Contact line dynamics of droplets under electrowetting actuation

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CONTACT LINE DYNAMICS OF DROPLETS UNDER ELECTROWETTING ACTUATION

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A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

January 31, 2019

Date

Vo Xuan Quoc

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

January 31, 2019

Date

Asst. Prof. Tran Anh Tuan

Authorship Attribution Statement

This thesis contains material from 2 papers published in the following peer-reviewed journals where I was the first author and Prof. Tran Anh Tuan is the corresponding author.

Chapter 4 is published as: Q. Vo and T. Tran, Contact line friction of viscous electrowetting droplets, *Physical Review E* **97**, 063101, (2018). DOI: 10.1103/PhysRevE.97.063101. The contributions of the co-authors are as follows:

- I co-designed the study with Prof. Tran Anh Tuan and performed all the laboratory work at the School of Mechanical and Aerospace Engineering. I also analyzed the data.
- I prepared the manuscript drafts. The manuscript was revised by Prof. Tran Anh Tuan.

Chapter 5 is published as: Q. Vo, H. Su, and T. Tran, Transient dynamics of electrowetting droplets *Scientific Report* **8**, 836, (2018). DOI: 10.1038/s41598-018-19167-7. The contributions of the co-authors are as follows:

- I co-designed the study with Prof. Tran Anh Tuan and performed all the laboratory work at the School of Mechanical and Aerospace Engineering. I also analyzed the data.
- I prepared the manuscript drafts. The manuscript was revised by A/Prof. H. Su and Prof. Tran Anh Tuan.

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Summary

The dynamics of droplets spreading and retracting on solid substrates are both of fundamental and industrial interests. With the motivations to broaden our current knowledge on contact line dynamics as well as to provide technical guidelines for related applications, this thesis focuses on contact line dynamics of droplets spreading and retracting on solid substrates due to the electrocapillary effects. First, in Chapter 4, contact line friction of electrowetting actuated droplets are investigated. The droplets are spread on the solid substrate using electrowetting actuation. Then, the voltage is released allowing the droplets to retract freely to study the retracting stages. The contact line friction coefficients of both the spreading and the retracting stages are found to depend *equally* on viscosities of the droplets and of the surrounding liquids. Therefore, it can be described by the geometric mean of the both viscosities. Based on the analysis of the contact line friction, a characteristic timescale for viscous droplets spreading and retracting on solid substrates is theoretically derived and experimentally verified. The subject of Chapter 5 is the transient behaviours of droplets under electrowetting actuation. These behaviours are categorised in either *underdamped* or *overdamped* regimes. Based on the force balance between driving forces and resisting forces of each regime, characteristic timescales for the transient dynamics of droplets for the two dynamical behaviours are established. The condition for the behaviours to change from one regime to the other is determined when the two timescales are comparable. Moreover, the actuation time, defined as the duration for the droplets to reach new equilibrium after actuation, is studied. It is theoretically and experimentally shown that the minimisation of the actuation time is only achieved at the transition between the two regimes. Also, the dependence of the actuation time on system parameters such as viscosity, droplet radius and the applied voltage are investigated in detail. In Chapter 6, the dependence of static and dynamical behaviours of droplets on substrate properties is studied. It is shown that it is possible to bring the applied voltage to as low as the logic-signal-voltage level while maintaining sufficient electrowetting effects. This investigation also reveals that dielectric materials have a minute effect on the contact

line friction coefficient, therefore, insignificantly affect to the transient dynamics of the actuated droplets. This result opens a great potential in numerous droplet-manipulating applications that requires low-voltage electrowetting actuation. Chapter 7 focuses on the detachment of droplets on solid substrates under electrowetting actuation. It is found that the detachment of droplets depends both on the hydrodynamical behaviours and contact line pinning of droplets. Particularly, droplets only can detach when the transient dynamics is in the underdamped regimes and the surface energy difference created by the electrowetting effect is higher than the sum of the contact line dissipation and an energy barrier created by the contact line pinning. Based on this, a theoretical model to predict the condition for the detachment is developed. Moreover, the study about droplet detachment is extended to using maximum deformation actuation with over-saturation voltage. It is found that although the static contact angle saturates with over-saturation voltage, the deformation of droplets in the transient states are still facilitated by the over-saturation voltage. Therefore, it helps to increase the surface energy difference and to assist the detachment of the droplets. As a result, the detachable regime is expanded significantly meaning that it is possible to detach droplets with smaller sizes and higher viscosity compared to non-saturation detaching methods. Finally, the initial velocity of detached droplets is investigated in detail. The initial detaching velocity can be characterised by the characteristic retracting velocity of the contact line. As a result, it is also can be predicted by using the characteristic timescales of the transient dynamics. In Chapter 8, contact line dynamics of droplets on dielectrowetting substrates is studied. In particular, this experiment focuses on investigating the spreading and retracting dynamics caused by the impinging of droplets on the dielectrowetting substrates. The dielectrowetting effect is created by an application of an AC voltage to an array of electrodes beneath the dielectric layer of the substrate. It is found that the strength of the electric field facilitates the spreading stage, whereas it has a negative effect on the retracting stage. Interestingly, the retracting dynamics is *asymmetrical*, i.e., it retracts faster along the electrode's direction compared to the electrode-perpendicular direction. A theoretical model determining the characteristic timescale of the asymmetrical retracting dynamic is proposed. The model is verified by the experimental data with a large range of the applied voltage. The presented results not only strengthen the current knowledge on contact line dynamics of droplets, but also provide important technical guidelines in design, control and optimisation of droplet manipulations using electrowetting. The results are also relevant in understanding other capillary driven phenomena such as wetting, droplet impact and evaporation.

Chapter 1

Introduction

1.1 Motivations

Droplet wetting and dewetting phenomena are ubiquitous in everyday life whenever a drop of liquid comes to contact to a solid surface. Examples of such phenomena include rain drops sliding on a windshield, small droplets keeping its spherical shapes on a lotus leaf, or bloods wetting a crime scene. One of the most important factors in the dynamics of such phenomena is the motion of the contact line, i.e., the boundary where the three phases meet. Contact line dynamics is not only a fundamental topic, but it also affects numerous key processes in many industrial applications. It plays a key role in applications at larger scales such as oil recovery [1], the efficient deposition of pesticides on plant leaves, drainage of water from highways [2], or cooling reactors [3]. In those of smaller scales, contact line dynamics is crucially important in solving technological problems of microfluidics or ink-jet printing [4]. A physical understanding of contact line dynamics therefore not only improves our knowledge of everyday events but also helps in developing new materials and technologies.

One of the technologies that requires understanding in contact line dynamics is using electric fields to control the spreading and retracting of droplets on solid substrates, and subsequently control the behaviours of the droplets, or the contact line. This method is based on the so-called electrowetting on dielectric (EWOD) effect [5, 6]. EWOD is the phenomenon whereby an application of a voltage between a conductive droplet and a hydrophobic, insulated electrode lowers the surface energy of the liquid-solid interface, therefore, changes the wetting of the droplet on the solid electrode. This technique of wetting modification has been successfully applied in many applications such as digital camera, light valves [7], liquid lens [8], fast response displays [9], optical films [10], and digital microfluidics [4, 11].

Figure 1.1: An example of 2D-DMF EWOD chip [15].

Among the above applications, digital microfluidics is a new technique to control small, discrete droplets digitally. Thus, it has a great potential in numerous applications such as chemistry, biological applications [12, 13] and tissue engineering [14]. Typically, digital microfluidics includes two types of droplet manipulations using EWOD as a core technique. They are horizontal and vertical actuations, or the so-called in-plane and out-of-plane actuations, respectively. The key idea of in-plane actuation is shown in Fig. 1.1 [15]. Applications of voltage to a series of adjacent electrodes can turn on or off the interfacial tension imbalance at the contact line of a droplet contacting with the electrodes. This imbalance in the interfacial tension drives the droplet to move from one position to another. By using a control algorithm that combines different actuations, this technique can be used to create droplets from a reservoir, to transport droplets to any desired position in an EWOD chip, to merge two or many droplets together or to split a large droplet to smaller ones [11, 14]. These form a set of manipulations on horizontal surfaces, or the so-called two-dimensional digital microfluidics (2D-DMF). Till now, 2D-DMF has shown an excellent ability in many biological applications such as cell culture/assays [12, 13, 16, 17] and DNA/protein analysis [18, 19].

More recently, three-dimensional digital microfluidics (3D-DMF) based on out-of-plane actuation induced by electrowetting [20, 21] has been introduced [22, 23]. To actuate a droplet vertically, a voltage difference is applied to a droplet-substrate EWOD system to spread the droplet and store energy to the droplet surfaces (see Fig. 1.2). Then, the voltage is released letting the droplet to retract freely. At the end of the retracting stage, the droplet can detach from the solid substrate vertically if some detaching criteria are satisfied [20] (see Fig. 1.2). Recently, 3D-DMF has been successfully applied in to various applications that requires vertical actuation of droplets such as droplet mixing [22], 3D manipulation of droplets containing bio-cells [23].

The growing number of applications using these droplet-manipulating methods

Figure 1.2: The principle of vertical actuation of droplets using EWOD.

requires a deeper understanding of the contact line dynamics in order to improve such processes. Taking a closer look to the physical nature of the phenomenon, the motion of a such droplet on the solid substrate is driven by an imbalance in the interfacial tensions at the contact line created by the electric field [5] and opposed by both liquid inertia and viscous dissipation. In such phenomenon, the contact line dynamics will determine the responses of the droplet under the external stimulation. Therefore, the contact line dynamics plays a crucial role in controlling and optimising the manipulations of the droplet.

Although many efforts have been devoted to understanding this simple-looking phenomenon, numerous standing questions remain open. In particular, how the transient dynamics of contact line depend on contributing factors such as contact line friction, liquid viscosity, and inertia of droplets, or what roles of the electric field affecting to the contact line dynamics. For the droplet manipulating problems, it is a non-trivial question how the contact line dynamics affect to the transient dynamics of the actuated droplet; or what criteria for the droplet to detach from a solid surface in the vertical actuation problem. As a consequence, a systematic investigation of the transient dynamics of droplets under an application of electric field is needed to address the aforementioned problems. Moreover, knowledge on dynamics of droplets under the electrowetting effect also helps in understanding other related interfacial-tension-driven phenomena such as natural wetting and dewetting problems [24], Marangoni-driven flows [3], droplet evaporation [25], or droplet impact on solid surfaces [3] due to the common physical natures. Some of these aspects are described in the present thesis.

1.2 Objectives

To provide a better understanding on the physics of the phenomena as well as to provide a technical guideline for designing and improving of the aforementioned processes, in this thesis, we aim to study various fundamental aspects of the dynamics of droplets

and contact lines under electrocapillary effects including contact line friction, transient dynamics of electrowetting droplets, droplet detaching by electrowetting actuation, and contact line dynamics of dielectrowetting droplets. The specific aims of the thesis are:

- Study contact line friction of droplets spreading and retracting by electrowetting and its role in the transient dynamics of the droplets;
- Systematically investigate the transient dynamics of electrowetting droplets considering various control parameters;
- Investigate contact line dynamics of droplets detachment under electrowetting actuation;
- Investigate spreading and retracting dynamics of droplets impinging on dielectrowetting substrates.

1.3 Scopes

In this thesis, we consider contact line motions of aqueous droplets on a solid surface under electric fields causing electrowetting and dielectrowetting effects. Regarding to the contact line dynamics of electrowetting droplets, we investigate various configurations that mostly used in droplet manipulating applications including in-plane and out-of-plane actuations. For the dielectrowetting effects, we focus on contact line dynamics of droplets spreading and retracting upon impact on dielectrowetting substrates. The scopes of our study are listed below.

Firstly, we limit our investigation in surface-tension-dominated regime where the gravitational effect is neglected. To do that, in all our experiment, we use droplets having radius R smaller than the capillary length λ_c , defined by the ratio of surface tension to gravitational force: $\lambda_c = \sqrt{\sigma/\rho g}$. Here, σ is the surface tension of droplets; ρ is density of liquid droplet; and g is the gravitational acceleration.

Secondly, in this thesis, we will work with small liquid droplets and most of the cases they are in ambient oils having viscosity that is much higher than that of air. As a result, the Reynolds number, i.e., the ratio of inertial forces to viscous forces, $Re = \rho UL/\mu$, is usually small. Here U , L are respectively characteristic velocity and length, μ is the viscosity of droplets.

Thirdly, we focus on the case in which the contact line motion is solely caused by interfacial tension imbalance caused by electrowetting and dielectrowetting effects, while excluding the Marangoni and evaporation effects. Thus, an assumption of volume conservation of droplets is accepted and will be used in many analyses of this thesis. Moreover, we also ignore the effects of temperature in all of our processes. In experimental point of view, as we will describe more detail in Chapter 3, we will keep the temperature of the surrounding environment fixed in all our experiments.

Finally, in our experiments, we consider parameters that listed in Table. 1.1 as our control factors. Any other parameter is assumed constant. Restricted by the above limits, Table. 1.1 shows the ranges of the varied parameters in this thesis.

Table 1.1: Ranges of investigated parameters

Parameter's name	Notation	Range
Droplet Radius	R	$50\text{ }\mu\text{m} \leq R \leq 1.5\text{ mm}$
Droplet viscosity	μ	$1.0\text{ mPas} \leq \mu \leq 615.0\text{ mPas}$
Oil viscosity	μ_o	$1.8\text{ mPas} \leq \mu_o \leq 1000.0\text{ mPas}$
Voltage	V	$0\text{ V} \leq V \leq 150\text{ V}$ for DC voltage or, $0\text{ Vpp} \leq V_{\text{pp}} \leq 600\text{ Vpp}$ for AC voltage

1.4 Guide through the thesis

Here, we give an outline describing each next chapter of the thesis. In Chapter 2, we review important studies of relevant aspects of contact line dynamics including contact line friction, transient dynamics of droplets under electrowetting actuation, effects of substrate's properties on dynamics of electrowetting droplets, jumping droplets under electrowetting actuation. We also review the contact line dynamics under non-uniform electric fields for droplet impacting on dielectrowetting substrates.

Chapter 3 shows our experimental setups, substrate's fabrications, experimental methods. This chapter also shows preparations and characterizations of materials that we use in our experiments. The measured properties of the materials are carefully characterised.

From Chapter 4 to Chapter 8 we show experimental results, theoretical analyses

and discussions of each aforementioned problem. They are

- Chapter 4: Contact line friction of viscous electrowetting droplets;
- Chapter 5: Transient dynamics of electrowetting droplets;
- Chapter 6: Effects of substrates on static and dynamics of electrowetting droplets;
- Chapter 7: Vertical actuation of droplets using electrowetting;
- Chapter 8: Contact line dynamics of droplets upon impact on dielectrowetting substrates.

