.5: Droplet size effect on elastowetting dynamics. Thickness of the soft layer is 104 μ m and the flux rate is 120 μ L/min.

Resting time effect

Here we would like to investigate whether the time the droplet remains on the soft gel surface before performing experiments affects the spreading dynamics. In fact, we have already seen previously that the resting time of the droplet affected the hysteresis of the contact angle. Does it play a role in the dynamics? Droplets are first deposited onto the soft layer within a closed chamber saturated with water for a controlled amount of time. Then we start to run the receding experiments. Droplets are deposited at different locations on the same soft layer to avoid the trace initiated by the previous drop that could lead to the contact line pinning. Results are shown in Figure <u>4.6</u>: hysteresis is observed again for zero wetting velocity as the starting dynamic contact angle is decreasing with the increasing of the resting time; initial resting of the contact line doesn't modify the receding dynamics. Those results can be interpreted as follows: the resting time induces a local growth that freezes of the wetting ridge, introducing contact

angle hysteresis for several degrees. However, this "freezing" ridge is a local event. Once the contact line surfs over it, the surface deformation accompanying the receding contact line will not be affected any more.



FIGURE 4.6: Resting time effect on elastowetting dynamics. Thickness of the soft layer is $104 \ \mu m$ and the flux rate is $120 \ \mu L/min$.

Thickness effect

We know from the static surface deformation study that the thickness of the soft layer exerts an effect on the surface deformation. If we turn to the Equation (3.29) and Figure 3.5, thickness of the soft layer will affect each integral term: the deformation induced by the contact line f_1 , the deformation induced by the contact line f_2 , and deformation induced by the Laplace pressure f_p . As a result, thickness of soft layers should also be a factor in determining the spreading dynamics because the dissipation is connected to the gel motion (gel deformation). Experimentally, we perform receding contact line experiments on soft layers with thickness ranging from 8.8 μm to 900 μm . Their dynamics, the relation between θ_d and V_d , is shown as scattered cross points in Figure 4.7(a). Multiple runs (> 3) are carried out to ensure the reproducibility. We reveal that the thickness modifies the receding dynamics in the following way: at fixed receding velocity, the smaller is the thickness, the larger the dynamic contact angle is, an indication of the capillary driving for the moving contact line. Our experimental results further imply that more driving force is needed to propel the same wetting speed on the thicker layer. As a result, more energy is dissipated for the spreading on the thicker layer. To see how exactly the spreading dynamics is modified by the thickness, we fix the receding velocity at $0.1 \, mm/s$ and the dynamic contact angle corresponding to this velocity is plotted as a function of the soft layer thickness in Figure 4.7(b-c). From Figure 4.7(b), we notice that the thickness effect is pronounced on thin layers (< 100 μ m) and there seems to be a saturation on thick layers (> 100 μm). A log-linear plot is further shown in Figure 4.7(c) to magnify the thickness effect for thin layers. The dissipation power, P, can be estimated from the capillary driving power for the unit length of the contact line: $\gamma_{LV}V_d(\cos\theta_d - \cos\theta_e)$. If we assume the static contact angle is 106°. Then for the thinnest layer ($h_0 = 8.8 \ \mu m$), it is calculated as 2.05 μ W; for the thickest one ($h_0 = 798 \,\mu$ m), it is calculated as 3.02 μ W. The increase is 47.3%.



FIGURE 4.7: Thickness effect on elastowetting dynamics. Flux rate: $120 \,\mu L/min.(a)$ Paranoma of the relation of θ_d and V_d as a function of thickness. (b) Linear-linear plot of the relation between the dynamic contact angle, θ_d , and soft layer thickness h_0 at fix receding velocity $V_d = 0.1 \,\text{mm/s}$. (c) Log-linear plot of the relation between the dynamic contact angle, θ_d , and soft layer thickness h_0 at fix receding velocity $V_d = 0.1 \,\text{mm/s}$.

As a short conclusion to the experimental observations, the spreading of liquid on soft layers $(G' \sim 1 \ kPa)$ is governed by the dissipation in the soft gel phase. At low spreading velocity $(\sim 0.1 \ mm/s)$, the capillary number is small and the spreading can be taken to be quasi-steady (no needle effect and flow rate effect). For an initially big droplet $(D > 2.5 \ mm)$, droplet size does not modify the spreading dynamics. This observation is likely due to the small contribution of the Laplace pressure on the surface deformation close to the contact line. We find a strong influence of the soft layer thickness on the spreading. Increasing thickness can aggrandize the dissipation in the gel by 47.3%. In the following, we are going to rationalize the viscoelastic braking and the thickness effect from theories.

4.3 Rationalization with the theory of linear viscoelasticity

In sharp contrast to the spreading on rigid substrate, the spreading of a liquid on a soft material will introduce a local deformation at the contact line that propagates with the moving of the contact line. The gel is thus subject to a cycling motion, which dissipates energy and can rule the wetting dynamics^{35,38,42}. In the following, we calculate the surface deformation marching

with the motion of the moving contact line and the associated energy dissipated in the soft material, and reach a spreading law for a moving contact line on soft layers.

4.3.1 Modeling



FIGURE 4.8: A line traction, \vec{f} , moving on a viscoelastic substrate.

General solution of dynamic deformation for arbitrary rheology

Experiments indicate droplet size exerts no effect on the spreading dynamics, which implies that the Laplace pressure is not crucial to the energy dissipation in the spreading. Hence, we neglect the Laplace pressure in the modelling. The picture of liquid spreading on gels can be simplified to a 2D case (Figure 4.8): a line traction, $\vec{f} = (f_x(x,t), f_y(x,t))$, which makes an angle θ_d to the horizontal direction, is propagating at a constant velocity, V_d , on a viscoelastic layer of thickness h_0 . Here t stands for the time. As is similar in the static case, we assume the material to be incompressible and solid surface tensions to be equal on the two sides of the contact line. For general linear viscoelastic materials, the stress, σ , and the strain, ε , are related through the linear relation:

$$\sigma(\vec{x},t) = \int_{-\infty}^{t} G(t-t') \frac{\partial \varepsilon}{\partial t'} dt' - P(\vec{x},t)I$$
(4.4)

with *I* being the identity matrix and *P* is the effect pressure introduced in Equation ($\underline{3.4}$). Its Fourier transform in temporal space is:

$$\hat{\sigma}(\vec{x},\omega) = G(\omega)\varepsilon(\vec{x},\omega) - \hat{P}(\vec{x},\omega)I$$
(4.5)

 $G(\omega)$ is the dynamic modulus or the Fourier transform of the instantaneous moduli G(t) of the soft material and is defined by:

$$G(\omega) = i\omega \int_0^\infty G(t)e^{-i\omega t}dt$$
(4.6)

The incompressibility of the material and the steady state of the moving contact line read in their Fourier transform as follows:

$$\vec{\nabla} \cdot \vec{\hat{u}} = 0 \tag{4.7}$$
$$\Delta \vec{\hat{u}} - \vec{\nabla} \hat{P} = 0$$

Similar to Equations (3.7-3.12) in statics, boundary conditions in their temporal Fourier forms are:

$$\hat{\sigma}_{yy} = 2G(\omega)\frac{\partial \hat{u}_y}{\partial y} - \hat{P} = \hat{f}_y(\omega) + \gamma_s \frac{d^2 \hat{\zeta}}{dx^2}$$

$$\hat{\sigma}_{xy} = G(\omega) \left(\frac{\partial \hat{u}_y}{\partial x} + \frac{\partial \hat{u}_x}{\partial y}\right) = \hat{f}_x(\omega)$$

$$\hat{u}_x(x, -h_0) = 0$$

$$\hat{u}_y(x, -h_0) = 0$$
(4.8)

where ζ is the surface deformation. This set of Equation is strictly identical to the boundary condition in statics. By following Equations (3.18-3.25), the temporal Fourier transform of the spatial Fourier transform at wave number *k* for ζ is straightforward and read as:

$$\tilde{\zeta}(k,\omega) = \frac{1}{\gamma_s} \left[k^2 + \frac{G(\omega)}{\gamma_s K(k)} \right]^{-1} \left[\tilde{f}_y(k,\omega) - i \tilde{f}_x(k,\omega) \frac{2h_0^2 k^2}{\sinh(2h_0 k) - 2h_0 k} \right]$$

$$= \tilde{f}_y(k,\omega) S(k,\omega) + \tilde{f}_x(k,\omega) Q(k,\omega)$$
(4.9)

where K(k) is expressed in Equation (3.24). If now we focus on the case of a contact line moving at constant speed:

$$f_x(x,t) = \gamma_{LV}(\cos\theta_e - \cos\theta_d)\delta(x - V_d t), f_y(x,t) = \gamma_{LV}\sin\theta_d\,\delta(x - V_d t)$$

then the double Fourier transform with respect to the time and space preserves the shape of the traction. In this case, we have:

$$\tilde{f}_x(k,\omega) = \gamma_{LV}(\cos\theta_e - \cos\theta_d)\delta(\omega + V_d k), \quad \tilde{f}_y(k,\omega) = \gamma_{LV}\sin\theta_d\,\delta(\omega + V_d k)$$

Now we reach the double Fourier transform for the surface deformation:

~

$$\hat{\zeta}(k,\omega) = \gamma_{LV} \sin\theta_d \,\delta(\omega + V_d k) S(k,\omega) + \gamma_{LV} (\cos\theta_e - \cos\theta_d) \delta(\omega + V_d k) Q(k,\omega)$$
(4.10)

The above solution can be shifted back to the time space with an inverse Fourier transform with respect to ω :

$$\tilde{\zeta}(k,t) = e^{-ikV_d t} \frac{\gamma_{LV} \sin \theta_d}{\gamma_s} \left[k^2 + \frac{G(-kV_d)}{\gamma_s K(k)} \right]^{-1} - ie^{-ikV_d t} \frac{\gamma_{LV} (\cos \theta_e - \cos \theta_d)}{\gamma_s} \left[k^2 + \frac{G(-kV_d)}{\gamma_s K(k)} \right]^{-1} \frac{2h_0^2 k^2}{\sinh(2h_0 k) - 2h_0 k}$$

$$(4.11)$$

Furthermore, with another inverse Fourier transform in real space, the surface deformation is recovered as:

$$\zeta(x,t) = \frac{\gamma_{LV} \sin \theta_d}{2\pi\gamma_s} \int_{-\infty}^{+\infty} e^{ik(x-V_d t)} dk \left[k^2 + \frac{G(-kV_d)}{\gamma_s K(k)} \right]^{-1} \\ + \frac{\gamma_{LV} (\cos \theta_e - \cos \theta_d)}{2\pi\gamma_s} \int_{-\infty}^{+\infty} e^{ik(x-V_d t)} dk \left[k^2 + \frac{G(-kV_d)}{\gamma_s K(k)} \right]^{-1} \frac{2h_0^2 k^2}{\sinh(2h_0 k) - 2h_0 k}$$
(4.12)

If we are traveling with the moving contact line at the same speed and define a new coordination system which is called co-moving frame $(x' = x - V_d t)$, we will cancel the time t. The profile of the deformation $\zeta(x')$ is then independent of t:

$$\zeta(x') = \frac{\gamma_{LV} \sin \theta_d}{2\pi\gamma_s} \int_{-\infty}^{+\infty} e^{ikx'} dk \left[k^2 + \frac{G(-kV_d)}{\gamma_s K(k)} \right]^{-1} + \frac{\gamma_{LV} (\cos \theta_e - \cos \theta_d)}{2\pi\gamma_s} \int_{-\infty}^{+\infty} e^{ikx'} dk \left[k^2 \right] + \frac{G(-kV_d)}{\gamma_s K(k)} - \frac{2h_0^2 k^2}{\sinh(2h_0 k) - 2h_0 k}$$

$$(4.13)$$

This expression is valid for arbitrary rheology at long time after the application of the line force and does not account for any transient regime that might occurs immediately following the application of the line force.