Finally, Chapter 9 will give our conclusions of the thesis and some possible perspectives that can be extend in future.

1.5 Publications

Journal papers

- Quoc Vo and Tuan Tran, Contact line friction of electrowetting actuated viscous droplets, *Physical Review E*, **97**, 063101 (2018).
- Quoc Vo, Haibin Su and Tuan Tran, Universal transient dynamics of electrowetting droplets, *Scientific Report*, **8**, 836 (2018).
- Quoc Vo and Tuan Tran, Critical condition for jumping of droplets under electrowetting, *submitted* (2018).

Conference presentations and papers

- Quoc Vo and Tuan Tran, Contact line friction of viscous droplets spreading and retracting in ambient oils, oral presentation and abstract at *EMN Orlando Meeting on Droplets*, USA, (2017).
- Quoc Vo and Tuan Tran, Transient electrowetting on dielectric for activating droplets in bioprinting applications, oral presentation and full paper at *Pro-AM*, Singapore, (2016).

Chapter 2

Literature review

2.1 Electrowetting on dielectric (EWOD)

2.1.1 Background of electrocapillary and EWOD

Electrowetting was first observed by Lippmann [26] who investigated capillary rises of mercury's level in a vertical experimental tube. In his experiment, he found that when a voltage is applied between the mercury and water-sulfuric acid which fills the upper part of the tube, the mercury level increases. In this configuration, due to the application of the voltage to the two contacted conductive liquids, an electrical current is generated directly through the liquids resulting in electrolysis of the liquids playing as electrodes [5]. Thus, the applied voltage is limited in order of millivolts. To prevent this unwanted current, Berge et al. proposed a solution that uses an insulating layer to separate the two electrodes [27]. Berge ingeniously applied this new configuration to a system having a conductive droplet resting on a flat electrode covered by a thin insulating layer. He observed that contact angles of the droplet reduce when a voltage difference between the droplet and the electrode is applied. Without the electrolytic current, the voltage can go up to thousands of volts to enlarge the electrowetting effect. This setting was then termed as electrowetting-on-dielectric (EWOD). As introduced in Chapter 1, recently, EWOD has become increasingly important in diverse applications requiring active controls of droplets such as digital microfluidics [4], liquid lens [8], light valves [7], fast response displays [9], and optical films [10].

In a typical EWOD setup (Fig. 2.1(a)), an electrically conductive substrate is coated with a thin insulating layer. A droplet deposited on the insulating layer is in contact with an electrode on top, which is usually a metal wire dipping into the droplet. The conductive substrate is connected to another electrode. When a voltage V is applied to

Figure 2.1: (a) Schematic of a typical EWOD setup [28]. (b) The linear relation between electrowetting number η and the applied voltage V of aqueous droplets under electrowetting actuation. The experiment is done in air. The solid line represents the plot of Young-Lippmann equation (Eq. 2.3) with parameters: $d = 2.5 \mu\text{m}$, $\epsilon = 1.93$, $\sigma = 72.18 \text{ mNm}^{-1}$ [28].

the two electrodes, surface energy at the liquid-solid interface changes an amount according to the energy stored in the two sides of the dielectric layer playing as a parallel-plates capacitor [5]:

$$\sigma_{\text{sl}}^{\text{eff}} = \sigma_{\text{sl}} - \frac{\epsilon\epsilon_0}{2d}V^2, \quad (2.1)$$

where ϵ_0 is the permittivity of the free space; and ϵ , d , respectively, are dielectric constant and thickness of the insulating layer; σ_{sl} and $\sigma_{\text{sl}}^{\text{eff}}$ are the solid-liquid interfacial tensions before and after the voltage V is applied, respectively. Giving the equilibrium contact angle of the droplet on the solid substrate before and after the voltage V is applied are, respectively, θ_0 and θ_e , Young's equation gives

$$\begin{cases} \cos \theta_e = \frac{\sigma_{\text{so}} - \sigma_{\text{sl}}^{\text{eff}}}{\sigma_{\text{lo}}}, \\ \cos \theta_0 = \frac{\sigma_{\text{so}} - \sigma_{\text{sl}}}{\sigma_{\text{lo}}}, \end{cases}, \quad (2.2)$$

where σ_{so} and σ_{lo} are, respectively, the interfacial tensions of the solid-oil and liquid-oil interfaces assuming that the system is immersed in oil. By combining Eqs. 2.1 and 2.2, ones achieve the famous Young-Lippmann equation that describes electrowetting effect for droplets on solid substrates [5, 26]:

$$\cos \theta_e - \cos \theta_0 = \frac{\epsilon\epsilon_0 V^2}{2d\sigma} = \eta. \quad (2.3)$$

Here, from now on in this thesis, we use σ instead of σ_{lo} to simply describe the liquid-oil interfacial tension. In Eq. 2.3, η denotes the so-called electrowetting number, which is the ratio of electrical energy, $\epsilon\epsilon_0 V^2/2d$, to the surface energy, σ , of droplets. Therefore, it

represents the strength in the electrical force over the interfacial tension of the droplets. Also, from Eq. 2.3, we can see that, η is always smaller than 2. This is also the limit of the electrical force that can apply to the droplet surfaces. As we will see later in this thesis, a droplet will split into smaller droplets in order to increase the total surface area when a voltage that causes $\eta \geq 2$ is applied. Fig. 2.1(b) shows a typical steady EWOD experiment. When V is smaller than a threshold voltage, e.g., $V < 100$ V in this case, the change in contact angle, which is now represented by the electrowetting number η , well follows the Young-Lippmann equation (Eq. 2.3). This result is confirmed by many works on static electrowetting [5, 29, 30]. However, when V is larger than the mentioned threshold voltage, η no longer has a quadratic relation with V . This phenomenon is called contact angle saturation and will be discussed in the following section.

2.1.2 Contact angle saturation

The parabolic relation between the change in contact angle and the applied voltage is only observed for low voltage applied. At high voltage, the contact angles are saturated [5, 31] (see Fig. 2.1(b), for $V > 100$ V). The saturating contact angles are observed about 30° to 80° depending on different configurations of the EWOD setup such as material of the dielectric layer [32], types of the applied voltage, e.g., AC or DC [32], or types of outer liquid, e.g., air or oil [32]. When AC voltage is used, it is reported that the contact angle saturation also depends on the frequency of the AC applied voltage [33, 34]. So far, the linear model of electrowetting cannot explain the contact angle saturation. Although numerous theories have been proposed to explain various experimental observations [35–39], no possible theory of contact angle saturation has been widely accepted [5]. Therefore, in most of our experiments, we limit the applied voltage in the Young-Lippmann regime that the Eq. 2.3 is still valid. We will have some experiments on the saturation regime, but only for the experiments of vertical actuation of droplets by electrowetting.

2.2 Dynamics of electrowetting actuated droplets

2.2.1 Basic of wetting dynamics and contact line friction

Despite the simple presence of wetting phenomenon when a liquid droplet contacts with a solid surface, the prediction of contact line evolution after the droplet touches the solid surface is nontrivial. A number of physical phenomena in the liquid's bulk and

Figure 2.2: The rates of dissipation and the rate of change in kinetic energy for a droplet spreading on a solid surface with the contact angle $\theta = 43^\circ$. The data is reproduced from Carlson et al. [41]. Here, $\dot{R}_{Dw}$, $\dot{R}_\mu$, $\dot{R}_D$ are, respectively, the rates of dissipation at the contact line, in the liquid's bulk and by chemical potential; $\dot{R}_\rho$ is the rate of change in kinetic energy of the droplet. We can see that $\dot{R}_{Dw}$ dominates other sources of dissipation in fast dynamics of the wetting phenomenon.

at the solid surface are involved in the spreading process. Generally, wetting is driven by the interfacial tensions imbalance at the contact line resulted from the difference in surface free energies of solid-liquid, solid-oil and liquid-oil interfaces [40]. In dynamical perspectives, when the spreading process is taking place, this energy will be converting to kinetic energy, presented by the contact line velocity, and eventually dissipated by viscous effects. Therefore, the energy dissipation plays a crucial role in wetting and spreading dynamics.

It is widely accepted that dissipation of a droplet spreading and retracting in a solid surface is one of the most difficult problems in wetting dynamics. Generally, this energy dissipation is contributed by three sources: viscous dissipation due to the shear flows in the bulk of the droplet; dissipation due to the shear stress in the region close to the surface because of the non-slip boundary condition; and contact line dissipation due to contact line friction [42, 43]. Among these sources, it is reported that in rapid dynamics of wetting and dewetting, the contact line dissipation caused by contact line friction dominates the

Figure 2.3: (a) Plot showing the linear dependence of the friction coefficients on viscosity of droplets for slow dynamics of wetting [48]. (b) Plot showing the relation $\lambda \sim \mu^{1/2}$ in fast spreading dynamics of droplets under electrowetting actuation [45].

others [41, 42, 44]. As a proof for this argument, Carlson et al. [41] carefully investigated the rates of change of different sources of dissipation in rapid wetting of droplets on solid substrates, both theoretically and experimentally, and showed that the dissipation caused by contact line friction is the most important compared to the dissipation of the liquid's bulk and chemical potential inside the droplets (Fig. 2.2). This dominance of contact line dissipation due to friction at the contact line region is also observed in droplets spreading on substrates with different wettability [41, 42].

In the high viscosity limit, the contact line friction was shown to depend on both the viscosity μ of the fluid in the droplet [42, 45] and the viscosity μ_o of the surrounding fluid [46]. The functional dependence of the contact line friction coefficient λ on μ and μ_o has been the subject of extensive, split research efforts. When μ_o is kept fixed, λ is typically represented in the form $\lambda \sim \mu^\alpha$, where α is a constant sensitive to the spreading velocity. On the one hand, $\alpha = 1$ was reported from theoretical [47] and experimental investigations for spreading at the later stage, i.e., low spreading velocity, of glycerol solution droplets on glass substrates [48] (Fig. 2.3 (a)). On the other hand, it was found experimentally that $\alpha = 1/2$ at the early stage, i.e., high spreading velocity, of capillary-driven spreading of droplets on solid surfaces in air [41, 42, 44]; a similar value of α was found for electrowetting-driven spreading of droplets in air [45] (Fig. 2.3 (b)).

The dependence of λ on μ_o has also been the subject of numerous theoretical and experimental studies. Miller et al. [49] showed equal contributions of both viscosities μ and μ_o to the decaying factor of droplet oscillations. Huh et al. [50] used a creeping flow model

Figure 2.4: Plot showing the relation $\lambda \sim \mu_o^{0.8}$ of droplets spreading under electrowetting actuation in silicone oil [46].

to describe the contact line velocity and found that the ratio of the two viscosities had an important role on the contact line motion. More recently, Hong et al. [46] reported a power law relation $\lambda \sim \mu_o^{0.8}$ from an experimental study of electrowetting actuated droplets on Teflon surfaces in silicone oils (Fig. 2.4).

The contact line friction coefficient is also found to depend on substrate's properties, e.g., substrate's chemistry or roughness. Carlson et al. studied contact line friction of droplets spreading on different substrates, i.e., Silicon dioxide, Silane and Teflon, and reported that although the friction coefficients follow the rule $\lambda \sim C\mu^{1/2}$ for all surfaces, the prefactor C is very different among the investigated substrates. In particular, C is greatest for the Silicon dioxide substrate, while it is smallest for the Teflon substrate. When considering the static contact angles of droplets on those substrates, it was revealed that contact line frictions of droplets spreading on hydrophilic solid surfaces are higher than those on hydrophobic ones (Fig. 2.5).

Although diverse theories and experimental data regarding to the dependence of the contact line friction coefficient on liquid viscosity, outer phase viscosity and substrate's properties have been proposed, it is hard to connect those theories together in order to provide a unique description of the friction coefficient. As a result, understanding of contact line friction of droplets spreading and retracting on solid substrates remains elusive.

Figure 2.5: Plot showing the friction coefficients versus viscosity of droplets for different substrates. The surface wettability is represented by the static contact angle θ_e . The data is collected from Carlson et al. [42]. The data shows that the friction is lower for hydrophobic surfaces compared to that of hydrophilic surfaces.

2.2.2 Transient dynamics of electrowetting droplets

2.2.2.1 Underdamped and overdamped behaviours of electrowetting droplets

While the Y-L equation (Eq. 2.3) gives predictions in good accord with the measured changes in contact angles of a droplet under an electric field [5] (Fig. 2.1(b)), it only relates the equilibrated contact angles before and after the electric field is applied. Thus, it cannot be used to describe the transient dynamics between the two equilibrium states. Understanding of droplet characteristics during actuation, however, plays a critical role in applications utilizing EWOD for droplet manipulation. In particular, the relations between the system parameters, e.g., droplet size, liquid properties, applied voltage, and the resulting transient characteristics, e.g., the actuation time, are of both fundamental and engineering interests.

Among system parameters that affect to the transient dynamics, droplet size is the first parameter that attracted concerns of researchers and keeps a direct link to applications. In most cases, the droplet radius is considered the length scale of the dynamics. As a result, for large droplets, the dynamics are determined by droplets' inertia resulting in strong capillary waves on the droplets' surfaces and oscillations at the contact lines [45] (Fig. 2.6, upper panel). When the droplets are small, e.g., toward micro-size, Re become

Figure 2.6: Snapshots showing the underdamped behaviours (top panel) and overdamped behaviours (bottom panel) of droplets under electrowetting actuation [45]. The viscosity of liquids in the two cases are, respectively, 1.0 mPas and 219.0 mPas.

smaller while Oh is larger representing the dominance of viscous effects in the resisting forces. Thus, there is no contact line oscillation in the dynamics, and the droplets react to the actuation slowly and monotonically [45, 51] (Fig. 2.6, lower panel). The former is stood for underdamped behaviours while the latter is called overdamped behaviours [8, 51]. Unfortunately, to achieve overdamped behaviours for droplets actuated in air ones need significantly small droplets that is usually out of the capability of experimental observations [45]. A possible way to observe the overdamped behaviours of water droplets is to immerse the droplets in silicon oil [51].

Droplet viscosity is an important parameter associating with types of materials, therefore, is determined by application requirements. Thus, understanding of the effects of viscosity on the transient dynamics is crucial in improving performance of electrowetting-based devices. It was shown that viscosity of droplets is associated with the dynamical behaviours of droplets, i.e., underdamped and overdamped behaviours [45]. Overdamped behaviours are typically observed for droplets having high viscosity, whereas low viscosity droplets usually have underdamped behaviours (Fig. 2.6). The transition between the underdamped behaviours and the overdamped behaviours has also been captured experimentally by varying viscosity of droplets [45]. More interestingly, for low viscosity, it was shown that the underdamped dynamics can be successfully normalised by the inertial timescale $\tau_i = (\rho R^3 / \sigma)^{1/2}$ representing the dominance of inertia in the resisting forces. However, there is no such timescale to characterise the dynamics of droplets in the overdamped regimes that has been proposed.

It was shown that the transient dynamics of a actuated droplet also depend on the applied voltage. It is observed that increasing the applied voltage changes the behaviours

Figure 2.7: Plot showing a linear relation between the maximum spreading velocity and the electrowetting number. The data are collected for different droplet volumes under electrowetting actuation [45].

of the actuated droplets from overdamped to underdamped regimes [45]. Unfortunately, no mathematical relation between the applied voltage and the dynamical behaviours has been proposed. Another parameter that affects to the transient dynamics of an electrowetting droplet is the viscosity of the surrounding fluids. Playing a same role as the viscosity of droplets, the outer fluid's viscosity was considered facilitating viscous dissipation of the system. Therefore, by immersing droplets that have underdamped behaviours in air into silicon oil, the behaviours of the droplets change to overdamped regime due to the increasing of viscous dissipation [46].

Using oil as the surrounding medium not only reduces the instability of the actuated droplet, but also brings numerous other advantages to applications using electrowetting actuation of droplets. First, the oil can impregnate onto the solid surfaces and reduces contact line stiction as well as substrate's hysteresis [11]. Another advantage of using oil is that, the oil will prevent direct contact of the solid substrates and the liquid droplets [46, 52]. It is essential in some biological applications due to bio-substances containing in the droplets may residue on the solid surfaces in the electrowetting chip and make the chip dirty [11]. Therefore, understanding of the effect of oil viscosity on the transient dynamics of droplets is necessary for electrowetting droplet actuations.

Figure 2.8: (a) Plot of settling time versus electrowetting number for droplets under electrowetting actuation in air [46]. (b) Plot of settling time versus viscosity of silicon oils for droplets under electrowetting actuation in silicon oil [46].

2.2.2.2 Actuation time of electrowetting droplets

In any actuating system, the actuation time, the so-called settling time, defined by the time that the system reaches the new equilibrium after actuated, always attracts attentions. The actuation time of droplets under electrowetting is reported having a close relation to the dynamical regimes, i.e., underdamped or overdamped regimes. It is observed that the fastest way for droplets to react upon an electrowetting actuation is that its dynamics is at the transition between the two regimes [8]. This minimisation of the actuation time had been observed and confirmed in a liquid lens system controlled by electrowetting [8]. However, no mathematical description capturing the minimum of the actuation time has been reported.

The dependencies of the actuation time t_a on EWOD system parameters such as electrowetting number η , droplet radius R , or viscosity of the outer fluid μ_o are also studied. First, it was theoretically shown that the maximum spreading velocity of an actuated droplet depends strongly on the applied voltage [53, 54]. In particular, it is linearly proportional to the electrowetting number regardless of droplet volumes (see Fig. 2.7) [45]. As a result, the actuation time of the droplet decreases with electrowetting number, i.e., $t_a \sim \eta^{-0.6}$ [46] (see Fig. 2.8). The viscosity of the outer fluid also affects to the actuation time that $t_a \sim \mu_o^{0.9}$ was experimentally observed for overdamped droplets immersed in oils under applications of various electrowetting numbers [Fig. 2.8(b)] [46]. Due to the same role of viscosity of the outer fluid and viscosity of the liquid of droplets, the dependence between

Figure 2.9: Plots showing linear relations of settling time versus droplet radius, respectively, reported by (a) Hong et al. [46] and (b) Smith et al. [55].

the actuation time with droplet viscosity is also expected a linear relation. However, no such experimental data is reported. Finally, for the dependence of actuation time on droplet radius, it was shown that, when the transient behaviours of droplets are in the overdamped regimes, $t_a \sim R^{0.9}$ regardless of the electroviscosity number [46, 55] (see Fig. 2.9).

In contrast to the plenty data of actuation time reported for droplets in the overdamped regimes, there is very few observations of actuation time conducted for droplets in the underdamped regimes. It might be due to the non-monotonic behaviours of the contact radius in this regime making it hard to measure the actuation time. A very rare observation relating to the actuation time of underdamped droplets showed that the time for reaching maximum contact radius of droplets under applications of a step voltage is independent from the voltage applied [56]. However, there is not adequate experimental data to support this argument.

2.2.3 Dependence of dynamics of electrowetting droplets on substrate's properties

2.2.3.1 Dependence of steady state of electrowetting droplets on substrate's properties

By introducing the insulating layer to electrowetting, the electrolytic current is eliminated resulting in that the applied voltage can be up to thousands of volts. On the one hand, a high applied voltage can maximise the electrowetting effect represented by high values of the electroviscosity number η . On the other hand, a high applied voltage causes

many technical problems such as electrical breakdown of the insulator, high actuation time and heavy equipment needed. Moreover, for most of applications using droplet manipulation, the voltage requirement needs to be in order of ten volts or lower. Hence, numerous attempts have been made to reduce the applied voltage [57–59].

The key idea of reducing the applied voltage is given in the Young-Lippmann equation (Eq. 2.3). Given that the required electrowetting number η is constant, the voltage applied V is proportional to the interfacial tension σ and the thickness of the insulating layer d . Whereas, it is inversely proportionate to the dielectric constant of the dielectric material ϵ . As a result, to reduce the voltage, ones can either reduce the dielectric layer thickness [60] or use higher dielectric constant materials [61, 62]. Since the thickness of the dielectric layer directly affects to the electrical breakdown voltage of the insulating layer, to choose the dielectric layer thickness, ones need to consider the electrical strength of the dielectric material [60].

Various materials and designs have been proposed to reduce the applied voltage. First, Parylene C thin films were used in many electrowetting experiments [5, 15] due to easy fabricating processes. Depending on the thickness of the films, the voltage can be varied from tens to hundreds of volts. However, due to the limit in the electrical breakdown threshold of Parylen C, about $267 \text{ V}/\mu\text{m}$, the lowest thickness that the films can achieve in EWOD is 800 nm resulting in the lowest applied voltage is 60 V [61]. Silicon dioxide was also tested for electrowetting substrates [60]. Silicon dioxide has higher electrical strength, i.e., $1000 \text{ V}/\mu\text{m}$, compared to Parylen C. As a result, the thickness of the Silicon Dioxide layer can be as thin as 100 nm . With this thickness, this setup can maintain the same change in contact angle with the system using Parylen C films [15] with only 25 V applied voltage. For super low voltage EWOD devices, e.g., lower than 10 V [11], high dielectric constant materials, such as tantalum pentoxide (Ta_2O_5) [62], aluminium oxide (Al_2O_3) [63] or barium strontium titanate (BST) [60] had been tested. It is reported that the voltages vary from 3 V for Al_2O_3 to 15 V for Ta_2O_5 . However, very complicated fabrication procedures for these high dielectric constant materials are required.

2.2.3.2 Dependence of transient dynamics of electrowetting droplets on substrate's properties

Effects of substrate's properties on transient dynamics of electrowetting droplets are presented via contact line friction and contact line pinning [47, 64, 65]. For the effects of substrate's properties on the contact line friction, it was shown that the contact line friction coefficients in short-time dynamics of droplets spreading on solid substrates mostly depend on surface's chemistry of the substrates [42]. Particularly, Carlson et al. [42] investigated the contact line friction coefficients of droplets spreading on three substrates, i.e., Silicon dioxide (SiO_2), Silane and Teflon. He found that the friction coefficients are highest in the Silicon dioxide substrate and lowest in the Teflon substrates (see Fig. 2.5). Taking into account the effects of wettability of the substrates, the contact line friction coefficients reduces with the hydrophobicity of the substrates. However, there is very little knowledge of how the substrate's properties affect to the contact line friction coefficient.

2.2.3.3 Effects of contact line pinning on the dynamics of electrowetting droplets

The ability to generate motion of a sessile droplet initially resting on a solid substrate directly ties to the dynamics of contact line (CL) between the liquid interface and the substrate, among other factors such as viscous dissipation in the bulk fluid and capillarity. For a moving contact line, its motion is resisted by viscous dissipation and pinning of part of the contact line to the substrate. While dissipation at the contact line shares similar viscosity and velocity dependence with that in the bulk flow [28, 41, 42, 51, 66], CL pinning originates from physical or chemical heterogeneity of the substrate. Contact line pinning therefore has little to do with the bulk properties but depends on microscopic characteristics of the substrate. Models considering the relation between contact line pinning and substrate heterogeneity typically describe CL motion as a series of hopping events over defects characterized by energy barrier E_b and typical size γ [47]. Following theoretical developments, experimental studies revealing the relation between CL pinning and microscopic characteristics of the defects start to emerge recently [67–70]. Although it is now possible to incorporate microscopic models of CL pinning to understand macroscopic wetting phenomena, e.g., contact angle hysteresis, a phenomenon in which the apparent receding and advancing contact angles differ from that at equilibrium [71], mechanistic understanding of various wetting phenomena, e.g., adhesion or actuation of droplets on solid

Figure 2.10: Principle of inducing droplet detachment from solid surfaces using electrowetting steady state actuation method [72].

surfaces, are still elusive due to entangled contributions from both the CL pinning and bulk flows [72].

2.3 Vertical actuation of droplets using electrowetting

Detachment of droplets from solid surfaces is also of importance of numerous applications such as anti-icing [73] self-cleaning surfaces [74, 75] or dropwise condensation [76]. Recently, electrowetting is also exploited to induce droplet detachment from solid surfaces which is the core technique in the vertical actuation of droplets for three-dimensional digital microfluidics applications. As briefly introduced in Chapter 1, when the applied voltage is released from an electrowetting-stretched droplet, the surface energy difference will drive the detaching motion of the droplet. In this section, we will review the vertical actuation of droplets using electrowetting in more details. We will consider theoretical and experimental works on different configurations including detaching droplets with and without the top electrode configurations. We also study different methods of detaching droplets using electrowetting effect such as detaching droplets from steady states and maximum deformation methods. We mostly focus on fundamental aspects of those interesting techniques including energy conversion and the role of contact line elasticity in a detaching droplet. We aim to explore the condition for a droplet to detach from a solid surface as well as to study other parameters of interests such as detaching velocity and detaching height.

2.3.1 Detaching droplets with top-electrodes configurations

2.3.1.1 Critical conditions for droplets to detach from solid substrates under electrowetting actuation

Fig. 2.10 shows the principle of detaching droplets from steady state using electrowetting actuation. A small droplet resting on a hydrophobic substrate of an EWOD configuration forms a spherical cap shape with contact angle θ_0 (stage (I)). When a voltage V is applied to the EWOD system, the electrowetting effects spread the droplet to a new equilibrium state having contact angle θ_e (state (II)). Then, the voltage is suddenly released leading in the solid-liquid interfacial tension restores back to its value before applying the voltage. As a result, the microscopic contact angle immediately restores back to θ_0 . However, the apparent contact angle is still θ_e since hydrodynamical motions have not yet occurred (state (III)). This restoration of the solid-liquid interfacial tension increases the surface energy of the droplet, therefore, drives the retraction of the droplet toward a new equilibrium where the surface energy is minimised (stage (IV)). At the end of the retracting stage, the droplet will detach (stage (V)) or not depending on relations between system parameters including driving surface energy, viscous dissipation and contact line elastic energy barrier [72, 77].

Regarding to the condition for a droplet to detach, both numerical [72, 77] and experimental [20, 21] works have been published. One of the methods to determine the detachment condition is based on energy conservation of the actuated droplet. First of all, the free energies of the droplet at every state in Fig. 2.10, i.e., E_I , E_{II} , E_{III} , E_{IV} , E_V , are determined by multiplying the corresponding interfacial tensions with the surface areas at each of the states [72]. The initial state of the detaching process is state (III) (see Fig. 2.10) that the voltage is already released but no hydrodynamical response occurs. The surface energy difference that drives the retracting and detaching motions is calculated by $E_{III} - E_V$, since E_V is the surface energy of a detached droplet. As a result, the condition for an inviscid droplet to detach is $E_{III} - E_V > 0$ [72]. Fig. 2.11 shows the normalised surface energy, $(E_{III} - E_V)/E_V$, versus different values of θ_e and θ_0 , that is considered a general phase diagram for a droplet to detach from an electrowetting substrate [72]. Based on this analysis the authors explained their experimental observation and pointed out the mismatches between the theory and the experimental data (few dots in Fig. 2.11) due to the lack of considering viscous dissipation and contact angle hysteresis of the retracting

Figure 2.11: A general phase diagram of jump and no-jump of droplets under electrowetting actuation [72]. Here, θ_Y and θ_0 are, respectively, θ_0 and θ_e in our notation. Dots represent experimental data. The blue circles are for successful detachments and red crosses are for unsuccessful detachments. The dash line shows the limit $\theta_Y = \theta_0$.

droplets. However, this calculation did not take into account the solid-oil surface when calculating the difference in free energy between the states. For example, in state (V), the surface energy is calculated as $E_V = \sigma 4\pi R^2$, which totally neglect the free energy on the solid surface. However, this solid surface absorbs a certain amount of energy when the droplet retracts from state (III) to state (V). As a result, the condition $E_{III} - E_V > 0$ cannot be used to explain the detaching condition of droplets even for the inviscid case.

Another approach to determine the condition of a detaching droplet for inviscid case was made by Lee et al. [20]. The authors argued that the droplet only can detach when the energy charged to the droplet by electrowetting effect $\eta\sigma$ must be larger than the adhesion work of the droplet on the solid substrate before the voltage is applied (state (I)). This adhesion work can be calculated using Young-Dupre equation [78]: $W_{ah} = \sigma(1 + \cos \theta_0)$. As a result, the condition for an inviscid droplet to detach

$$\eta \geq 1 + \cos \theta_0. \quad (2.4)$$

Eq. 2.4 was reported that is in good agreement with an experimental observation (Fig 2.12) [20]. However, there are few points that this approach did not take into account. First, in this approach, the voltage was released at maximum deformation of droplets, while

Figure 2.12: Plot of the variations in the threshold electrowetting number for droplet to detach with different droplet volume. The dot-dash line represents Eq. 2.4 [20].

the electrical energy $\eta\sigma$ is the energy difference at the droplet steady state. Moreover, the adhesion energy, which is the work done to detaching the droplet, is essentially the difference in surface energies between state (I) and state (V) (see Fig. 2.11). In other words, it is $E_I - E_V$. Thus, based on the approach of Cavalli et al. [72], this energy is actually the energy difference that drives the detaching motion and cannot be considered as the work done of the process.