Dissipation in the soft film described by the Chasset-Thirion model for viscoelasticity

The dissipation with a traveling traction \vec{f} at the speed V_d on a soft film with finite thickness can be calculated by:

$$P_{film} = \iint_B \sigma: \dot{\varepsilon} \, dx dy \tag{4.14}$$

It is integrated for the overall body, B, of the soft material. Since we assume it is a steady problem, the deformation should be independent of the time. Now Equation (4.14) can be expressed in terms of its temporal Fourier space:

$$P_{film} = \frac{1}{4\pi^2} \iint_B dxdy \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} d\omega'$$

$$\times (i\omega')e^{i(\omega+\omega')t}G(\omega)\hat{u}_{ij}(\vec{x},\omega)u_{ij}(\vec{x},\omega')$$
(4.15)

Following Long et al^{41,42}, we assume that the four terms in the integral above contribute equally to the dissipation and we will only retain the variation along the *x*-direction of the displacement in the *y*-direction. Dropping the factor $1/4\pi^2$, we get:

$$P_{film} \sim \iint_{B} dx dy \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} d\omega'$$

$$\times (i\omega') e^{i(\omega+\omega')t} G(\omega) \frac{\partial \hat{\zeta}}{\partial x}(\vec{x},\omega) \frac{\partial \hat{\zeta}}{\partial x}(\vec{x},\omega')$$

$$(4.16)$$

According to the Plancherel theorem, the previous integral can be rewritten as:

$$P_{film} \sim \int_{-h_0}^{0} dy \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} (i\omega') e^{i(\omega+\omega')t} d\omega' G(\omega) d\omega'$$

$$\times \int_{-\infty}^{+\infty} k^2 \tilde{\zeta}(-k,\omega') \tilde{\zeta}(-k,\omega') dk$$
(4.17)

This dual integral can be solved out of the temporal domain with Equation (4.10). For the sake of simplicity, the vertical traction is only retained and we will thus have:

$$P_{film} \sim \int_{-h_0}^{0} dy \int_{-\infty}^{+\infty} -ikV_d \, G(-kV_d) k^2 \gamma_{LV}^2 \sin \theta_d \, S(k, -kV_d) S(-k, kV_d) dk \tag{4.18}$$

Because the deformation penetrates to a depth $|k|^{-1}$, the integration above is further simplified to:

$$P_{film} \sim \gamma_{LV}^2 V_d \sin^2 \theta_d \int_{-\infty}^{+\infty} ik \ G(-kV_d) ksign(k) S(k, -kV_d) S(-k, kV_d) dk$$
(4.19)

For a purely elastic material, $G(\omega) = constant$ and the above integral will be an imaginary. Since the rheology of the soft material we use can be fitted with the empirical Chasset-Thirion model:

$$G(\omega) = G_0(1 + (i\omega\tau)^m) \tag{4.20}$$

where G_0 is the equilibrium modulus and τ is the relaxation time of polymer chains, by inserting this viscoelastic model into Equation (4.19) we obtain:

$$P_{film} \sim G_0 \gamma_{LV}^2 V_d \sin^2 \theta_d \, |V_d \tau|^m \int_0^\infty |k|^{m+2} S(k, -kV_d) S(-k, kV_d) dk \tag{4.21}$$

or equivalently,

$$P_{film} \sim \left(\frac{\gamma_{LV} \sin \theta_d}{\gamma_s}\right)^2 G_0 V_d |V_d \tau|^m \int_0^\infty \frac{|k|^{m+2}}{(k^2 + \frac{G(-kV_d)}{\gamma_s K(k)})(k^2 + \frac{G(kV_d)}{\gamma_s K(-k)})} dk$$
(4.22)

Spreading

We balance the dissipation power with the capillary driving power $V_d \gamma_{LV} (\cos \theta_d - \cos \theta_e)$ and we arrive at a full expression for the spreading:

$$\Psi(\theta_d) \sim \frac{\gamma_{LV}}{\gamma_s} \frac{G_0}{\gamma_s} |V_d \tau|^m \int_0^\infty \frac{|k|^{m+2}}{(k^2 + \frac{G(-kV_d)}{\gamma_s K(k)})(k^2 + \frac{G(kV_d)}{\gamma_s K(-k)})} dk$$

$$\Psi(\theta_d) = \frac{\cos\theta_e - \cos\theta_d}{\sin^2\theta_d}$$
(4.23)

4.3.2 Results

To solve the Equation (4.23), we need to know the rheology of the soft material. As is shown in Figure 4.9, the shear loss modulus of the gel can be well fitted with a power law of the

frequency ω with an exponent *m*. The best fit of Equation (4.20) to the rheology data ($G(\omega) = G'(\omega) + iG''(\omega)$) gives a shear storage modulus at the plateau $G_0 = 1240 Pa$, an exponent m = 0.615, and a relaxation time of polymer chains $\tau = 8.6 ms$. Nevertheless, γ_s is an unknown parameter. As we already find a quite reasonable value for it in the static case, in the following we will constantly set it as 40 mN/m if it is not specially specified. The static contact angle θ_e is experimentally found to be weakly dependent on the soft layer thickness and droplet size (section 4.3.3), and thus it is taken to be a constant 106° as well.



FIGURE 4.9: Chasset-Thirion model accounting for the viscoelasticity of soft PDMS gel. Triangles are from rheology measurement and the red solid line is from the fitting with the Chasset-Thirion model.

With all the above parameters, we will be able to solve Equation (4.23). In the following, the elastowetting dynamics will be described by the relation between the difference of the dynamic contact angle and the static contact angle ($\theta_e - \theta_d$), and the wetting velocity V_d . We define the receding velocity as a positive and the advancing velocity to be a negative.

It is found that our model predicts very well experiments (Figure 4.10). Not only can it recover the "viscoelastic braking" effect, but also it captures the thickness effect for the spreading. Figure 4.10(a) shows two limits of our experiments and calculations: spreading on very thin layer and on very thick layer. The range of the thickness covers two orders of magnitude from 15.9 μ m to 900 μ m. As our experimental precision of wetting velocity is 0.03 mm/s, comparison with our data shows that the model works well for the velocity from 0.03 mm/s to 0.3 mm/s, with a capillary number ($Ca = \mu V_d / \gamma_{LV}$) ranging from 4.2 × 10⁻⁷ to 4.2 × 10⁻⁶. However, in this Ca regime, for the spreading on rigid substrates, ($\theta_e - \theta_d$) \rightarrow 0 (Section 4.2.1). This result clearly shows the spreading on a soft material is governed by the dissipation in the solid phase.

Figure 4.10(b) demonstrates that $(\theta_e - \theta_d)$ is smaller if the soft layer is thinner. $(\theta_e - \theta_d)$ indicates the deviation of the dynamic contact angle from the static one such that it can be approximately taken to be the capillary driving force in the system. At fixed wetting velocity (0.1 mm/s), a larger value of $(\theta_e - \theta_d)$ means a higher capillary driving force/energy is needed to promote the same spreading speed or equivalently a higher friction/dissipation will be felt by the contact line. As a result, less force/energy is required to maintain the spreading for layers with smaller thickness. Less energy (smaller P_{film}) is dissipated on thinner layers (smaller h_0). Besides, the dependence of the dissipation on the thickness is strong for thin layers $(h_0 < 100 \ \mu m)$ and it is becoming weak for large thickness (Figure 4.7 and Figure 4.10(b)). This is also captured by our calculation. A plateau is found for large thickness $(h_0 > 100 \ \mu m)$ and a sharp plunge is revealed for small thickness. For the model, we numerically change the

surface tension of the soft gel (γ_s) from 38 mN/m to 42 mN/m, and all the experimental data falls into the region between the two curves predicted by the two γ_s . Both values are close to the reported value for PDMS⁵³. This prediction further supports that our model is a success.

In addition, we only consider the vertical component of γ_{LV} in calculating the surface deformation induced by a single moving contact line (Equation (4.18)). Laplace pressure, the tangential component of the liquid-vapor surface tension, surface tension from the far-away contact line (Figure 3.5) are all neglected. Still we have a very good prediction for the elastowetting spreading. This implies that the dissipation mainly happens in the close region of the contact line where the surface deformation is governed by the vertical component of the surface tension from the close contact line (Figure 3.9 and Figure 3.11).



FIGURE 4.10: Receding dynamics and thickness effect. $\theta_e = 106^{\circ}$. (a) Comparison of experiments and calculations for the elastowetting dynamics on soft layers with different thickness. Flux rate: $120 \ \mu$ L/min. (b) Thickness effect for the spreading dynamics at fixed receding velocity (0.1 mm/s).

4.3.3 Discussion

Static contact angle

Experimentally, the dissipation in the spreading is evaluated from the capillary driving power: $V_d \gamma_{LV} (\cos \theta_d - \cos \theta_e)$. For the thickness effect to be valid, it would be necessary to confirm that, as theoretically θ_e does not have a dependence on the thickness and droplet size.

We perform liquid inflation-deflation experiments by changing the initial droplet diameter from 2.5 mm to 4.4 mm. Thickness of the soft layers is controlled from 29 μ m to 2745 μ m. The flux rate is fixed at 120 $\mu L/min$. All the experiments are implemented in the open surroundings and the duration for each run is less than 2 minutes. A side view camera is mounted to record the moving of the contact line and contact angle. A panorama of the spreading dynamics at small velocity to check θ_e is shown in Figure 4.11: each data set stands for the spreading on the same layer (hence the same thickness); the wetting velocity is translated horizontally to separate from the others for a better visual effect; the equilibrium state for droplets (zero velocity) is marked by the grey dotted line for each data set; the black, red and green dotted datasets stand for an initial droplet size of $\sim 3 mm$, $\sim 2.5 mm$ and $\sim 4 mm$, respectively. A very high reproducibility of spreading dynamics at small velocity (< 10 $\mu m/s$) is observed on layers with thickness ranging from 45 μm to 457 μm . This reinforces our previous observation of the droplet size effect on the spreading dynamics (section 4.2.2). For the static contact angle, we show its distribution at $V_d < 0.05 \,\mu m/s$ in Figure 4.11(b) which demonstrates that the thickness does not have any influence on the mean value of static contact angle although some perturbations are found for $h_0 = 295 \ \mu m$, $h_0 = 380 \ \mu m$ and $h_0 = 1605 \ \mu m$. Figure <u>4.11(c)</u> is obtained from another droplet inflation-deflation test. It attests again that neither the droplet size nor the soft layer thickness will modify the static contact angle.

As a short summary, the inflation-deflation experiments that mimic experimental conditions for receding dynamics in section 4.2 certify the static contact angle θ_e depends neither on the droplet size nor the soft layer thickness. It is safe to take it as a constant (106°) in our calculations.



FIGURE 4.11: (a) Receding dynamics at small velocity. Each dataset characterizing the relation of θ_d and V_d is horizontally translated and the zero velocity at the local x-coordination is marked by the dotted gray line. The thickness for each curve from left to right is 29 µm, 45 µm, 144 µm, 162 µm, 225 µm, 295 µm, 380 µm, 457 µm, 570 µm, 1365 µm, 1605 µm, 2745 µm. (b) Thickness effect on the contact angle at $|V_d| < 0.05 \mu m/s$.

Previous models

Now we are going to briefly summarize three available models that attempt at describing the elastowetting dynamics up to now and highlight the insights that our model brings.



FIGURE 4.12: (a) Comparison among experiments (scatted dots), D. Long model⁴² (blue solid line) and "Elastic" model^{35,39} (black solid line). (b) Comparison among experiments, our dissipation model and the phenomenological model⁴⁵.

"Elastic" model

This model^{32,33,35,38,39,79} assumes that surface deformation of a moving contact line on a viscoelastic material is approximated by the elastic deformation induced by a vertical concentrated force $\gamma_{LV} \sin \theta_d$ on a half-infinite plate. The elastic energy, W, is calculated from this deformation and the viscoelastic dissipation is simply taken to be a fraction Ω of this supplied strain energy:

$$W\Omega \sim \frac{2\Omega\gamma_{LV}^2(1-\nu^2)V_d}{\pi E} \left\{ \frac{1}{\varepsilon} + \frac{3\theta_d^2}{r} \left[2\ln\left(\frac{d}{\varepsilon}\right) - 1 \right] \right\}$$
(4.24)

 Ω can be taken as $(V_d/V_0)^n$, where V_0 and *n* are material constants characterizing the damping properties of solids; relevant parameters in this equation have been addressed in section <u>1.4.2</u>. It has a more general simple form for elastomers (Poisson's ratio is 0.5, close to the PDMS gel):

$$W\Omega \sim \frac{\gamma_{LV}^2 V_d}{2\pi G_0 \varepsilon} \left(\frac{V_d}{V_0}\right)^n \tag{4.25}$$

When the solid dissipation dominates upon the liquid spreading, this simplified equation should be balanced with the capillary driving power: $V_d \gamma_{LV} (\cos \theta_d - \cos \theta_e)$. Hence, we will arrive at the following relation from the "elastic" model:

$$\cos\theta_d - \cos\theta_e \sim \frac{\gamma_{LV}}{2\pi G_0 \varepsilon} \left(\frac{V_d}{V_0}\right)^n \tag{4.26}$$

Long et al.'s model

In this model⁴⁰⁻⁴², the dissipation in the soft material phase is calculated from its viscoelasticity. The surface deformation in dynamics integrates both the viscoelasticity and surface tension, and it is simplified with the first order approximation as to the indention depth ϵ at the wavenumber k. The kernel for the dynamic deformation on the rubber⁴² is approached from the solution for the molten polymer brush⁴⁰, where high orders of ϵ (check section <u>1.4.2</u>) are dropped for the surface energy and elastic energy. The traction for inducing surface deformation is similar to that from "elastic" model: only the vertical component $\gamma_{LV} \sin \theta_d$ is accounted. We take the expression for the dissipation from section <u>1.4.2</u> and balance it with the capillary driving power and reach the following prediction for the elastowetting spreading at small velocity where the dissipation in the soft layer dominates:

$$\cos\theta_{e} - \cos\theta_{d} \sim \frac{\gamma_{LV} \tau^{m} G_{0}^{2} \sin^{2} \theta_{d}}{\gamma_{s}^{m+1}} V_{d}^{m}$$

$$, \text{ when } V_{d} < \left[\frac{\gamma_{LV} (\cos\theta_{d} - \cos\theta_{e})^{2}}{\gamma_{s}} \left(\frac{\tau G_{0}}{\gamma_{s}} \right)^{m} \frac{\theta_{d}}{3\mu \ln(\frac{L}{L_{m}})} \right]^{\frac{1}{1-m}}$$

$$(4.27)$$

Phenomenological model⁴⁵

Inspired by the finding of the universal Neumann's triangle at the wetting tip in statics^{53,80}, this model hypotheses that this relation still holds in dynamics. The surface dynamic surface deformation is assumed to be caused by the vertical component of the liquid-vapor traction in spreading (Equation (3.1-3.25)). Upon spreading, the ridge rotates by an angle, ϕ , to ensure the balance of surface tension at the tip (Neumann's triangle) and the liquid-vapor interface has to

bend to accommodate this rotation ($\phi = \theta_d - \theta_e$). The dynamic surface deformation is deduced by imposing the Neumann's relation as a boundary condition instead of the energy balance. Hence the rotation of the ridge ϕ is given by the symmetric part of the dynamic surface deformation profile in the co-moving frame:

$$\tan \phi = \lim_{x \to 0} \frac{1}{2} \left(\zeta'(x) - \zeta'(-x) \right) = \frac{\gamma_{LV} \sin \theta_d}{2\pi\gamma_s} \int_{-\infty}^{+\infty} \Re \left[\frac{-ik}{k^2 + \frac{G(-kV_d)}{\gamma_s K(k)}} \right] dk$$
(4.28)

At low velocity, the above relation reduces to:

$$\frac{\tan(\theta_d - \theta_e)}{\sin \theta_d} = \left(\frac{\gamma_{LV}}{\pi \gamma_s}\right) \frac{G_0}{\gamma_s} |V_d \tau|^m \int_0^\infty \frac{|k|^{m+1}}{K(k) \left(k^2 + \frac{G_0}{\gamma_s K(k)}\right)} dk$$
(4.29)

All the experimental parameters are planted into the "elastic" model (Equation (4.26)), Long et al.'s model (Equation (4.27)) and the phenomenological model (Equation (4.29)). Their comparisons with experiments are shown in Figure 4.12. Both the "elastic" model and Long et al.'s model are able to capture experimental features: reasonable value for dynamic contact angle is recovered for the wetting velocity compared to the hydrodynamic model; the higher is the velocity, the more energy is dissipated by the moving contact line; both models use the same power (0.615) for the relation of θ_d and V_d ; the fitting parameter γ_s for the D. Long model is 26 mN/m, which is a reasonable value for PDMS. However, neither the "Elastic" model nor Long et al.'s model account for the thickness of the soft layer; an error as high as 10° (~60%) is observed for the two models when trying to describe the dependence of the dynamic contact angle on the thickness at fixed velocity (0.1 mm/s). For the phenomenological model, it captures well the spreading on thick layer, as is the plateau $(h_0 > 100 \,\mu m)$ shown in Figure <u>4.12(b)</u>. Nevertheless, it underestimates the thickness effect at small thickness limit ($h_0 <$ 100 μ m). We here show two curves for its prediction: one is for the fitting for the spreading on thick layer limit, and another one frim the value (40 mN/m) which we inject in our dissipation model (Equation (4.23)). The mismatching at small thickness limit for the phenomenological model may originate from its imposition of the Neumann's relation at the wetting tip.

From the above results, we conclude that our dissipation model not only captures the viscoelastic braking, but also it is able to properly find the thickness effect with a reasonable γ_s (40 mN/m). However, the full dissipation model is not easy to apply directly because of its complex integration (Equation (4.23)). In the next section, we are going to show how it can be simplified at specified conditions.

Scaling for the spreading velocity

From the full solution in Equation (4.23), we define the left side of the equation as $\Psi(\theta_d)$ to avoid the presence of contact angle on the right side. Additionally, there are two parts for the term on the right side of the equation: $\frac{\gamma_{LV}}{\gamma_s} \frac{G_0}{\gamma_s} |V_d \tau|^m$ and the long complicate integration term. The first part $\frac{\gamma_{LV}}{\gamma_s} \frac{G_0}{\gamma_s} |V_d \tau|^m$ gives us a power law for the spreading as to V_d , though the later integral may also have a spreading velocity dependence since V_d is also present in the viscoelastic term $G(kV_d)$. To check this, we plot the experimental data in a log-log fashion in Figure 4.13(a). It clearly shows a linear relation between the log($\Psi(\theta_d)$) and log(V_d) except that there is a shifting between each data set due to the thickness. The experiments imply a power law between the $\Psi(\theta_d)$ and V_d . The best fit of the curve (Figure 4.13(b)) gives us the value of the power: 0.62 ± 0.2 , which is exactly the same value of m = 0.615 from the rheology measurement.



FIGURE 4.13: Scaling for the spreading dynamics on soft PDMS layers. (a) Universal power behavior for spreading dynamics on soft layers with thickness ranging from 8.8 µm to 798 µm by three orders' magnitude. (b) Comparison between our experiment and simplified model.