The contradictory between the two aforementioned approaches represents the gap in the current understanding on the condition for droplets to detach under electrowetting actuation. When viscosity μ of droplets and μ_o of the outer phases are involved, the problem becomes more complicated. In this case, the energy dissipation caused by viscous effects becomes an important factor determining the efficiency of the conversion between surface energy and kinetic energy. Moreover, energy barrier E_b caused by the distortion of contact line due to chemical contamination or roughness of solid substrates may significantly contribute to the energy barrier that the droplets must overcome to detach from the substrates. Till this point, to the best of our knowledge, there is no theoretical or experimental study that proposes an appropriate explanation for the detaching condition of electrowetting actuated droplets. Therefore, it is necessary to investigate the critical condition that is required for a droplet to detach from a solid surface using electrowetting actuation in ambient oils and consider the most important parameters, i.e., viscosity, droplet size and magnitude of the applied voltage altogether.

Figure 2.13: A schematic showing the principle of detaching a droplet using maximum deformation actuation. T is the duration that the voltage is applied to the system to force the droplet to spread to maximum deformation. After that, the voltage V is released to let the droplet to retract freely and detach from the solid substrate.

2.3.1.2 Droplets detachment using maximum deformation electrowetting actuation

Due to the limit of contact angle saturation, the minimum of θ_e in most of electrowetting configurations is about 30° to 60° [32]. Thus, it limits the ability of using electrowetting effect to induce droplet detachment from steady states. One of the effective ways to enlarge the detachable regime is releasing the applied voltage when the droplet reaches its maximum deformation [20, 22, 79, 80]. Fig. 2.13 shows the principle of this method. After a voltage is applied, the resting droplet is spreading on the solid substrates. When the droplet reaches its maximum deformation, the voltage is release letting the droplet to retract. The surface energy difference that drives the detaching motion of the droplet is enhanced by the additional deformation of the droplet. As a result, the detachment is facilitated. It is worth to note that this method is only efficient for actuating droplets in the underdamped regime when overshoots of the droplet deformation occur. If the droplets are in overdamped regimes, the maximum deformation states are also the steady states. From now on, we presume that we only apply this method to droplets in underdamped regimes.

One important point in this technique is the time for an actuated droplet to reach

Figure 2.14: Snapshots showing a demonstration of detaching a droplet by maximum deformation actuation using electrowetting effect [20]. The applied voltage is 135 V. The water droplet volume is 5 μL . The actuating duration $T = 7$ ms.

its maximum deformation denoted by τ_p . It was reported that τ_p is directly related to the natural frequency of oscillating droplets [21]. One way to find the natural frequencies of a droplet is using the analysis of shape oscillation theory in AC electrowetting [81]:

$$\omega_0 = \frac{1}{2\pi} \left(\frac{n(n-1)(n+2)\sigma}{\rho R^3} \right)^{1/2}, \quad (2.5)$$

where n is the oscillation mode [81]; ρ is the density of the droplet. For droplet detaching from solid substrates, usually, $n = 2$ [20]. We can see that this expression of ω_0 is actually very similar to the inertial frequency of droplets bouncing on solid surfaces [82], excepting that it includes the shape mode number n . It is noted that, in the shape oscillation theory, $n = 2$ is corresponding to P_2 oscillation mode [81]. Follow this theory, Lee et al. had successfully applied a voltage V with period $\tau_p = 1/\omega_0$ to detach water droplets in air [20]. The calculated applied period for 5 μL water droplets to force them to reach maximum deformation is $\tau_p = 7$ ms (Fig. 2.14). More interestingly, the authors also varied the apply duration T in the range from $0.5\tau_p$ to $1.5\tau_p$ and observed that the required electrowetting number is lowest at $T = \tau_p$. Either increasing or decreasing the pulse width T makes the required electrowetting number rise. Moreover, it was shown that by using the double pulses, the required electrowetting number for droplets to detach is lower compared to the case of using single pulse voltage [20].

Figure 2.15: (a) Plot of dimensionless jumping height versus applied voltage for detached droplets under maximum deformation actuation [20]. Here, the dimensionless jumping height is defined by the ratio of the distance between the substrate and the centre of mass of the droplets to the droplet radius R . (b) Plot of maximum dimensionless height versus droplet volume for detached droplets under maximum deformation actuation [22]. The maximum dimensionless height is defined by the ratio of the maximum apex height of the detached droplets to the droplet diameter.

2.3.1.3 Droplets detachment using oversaturation electrowetting

Contact angle saturation is an interesting phenomenon of electrowetting and attracted many attentions [5, 29, 31, 83]. Unfortunately, due to the complication of this problem, there is yet a widely accepted model for contact angle saturation in electrowetting. As a result, in all electrowetting related studies, particularly, in detachment of droplets by electrowetting, the applied voltage is always limited under the saturation voltage. Therefore, how an over-saturation voltage affects to the transient behaviours of droplets and subsequently influences on its detachment is still unknown. We will also have a study regarding to this interesting problem in this thesis.

2.3.1.4 Jumping height of detached droplets using electrowetting actuation

The kinetic energy of a droplet after detaching from an EWOD substrate is an important parameter in applications. This kinetic energy is represented by the detaching velocity and is eventually converted to the jumping height of the droplet. As a result, in order to quantitatively characterise the detaching behaviours, most of the works consider

Figure 2.16: Plot of dimensionless jumping height versus applied voltage for detached droplets by maximum deformation actuation (red circles) and steady state actuation (blue triangles) [79]. The dimensionless jumping height is defined by the ratio of the distance between substrate and the centre of mass of the droplets to the droplets radius. Here, red circles are data for droplets in n-decane oil detaching from maximum deformation, while blue triangles denote data for droplets in n-decane oil detaching from steady state. The green squares are for droplets detaching from maximum deformation actuation in air.

the maximum jumping heights of droplets defined either by apex heights [22] or by the heights of centre of mass [20, 79] of the detached droplets.

The relations between the jumping height of a droplet and the applied voltage as well as the droplet radius are investigated by recent works [20, 22, 79]. It was reported that the jumping height mostly linearly increase with the voltage applied [20, 22] (Fig. 2.15(a)). Besides, dimensionless jumping height define by the ratio of the apex height to the droplet diameter is independent from the droplet volume [22] (Fig. 2.15(b)). This can be postulated to a quadrature dependence between the jumping height and the droplet's radius. It was also shown that maximum deformation actuation gives higher jumping height compared to that of steady state actuation (Fig. 2.16) [79].

Unfortunately, none of the presented works proposes a validated theoretical description for the dependencies of the jumping height or the detaching velocity on the system's parameters. In addition, by using the jumping height as a quantitative parameter to represent the kinetic energy of the detached droplets, a consideration on the outer phase's properties is needed. Instead, the detaching velocity which is calculated when the droplets

Figure 2.17: Demonstration of droplets detaching with different EWOD configurations: (a) with top-needle electrode; (b) with bottom-needle electrode; (c) with integrated electrodes [80].

detach from the substrate is a more appropriate parameter to describe the kinetic energy of the detached droplets. In this thesis, we will use detaching velocity as the characteristic parameter to quantitatively describe detachment process.

2.3.2 Detaching droplets with top-electrode-free configurations

An EWOD configuration with a top-electrode, e.g., a conductive needle dipping into the droplet (Fig. 2.1), cannot be used for microfluidics chips. Therefore, it is required another configuration for vertically actuating of droplets without the top electrode in order to make the method become feasible for applications. The first attempt of using a top-electrode-free EWOD configuration for vertically detaching droplets had been made by Lee et al. [80]. Fig. 2.17 shows three different configurations that Lee et al. used to detach droplets. In Fig. 2.17(c), the top electrode is removed, and the voltage is now applied to two buried electrodes underneath the dielectric layer. Further investigation on the buried-electrode configuration was made by Lee et al. [20]. In this work, it was observed that the detaching voltages in the buried-electrode configurations, or the so-called integrated-electrode configurations, are typically higher than that in the top-electrode configurations.

Figure 2.18: (a) Left figure: Schematic of the experimental chamber for mixing applications using vertical manipulation of droplets by electrowetting effect. (a) Right figure: the design of the with integrated electrodes. (b) Snapshots showing the mixing process of two water droplets in oil [22].

Moreover, small droplets are ejected during the detaching processes letting some residue materials on the solid surface [20]. Although, this method later was successfully applied to droplet-based mixing applications [22] and enable 3D-DMF [22] (Fig. 2.18), there are still many remaining problems need to be solved in order to improve and optimise this method for 3D-DMF. They include the conditions for droplets to detach in this configuration, or how to reduce the applied voltage and small droplets ejection during the detaching process.

2.4 Fundamentals of dielectrowetting and its applications

An alternative way of using electrowetting for assisting liquid spreading and super-spreading on solid substrates in top-electrode-free EWOD configurations is using dielectrowetting effects. In this section, we first look at the fundamental aspects of dielectrowetting phenomenon.

The fundamental difference between electrowetting and dielectrowetting is that in electrowetting, the electric field is spatial uniform, while in dielectrowetting the electric field is non-uniform both in space and time. For two charges of a dipole placed in a uniform electric field, the forces of the electric field acting on the two charges balance each other

Figure 2.19: Schematic of a typical setup of dielectrowetting experiments.

resulting in the net force vanishes. When the electric field is non-uniform, dielectrophoretic forces occur making the net force applying on the dipole non-zero. Given a droplet of dielectric liquid resting on a substrate with a non-uniform electric field create by an array of electrode beneath the substrate, the non-zero dielectrophoretic acting on liquid volume close to the contact line pulls the contact line out resulting in spreading of the droplet on the substrate. This phenomenon is termed as dielectrowetting, which is a combination between dielectrophoresis and electrowetting. The uses of dielectrowetting effects have also been reported in various applications such as variable focus lens [84] or microlen arrays [85], however, at that time, the theoretical relationship between the spreading of the droplets, usually represented by contact angles, and the strength of the electric field, represented by the applied voltage to the electrodes, had not been understood.

The relation between contact angles and applied voltage in dielectrowetting is discovered recently [86, 87]. To understand the physic of this phenomenon, we first consider a system that includes a uniform layer of dielectric liquid with a depth h on a solid surface and an electrical potential decaying with a depth of penetration of the electric field into the liquid. The electrical potential at a distance z above the solid surface is expressed by $V(z) = V_0 e^{-2z/\delta}$, where δ is the penetration depth; V_0 is the electric potential at the solid surface where $z = 0$. Electrostatic energy per unit area stored in the dielectric liquid layer is [86]

$$w_e = -\frac{\epsilon_0 \epsilon_l V_0^2}{2\delta} [e^{-4h/\delta} - 1] \quad (2.6)$$

given by integrating the dielectric energy density, $1/2\epsilon_0\epsilon_1 E \cdot E$, over the volume of the liquid layer [86]. Here, ϵ_1 is the dielectric constant of the dielectric liquid and $E = -\nabla V$ is the electric field. For $h \gg \delta$, the electrostatic energy w_e can be approximated to $w_e = \epsilon_0\epsilon_1 V_0^2/2\delta$. In the case of liquid droplets on solid surfaces, w_e is the equivalent energy change in the solid-liquid interface by the effect of the non-uniform electric field. This can be compared to the term $\epsilon\epsilon_0 V^2/2d$ (Eq. 2.1) in the case of electrowetting. By taking a same analysis as being done in the case of electrowetting, ones can come up with the relation between the applied voltage and the reduction in contact angle in dielectrowetting phenomenon:

$$\cos \theta_e - \cos \theta_0 = \frac{\epsilon_0(\epsilon_1 - 1)V_0^2}{2\sigma\delta}. \quad (2.7)$$

In the case of using an AC voltage, the amplitude of the electrical potential at the solid surface, V_0 , can be approximated to the peak voltage of the AC voltage V_p , i.e., $V_0 \sim V_p$.

In facts, Eq. 2.7 is a modification of the Young-Lippmann Equation (Eq. 2.3) applied for the case of a dielectric liquid droplet in a non-uniform electric field. The properties of dielectric layer, i.e., d and ϵ in Eq. 2.3, are now replaced by the equivalent properties of the dielectric liquid, i.e., δ and ϵ_1 in Eq. 2.7. More interestingly, while the dielectric constant ϵ_1 is a property of the liquid, the penetration depth, δ depends on the configuration of the setup. As a result, to calculate δ , ones need to consider the geometry of the electrodes and the characteristics of the electrical potential. Fig. 2.19 shows a typical dielectrowetting substrates. The width of each electrode and the gap between the electrodes are Φ . Giving an AC voltage applied to the electrodes, the electrical period is 4Φ (Fig. 2.19) resulting in a wave number $\kappa = 2\pi/4\Phi = \pi/2\Phi$. The penetration depth $\delta = 4\Phi/\pi$ can be resulted from the solution of Poisson's equation for the potential in a semi-infinite dielectric liquid which is of the form $-\cos(kx) \times e^{-kz}$. From this solution, ones can see that because the field is across the electrodes, the dielectrophoretic forces is applied along the electrodes. This results in the liquid will spread in the longitudinal direction as in Fig. 2.20(a). In Fig. 2.20(b), the dependence of the contact angle on the applied voltage is shown. The curve of increasing voltage is a little different with that of decreasing voltage. It is due to the contact angle hysteresis of the substrate [86]. Interestingly, there is no contact angle saturation observed in dielectrowetting actuation [87].

In practices, to avoid electrolytic currents through the electrodes, an insulating layer is also introduced [27, 86]. With the presence of this insulating layer, usually in order of micrometers of thickness, the penetration depth of the field into the dielectric liquid

Figure 2.20: (a) Snapshots showing the spreading of droplets by dielectrowetting effect viewed from the top (left figure) and from side (right figure) [86]. The liquid is 1, 2-propylene glycol. The dielectrowetting substrate is a glass wafer with interdigital electrodes on top. The width of each electrode and the gaps between two adjacent electrodes are all $80\ \mu\text{m}$. The applied voltage is a 10 kHz sinusoidal voltage with peak-to-peak amplitude varied in the range 0 V to 312 V. The arrows show direction of increasing or decreasing the applied voltage. (b) Plot of the contact angle versus voltage for the dielectrowetting experiment. Solid symbols indicate the increasing voltage data; open symbols indicate the decreasing voltage data [86]. Inset: plot of the contact angle versus the square of the voltage.

reduces accordingly to the dielectric constant of the insulator. Therefore, a compensating coefficient is introduced [86]:

$$m_e = \frac{(1 + \Delta\epsilon)e^{-2d/\delta}}{1 + \Delta\epsilon e^{-4d/\delta}}, \quad (2.8)$$

where d is the thickness of the insulating layer; $\Delta\epsilon = (\epsilon - \epsilon_1)/(\epsilon + \epsilon_1)$. As a result, the final relation between contact angles and the AC applied voltage in dielectrowetting in the presence of the insulating layer is

$$\cos \theta_e - \cos \theta_0 = m_e \frac{\epsilon_0(\epsilon_1 - 1)V_p^2}{2\sigma\delta}. \quad (2.9)$$

This modification is proven valid for different insulating layer thicknesses [86] opening a feasibility to applied dielectrowetting phenomenon into applications such as dynamically

Figure 2.21: (A-F) Snapshots showing the dewetting of a liquid droplet on a solid substrate. The droplet is spread to a liquid film using dielectrowetting effect. When the voltage is released, the droplet retracts freely. (G) Schematic of the contact radius versus time of the dewetting droplet. (H) Schematic of the dynamic contact angle versus time of the dewetting droplet. All the figures here are reproduced from the work of Edwards et al. [88]

controlling droplets spreading [87] and retracting [88] (Fig. 2.21). More recently, dielectrowetting has been successfully applied into various applications such as microfluidics optical shutters [89] or manipulating droplets in horizontal surfaces [90] (Fig. 2.22). So far, no study about droplets detaching or jumping taking advantages of the dielectrowetting effects has been reported.

In short, enormous efforts have been devoted in investigating contact line dynamics of droplets under electrowetting and dielectrowetting actuation in the recent years. Nonetheless, big gaps still stand between our understanding and the nature of the problem. The diverse theories and experimental data of the dependence of the contact line friction coefficients on liquid viscosity, outer phase viscosity and substrate properties reveal the controversial nature of the current understanding on the contact line friction. In the transient dynamics of electrowetting droplets, there is very little knowledge about a characteristic timescales that can describe the dynamic. There is also very few experimental data reported for the actuation time of droplets. For the transition between the two

Figure 2.22: Snapshots showing different manipulation of droplets using dielectrowetting effect including splitting (from (a) to (c)) and transporting (from (d) to (g)) [90]. The blue arrow shows the time sequence. Scale bar is 2 mm.

dynamical behaviours, there is no mathematical expression determining the condition of system parameters for the transition to occur. And, how the transient dynamics affects to the actuation time of droplets is still an open question. For the droplet detachment using electrowetting effect, an appropriate explanation for the detaching condition is still elusive. These gaps are the motivations of our work in experiments on the contact line dynamics of electrowetting droplets.

Chapter 3

Methods and materials

In this chapter, we will describe in detail our experimental setup used in the study. We first introduce the set of experiments on transient dynamics of electrowetting droplets serving as our fundamental understanding of dynamics of electrowetting phenomenon. We then show experimental procedures and methods on vertical actuation of droplets. We also show the experimental setup of the study on the spreading and retracting dynamics of droplets upon impact on dielectrowetting substrates. Finally, the characterisation of materials used in the study is presented.

3.1 Experimental methods

3.1.1 Experiments on transient dynamics electrowetting droplets

In this set of experiments, we aim to reveal the dependence of the actuation dynamics on various system parameters including hydrodynamical properties, e.g., droplets' radius, viscosity of liquid of droplets, viscosity of outer liquid, and electrical properties, e.g., applied voltage, electrical conductivity of droplets. We also study the dependence of droplet behaviours actuated by electrowetting on substrate's properties. We take all these variables as our control parameters. In order to characterise the dynamics, we will instantaneously examine the spreading radius r and the contact angle θ of the droplet. In some of our experiments, centre of mass of the actuated droplets is also investigated.

In the setup illustrated in the Fig. 3.1, the electrowetting substrate is made of an indium tin oxide (ITO) glass slide covered by a fluoropolymer layer (Teflon AF-1600, DuPont) with thickness $d = 2.5 \mu\text{m}$. The Teflon layer which is fabricated by spin coating technique acts as a hydrophobic coating and an insulator. The thickness of the Teflon layer is measured by a surface profiler. The substrate is placed in a closed experimental

Figure 3.1: (a) Schematic of experimental setup of the electrowetting experiments. (b) Experimental chamber.

chamber filled by a fluid which is immiscible with the droplet. In most of our experiments, the filled fluid, the so-called outer fluid, is silicone oil. In order to maintain consistent experimental conditions, we fix the temperature of the outer fluid at $20 \pm 0.5^\circ\text{C}$ by using a temperature controller. The contact angle of an aqueous droplet on the substrate is about 120 degrees measured in air. In the case droplets immersed in oil, the solid surface become super-hydrophobic that the contact angle is close to 180 degrees. The oil also prevents evaporation of droplets during the experiments.

Droplets are deposited on the electrowetting substrate using a micro-needle. The radius of the droplets is controlled precisely using a high-resolution camera with a fixed-magnification lens. In order to spread the droplets by electrowetting effect, we immerse a $18\text{ }\mu\text{m}$ diameter tungsten wire into the bulk of the droplets. The wire is then connected to the positive terminal of a control box including an externally-controlled solid-state-relay (SSR) to close or open the circuit. The negative output terminal of the control box is connected to the ITO layer acting as a ground electrode. We connect input terminals of the control box to corresponding terminals of a fine-voltage-profile DC power supply. The SSR inside the control box is directly controlled by a signal generated from a function generator (Fig. 3.1). By using the SSR to close or open the circuit momentarily, we generate an electrical pulse in the form of a step function between the wire and the ITO layer. We monitor the actual voltage that applied to the droplets by using an oscilloscope connected to two terminals of the experimental chamber, i.e., the needle and the ITO layer. In all our experiments, the actual applied voltage is well defined.

To capture the transient deformation of the actuated droplets, we use a high-speed camera (SAX2, Photron) running at 5000 frames per second (Fig. 3.1). The magnification of our lens system gives four microns-per-pixel for the spatial resolution of the recorded images. We observe that the droplets react almost immediately after the circuit is closed or opened, suggesting that the time for the system to be electrically charged or discharged is negligible compared to its hydrodynamical response time [11, 91]. The data collected from the camera are then sent to a computer for storage and post-processing after each run of the experiments. The recorded images are then processed by using MATLAB image processing toolbox to extract desired parameters. The signal generated from the function generator is also used to trigger the high-speed camera to capture the deformation of the droplets and to synchronise with the voltage application. We note that in this study, we carry out all our experiments with voltage lower than contact angle saturation voltage [5].

3.1.2 Experiments on vertical actuation of droplets using electrowetting

This set of experiments typically includes two main experiments: detaching droplets from steady state experiment and detaching droplets from maximum deformation experiment. All these experiments are conducted using the setup described in Fig. 3.1. The duration of the voltage application is tailored particularly for different system parameters. We vary three main control parameters, i.e., droplets' radius, droplets' viscosity and the

applied voltage in these experiments. We characterise droplets' behaviours as detachable and non-detachable and determine the condition for droplets to change from one behaviour to another. We also examine some dynamical aspects of the detached droplets such as jumping height and initial detaching velocity.

In Fig. 2.10, we demonstrate the procedure to detach a droplet from steady state using electrowetting. We first apply a voltage to the tungsten wire dipping into the bulk of the droplet by closing a solid-state relay (SSR) in the control box to force the droplet spread. We keep the voltage applied to the system long enough, i.e., typically from 50 ms to 100 ms depending on viscosity of the droplet. This is to make sure that the droplet reaches its equilibrium. Then, we release the voltage by suddenly opening the SSR to let the droplet freely retract. We slowly increase the applied voltage V to decrease the contact angle θ_e to the point that the droplet can detach from the substrate (see Fig. 2.10). The amplitude of the applied voltage is varied in the range $60 \text{ V} \leq V \leq 120 \text{ V}$. We note that all of our experiments of droplet detachment are carried out without contact angle saturation [5], which occurs at $V = 120 \text{ V}$ in our experimental configuration.

In the experiment for detaching droplets by maximum deformation (Fig. 2.13), we release the voltage when the droplets reach its maximum deformation. This experiment is only done for droplets having underdamped behaviours, because this method is only efficient for behaviours that have overshoots in droplets' deformation. For those without maximum deformation, e.g., droplets with monotonic behaviours, we release the voltage immediately when the droplets reach its steady states. The duration of voltage application for droplets to reach maximum deformation are experimentally measured in the transient dynamics experiment. The amplitude of the applied voltage is varied in the range $60 \text{ V} \leq V \leq 140 \text{ V}$. We also examine behaviours of actuated droplets for over-saturation voltage.

3.1.3 Particle image velocimetry (PIV) experiment

As a part of our analysis on the energy conversion of a spreading and retracting droplet, we conduct a particle image velocimetry (PIV) experiment to investigate internal flows of a spreading and retracting droplet. From these data we can able to calculate kinetic energy and viscous dissipation of different regions inside the droplet. These data will be served as additional information for our analysis on the energy conversion of a spreading and retracting droplet.

Figure 3.2: Experimental setup of droplet impact on dielectrowetting substrates experiments.

In order to observe inside a droplet immersing in oil, we have to use a liquid that has a same refracted index with the oil. To do that, we use 41.5%wt glycerol-water mixture having its refracted index $n = 1.39$ which is very similar to the refracted index of silicone oil 2 cSt (a Clearco's product). We then mix polyethylene (PE) particles having characteristic diameters $1\ \mu\text{m}$ with a very dilute concentration to the glycerol solution. The particles will appear as black dots in the recorded images while liquid droplets and outer phase appear as the white background due to the similarity in their refracted indexes. To capture the images, we use the same high-speed camera that is used in the previous experiments but with a lens having higher magnification that creates two microns-per-pixel spatial resolution to see small particles. The image is then processed using PIVlab MATLAB package that has been proven its appropriation in processing research PIV data [92].

Figure 3.3: Schematic of the dielectrowetting substrate and the internal electrodes.

3.1.4 Experiments on behaviours of droplets on dielectrowetting substrates

The aim of this experiment is to investigate the dynamics of droplets spreading and retracting on dielectrowetting substrates. We focus on behaviours of droplets upon impact on solid surface under dielectrowetting effects caused by an application of an AC voltage to an electrode array manufactured beneath the substrate.

Fig. 3.2 illustrates the schematic of our experimental setup of the droplets spreading and retracting on dielectrowetting substrate experiment. A needle is connected to a syringe pump and placed at 25 cm above the experimental substrate. The substrate is connected to two output terminals of a high voltage amplifier which can amplify 100x the input voltage. The input voltage is a sine wave signal having frequency 10 kHz generated from a sine wave generator. The output voltage of the generator can be varied up to 6 V peak-to-peak which can be amplified up to 600 Volts peak-to-peak to apply to the substrate.

To observe the spreading and retracting processes, we use two high-speed cameras, (SA5 and SAX, Photron) placed at the two sides of the substrate. One of them captures the deformation on the longitudinal direction D_L , which is the same direction with the electrodes. The other one observes the deformation in the transverse direction D_T which is perpendicular to the electrodes (see Fig. 3.3). A function generator is used to synchronize the two high-speed cameras and the application of the high voltage into the substrate (Fig. 3.2). Both high-speed cameras are run at 5000 frames-per-second with 5X magnification of the lens systems giving spatial resolutions of the recorded images of 4 microns-per-pixel.

Fig. 3.3 illustrates the schematic of our experimental substrate. We deposit gold electrodes on glass wafers using gold sputtering technique on the glass wafers that is photolithographed. The width of each electrode and the gap between the electrodes are $\Phi = 50\text{ }\mu\text{m}$ (see Fig. 3.3). We then cover the substrate with a Silicon nitride (Si_3N_4) layer. The thickness of the Silicon nitride layer is $d = 500\text{ nm}$ deposited on the substrate using plasma-enhanced chemical vapor deposition (PECVD) technique. On top of the Silicon nitride layer, we spin coat a 50 nm fluoropolymer layer [60] to make the substrate become hydrophobic, i.e., contact angles of glycerol-water droplets in the case of without applied voltage is as high as $\theta_0 \approx 110^\circ$.

3.2 Image processing and data analysis

In most of our experiment results, we deal with images taken by high-speed cameras. Thus, we develop MATLAB scripts based on the MATLAB image processing toolbox to analyse the recorded images and extract desired parameters. The extracted parameters are usually contact line radius r , dynamic contact angle $\theta(t)$, and centre of mass of droplets. Fig. 3.4 shows typical steps of the image processing and analysis for the transient dynamics experiments. From the original image as shown Fig. 3.4(a), we remove the image's background. Then, we convert the image to a binary image. We also remove small objects appearing in the image due to dusts in the optical system. We calculate the centre of mass of the droplet from the final image (Fig. 3.4(b)), assuming that the liquid is homogeneous in density. The contact radius and contact angle measurements are shown in Fig. 3.4(c). From the binary image in Fig. 3.4(b), a thin region of the image near the contact line is extracted to calculate the dynamic contact angle. The left and right boundaries of the white part of the new image are found using MATLAB 'edge' function. The orientations of these boundaries respecting to the horizontal direction represent the dynamic contact angles. To find those orientations, we use the function MATLAB 'regionprops' with the 'Orientation' property. By doing that, we calculate both left contact angle and right contact angle. The dynamic contact angle $\theta(t)$ used for other analyses is an average of these left and right contact angles.

Figure 3.4: (a) A typical original image of a droplet spreading by electrowetting actuation. (b) The image after processed. The blue square indicates the centre of mass of the droplet. (c) A snapshot showing the calculating of contact diameter and contact angles. We calculate both left contact angle and right contact angle. The dynamic contact angle $\theta(t)$ is an average of these contact angles.

3.3 Materials

3.3.1 Working liquids for generating droplets

In our experiments, we use aqueous glycerol solutions consisting of glycerol, DI water, and 0.125 Molar sodium chloride as working liquids for generating droplets. In order to achieve different viscosity of droplets, we vary the concentration of glycerol in the solutions. The range of glycerol concentration is from 0 % to 95 %. Due to the importance of liquid properties, we characterise the properties of the working liquid by measuring liquid's electrical conductivity, viscosity, density and interfacial tensions of liquid droplets in different types of silicone oils (see Table. 3.1). To measure viscosity of liquid, we use a rheometer (TA DHR-2) which is using the rotating disk method. By adjusting the glycerol concentrations, the viscosity μ of the solutions is varied from 1.0 mPas to 615.0 mPas (Table. 3.1). The electrical conductivity of the solutions of DI water and 0.125 Molar sodium chloride is ≈ 8.8 EC measuring by using an electrical conductivity meter. All the properties of the liquids that are used to generate droplets are given in Table. 3.1.

To study the effect of outer phase, we use silicone oils with different viscosity μ_o varying in the range $1.75 \text{ mPas} \leq \mu_o \leq 98.9.0 \text{ mPas}$. We then measure the interfacial tensions of the glycerol solutions in air and in different silicone oils using the pendant

Table 3.1: Measured values of viscosity μ , density ρ , and the interfacial tensions σ of the glycerol solutions. Here, $\sigma_{(2\text{ cSt})}$ and $\sigma_{(5\text{ cSt})}$, respectively, denote the interfacial tensions of the solutions in 2 cSt and 5 cSt silicone oils.