This result shows that the integral $\int_0^\infty \frac{|k|^{m+2}}{(k^2 + \frac{G(-kV_d)}{\gamma_5 K(k)})(k^2 + \frac{G(kV_d)}{\gamma_5 K(-k)})} dk$ is indeed almost independent

of V_d in the velocity range that we study. Therefore, Equation (4.23) can be approximated by a simpler expression at small velocities in the following:

$$\Psi(\theta_d) \sim \frac{\gamma_{LV}}{\gamma_s} \frac{G_0}{\gamma_s} |V_d \tau|^m \int_0^\infty \frac{|k|^{m+2}}{(k^2 + \frac{G_0}{\gamma_s K(k)})^2} dk$$

$$\Psi(\theta_d) = \frac{\cos\theta_e - \cos\theta_d}{\sin^2\theta_d}$$
(4.30)

Scaling for thickness effect at small thickness limit

Now we are able to separate the thickness effect in the Equation (4.30) and find it to be the integral $\int_0^\infty \frac{|k|^{m+2}}{(k^2 + \frac{G_0}{\gamma_S K(k)})^2} dk$. When the velocity is small, we find a concise scaling at small thickness limit by keeping the leading term of the integrand (details can be found in Appendix **B**):

$$\Psi(\theta_d) \sim \frac{\gamma_{LV}}{\gamma_s} \left(\frac{V_d \tau G_0}{\gamma_s}\right)^m \left(\frac{h_0 G_0}{\gamma_s}\right)^{\frac{3(1-m)}{4}}$$
(4.31)

This equation should work in the whole range for the velocity that we are investigating in this study because it is a low order approximation of the thickness effect to the Equation (4.30), which predicts very well our experimental result for all the experimental velocity. This scaling is compared with our experiments in Figure 4.14. It turns out that thickness effect is quite well predicted in Figure 4.14(a) for small thickness ($h_0 < 50 \ \mu m$) when $V_d = 0.1 \ mm/s$. Besides, the scaling is further verified in Figure 4.14(b) with two dimensionless numbers.



4.4 Summaries and conclusions

In this chapter, we experimentally and theoretically study the spreading dynamics of liquid on a soft material. We find that the thickness of the soft layer on which liquid spreads is an important parameter. We develop a model based on the theory of linear viscoelasticity theory that captures very well all the experimental features. Furthermore, we derive a scaling accounting for the spreading velocity and another simpler scaling accounting for the thickness effect at small thickness limit. Both scaling laws match our observations very well.

First, we observe the forced receding dynamics of a water droplet on a soft PDMS layer with thickness of 150 μm at fixed flux rate 120 $\mu L/min$. From an estimation from hydrodynamic model, we find that the cut-off length is non-physical, and further we conclude that the elastowetting spreading in our system is controlled by the dissipation in the soft gel phase.

Then we prove the spreading at small velocity ($V_d < 0.35 \text{ mm/s}$) is quasi-steady because of the small capillary number (~ 1.4×10^{-6}) and we experimentally verify this quasi-steady state by checking the flux rate effect from 20 $\mu L/min$ to 120 $\mu L/min$. Besides, it is also testified by "Needle effect" experiments.

Next, we investigate various factors that may affect spreading dynamics in the aspiration of elastowetting statics in the previous chapter. We check the droplet size effect (> 2 mm), resting time effect and the layer thickness effect at fixed flux rate $120 \,\mu L/min$. We find that neither will the initial droplet size modify the spreading, nor will the resting time except that it modifies the contact angle hysteresis; However, the thickness of the soft layer does affect the spreading; the dynamic contact angle is larger when the film is thinner at a fixed receding velocity; it means less energy is dissipated on the thinner layer.

Further, we develop a dissipation model based on the linear viscoelasticity theory accounting for the elastowetting spreading. We inject the full expression of dynamic surface deformation induced by a vertical traction from the propagating contact line and the Chasset-Thirion model describing the viscoelasticity of the soft material into the calculation of the energy dissipation power and balance it with the capillary driving power. We obtain a complete equation for the spreading on soft materials. This model is then compared with our experiments and shows excellent agreement.

Finally, we demonstrate our dissipation model stands out of the several other existing models, including the "elastic" model, D. Long model and phenomenological model. We further show our model can be simplified to a general scaling law accounting for the spreading velocity and another further simpler scaling law for the thickness effect at small thickness limit. Both successfully predict our experiments.

4.5 Perspectives

In our model, we neglect the tangential force for estimating the dynamic surface deformation, as can be seen in Equation (4.18). However, this tangential component of the liquid-vapor surface tension is found to be important in inducing the static long-range surface deformation. With the fact that our model successfully captures all the experimental features for the spreading, it seems that this long-range surface deformation is not very crucial to the elastowetting dynamics. This guess is also supported by the droplet size effect experiments in which it doesn't not play any role while it affects the long-range deformation in statics. As our calculation shows in the last chapter, the vertical component of the surface tension from the close contact line dominates the short-range deformation at the contact line, which is barely affected by the tangential force and the Laplace pressure. What's more, we find a thickness dependent wetting ridge in the vicinity of the contact line for both statics and dynamics, as is shown in Figure 4.15. The two pictures are taken by a side view camera with the pixel resolution of 4.5 $\mu m/pixel$ in the same illumination condition when the contact line is not moving. Water droplets are deposited onto a soft layer that is bounded onto glass slides. The thickness of the PDMS layers $(G' \sim 1.2 \ kPa)$ in Figure 4.15(a) and Figure 4.15(b) is 24 μm and 301 μm , respectively. The wetting ridge at the contact line distinguishes for the two cases: it is not observable on the thin layer $(24 \,\mu m)$ while a shadow of $\sim 20 \,\mu m$ high at the liquid-vapor-solid junction with a horizontal extension of $\sim 100 \ \mu m$ is formed in the vicinity of the contact line on the thick layer. This experimental result regarding to the thickness dependent wetting ridge has been reported years ago⁵⁹. Here we reinforce the importance of it. A detailed experimental study on its shape is in emergent demand because it seems to be related to the thickness dependent spreading/dissipation. Combining this observation, the calculation in static deformation and our results in dynamics, we speculate that the dissipation at dynamics mainly occurs in the close region of the contact line and the long-range surface deformation plays a less effect.

The above conjecture requires a precise experimental measurement of the surface deformation both at small scale ($< l_s$) and large scale ($> l_s$) when the contact line is moving. Our Schlieren optics provides a useful tool for the long-range dynamic surface deformation. For the shortrange one, proper experimental technique needs to be designed first to track its dynamics.



FIGURE 4.15: Comparison of the small-scale deformation on the thin layer and thick layer. (a) A resting droplet on a thin PDMS layer ($G' \sim 1.2 \text{ kPa}$); the thickness is 24 µm. (b) A resting droplet on a thick PDMS layer ($G' \sim 1.2 \text{ kPa}$); the thickness is 301 µm. (c) Zoom-in of the red rectangle from (a). (d) Zoom-in of the yellow rectangle from (b).

Chapter 5 Sliding and drifting of droplets on soft films

5.1 Introduction

Based on the thickness effect we have discovered in the previous chapter, we are going to explore how the thickness profile of a soft layer can be used to control the sliding of droplets. This chapter is split into two sections: the first part is about the sliding of droplets on soft films with homogeneous thickness; the second part is on the behavior of sliding droplets on soft films with thickness gradient.



FIGURE 5.1: Experimental setup for the sliding experiment.

The experimental setup for this chapter is drawn in Figure 2.14 and is shown in Figure 5.1. Here we will elaborate on the configuration of the sample and the humidity control. Soft films are bounded on glass slides, which are vertically tilted, hence inducing a 90° sliding angle for droplets. The substrate tilting is monitored by an electronic level with a precision of 0.1°. A front view camera (DFK 23UX174, IMAGING SOURCE, Germany) is installed facing the soft film to track the droplet motion with a resolution of $19 \, \mu m/pixel$. The glass slide bounded with the soft film is placed in a petri-dish which is vertically mounted. During the experiment, the petri-dish will be closed and deposited with extra water (Figure 5.1). Thus, evaporation of sliding droplets is mostly inhibited, which is demonstrated in Figure 5.2: during the $\sim 1 hour$ sliding, the diameter D of the smallest droplet $(1 \,\mu L)$ we will use decreases from 1.25 mm to 1.23 mm and the change is only 1.6%. For other droplets, the change is found to be less than 1.6%. As a consequence, we will assume that the sliding experiments are performed in an environment saturated with liquid vapor and the droplet evaporation is neglected. The liquid we employ in this chapter is distilled water (Milli-Q Integral; Millipore, USA) and the shear elastic modulus of the soft PDMS gel is 1.2 kPa, whose rheology is the same as that used in chapter 4.


FIGURE 5.2: The sliding of a 1 µL droplet in 62 minutes. Black arrow indicates the gravity direction.

5.2 Droplets sliding on viscoelastic films

5.2.1 Droplet size effect

We will show how the droplet size affects the sliding velocity of droplets on vertically titled soft films and their morphology in the steady state.

On the sliding velocity



FIGURE 5.3: Droplet size effect on the sliding velocity. The thickness of the soft film is 18.5 μ m. Time duration between the two superimposed pictures is 340 seconds. Red arrow indicates the displacement of each droplet. The green arrow points to the gravity direction.

Figure 5.3 depicts the sliding of water droplets over a soft film of 18.5 μm thick. Their size varies from 0.9 μL to 6 μL . The red arrows indicate the displacement of each droplet during the

340 seconds. The first image is taken ~1 minute after the droplet deposition. All droplets move along the gravity direction on the uniformly thick soft layer; the larger the droplet is, the faster the sliding velocity is. To see how the sliding velocity evolves during the sliding, we plot the sliding velocity, V_s , as a function of droplet position in Figure 5.4. All the droplets move from left to right in time sequence. For sliding on both the thin layer (Figure 5.4(a)) and thick layer (Figure 5.4(b)), V_s barely changes with the sliding time and location. However, it increases with the increase of the droplet size. Next, we will analyze how the sliding velocity is determined by it.



FIGURE 5.4: Sliding velocity, V_s , as a function of displacement. Droplets slide from left to right. (a)The thickness of the soft layer is 18.5 μ m. (b) The thickness of the soft layer is 1680 μ m.

When a droplet slides over a soft layer, the driving energy comes from the gravity. And it is always balanced with the overall dissipation in the system for the steady state. This dissipation, as is demonstrated in previous chapter, is dictated by the dissipation from the soft gel close to the contact line. Assuming the droplet keeps a circle shape during the steady sliding, dissipation during certain time Δt can be estimated as^{37,38}:

$$E_{overall} \sim D\Delta t P_{film} \tag{5.1}$$

where *D* and P_{film} are the diameter defined in Figure 5.2 and Figure 5.6, and the dissipated power for a single contact line, respectively. It shall be equal to the gravitational energy:

$$E_{overall} \sim D\Delta t P_{film} = mgV_{\rm s}\Delta t \tag{5.2}$$

here, *m* is the mass of the liquid and it scales as $\sim \rho D^3 \sin \theta_d$; ρ and *g* are the water density and the gravitational acceleration, respectively. Using Equation (4.22), Equation (4.30) at small sliding velocity ($V_s < 0.1 \text{ mm/s}$), we reach:

$$D\Delta t \left(\frac{\gamma_{LV}\sin\theta_d}{\gamma_s}\right)^2 G_0 V_s |V_s\tau|^m \int_0^\infty \frac{|k|^{m+2}}{(k^2 + \frac{G_0}{\gamma_s K(k)})^2} dk \sim \rho D^3 g \sin\theta_d V_s \Delta t$$
(5.3)

 θ_d is the dynamic contact angle. Since the integral $\int_0^\infty \frac{|k|^{m+2}}{(k^2 + \frac{G_0}{\gamma_S K(k)})^2} dk$ is not sensitive to V_s , we replace it with a function $\Theta(h_0)$. Hence,

$$V_s^m \sim \frac{\rho D^2 g}{G_0 \Theta(h_0) \tau^m \sin \theta_d} \left(\frac{\gamma_s}{\gamma_{LV}}\right)^2$$
(5.4)

For this scaling law, the local dynamic contact angle, θ_d , around the contact line is not accessible with our experimental technique. However, it is possible to solve it numerically by combining with Equation (4.30). Here, we take a simple approach and assume that its variation is not strong during the droplet sliding. Then, Equation (5.4) leads us to:

$$V_{s} \sim \left(\frac{\rho g}{G_{0}\Theta(h_{0})\tau^{m}}\right)^{\frac{1}{m}} \left(\frac{\gamma_{s}}{\gamma_{LV}}\right)^{\frac{2}{m}} D^{\frac{2}{m}}$$
(5.5)

From the rheology in the previous chapter, we know that m = 0.615. Hence, $V_s \sim D^{3.3}$. This scaling captures very well our experiments (Figure 5.5) for small droplets. When droplet size becomes large (> 2.5 mm), it starts to deviate. This is likely due to the fact that droplet shape is elongated, as will be demonstrated in the next.



FIGURE 5.5: Log-log plot of the droplet size effect on the sliding velocity.

On the morphology

During our experiment, we notice that the morphology of sliding droplets from a front view is varying with the change of the droplet volume $(1 \ \mu L - 20 \ \mu L)$ /sliding velocity $(2.5 \ \mu m/s - 1.8 \ mm/s)$. Their steady shape at sliding is shown in Figure 5.6. Droplet shape is elongated in the sliding direction, and this elongation is more and more obvious with the increasing of the droplet volume/sliding velocity. A quasi-round shape is found for droplets smaller than 7 μL ($V_s < 42.5 \ \mu m/s$). A neck that connects the rear of the droplet and the front of the droplet starts to develop when volume increases.



FIGURE 5.6: Droplet size effect on the its morphology at sliding. The thickness of the soft layer is 18.4 μm. When the volume increases from 1 μL to 20 μl, the diameter for each droplet in the figure increases as:
1.2 mm, 1.53 mm, 1.68 mm, 1.97 mm, 2.17 mm, 2.35 mm, 2.49 mm, 2.57 mm, 2.65 mm, 2.82 mm, 3.09 mm, 3.2 mm, 3.25 mm, 3.3 mm.

5.2.2 Thickness effect

We run droplet sliding experiments on soft films with thickness ranging from 8.3 μm to 1680 μm . And the droplet size varies from 1.5 μL to 14 μL . The thickness effect on the sliding (Figure 5.7) is found to be similar to that on the spreading dynamics as we have revealed in previous chapter. Less energy dissipation is found on a thinner layer, thus the faster the sliding velocity is on a thinner layer. The thickness effect is pronounced at $h_0 < 100 \,\mu m$ as is denoted by the sharp increase, possibly by a factor of 3.4, on all the curves in Figure 5.7. The dependence of V_s on the thickness h_0 is becoming weak for large thickness ($h_0 > 100 \,\mu m$). The full calculation from Equation (5.4) and Equation (4.30) remains to be performed to understand all those features.



FIGURE 5.7: Linear-log plot of the thickness effect on the sliding velocity.

5.3 Drifting droplets with thickness gradient

We also investigate how droplets would move over coatings with gradients of thickness. Because the dynamic contact line at different location would experience different friction/dissipation, this might generate a net drifting force when the droplet is moving. In the following, we will show our experimental design and results.

5.3.1 Experimental setup

The experimental setup is the same as the one used in the sliding experiments (section 5.1) except that the soft films are specially designed (section 2.5). Soft films are prepared on transparent glass slides and they are vertically tilted along the gravity. Droplets will slide down the soft layer because of gravity (Figure 5.8). During experiments, evaporation is controlled and a front view camera (DFK23UX174, IMAGING SOURCE, Germany) is mounted to record droplet motion. Important parameters we will use are defined as follows: the diameter of the liquid-solid interface is D; the vertical sliding velocity of droplets is indicated as V_s ; the thickness of the soft layer where the contact line stands on the thin side of the soft layer is called h_m ; the thickness profile of the soft layer is h(x) and x = 0 means the edge of the soft film (h(0) = 0); the surface slope angle of the soft film is α .



FIGURE 5.8: Droplet sliding down on a soft layer with a thickness gradient.

5.3.2 Drifting

Observation

Droplets on a soft film with thickness gradient not only slide down along the direction of gravity, but also, they drift to the thick side of the film. Figure 5.9 is the superimposition of six pictures with the time interval of 24 *minutes* between each successive two. The droplet volume is $1.5 \ \mu L$. The thickness profile is on the top of Figure 5.9 and it corresponds to the film below.

As can be seen, the three droplets are in general moving at the same sliding velocity. This is expected from our previous results (Chapter <u>4</u> and section <u>5.2.2</u>) because the thickness of soft gel beneath them is larger than 100 μ m: sliding/receding velocity weakly depends on the

thickness when the soft layer is thick ($h_0 > 100 \ \mu m$). However, droplets I and II drift to the thick side of the soft layer while the droplet III moves only along the gravitational direction. The thickness of soft layers at the initial position of the three droplets, h_m , increases from ~80 μm to ~190 μm for droplet I, from ~280 μm to ~395 μm for droplet II and from ~440 μm to ~560 μm for droplet III. The drifting effect for droplet I is always stronger than droplet II. It seems that the thinner the layer is, the stronger the drifting would be.



FIGURE 5.9: Drifting of droplets on a soft film with thickness gradient. Droplet volume is 1.5 μ L. The thickness of the soft layer corresponds to the thickness profile on top. The yellow arrow points to the gravity direction.

For the drifting origin, is it a static effect or a dynamic one? Style et al⁷², observed the spontaneous moving of small droplets (diameter < 100 μ m) from thin part to the thick part on soft films with thickness gradient. This phenomenon comes from the dependence of the static contact angle on the soft layer thickness for small droplets ($D \sim l_s$): the static contact angle decreases as the layer becomes thicker so that droplets spontaneously move from lyophobic part (high contact angle on thin layer) to the lyophilic part (low contact angle on thick layer). In the following, we will show that this effect is not relevant to our observations of the drifting.

Static origin

The experimental design we use to investigate the effect of thickness gradient is shown in Figure 5.10(d): a mold made of PMMA glass is machined into a block with a canal with a well-controlled cross-section (Figure 5.10(d)). Sylgard 527 is prepared according to section 2.6.1 and poured onto the mold on which a pre-layer of Sylgard 527 liquid has been spin-coated (see section 2.5). During the crosslinking, the flatness of the surface is monitored with a level which has a precision of 0.1°. The surface of the soft film is always exposed to air, thus it is flat and the surface roughness is very small. When the sample is ready, droplet sliding (titling angle 90°, Figure 5.10(a)) and horizontal resting (titling angle 0°, Figure 5.10(b)) experiments are performed with the same droplet volume (2 μ L), respectively. A side view of the sliding is shown in Figure 5.10(c). Black shadow line in Figure 5.10(a-b) corresponds to the thickness jump on the cartoon drawing of the substrate below each image. Figure 5.10(a) is the superimposition of two pictures with a time interval 207 minutes. The drifting angle δ is defined as the angle between the sliding trajectory and the gravity direction.



FIGURE 5.10: Drifting origin. Droplet volume is 2 μ L. (a) Drifting of a sliding droplet. (b) A resting droplet on a soft layer with step thickness design. (c) Schematic of sliding experiment of (a). (d) Schematic of resting experiment of (b) and the cross-section view of sample. h₁ = 120 μ m; h₂ = 400 μ m;

We observe that the drifting occurs in the sliding case, i.e. in a dynamic situation (Figure 5.10(a) and 5.10(c)). On the one hand, the droplet slides down because of gravity pulling; on the other hand, it drifts from the thin side $(120 \ \mu m)$ to the thick side $(360 \ \mu m - 400 \ \mu m)$ of the soft gel in 41 *minutes*. In the sessile case, two droplets are barely moving except for the evaporation-induced shrinking. One droplet (left-side droplet in Figure 5.10(b)) is placed on a soft layer whose thickness increases linearly from 272 μm to 320 μm and the other one (right-side droplet in Figure 5.10(b)) is deposited on a soft layer with a thickness jump from 120 μm to 400 μm . Both droplets remain immobile over the 207 *minutes* during the experiment. These results justify that the drifting of sliding droplet is not due to the spontaneous motion of the droplet. Rather, it should be a dynamic effect which originates from the asymmetrical dynamic surface tension around the contact line (Figure 5.11).

A simple way to understand the observed drifting is depicted in Figure 5.11. Note that the droplet is moving towards us. If the droplet is moving steadily, the wetting velocity, at each liquid-solid-vapor junction, should be symmetric with respect to the centerline along the sliding direction. With the results from chapter 4, we know that dynamic contact angles on the two sides on the droplet will be different: the dynamic contact angle, θ_{thin} , should be smaller than the dynamic contact angle, θ_{thick} , on the thick side. As a consequence, the asymmetrical dynamic contact angle indicates the asymmetrical friction around the contact line, resulting into an unbalanced net translation force, which drives the droplet to the thick side of the soft layer.