%wt glycerol	μ (mPas)	ρ (kg.m ⁻³)	$\sigma_{(5\text{ cSt})}$ (mN.m ⁻¹)	$\sigma_{(2\text{ cSt})}$ (mN.m ⁻¹)	$\sigma_{(\text{air})}$ (mN.m ⁻¹)
0	1.0	1000	35.7 ± 0.2	37.2 ± 0.5	72.18 ± 0.5
20	2.2	1053	33.5 ± 0.2	32.4 ± 1.0	71.8 ± 2.3
41	4.8	1106	31.6 ± 0.2	30.4 ± 0.9	67.3 ± 0.2
55	8.2	1141	30.8 ± 0.1	29.7 ± 0.5	66.9 ± 0.2
67	17.6	1174	26.9 ± 0.2	26.9 ± 0.4	66.8 ± 0.3
74	32.7	1192	27.4 ± 0.1	25.9 ± 0.5	64.1 ± 0.4
80	68.7	1210	26.3 ± 0.3	26.8 ± 0.1	65.3 ± 0.3
86	136.0	1228	25.6 ± 0.2	24.9 ± 0.5	64.2 ± 0.3
91	258.8	1244	25.2 ± 0.1	26.0 ± 0.3	62.2 ± 0.2
95	615.0	1281	28.2 ± 0.2	27.5 ± 0.3	63.6 ± 0.2

drops method (Fig. 3.5). As illustrated in Fig. 3.5, the interfacial tension that attaches the droplet to the needle is balance with the gravity. Based on this force balance, we can measure the interfacial tension of the droplet by measuring maximum mass of the droplet when it still attaches to the needle. To do that, we measure droplets volume using image processing and then multiply by the relative density, i.e., the density difference between the liquid and the outer phase. The surface tensions of the glycerol solutions and their interfacial tensions in 2 cSt and 5 cSt silicone oils are given in Table. 3.1. We observe that changing the concentrations of glycerol in the explored range has a minute effect on the interfacial tension σ between the working liquids and the oils, i.e., σ only varies in a narrow range from 35.7 mNm^{-1} to 25.2 mNm^{-1} when the concentrations of glycerol increase from 0 % to 95 %, or equivalently μ increases from 1 mPas to 615.0 mPas and μ_o is fixed (Table. 3.1).

As described previously, in transient dynamics of electrowetting droplets experiments, we also vary electrical conductivity (EC) of the liquid droplets. To do so, we change the concentrations of sodium chloride (NaCl) in deionized water as 0.065 M, 0.0125 M,

Figure 3.5: A snapshot showing the principle of the pendant drops method that is used to measure interfacial tensions of a droplet and outer fluid. The interfacial tensions that attaches the droplets to the needle is balance with gravity. Based on the force balance between the interfacial tension and the gravity, the interfacial tensions are measured. To do that, we measure droplets volume using image processing and then multiply by the relative density, i.e., density of liquid minus density of the outer phase.

0.25 M, and 0.5 M. We measure the electrical conductivity using an EC meter. The measured values of EC of liquids are 0.43 S/m, 0.88 S/m, 1.5 S/m, and 3.02 S/m, respectively, to the increasing concentrations of sodium chloride in the solutions.

3.3.2 Substrates in electrowetting experiments

We characterise various substrates with different materials and thicknesses of the dielectric layer in this study. As illustrated in Fig. 3.6(a), the substrates are made of indium

Table 3.2: Designs and fabrication of substrates in the experiments.

Samples	Dielectric layer	ϵ	Fabrication	Hydrophobic Layer
Teflon	Teflon, 2.5 μm	1.93	Spin coating	Teflon
SU-8	SU-8 2000, 2.0 μm	4.1	Spin coating	Teflon, 50 nm
SN	Silicon nitride, 100 nm	7.5	PE-CVD	Teflon, 50 nm

Figure 3.6: (a) Design of substrates for electrowetting experiments. (b) A SEM image of the substrate's surface.

tin oxide (ITO) glass slides covered by a dielectric layer of either fluoropolymer (Teflon AF-1600, DuPont), SU-8 2000 class or Silicon nitride (SN). To fabricate these substrates, we use different manufacturing techniques listed in Table. 3.2. On top of the dielectric layer, we spin coat a 50 nm fluoropolymer layer [60]. This Teflon layer acts as a hydrophobic coating that bring contact angles of small water droplets to about 120° in air or close to 180° in oil. Other properties of the substrates are given in Table. 3.2. Fig. 3.6(b) shows a typical scanning electron microscope (SEM) image of the surfaces of the substrates. The surfaces are observed smooth with typical roughness 10 nm. This is a typical roughness for Teflon surfaces manufactured by spin coating technique [93, 94]. Thus, we can ignore the effect of surface roughness in our analyses.

Chapter 4

Contact line friction of electrowetting droplets *

We examine the contact line friction coefficient of viscous droplets spreading and retracting on solid surfaces immersed in ambient oil. By using the electrowetting effect, we generate a surface tension imbalance to drive the spreading and the retracting motion of the three-phase contact line (TCL). We show that neither the driving force intensity nor TCL direction significantly influences the friction coefficient. Instead, the friction coefficient depends equivalently on the viscosity of liquid droplets and the surrounding oil. We derive and experimentally verify a transient timescale that can be used to characterise both the spreading and retracting dynamics.

4.1 Introduction

When a liquid droplet comes into contact with a solid substrate, its spreading motion is driven by an imbalance in interfacial tensions at the three-phase contact line and opposed by both friction at the contact line and liquid inertia. Contact line motion is found not only in natural spreading or retracting of liquid [40], but also in other capillary-related phenomena such as evaporation, Marangoni-driven flows, and electrowetting [3, 5, 6, 25]. Contact line motion also plays a central role in numerous technological and industrial applications ranging from digital microfluidics [95], dip coating, oil extraction to pesticides deposition [3]. A physical understanding of contact line dynamics is therefore of both fundamental and practical interests.

The contact line dynamics of a droplet spreading on a solid substrate are typically

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categorised into two main regimes. In the so-called underdamped regime, liquid inertia dominantly resists the contact line motion, resulting in apparent oscillations at the droplet surface [45, 51, 96], whereas in the so-called overdamped regime, the viscous effect becomes dominant causing the droplet to spread or retract gradually to its equilibrium state [28, 47, 51, 97, 98]. In particular, contact line friction mostly dissipates excessive interfacial energy in the overdamped regime [42, 99, 100].

In this chapter, we investigate the contact line motion of aqueous droplets on a solid surface. We focus on the case in which the contact line motion is solely caused by interfacial tension imbalance, while excluding the Marangoni and evaporation effects by immersing the tested droplet and surface in an oil pool. We use the electrowetting effect to induce the contact line motion of droplets. By applying a potential difference between a droplet and the surface we generate an interfacial tension imbalance at the contact line, causing the droplet to spread to a new equilibrium state (Fig. 4.1a). Once the droplet is in the new equilibrium state, removing the potential difference restores the surface energy to the original state, thus imposing a surface tension imbalance in the opposite direction and drives the droplet to retract (Fig. 4.1b). We then investigate the contact line friction and its role in the transient dynamics in both the spreading and retracting stages. By considering this system in a parameter space of viscosities μ , μ_o , and driving force intensity set by the applied voltage, we aim to achieve a unified description of the dependence of λ on both μ and μ_o at the high viscosity limit.

4.2 Materials and methods

In our experiments, we use aqueous glycerol solutions consisting of glycerol, DI water, and 0.125 M sodium chloride as the working fluids to generate droplets. By adjusting the glycerol concentration, we vary the viscosity μ of the solutions from 8.2 mPas to 615.0 mPas. The exact concentrations and corresponding physical properties are given in Table. 3.1. We use silicone oils with viscosity in the range $1.8 \text{ mPas} \leq \mu_o \leq 970.0 \text{ mPas}$ as the surrounding fluids. The temperature of the oil pool is kept at $20 \pm 0.5^\circ\text{C}$ to maintain consistent experimental conditions. We note that varying glycerol concentration has a minute effect on the interfacial tension σ between the working fluids and the surrounding oils [46]; we experimentally measured σ and verified that it varied in a narrow range, from 30.8 mNm^{-1} to 24.9 mNm^{-1} , for glycerol concentration varying from 55 % to 95 % (Table. 3.1).

Figure 4.1: (a) When a potential difference between a droplet and a substrate is applied, the droplet spreads from an initial state with contact angle θ_0 to a new equilibrium state with contact angle θ_e . At any transient state with contact angle θ_t , the driving force per unit length at the contact line is calculated as $F = \sigma(\cos\theta_e - \cos\theta_t)$. The positive direction of the contact line motion is indicated by the $\oplus$ sign. (b) When the voltage is released, the droplet retracts freely and the contact angle changes from θ_e to θ_0 , assuming sufficiently small hysteresis. The driving force is now $F = \sigma(\cos\theta_0 - \cos\theta_t)$. (c) Typical plots of the contact radius r versus time t (left axis) and contact angle θ_t versus time t (right axis) for a droplet of initial radius $R = 0.5$ mm when a voltage $V = 100$ V is applied for 50 ms and then released. Inset: schematic of the experimental setup. The liquid used to generate droplets is water-glycerol solution having viscosity $\mu = 17.6$ mPas. The outer phase is silicone oil having viscosity $\mu_o = 4.6$ mPas.

In the inset of Fig. 4.1(c), we show a schematic of our experimental setup. A droplet is seated on an indium tin oxide (ITO) glass slide covered by a fluoropolymer layer (Teflon AF-1600, DuPont) of thickness $d = 2.5$ μm . The Teflon layer acts as a hydrophobic and electrically insulating cover. By immersing both the droplets and the substrate in silicone oil, the static contact angles of droplets are close to 180° . To induce the electrowetting effect on a droplet, we immerse one end of a 18 μm diameter tungsten

Figure 4.2: Plots of contact line velocity u versus time t (left axis) and contact line force, F versus time t (right axis) for the spreading stage (a) and the retracting stage (b). Insets: data in the main plots are re-plotted to show the relation between F and u . The results were obtained by applying 80 V to a 1 mm diameter droplets ($\mu = 8.2$ mPas) immersed in silicone oil ($\mu_o = 4.6$ mPas). The best fits to the data in the insets give $\lambda = 0.19 \pm 0.01$ Pas for the spreading stage and $\lambda = 0.17 \pm 0.02$ Pas for the retracting stage.

wire into the droplet and connect the other end of the wire to the positive terminal of a DC power supply. The negative terminal of the power supply is connected to the ITO layer which acts as the ground electrode. We generate an electrical pulse in the form of a step function between the wire and the ITO layer by using a solid-state-relay (SSR). The amplitude V of the applied voltage is varied in the range $20 \text{ V} \leq V \leq 100 \text{ V}$. We note that all our experiments are carried out without contact angle saturation [5], which occurs at $V = 115 \text{ V}$ with our experimental configurations [51]. To make sure that the droplet reaches its new equilibrium, the applied voltage is maintained for a sufficient period, i.e., 50 ms (see Fig. 4.1(c)). Subsequently, we release the voltage for the droplet to retract freely

Figure 4.3: Driving force F at the contact line versus contact line velocity u for different applied voltages ($20\text{ V} \leq V \leq 100\text{ V}$). Inset: zoom in of data near the origin. The working fluid's viscosity is $\mu = 17.6\text{ mPas}$, while the oil viscosity is $\mu_o = 4.6\text{ mPas}$. The radius of droplets is 0.5 mm . The friction coefficient $\lambda = 0.28 \pm 0.05\text{ Pas}$ is calculated from the slope of the solid line.

and observe the retracting stage. We observe that the droplet reacts almost immediately after the circuit is closed or opened, suggesting that the time duration for the system to electrically charge or discharge is negligible compared to its hydrodynamical response time [11, 91]. We use a high-speed camera (SAX2, Photron) to record both the spreading and retracting motions. The recording is taken from side view (see snapshots in Figs. 4.1(a), (b)) with a typical frame rate 5000 frames per second and a spatial resolution of 4 microns per pixel.

We repeat the experiment three times for each set of the control parameters, (V, μ, μ_o) , and extract both the base radius r and the contact angle θ_t as functions of time t . Here, θ_t is the so-called Lippmann contact angle [101], which is measured at some distance away from the contact line vicinity. Repetitive measurements of r and θ_t typically result in less than 5% deviation. We observe insignificant hysteresis of the system evidenced by the negligible difference between the initial state before spreading and the final state after retracting (e.g., see first of Fig. 4.1(a), and last snapshots of Fig. 4.1(b)). This may result from entrapment of a thin oil layer between the droplet and the substrate during the spreading stage [11, 35, 46, 52]. We also observe that r and θ_t vary monotonically with time in both the spreading and the retracting stages due to the high viscosity of working fluids (Fig. 4.1(c)). In other words, the contact line dynamics in the both stages are overdamped.

In the absence of hysteresis, one can write the expression for the driving force per unit length F at the contact line based on the interfacial tension imbalance in the horizontal direction:

$$F = \begin{cases} \sigma(\cos \theta_e - \cos \theta_t), & \text{(spreading stage)} \\ \sigma(\cos \theta_0 - \cos \theta_t), & \text{(retracting stage)} \end{cases}, \quad (4.1)$$

where θ_0 and θ_e respectively are the initial contact angle and the equilibrium contact angle after spreading, and θ_t is the contact angle at time t . Here the spreading direction is assigned positive (Figs. 4.1(a),(b)). Both values of F and contact line velocity $u = dr/dt$ can be calculated using the measured values of θ_t and r at time t . In Fig. 4.2, we show the dependence of F and u on t in both the spreading stage (Fig. 4.2(a)) and the retracting stage (Fig. 4.2(b)). The similarity between two functions $F(t)$ and $u(t)$ suggests a linear relation:

$$F = \lambda u. \quad (4.2)$$

Here λ is the so-called friction coefficient representing the three-phase contact line (TCL) friction, which originates from interactions between the liquid molecules and the solid surface at TCL [47]. We note that the linear relation between F and u is applicable for small TCL velocity [47] and is consistent with the data shown in the insets of Figs. 4.2(a) and 4.2(b).

4.3 Effects of motion direction and driving force on contact line friction coefficient

For a fixed set of the parameters (V, μ, μ_o) , we obtain the friction coefficients in both the spreading and retracting stages. The difference between these coefficients is typically within 15% of their mean value, suggesting that the friction coefficient is independent of the TCL direction. This result is consistent with the negligible hysteresis observed before and after applying the electrowetting effect.