FIGURE 5.11: Schematic for the drifting origin. Black dashed line is the trajectory of the droplet, white dashed line is the vertical. The orange arrow represents the rotation of the droplet as it moves down the coating.

5.3.3 Results

Now we will report our experimental results on the thickness effect and the thickness gradient effect on drifting. The soft layers we will use are shown in Figure 2.21. Figure 2.21(a) indicates the thickness profiles of them, and Figure 2.21(b) consists two cross-section views of the soft films. A meniscus at the edge is found to extend to its capillary length, $l_c \sim \sqrt{\gamma_{PDMS}/\rho g} \sim 1.4 \text{ mm}$. The thickness gradient of the sample I is $\tan \alpha 1 = 0.11 - 0.16$, and that of the sample II is $\tan \alpha 2 = 0.04 - 0.08$.

Thickness effect

Figure 5.12 (a) summarizes the thickness effect for the droplet drifting. δ indicates the drifting angle. h_m is the initial position of a droplet, and it is defined in Figure 5.8, standing for the smallest layer thickness over which the droplet slides. We find that an increasing thickness results into a decreasing drifting angle δ . This can be qualitatively understood from the fact that the dependence of the dynamic contact angle (drifting force) on the thickness is decreasing with the increasing of the thickness (section 4.3.2).

Droplet size effect

When the liquid volume increases, the drifting angle decreases (Figure 5.12(a)). This is due to the decreasing ratio of the drifting force $F_{drifting}$ to the sliding force $F_{sliding}$. To understand a bit the trend of the volume effect, we assume that the $\cos \theta_d$ is linearly inversely proportional to the thickness for a fixed sliding velocity. For the drifting force, it is the integration of the dynamic surface tension difference ($\sim D$) over the whole contact line (πD) and should scale like $\sim D^2$. For the sliding force, it comes from gravity that scales with the volume (V) of the droplets ($\sim D^3$). Thus, drifting angle δ should be approximated related to $F_{drifting}$ and $F_{sliding}$ as:

 $\tan \delta \sim F_{drifting}/F_{sliding} \sim 1/D \sim 1/V^{\frac{1}{3}}$. This simple scaling is verified by experiments (Figure 5.12(b)).



FIGURE 5.12: Thickness effect and thickness gradient effect on the drifting. (a) Drifting on sample II ($\tan \alpha = 0.04 - 0.08$); h_m is defined in Figure 5.8, standing for the thickness of the soft layer beneath the contact line on the thin side. (b) Scaling.

Thickness gradient effect

Two soft layers with different thickness gradient, $\tan \alpha$, are employed to investigate the thickness gradient effect (Figure 5.13). The thickness gradient of the solid curve (0.11 - 0.16) is almost twice that of the dotted curve (0.04 - 0.08). we find that: at small thickness, $\tan \delta$ is larger for a larger $\tan \alpha$ at a fixed V; however, at large thickness, $\tan \delta$ is smaller for a larger $\tan \alpha$ at a fixed V.



FIGURE 5.13: Thickness gradient effect on the drifting. Drifting on sample I ($\tan \alpha 1 = 0.04 - 0.08$) and sample II ($\tan \alpha 2 = 0.11 - 0.16$).

5.4 Conclusions and perspectives

This chapter is mainly an experimental report of the droplet sliding on soft films.

First, we experimentally investigate the sliding of droplets on soft films with homogenous thickness. We systematically study the droplet size effect and thickness effect on the sliding velocity. For the droplet size effect, we vary the liquid volume from $1.5 \,\mu L$ to $14 \,\mu L$, and we find a scaling law by assuming that the intersection of the liquid-solid is a circle. This scaling works well for small droplets. For the thickness effect, we change the thickness of soft layers from 8.3 μm to 1680 μm . A similar result is recovered as that in receding dynamics: its effect is pronounced at small thickness (< 100 μm) and becoming weak for large thickness (> 100 μm). Besides, we report the morphology of the sliding droplet depends on the droplet volume (1 $\mu L - 20\mu L$)/sliding velocity (2.5 $\mu m/s - 1.8 \,mm/s$). It is a round shape at small droplet ($V < 7\mu L$)/velocity ($V_s < 42.5 \,\mu m/s$) and becomes elongated along the sliding direction at large droplet ($V > 7\mu L$)/velocity ($V_s > 42.5 \,\mu m/s$).

Next, we report the droplet sliding on soft films with thickness gradient. We find that a dynamic drifting phenomenon: sliding droplets not only move in the gravity direction, but also are horizontally translated. The origin of it is checked. We rule out the durotaxi effect by looking at a resting sessile droplet on a flat soft film with a sharp thickness jump. Further, we show the thickness effect, droplet size effect and thickness gradient effect on the drifting angle: large thickness decreases the drifting angle; increasing droplet size also inhibits the drifting; high thickness gradient promotes the drifting at small thickness.

We have investigated sliding on soft films with homogeneous thickness mostly through experiments. However, the value of θ_d around the whole contact line in Equation (5.4) remains unsolved. In theory, it can be acquired from Equation (4.30). By combining the above two equations, it is possible further to check the droplet size effect and thickness effect for small V_s . Besides, the theoretical value of θ_d from the 2D model needs to be compared with experiments, which can be obtained at the advancing front and the receding rear of sliding droplets from a side view.

We don't understand the shape of the sliding droplet at large V_s on soft substrate, which has not been solved yet. The energy dissipation for the high velocity sliding needs an exact solution of it, as is the same with the relation of V_s and V.

For the sliding and drifting on soft films with thickness gradient, a full calculation on the drifting force has not been carried out yet. Nevertheless, we think that this feat should be possible with our dissipation model: Equation (4.23) can be solved together with a round-shape assumption of the liquid-solid intersection. How exactly the droplet size, thickness of soft layer and the gradient of soft layer affect the drifting remains to be numerically compared with experiments. At high velocity, the sliding droplet shape will be elongated and the resultant drifting force will be modified as a consequence. This would be another challenging task to tackle.

Chapter 6 General conclusions and perspectives

6.1 Conclusions

In this thesis, we have experimentally and theoretically studied the statics and dynamics of elastowetting: static surface deformation, contact angle hysteresis, spreading dynamics and sliding of droplets.

First, we have built a quantitative Schlieren optics, with which we are able to directly measure the surface slope of a deformed gel in real time. This setup is sensitive to the light beam deflection $(7 \times 10^{-4} rad)$ with a scope up to 0.05 rad. For the PDMS gel with the refractive index of 1.4, it can detect the surface slope up to ~7° with a precision of 0.1° (7.1 nm in spatial precision). Besides, we develop a set of other techniques to detect the dynamic contact angle and wetting velocity, to control the viscoelasticity ($E: 3.6 \times 10^3 - 1.8 \times 10^6 Pa$) and thickness ($h_0: 8 - 3 \times 10^3 \mu m$) of soft gels.



FIGURE 6.1: Liquid droplet on a soft substrate.

Then, we experimentally investigate the long-range surface deformation induced by a sessile droplet (Figure 6.1) in the dry side $(> l_s)$ of the contact line by varying the droplet size (D: 0.42 - 2.95 mm), the thickness of soft layers $(h_0: 44 \mu m - 3 mm)$, elasticity of soft PDMS (G': 1.2 - 15.7 kPa) with the Schlieren setup. Experimental results are rationalized with a 3D model based on linear elasticity theory with the solid surface tension considered. The analytical solution for a single contact line on a soft slab with finite thickness h_0 is applied as a Green function to the 3D problem which is approximated by a rivulet (width D/2) on a soft slab with finite thickness h_0 . The contribution of each component of the applied stresses is analyzed: the short-range surface deformation ($< l_s$) is dominated by the vertical component of γ_{LV} from the close contact line; the long-range surface deformation (> l_s) is equally determined by the vertical and tangential components of γ_{LV} from the close contact line, and the Laplace pressure inside the droplet. However, the long-range surface deformation induced by the tangential traction $\gamma_{LV} \cos \theta_e$ is sensitive to θ_e . This is also verified by the hysteresis experiment on the surface deformation. We finally conclude that: to establish a model to capture the full range of the surface deformation, it is necessary to take the tangential component of the liquid-vapor traction at the contact line into account.

Wetting on soft gels is found to be related with the resting time of a sessile droplet. A trace left behind by a resting droplet on soft PDMS gel is observed and its lifetime (from ~seconds to ~hours) depends on the resting time (from ~seconds to ~30 minutes). It can pin the contact line and introduce a contact angle hysteresis. On a soft layer of 20 μm thick, height of the trace

induced by a droplet with the resting time of 2 hours, is found to be 700 nm after ~20 seconds' relaxation. This surface deformation is much higher than the surface roughness. The wetting ridge at the contact line grows with the presence of the contact line. To identify the origin for its growth, we track the relaxation of a trace on PDMS, which points us to the importance of poroelasticity in this problem.

Receding dynamics of the contact line on a soft PDMS gel with controlled thickness (8.8 – 1011 μm) is experimentally studied. We confirm the receding at small velocity ($V_d < 0.35 \text{ mm/s}$) is quasi-steady by checking the flux rate effect (from 20 $\mu L/min$ to 120 $\mu L/min$) as well as the needle position effect ("Capping" and "Penetrating"). We show that the droplet size does not affect the spreading dynamics, which implies that the gel dissipation mainly comes from the region surrounding the contact line. In contrast, the thickness of soft layers modifies the receding dynamics. From those results, we build a dissipation model based on the linear viscoelasticity theory and fit our soft gel rheology with the Chasset-Thition model. It turns out this dissipation model captures well all the experiments and stands out among the "elastic" model, Long et al.'s model and the phenomenological model. Not only can it recover the viscoelastic braking, but also it is able to predict the thickness effect. In the end, we simplify our full calculation into two scaling laws: one holds for small velocity ($V_d < 0.35 \text{ mm/s}$) and the other one holds for small thickness ($h_0 < 50 \mu m$) at small velocity ($V_d < 0.35 \text{ mm/s}$).

Finally, under the inspiration of the thickness effect in the spreading dynamics, we experimentally investigate the sliding of droplets on two types of vertically tilted substrates: one is the soft film with homogeneous thickness and the other one is designed with thickness gradient. For the sliding on uniform thick layers, we study effects of the droplet size ($V: 1.5 - 14 \,\mu L$) and thickness ($h_0: 8.3 - 1680 \,\mu m$). A scaling law for the droplet size effect on the sliding velocity is deduced at small droplet size ($V < 7 \,\mu L$)/velocity ($V_s < 42.5 \,\mu m/s$). Thickness effect on V_s is similar to that in receding dynamics. Droplet size or V_s also modifies the morphology of sliding droplets: droplets are elongated along the sliding direction at large V or high V_s . For the sliding on soft layers with thickness gradient, we observe a drifting of droplet in the direction perpendicular to the sliding. Its static origin is checked and ruled out. We propose a dynamic model which is in charge of this translation motion.

6.2 Perspectives

Motivated by studies on the surface deformation and contact angle hysteresis in statics, it is time now to wonder what could happen to the contact angle hysteresis when the soft materials become more viscous and how the diffusion of liquids into the polymer network modifies the surface deformation. We will now show our preliminary results of the contact angle hysteresis, θ_h , on the SBS-paraffin gel and demonstrate why it is important to take the rheology of gels into account when it comes to θ_h . Besides, we will show how the poroelasticity can significantly modify the surface deformation, though many questions remain to be addressed.

6.2.1 Contact angle hysteresis on SBS-paraffin gels

Inspired by the resting time effect of the PDMS gel in section <u>3.6</u> and the report of "stick-slip" motion observed during water spreading on viscoelastic materials^{68,69}, we try to see how the resting time may affect the contact angle hysteresis of a viscoelastic gel.

We use the 15% SBS-paraffin gel in the current study. Its preparation has been detailed in Section 2.6.2. The thickness of the paraffin layer is 2.6 mm. A chamber which control the humidity is used for inhibiting the droplet evaporation. During the hysteresis test, water is injected into or extracted from droplets at fixed flux rate $10 \,\mu L/min$.



FIGURE 6.2: Resting time effect on the contact angle hysteresis of a water droplet on SBS-paraffin gel layer.

The relevant result is shown in Figure 6.2. The advancing contact angle and receding contact angle at *Resting time* = 0 *s* are acquired by a fast inflation and deflation test. The duration of the contact line resting is very short (~seconds). We simply take their resting time as 0 second as an approximation. As a result, we see that the advancing contact angle increases and receding contact angle decreases with the increasing of resting time. After 700 seconds, the contact angle hysteresis reaches 73°. This is in sharp contrast to the case of soft PDMS where θ_h increases to 14° with a resting time of 1800 seconds.

After performing the hysteresis experiments, we observe the traces are still visible within our camera even after 84 minutes relaxation! As is revealed in Figure 6.3(a), dark circles on the gel interface are the traces induced by the long-resting droplets.



FIGURE 6.3: Trace left by resting droplets. (a) Relaxation time for the traces from the inner to outer (red arrow direction): 84 minutes, 43 minutes, 30 minutes, 20 minutes, 13 minutes, 9 minutes, 3 minutes, 2 minutes; the resting time for creating those traces are 15 minutes, 15 minutes, 12 minutes, 9 minutes, 6 minutes, 3 minutes, 0.5 minutes. The black spots on (a) are from the bottom of the glass slide. They won't affect the wetting hysteresis measurement. (b) 3D reconstruction of the trace induced by a resting water droplet. Resting duration is 10 minutes and the relaxation time after the droplet removal at the measurement is 77 seconds.

To see the exact shape of this trace, we perform 3D profilometry measurement for the gel film with a 3D profiler (Microsurf 3D, Fogal Nanotech, France) after 77 seconds' relaxation of the trace, which is induced by a 10-minute resting water droplet. The shape of this trace is shown in Figure 6.4(a). The width is around 70 μm , and its height is 4.2 μm , which is much bigger than the size of the surface roughness $(10 nm)^{68}$. In addition, to have an idea of how the ridge grows with the resting time, we measure the relaxation of the trace in Figure 6.4(a) and the corresponding result is plotted in Figure 6.4(b). Since the hysteresis is very different from that on the PDMS substrate, the relaxation test of the trace on PDMS gel is also tracked (Figure <u>6.4(c)</u>). By comparing Figure <u>6.4(b)</u> and Figure <u>6.4(c)</u>, we find the following relaxation behaviors: both of them relax very fast in the beginning and then it takes hours to reach full relaxation; for the trace on SBS-paraffin gel to reach 0.4 μm height, it takes ~1000 seconds; while for the trace on PDMS gel to reach the same height, it take 20 seconds. Note that the resting time (ridge growth time) is 10 minutes for SBS-paraffin gel and 30 minutes for the soft PDMS gel. It can be deduced that it takes much more than 1000 seconds for the trace on SBS-paraffin gel to relax to a height of 0.4 μm if the resting time increases to the same (30) minutes) as that on the PDMS gel.

By checking the two types of polymer rheology from section 2.6.1 and the data by T. Kajiya^{68,69}, we notice that the PDMS gel has an elastic response at low frequencies ($\tan \delta = G''/G' < 1$) while SBS-paraffin gel has a viscous response at such frequencies ($\tan \delta = G''/G' > 1$). When a constant stress is applied to the two gels, PDMS gel will reach equilibrium in short time and SBS-paraffin gel will flow for a long time. This mechanism should also work in a similar way for the relaxation and thus predict the relaxation we have observed.



FIGURE 6.4: (a) The shape of the trace after 77 seconds' relaxation on SBS paraffin gel. (b)Relaxation of the trace on the soft SBS-paraffin layer. The point that is marked in blue from (a) is tracked. The resting duration

of the water droplet is 10 minutes. (c) Relaxation of the trace on a soft PDMS layer (G' = 1.2 kPa). Droplet volume, resting time, and soft layer thickness are 5 μ L, 30 minutes and 1358 μ m, respectively.

The relaxation measurements of the two gels are inspiring. However, how to theoretically relate their mechanics to the relaxation and growth remains to be done. This will be the first step to understand the relation between the mechanics of soft materials and their contact angle hysteresis. The next question to be addressed is how the growth (relaxation) of the local ridge pins the contact line and induces the contact angle hysteresis.

6.2.2 Elastowetting on hydrogels

Static deformation

We have investigated the simplest elastowetting case on soft PDMS gel: neutral wetting condition, no liquid diffusion. Now, we try to break those experimental constraints. In the following, we will present our first results of elastowetting on hydrogels.

A. Nonneutral wetting

We prepare PVA-SbQ/GA hydrogel films with a tunable G'ranging from 1 to 1.9 kPa. For the maneuverability of the soft hydrogel films, they are adhered on a microscopy glass slide presumably by interactions between the glass and SbQ under UV exposure. Those gels are above the gelation limit in terms of the polymer concentration and in equilibrium swelling with water. With increase in the crosslinking ratio, small water droplets can be observed on their surfaces. This apparition of water droplets is due to the deswelling of the polymer network at the condition where the equilibrium polymer concentration is higher than the polymer concentration at preparation. Further increase in the crosslinking ratio induces fracturing the gel as it is fixed to the glass slide, not suitable for wetting experiment. For the polymer preparation, we fix the mass ratio of PVA-SbQ as 4.4% and change the crosslinker GA (glutaraldehyde) molar concentration from 0.01 M to 0.09 M. After the polymerization, those hydrogel films are kept in closed petri dishes saturated with water vapor. They will not be taken out until we start to run experiments. The surface deformation is measured ~ 30 seconds after the water droplet deposition, as is demonstrated in Figure 6.5(a) and Figure 6.5(c). At the measurement, the contact line is already pinned. As a result, $V_d = 0 \ \mu m/s$. This can be further verified by Figure 6.7. The contact angle is observed by a side view camera (Figure 6.5(b)).



FIGURE 6.5: (a) Schlieren view of a water droplet on a PVA SbQ-GA hydrogel layer. PVA SbQ mass ratio is 4.4 % and the GA molar concentration is 0.03 M. (b) Side view of the (a). (c) Surface deformation measured 30 seconds after droplet deposition along the red line marked in (a).

Surface deformation for each measurement is shown in Figure <u>6.5(c)</u>. The experimental parameters for each curve are summarized in TABLE 6.1. The thickness for the five films is almost the same, $\sim 1200 \,\mu m$. A dimple is formed when GA molar ratio is more than 0.03 *M*. We observe that depth of the dimple increases when gels become more rigid. This observation seems to contradict PDMS results. However, the contact angle results should not be neglected. θ_e decreases when the concentration of GA increases. With the reminiscent of the hysteresis effect on the surface deformation from elastic gel, it is not surprising that the dimple becomes deeper with the increase of GA concentration. After all, the increase of *G'* is less than a factor 2 for our measurements.

Sample	PVA-SbQ (%)	GA (M)	Contact angle (°)	G' (kPa)	Diameter (<i>mm</i>)
PVA4.4GA0.01	4.4	0.01	66.7	0.93	3.5
PVA4.4GA0.03	4.4	0.03	60.8	1.3	3.5
PVA4.4GA0.05	4.4	0.05	52.9	1.1	3.8
PVA4.4GA0.07	4.4	0.07	53.4	1.9	3.9
PVA4.4GA0.09	4.4	0.09	55.7	1.5	4.4

TABLE 6.1 Parameters for the surface deformation

We apply our model written as Equation (3.29) to the hydrogel surface deformation. Since we do not measure the surface tension of the hydrogel, we calculate two limits for the surface tension of γ_s : 10 mN/m and 100 mN/m. In Figure 6.6, the comparison of the theoretical predictions and the experimental result (PVA4.4GA0.09) is shown. The model fails to capture the surface profile of the experimental results whatever the surface tension is.



FIGURE 6.6: Comparison between our model and experimental deformation for the test PVA4.4GA0.09. All experimental parameters are injected into Equation (3.29) except the surface tension γ_s . Blue solid curve is the calculation when $\gamma_s = 10 \text{ mN/m}$ and the black solid curve is the calculation when $\gamma_s = 100 \text{ mN/m}$.

In the model, we assume that the surface tension of liquid-gel interface and that of gel-vapor interface are the same. This assumption is reasonable for PDMS gels as its static contact angle is close to 90° . On the other hand, for the hydrogel it is 56° , thus it will be necessary to develop a model accounting for the asymmetry of the solid surface tension on both sides of the contact line. In the perspective of this work, it will be important to incorporate this asymmetry surface tension into the model. It would also be interesting to see how the geometry of the system and the material properties affect the surface deformation.

B. Poroelasticity effect

To study the diffusion-induced surface deformation, we prepare a hydrogel above the gelation limit and out of the swelling equilibrium. The hydrogel can absorb water when it is in contact with water in liquid or vapor phases. Here we prepare a PVA-SbQ hydrogel without GA, and the mass concentration of the PVA-SbQ polymer is 3.3%, which can swell in water.