We now examine the effect of driving force on the friction coefficient. The magnitude of F , which is varied by changing the applied voltage, may be characterised by the maximum force per unit length acting on the TCL

$$F_{\max} = \sigma(\cos \theta_e - \cos \theta_0) = \eta \sigma, \quad (4.3)$$

where $\eta = \cos \theta_e - \cos \theta_0$ represents the change in wettability of the solid surface when the contact angle changes from the initial value θ_0 to the new equilibrium one θ_e . In electrowet-

Figure 4.4: (a) Log-log plot of λ versus viscosity μ when μ_o is fixed at 4.6 mPa s. The solid line represents the scaling law $\lambda \sim \mu^{1/2}$. (b) Log-log plot of λ versus μ_o when μ is fixed at 17.6 mPa s. The solid line represents the scaling law $\lambda \sim \mu_o^{1/2}$. (c) Log-log plot of λ versus $\mu\mu_o$ for our experimental data shown in (a) and (b). The solid line represents the scaling law $\lambda \sim (\mu\mu_o)^{1/2}$. Inset: Linear plot of λ versus $(\mu\mu_o)^{1/2}$. The solid line represents the relation $\lambda = C(\mu\mu_o)^{1/2}$, where $C = 26.24 \pm 4.6$ is the fitting parameter.

ting context, η is termed electrowetting number and is related to electrical properties of the system by the Young-Lippmann equation (Eq.2.3). It follows that η also represents the

electrical strength compared to the interfacial tension between the glycerol solution and the surrounding oil [5]. As a result, by varying the voltage V , we change the characteristic force $F_{\max}$ acting on the contact line.

In Fig. 4.3, we plot the dependence of F on u for various applied voltages. In this particular experiment, we generate droplets from a mixture of glycerol solution and sodium chloride with viscosity $\mu = 17.6$ mPas. The surrounding oil has viscosity $\mu_o = 4.6$ mPas (see Table. 3.1 for material properties). The varying range of V is $20 \text{ V} \leq V \leq 100 \text{ V}$, resulting in $0.05 \leq \eta \leq 1.27$ and subsequently $1.37 \text{ mN.m}^{-1} \leq F_{\max} \leq 34.2 \text{ mN.m}^{-1}$. The overlapping of different datasets obtained using various values of V regardless of the TCL direction indicates that both the characteristic driving force $F_{\max}$ and TCL direction, i.e., spreading or retracting, have no significant effect on the contact line friction coefficient λ . This is also consistent with the reported results of water droplets spreading in air using electrowetting [102].

4.4 Effects of viscosity on contact line friction coefficient

to study the effect of viscosities of the two involving phases on λ , we fix the applied voltage at 80 V and vary both μ and μ_o to observe the resulting change in λ . In Fig. 4.4(a), we show a log-log plot of the measured values of λ versus μ while keeping μ_o fixed at 4.6 mPas. The viscosity μ is varied from 8.2 mPas to 615.0 mPas. The data obtained in both spreading and retracting stages are consistent with the scaling law $\lambda \sim \mu^{1/2}$. We note that the 1/2–scaling is also consistent with several previously reported datasets, e.g., for spreading of glycerol droplets on surfaces coated by Teflon [42, 45], Silicon dioxide (SiO_2) [42], and Silane [42]. The vertical shifts between datasets reflect variations in surface properties, e.g., roughness, surface chemistry, and the surrounding phase, e.g. air or silicone oil. Similarly, we show in Fig. 4.4(b) the dependence of λ on μ_o in log-log scale for $1.8 \text{ mPas} \leq \mu_o \leq 970.0 \text{ mPas}$, while keeping μ fixed at 17.6 mPas. Our data are also consistent with the scaling law $\lambda \sim \mu_o^{1/2}$ and agree well with the data collected for aqueous sodium chloride droplets on surfaces coated by Teflon and surrounded by silicone oils [46]. Our data therefore reveal that the dependence of λ on either μ or μ_o follow scaling laws with the same exponents, suggesting that μ and μ_o contribute *equally* to variations in λ . In other words, the dependence of λ on μ and μ_o reduces to

$$\lambda = C(\mu\mu_o)^{1/2} \quad (4.4)$$

Figure 4.5: Linear plots of the collapsed data of experiments with different droplet viscosity μ for spreading stage (a) and retracting stage (b). The raw data of each plot is shown by the corresponding inset.

for the tested ranges of μ and μ_o . Here C is a constant that depends on surface properties [42]. In Fig. 4.4(c), we show a log-log plot of λ versus $\mu\mu_o$ for our datasets, which collapse to a single curve, confirming that Eq. (4.4) can be used to unify the dependence of λ on both μ and μ_o . A best fit to our data gives $C = 26.24 \pm 4.6$, a constant specific to the properties of our substrate (Fig. 4.4(c), inset). Although the Eq. (4.4) works for the spreading and retracting dynamics of aqueous droplets in oils, it should be used with caution when the inner and outer phases have highly contrasted properties, e.g. aqueous droplets in air [50]. An extrapolation of this scaling law to such situation may require significant investigations towards the lower limit of μ_o , thus merit a separate study.

4.5 The role of contact line friction on transient dynamics

We now examine effects of contact line friction on transient dynamics of the spreading and retracting stages. We note that beside contact line friction, viscous dissipation caused by large velocity gradient in liquid bulk may contribute significantly to the transient dynamics, e.g., in the case of droplet oscillations [103] or imbibition of liquid in microchannels by electrowetting [104]. In our present analysis, the viscous dissipation in the bulk is assumed negligible as the system is in the overdamped regime with small velocity gradient. This assumption enables us to determine the characteristic timescale of the transient dynamics. On one hand, the characteristic velocity of the three-phase contact line (TCL) can be defined as $U = F_{\max}/\lambda$, or by incorporating Eqs. (4.3) and (4.4): $U = \eta\sigma/C(\mu\mu_o)^{1/2}$. On the other hand, if we denote τ the characteristic timescale for a

Figure 4.6: Linear plots of the collapsed data of experiments with different oil viscosity μ_o for spreading stage (a) and retracting stage (b). The raw data of each plot is shown by the corresponding inset.

droplet to switch between two equilibrium states, τ can be calculated as $\tau = (r_e - r_0)/U$, or

$$\tau = \frac{C(\mu\mu_o)^{1/2}(r_e - r_0)}{\eta\sigma}. \quad (4.5)$$

In Figs. 4.5 and 4.6, we respectively show the plots of $(r - r_0)/(r_e - r_0)$ versus t/τ for different values of μ and μ_o . The data collapse in both spreading and retracting stages, confirming that τ is indeed the characteristic timescale for the transient dynamics of viscous droplets actuated in ambient oils. We note that the dependence of τ on the electrical parameter η has two interesting implications: the transient dynamics of a droplet depends on 1) the strength of the electrical driving force when the droplet spreads due to the electrowetting effect because $\eta = \epsilon\epsilon_0 V^2/2d\sigma$, and 2) the initial condition when the droplet retracts from an equilibrium state where the contact angle is θ_e because $\eta = \cos\theta_e - \cos\theta_0$. This observation may be helpful in considering the spreading and retracting dynamics of droplets in other phenomena such as droplet impact [105] or wetting and dewetting of liquid films and droplets [3, 106].

The spreading and retracting rates, defined as $\gamma = U_{\max}/|r_e - r_0|$, are key parameters to determine how fast a droplet can spread or retract [100]. Here $U_{\max} = \max[u(t)]$ is the TCL's maximum velocity and is measured experimentally. To reveal the dependence of γ on both the hydrodynamical and electrical parameters, we note that γ can be estimated as $\gamma \sim \tau^{-1}$. In Fig. 4.7, we show a plot of γ versus τ for our data in both the spreading and retracting stages. Best fits of our experimental data give $\gamma = (0.78 \pm 0.07)\tau^{-1}$ for the

Figure 4.7: Log-log plot shows the inverted proportion between spreading rate (open markers) and retracting rate (filled markers) γ versus characteristic time scale τ . The solid line represents the scaling $\gamma \sim \tau^{-1}$.

spreading stage, and $\gamma = (0.43 \pm 0.06)\tau^{-1}$ for the retracting stage. We therefore conclude that both the spreading and retracting rates are represented by the proposed transient timescale τ .

4.6 Summary

In summary, we investigate the friction coefficient λ of viscous droplets in both the spreading and retracting stages: the spreading motion is driven by the electrowetting effect, whereas the retracting motion is purely driven by capillarity. We show that while λ depends weakly on either the driving force's strength or the moving direction of the contact line, it depends equally on both the viscosity μ of the droplets and the viscosity μ_o of the surrounding oils. Based on the dependence of λ on μ and μ_o , we derive and experimentally verify a unifying characteristic timescale for both the spreading and retracting stages. The proposed timescale is valid in both spreading and retracting stages suggesting that it may be applied in other interfacial tension driven problems such as droplet wetting or impacting on solid surfaces. This result will serve as background knowledge for our investigations on the transient dynamics of electrowetting droplets as well as droplet detachment using electrowetting actuation.

Chapter 5

Transient dynamics of electrowetting droplets

In this chapter, we systematically investigate the transient dynamics of typical EWOD droplets. We first investigate different dynamical regimes, i.e., underdamped and overdamped regimes, of droplets under electrowetting actuation and show that the dynamics are mainly determined by the hydrodynamical properties but not by the electrical properties of the system. We then study the transition between these hydrodynamical regimes by proposing universal timescales for two types of transient dynamics. The description of critical viscosity at which the transition occurs is determined. We find that the critical viscosity has a subtle and often hidden dependence on the electrical properties of the system. We next investigate the dependence of droplets' actuation time on system parameters. We experimentally verify that the condition for minimisation of the actuation time is only achieved at the transition. The effect of outer fluids, i.e., oil or air, is also investigated. We find that using oil instead of air reduces oscillations of the contact line significantly, while, it does not increase the friction coefficients of the contact line. We also verify our proposed timescales of the transient dynamics of droplets for the case of EWOD in air. Electrical conductivity of droplets appears an insignificant influence on the droplet dynamics.

5.1 Introduction

While the Y-L equation gives predictions in good accord with the measured changes in contact angles of a droplet under an electric field [5], it only relates the equilibrated contact angles before and after the electric field is applied. Thus, it cannot be used to describe the transient dynamics between the two equilibrium states. Understanding of

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Figure 5.1: (a) Schematic of the EWOD experimental setup. (b) A SEM image the substrate's surface. (c) Plot of the equilibrium contact angle θ_e versus applied voltage V .

droplet characteristics during actuation, however, plays a critical role in applications utilizing EWOD for droplet manipulation. In particular, the relations between the system parameters, e.g., droplet size R , liquid properties μ , applied voltage V , oil viscosity μ_o , electrical conductivity of liquid, and the resulting transient characteristics, e.g., the actuation time, are of both fundamental and engineering interests. The goal of this chapter is to investigate these relations experimentally and analytically. We will also investigate the transient dynamics of electrowetting droplets ambient air and compare it with the case in oil.

In our experiments, illustrated in Fig. 5.1(a), a droplet is seated on an indium tin oxide (ITO) glass slide covered by a $d = 2.5 \mu\text{m}$ fluoropolymer layer (Teflon AF-1600, DuPont). The Teflon layer acts as a hydrophobic coating and electrically insulates the ITO layer. Fig. 5.1(b) shows a scanning electron microscope (SEM) image of the Teflon surface. The typical roughness of the surface is about 10 nm that is considered smooth and morphologically homogeneous.

Figure 5.2: (a) Snapshots showing the deformations of droplets with different radius under electrowetting actuation. The scale bar in the last row represents 100 microns. (b) Snapshots showing the deformations of 1 mm radius droplets under different viscosity. All experiments are done in silicone oil having viscosity $\mu_o = 4.6$ mPas. The applied voltages are all 100 V.

In order to spread the droplet by electrowetting effect, we immerse a 18 μm diameter tungsten wire, connected to the positive terminal of a DC power supply, into the bulk of the droplet while the negative terminal of the power supply is connected to the ITO layer acting as the ground electrode. By using the solid-state relay (SSR) to close the circuit momentarily, we generate an electrical pulse in the form of a step function between the wire and the ITO layer. We immerse both the droplets and the substrate in silicone oils. By doing this the solid surface become super hydrophobic with contact angle is close to 180° . The oil also prevents evaporation of droplets during the experiment. We keep the temperature of the surrounding oil fixed at $20 \pm 0.5^\circ\text{C}$ to maintain consistent experimental conditions. In our experimental configuration, we note that the hysteresis of the system is small caused by a thin layer of oil entrapped between the droplet and the substrate when the droplet spreads [46, 52]. As a result, the hysteresis is reduced by the oil impregnation on the substrate [11, 35].

To capture the deformation of the droplets (Fig. 5.2), we use a high-speed camera

Figure 5.3: Plots of r versus t of droplets in underdamped regime for four control parameters: (a) electrowetting number η , (b) droplet viscosity μ , (c) droplet radius R and (d) oil viscosity μ_o .

(SAX2, Photron) running at 5000 frames per second. The magnification of our lens system gives four microns per pixel for the spatial resolution of our images. The recorded image is then processed by using MATLAB image processing toolbox and extract the desired parameters. We first study the effect of the amplitude of the applied voltage on the change in equilibrium contact angle θ_e by varying the voltage in the range $0 \text{ V} \leq V \leq 130 \text{ V}$. In Fig. 5.1c, we show the change in the equilibrium contact angle θ_e upon the applied voltage V of 1 mm water droplets in 5 cSt silicone oil. The change in θ_e is well described by the Young-Lippmann equation (Eqn. 2.3). The result confirms the validity of our experimental setup. Contact angle saturation occurs at $V \approx 115 \text{ V}$. We note that in this study, we carry out all our experiments with voltage lower than the saturation point.

5.2 Transient dynamics of electrowetting droplets

In Fig. 5.2, we show snapshots of droplets with different radius R (Fig. 5.2(a)), and liquid's viscosity μ (Fig. 5.2(b)) under applications of electrowetting. We observe that the responses of droplets with large R and low μ (first rows in Figs. 5.2(a), (b)) are always accompanied by capillary waves at the liquid-oil interfaces resulting in overshoots of the contact radius. This behaviour can be associated with the so-called *underdamped*

Figure 5.4: Plots of r versus t of droplets in overdamped regime for four control parameters: (a) electrowetting number η , (b) droplet viscosity μ , (c) droplet radius R and (d) oil viscosity μ_o .

behaviour [8, 45, 51]. In contrast, for small radius or high viscosity droplets (last rows in Figs. 5.2(a), (b)) the droplets response slowly and monotonically. Neither overshoot of the contact line radius nor capillary wave on the droplet surface is observed. This behaviour can be named as *overdamped* behaviour [8]. We note that the transition between the two distinct behaviours can also be observed when we increase viscosity of the outer phase.

In order to investigate these transient behaviours quantitatively, we extract contact radius r from the recorded images for each set of the control parameters, (η, μ, R, μ_o) . In Fig. 5.3, we show the contact radius r changed with time t of droplets in the underdamped regimes for the four control parameters. Obviously, these behaviours are associated droplet having either large radius or low viscosities. Similarly, in Fig. 5.4 we show the contact radius r versus t of droplets in the overdamped regime for the four control parameters. The overdamped regime is shown to accompany with small radius and high viscosity droplets. More interestingly, we observe that changing the applied voltage in the range from 60 V to 110 V, which results in the electrowetting number $0.35 \leq \eta \leq 1.18$, does not change the dynamics of the $R = 1.0$ mm droplets in both underdamped (Fig. 5.3(a)) and overdamped behaviours (Fig. 5.4(a)).