Thanks to the quantitative Schlieren setup, we can track the surface deformation in real time. We perform the diffusion test in the open surroundings with distilled water on the 3.3% PVA-SbQ hydrogel film and observe the evolution of the surface deformation in 9 *minutes*. As is shown in Figure <u>6.7(a)</u>, the white region close to the contact line propagates to the far region, indicating that the surface deformation increases when water diffuses from droplet bulk to the hydrogel network. The diffusion induces a growing surface deformation, extension of which increases from hundreds of microns to the several millimeters. At contact, there is a dimple around the contact line, pointed by the red arrow from Figure <u>6.7(a)</u>, which is a darker region than the surroundings. This is possibly due to the instantaneously elastic response of the hydrogel film. In the following stage, this dimple disappears and the interface around the contact line is swollen up, shown as the growing white annulus. With a side view camera, we are able to synchronize the contact angle evolution with the surface deformation, as is shown in Figure <u>6.7(b)</u>. Although a meniscus and the interface deformation can also be apparently visualized from a side view, the resolution of it is far worse than that of the Schlieren camera



FIGURE 6.7: Diffusion of water droplet on a 3.3% PVA-SbQ hydrogel film (thickness~1300 μm). (a) Schlieren view of the diffusion process. Scale bar is 1 mm.(b) Side view of the diffusion droplet. Scale bar is 0.5 mm.

Our quantitative Schlieren setup demonstrates a super-resolution ability in monitoring a tiny surface deformation on a large spatial scale. Thus, it would be very useful to study the diffusion effect on the interface deformation when liquid is absorbed into a polymer network.

The growing of neighbor droplets

Here we briefly describe the growth of small droplets observed during a wetting experiment. We identify a growing neighbor droplet close to the droplet that we deposit on a hydrogel film. The reason is unclear.

We prepare a PVA-SbQ/GA hydrogel with PVA-SbQ of mass ratio 4% and GA of molar concentration 0.1 M, which is sufficiently crosslinked to induce slight deswelling after the crosslinking reaction (the equilibrium polymer concentration is higher than the preparation polymer concentration, thus the gel deswells). We store it in a closed petri-dish which is saturated with water vapor. When we start experiments, the hydrogel film is placed in the open surroundings and a water drop is deposited close to small droplets onto the gel film interface. Both the Schlieren view and side view are recorded for 25 minutes, as is displayed in Figure 6.8. The small droplet (indicated by the red arrow in Figure 6.8) grows continuously in the first 10 minutes, and later it seems to be in equilibrium in evaporation and absorption.

Since the hydrogel is in open air, the mother droplet, the small droplets and the hydrogel should be all evaporating. We observe that: the gel surface is swollen up, indicated by the growing bright annulus in Figure 6.8(a); the small droplets grow as well; the deposited water droplet is losing its volume. It would be reasonable to draw a conclusion that the principle droplet not only provides all the liquid volume for the system's evaporation but also compensates the volume for growing neighbor small droplets. It seems that: (1) the solvent (water) is transported from this mother liquid reservoir to the polymer network; (2) some amount is extracted onto the surface. There is no surprise for the first diffusion effect. It is surprising for the second phenomenon. The exact mechanism for this is still not clear for the moment. A guess is that there is an osmotic pressure due to the surface deformation and this pressure competes with the Laplace pressure inside the small droplet. The dominance of the two decides whether droplet volume grows or not. A further study with the aid of the Schlieren optics in affirming the exact mechanism remains to be done.



FIGURE 6.8: Growing of a small liquid drop around the mother bulk on 0.04PVA SbQ-0.1GA gel film. (a) Schlieren view of the surface deformation with the growing of nearby small droplets. (b) Side view of the growing droplets.



Appendix A: Deflection of the parallel light beam

Figure A.1 Diagram of the relation between deflection distance and deflection angle

A collimated light beam, without any disturbance, follows the dotted green line in Figure A.1 when it passes through a lens of the focal length f_0 and will focus at the focal point where the red line meets the green dotted line. When this incident light beam is deflected by an angle ε , it will be deflected by a distance Δa on the focal plane, as is demonstrated by the grey solid line. From Figure A.1, it can be easily found the following angle relations:

$$\varepsilon = \varepsilon_1 = \varepsilon_2 = \varepsilon_3$$

Hence,

$$\Delta a = \varepsilon_3 f_0 = \varepsilon f_0$$

Appendix B: Scaling for the thickness effect at small thickness limit

The spreading of liquid on soft layers at small velocity can be described by the following relations:

$$\Psi(\theta_d) \sim \frac{\gamma_{LV}}{\gamma_s} \frac{G_0}{\gamma_s} |V_d \tau|^m \int_0^\infty \frac{|k|^{m+2}}{(k^2 + \frac{G_0}{\gamma_s K(k)})^2} dk$$
$$\Psi(\theta_d) = \frac{\cos\theta_e - \cos\theta_d}{\sin^2\theta_d}$$
$$K(k) = \frac{1}{2k} \left[\frac{\sinh(2h_0k) - 2h_0k}{2h_0^2k^2 + \cosh(2h_0k) + 1} \right]$$
(B.1)

We will start with the term $\frac{G_0}{\gamma_s K(k)}$ because it is the single term that contains h_0 . Its Taylor series in respect to h_0 is:

$$\frac{G_0}{\gamma_s K(k)} = \frac{2kG_0}{\gamma_s} \left[\frac{2h_0^2 k^2 + \cosh(2h_0 k) + 1}{\sinh(2h_0 k) - 2h_0 k} \right]$$
$$= \frac{3G_0}{k^2 \gamma_s h_0^3} + \frac{27G_0}{5\gamma_s h_0} - \frac{24k^2 G_0 h_0}{175\gamma_s} + \frac{431k^4 G_0 h_0^3}{7875\gamma_s}$$
$$- \frac{1263k^6 G_0 h_0^5}{336875\gamma_s} + O(h_0^7)$$
(B.2)

At small thickness, the first term rules. Hence the other terms will be dropped. Now we arrive at a simpler expression for the integrand in Equation ($\underline{B.1}$):

$$\int_{0}^{\infty} \frac{|k|^{m+2}}{\left(k^{2} + \frac{G_{0}}{\gamma_{s}K(k)}\right)^{2}} \sim \int_{0}^{\infty} \frac{|k|^{m+2}}{\left(k^{2} + \frac{3G_{0}}{k^{2}\gamma_{s}h_{0}^{3}}\right)^{2}} dk \sim \left(\frac{h_{0}^{3}\gamma_{s}}{G^{0}}\right)^{\frac{1-m}{4}}$$
(B.3)

By inserting Equation ($\underline{B.3}$) into Equation ($\underline{B.1}$), we will have:

$$\Psi(\theta_d) \sim \frac{\gamma_{LV}}{\gamma_s} \frac{G_0}{\gamma_s} |V_d \tau|^m \left(\frac{h_0^3 \gamma_s}{G^0}\right)^{\frac{1-m}{4}}$$
(B.4)

With proper dimensionless rearrangement of all terms, we find a scaling for the thickness effect for the spreading on soft layer at small thickness limit:

$$\Psi(\theta_d) \sim \frac{\gamma_{LV}}{\gamma_s} \left(\frac{V_d \tau G_0}{\gamma_s}\right)^m \left(\frac{h_0 G_0}{\gamma_s}\right)^{\frac{3(1-m)}{4}}$$
(B.5)

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Résumé

Dans cette thèse, nous nous sommes intéressés à la statique et la dynamique du mouillage de gouttes d'eau sur des substrats mous tels que des gels, encore connu sous le nom d'élastomouillage. Pour ce faire, nous avons d'abord développé une méthode quantitative de visualisation par strioscopie permettant de mesurer la déformation de la surface d'un film de gel transparent avec une précision élevée quelque soit l'épaisseur du substrat et sur de grandes distances. Nous montrons que la déformation superficielle de films mous de silicone (PDMS) dépend de la taille des gouttelettes déposées ainsi que de l'épaisseur et de l'élasticité de ces films. Nous avons construit un modèle basé sur la théorie de l'élasticité linéaire tenant compte de la tension superficielle des gels qui prédit bien la forme et l'amplitude de la déformation de surface. Nous apportons aussi la preuve expérimentale et l'analyse théorique de l'importance de l'hystérèse de l'angle de contact dans la description de la déformation en démontrant que la force tangentielle due à la tension superficielle entre liquide et vapeur à la ligne de contact, souvent négligé, contrôle la déformation de la surface. La dynamique de mouillage est étudiée en dégonflant des gouttelettes sur des films de PDMS avec une épaisseur bien contrôlée. Il est démontré que la dissipation d'énergie dans le gel dépend fortement de l'épaisseur lorsque cette dernière est inférieure à 100 µm. L'effet de freinage viscoélastique et l'effet d'épaisseur sont bien rationalisés avec un modèle basé sur la viscoélasticité linéaire et une simple loi l'échelle qui tient compte de l'effet d'épaisseur capture très bien nos expériences. Enfin, nous démontrons que nous pouvons dériver et guider les gouttelettes en mouvement avec la conception de surfaces couvertes de couches de gels ayant des gradients d'épaisseur.

Mots Clés

Elastomouillage, optique de Schlieren, déformation de surface, élasticité linéaire, dissipation, viscoélasticité.

Abstract

In this thesis, we aim at obtaining a better understanding of the statics and dynamics of the wetting of liquids on soft gels, otherwise known as elastowetting. First, we develop a quantitative Schlieren set-up to measure the surface deformation of a transparent gel film with a high precision over large areas and for all thicknesses in real time. The long-range surface deformation of soft PDMS films is found to be dependent on the sessile droplet size, and the thickness and elasticity of soft films. We build a model based on linear elasticity theory that accounts for the surface tension of soft materials. It predicts the longrange surface deformation in excellent agreement with the experimental data. We also bring the experimental proof and theoretical analysis of the importance of contact angle hysteresis in the description of the deformation of the surface of the gel. We demonstrate that the tangential component of the liquid-vapor surface tension at the contact line, whose contribution are often neglected, significantly affects the surface deformation. Wetting dynamics is investigated by deflating droplets on PDMS films with well-controlled thickness. It is shown that energy dissipation in the soft gel depends on the thickness when the latter is smaller than $100 \ \mu m$. The viscoelastic braking effect and the thickness effect are both well rationalized with a model based on the theory of linear viscoelasticity and a simple scaling law accounting for the thickness effect captures very well our experiments. Finally, we demonstrate that we are able to guide moving droplets with coatings having a gradient of their thickness.

Keywords

Elastowetting, Schlieren optics, surface deformation, linear elasticity, dissipation, viscoelasticity.