We now examine the transient dynamics in each of the underdamped and over-

Figure 5.5: Plots of normalised spreading radius r/r_e versus normalised time t/τ_u in the *underdamped* regime for four varying control parameters: (a) - Electrowetting number η , (b) - Droplet size R , (c) - Liquid viscosity μ , (d) - Silicone oil viscosity μ_o . Experimental conditions and properties of fluids are given in each plot.

damped regimes. In both regimes, the concentrated charge density along the liquid-oil interface at the vicinity of the three-phase contact line (TCL) causes a net horizontal force at time t

$$F = \sigma(\cos \theta_e - \cos \theta_t), \quad (5.1)$$

where θ_e is the equilibrium contact angle, and θ_t is the dynamic contact angle at time t [28]. Here the spreading direction is assigned positive. As a result, the characteristic force pulling the contact line horizontally can be approximated by the maximum force: $F_{\max} = (\cos \theta_e - \cos \theta_0)\sigma = \eta\sigma$ [5, 29] (Eq. 4.3).

In the underdamped regime, we assume that viscosity is negligible, and the driving force is only resisted by the droplet inertia. Thus, by balancing the driving force and the inertia: $\eta\sigma 2\pi r(t) \sim \rho 4/3\pi R^3 \ddot{r}(t)$, ones find that contact lines in this regime oscillate with characteristic frequency $\omega = (\eta\sigma/\rho R^3)^{1/2}$ [107]. As a result, the characteristic timescale

for the droplets to reach maximum deformation, which is the time for the contact line to reach the first peak of the oscillation, is

$$\tau_u = \pi \left(\frac{\rho R^3}{\eta \sigma} \right)^{1/2}. \quad (5.2)$$

In Fig. 5.5, we show the normalised spreading radius $r(t)/r_e$ versus the normalised time t/τ_u of the data in the underdamped regime for the four control parameters: η (Fig. 5.5(a)), μ (Fig. 5.5(b)), R (Fig. 5.5(c)), and μ_o (Fig. 5.5(d)). We observe excellent data collapses for all the control parameters. We also observe that all the overshoots of $r(t)$ occur at $t/\tau_u = 1$. This strongly suggests that τ_u is the characteristic time of the underdamped regime where the inertia of whole droplets dominates the resisting factors of the dynamics.

In the overdamped regime, the dominant factor opposing to the driving force is viscous force. We note that the viscous dissipation in the bulk can be assumed negligible as the internal flows of droplets have small velocity gradient [28, 42]. This assumption enables us to determine the characteristic timescale of the transient dynamics. As a result, the main force that opposing to the driving force is the contact line friction, which is estimated by Eq. 4.2. If we denote τ_o the characteristic timescale for the spreading motion in the overdamped regime, the TCL velocity is $u \approx r_e/\tau_o$, where $r_e = \beta R$ is the spreading radius at equilibrium. Here, β can be derived based on the assumptions that the shape of a droplet remains spherical at its equilibrium states and its volume is conserved:

$$\beta = \frac{r_e}{R} = (1 - \cos^2 \theta_e)^{1/2} \left(\frac{4}{(1 - \cos \theta_e)^2 (2 + \cos \theta_e)} \right)^{1/3}, \quad (5.3)$$

where $\cos \theta_e = \cos \theta_0 + \eta$ (Young-Lippmann equation, (Eq. 2.3)). By balancing the friction λu (Eq. 4.2) with the characteristic driving force $\eta \sigma$ (Eq. 4.3), we obtain

$$\tau_o = \frac{\lambda \beta R}{\eta \sigma}. \quad (5.4)$$

The friction coefficient λ is a function of both viscosities μ and μ_o , and can be measured experimentally by using the method proposed in Chapter 4. In this experiment, we also experimentally calculate λ and fit the experimental data into Eq. 4.4 to find the fitting parameter C . A best fit to our data gives $C = 30.9 \pm 3.2$, a constant specific to the properties of the substrate. We therefore arrive at the expression for the characteristic timescale in the overdamped regime

$$\tau_o = C \frac{(\mu \mu_o)^{1/2} \beta R}{\eta \sigma}. \quad (5.5)$$

Figure 5.6: Plots of normalised spreading radius r/r_e versus normalised time t/τ_o in the *overdamped* regime for four varying control parameters: (a) - Electrowetting number η , (b) - Droplet size R , (c) - Liquid viscosity μ , (d) - Silicone oil viscosity μ_o . Experimental conditions and properties of fluids are given in each plot.

In Fig. 5.6 we show the normalised spreading radius $r(t)/r_e$ versus the normalised time t/τ_o of the data in the overdamped regime for the four control parameters: electrowetting number η (Fig. 5.5(a)), liquid's viscosity μ (Fig. 5.5(b)), droplet radius R (Fig. 5.5(c)), and oil viscosity (Fig. 5.5(d)). We obtain an excellent data collapse for the spreading radius $r(t)$ indicating that τ_o characterises the transient dynamics in the overdamped regime.

5.3 Transition between overdamped to underdamped regime

Let us discuss parameter relations at the overdamped-to-underdamped (O-U) transition. We argue that the characteristic timescales of the two regimes are comparable at the O-U transition. In other words, the condition for the O-U transition to occur is

$$\xi = D \frac{\tau_o}{\tau_u} = 1, \quad (5.6)$$

Figure 5.7: Phase diagram showing different transient dynamics for EWOD actuated droplets. The varying parameters are droplet radius R , viscosity μ , and electrowetting numbers η . The surrounding liquid is silicone oil having viscosity $\mu_o = 4.6$ mPas. The transitional regime includes experiments in which the transient dynamics switch between overdamped and underdamped behaviours. The extent of the transitional regime indicates the experimental uncertainty in determining the overdamped-to-underdamped (O-U) transition.

where D is a prefactor independent from the control parameters. It is necessary to introduce the prefactor D in Eq. 5.6 due to the ignorance of the viscous dissipation in the bulk when balancing the driving force and resitting force in the overdamped dynamics. Nevertheless, we expect that D is of unity order. Here, the so-called damping ratio ξ can be fully expanded as

$$\xi = \left(\frac{DC}{\pi} \right) \left(\frac{\beta}{\eta^{1/2}} \right) \left(\frac{\mu\mu_o}{\rho\sigma R} \right)^{1/2}, \quad (5.7)$$

revealing similar physical significance as the Ohnesorge number with an additional electrical term $\beta\eta^{-1/2}$. The damping ratio is used to indicate whether the droplet behaviour is in the underdamped regime ($\xi < 1$), or in the overdamped regime ($\xi > 1$). The condition for the O-U transition to occur, $\xi = 1$, translates to a linear relation between the *critical viscosity* μ_c , defined as the viscosity at the transition, and the droplet radius R :

$$\mu_c = \left(\frac{\pi}{CD} \right)^2 \frac{\eta}{\beta^2} \frac{\rho\sigma}{\mu_o} R. \quad (5.8)$$

In Fig. 5.7, we show the phase diagram of these behaviours for wide ranges of control parameters: $0.05 \text{ mm} \leq R \leq 1.6 \text{ mm}$, $1 \text{ mPas} \leq \mu \leq 258.8 \text{ mPas}$, and $0.35 \leq \eta \leq 1.18$. The overdamped and underdamped regimes are clearly separated by the *transitional* regime.

Figure 5.8: Plot showing the O-U transition, with error bars representing the extent of the transitional regime. The straight line is a linear fit to the O-U transition (Eq. 5.8).

Here, the transitional regime is categorised by droplet behaviours having alternative characteristics in the case of repetitive runs of the same parameters (Fig. 5.3, $\mu = 17.6$ mPas). Among the control parameters, η has a negligible effect on the transition between these regimes. We attribute the extent of the transitional regime to irregularities in physical and chemical properties of the substrate; such effects could be minimised with better surface treatments. Thus, the overdamped-to-underdamped transition is possible with an uncertainty indicated by the extent of the transitional regime (Fig. 5.8).

By comparing the experimental data and the theory, we observe that Eq.5.8 is consistent with the O-U transition shown in Fig. 5.8. Fitting μ_c to the data at the transition in the phase diagram gives $D = 1.49 \pm 0.21$ for all tested values of the control parameters. Moreover, we note that the composite term $\eta\beta^{-2}$ carries the dependence of μ_c on both the applied voltage and the inherent electrical properties of the system, e.g., the thickness and the dielectric constant of the dielectric layer. For η varying from 0.35 to 1.18 in our experiments, the value of $\eta\beta^{-2}$ changes in a narrow range, from 0.55 to 0.62. Thus, we conclude that μ_c varies linearly with R and depends weakly on η for the explored ranges of parameters.

5.4 Actuation time of electrowetting droplets.

To obtain a quantitative description of the actuating motion of droplets under EWOD conditions, we measure the actuation time t_a , defined in practice as the duration for the spreading radius to reach 95% of the radius at equilibrium state after a voltage is

Figure 5.9: Spreading radius r versus time t for underdamped droplets (open squares), overdamped droplets (open diamonds), and droplets with transitional behaviour (open circles).

applied. As illustrated in Fig. 5.9, t_a depends strongly on viscosity of droplets. When the viscosity increases from $\mu = 1.0$ mPa.s, t_a reduces. But when it exceeds a certain value, e.g., $\mu = 17.6$ mPa.s, t_a starts increasing. As a result, t_a appears minimum at $\mu = 17.6$ mPa.s which can be considered a critical viscosity of the system. More generally, it suggests that t_a is closely linked to the transient dynamics, i.e., overdamped or underdamped.

We explore this link by investigating the dependence of t_a on different control parameters. In Fig. 5.10(a), we show a plot of t_a versus μ for a fixed applied voltage ($\eta = 0.98$) and various droplet sizes ($0.05 \text{ mm} \leq R \leq 1.6 \text{ mm}$). Indeed, different transient dynamics result in distinctive behaviours for the actuation time: t_a decreases with μ in the underdamped regime but increases in the overdamped regime. We study this dependence, i.e., between t_a and μ , R , η for different transient dynamics, by making an analogy between an actuating droplet and a mass-spring system. We take ω as the natural frequency and the ratio $\xi = D\tau_o/\tau_u$ as the damping ratio of the analogous mass-spring system. We note that for a mass-spring system of natural frequency ω and damping ratio ξ , the actuation time, i.e., the duration for the system to reach an equilibrium state, is specified as [108]

$$\tau_s = \frac{4}{\xi\omega} = \frac{4\pi}{DC} \frac{\rho R^2}{\beta(\mu\mu_o)^{1/2}}. \quad (5.9)$$

This suggests that τ_s is the characteristic timescale for the actuating motion of droplets in both transient dynamics. As a result, we nondimensionalise t_a and μ as $t_a/\tau_s = t_a\xi\omega/4$ and $\mu/\mu_c = \xi^2$, respectively. The link between t_a and μ , in a power form, is therefore equivalent to that of $\omega t_a/4$ and ξ . In Fig. 5.10(b), we show a log-log plot of $\omega t_a/4$ versus ξ

Figure 5.10: (a) Log-log plot of the actuation time t_a versus μ for different droplet size and at $\eta = 0.98$. The coloured areas are indicative of different transient dynamics. (b) Log-log plot of $\omega t_a/4$ versus ξ . The minimum point $\omega t_a/4 = 1$ occurs at $\xi = 1$.

for all the data shown in Fig. 5.10(a). In both the underdamped and overdamped regimes, excellent data collapses confirm that τ_s indeed represents the actuation time of droplets regardless of transient dynamics. In addition, the minimum value of the cloud of data occurs at $\xi = (\mu/\mu_c)^{1/2} = 1$ and $\omega t_a/4 = 1$. We conclude that for fixed values of R and η , minimisation of t_a is *always* achieved at $\mu = \mu_c$ and the minimum actuation time is

$$t_{a \min} = \frac{4}{\omega} = 4\tau_u. \quad (5.10)$$

We next investigate the dependence of t_a on R and η . In Fig. 5.11(a) we show the actuation time t_a versus droplet radius R . Generally, the data is consistent with the prediction on the previous part that t_a increases when R increases. We further investigate this relation by using the dependence of t_a on τ_s as suggested from the previous investiga-

Figure 5.11: (a) Log-log plots of the actuation time t_a versus droplet radius R . (b) Log-log plots of $t_a \eta^{(\alpha+1)/2} \beta^{-\alpha}$ for the underdamped regime ($\alpha = -1/2$, left plot), and overdamped regime ($\alpha = 1$, right plot). The working liquid is 0.125 M aqueous sodium chloride solution.

tion. From the collapsed data of t_a (Fig. 5.10(b)), we note that the dependence of $\omega t_a/4$ on ξ can be described using a power law $\omega t_a/4 \sim \xi^\alpha$, in which the exponent α takes the value $\alpha = -1/2$ in the underdamped regime and $\alpha = 1$ in the overdamped regime. The relation $\omega t_a/4 \sim \xi^\alpha$ can be fully expanded as

$$t_a \frac{\eta^{(\alpha+1)/2}}{\beta^\alpha} \sim A R^{(3-\alpha)/2}, \quad (5.11)$$

where $A = 4(DC/\pi)^\alpha (\mu\mu_o)^{\alpha/2} \sigma^{-(\alpha+1)/2} \rho^{(1-\alpha)/2}$. For the two values of α , we obtain the relations $t_a \eta^{1/4} \beta^{1/2} \sim R^{7/4}$ for the underdamped behaviour, and $t_a \eta \beta^{-1} \sim R$ for the overdamped behaviour. These relations are consistent with the experimental data shown in Fig. 5.11(b) for the wide ranges of η ($0.19 \leq \eta \leq 1.22$) and R ($0.05 \text{ mm} \leq R \leq 1.6 \text{ mm}$). The stronger dependence of t_a on R in the underdamped regime attests our initial assumption that the spreading motion is resisted by inertia of the entire droplet. In addition, we note that the term $\eta^{(\alpha+1)/2} \beta^{-\alpha}$ carries the dependence of t_a on the applied voltage V . Since $\beta^2 \eta^{-1}$ is roughly constant in the explored range of η , it follows that $t_a \sim \eta^{-1/2} \sim V^{-1}$ for

Figure 5.12: Snapshots showing the deformations of droplets actuated on a same substrate in air at 120 V (the upper panel) and in oil at 100 V (the lower panel). The liquid is 0.125M aqueous sodium chloride solution.

Figure 5.13: Underdamped behaviours of a droplet actuated in air (open circles) and another one actuated in 4.6 mPas silicone oil (solid squares). Both experiments are conducted on a same substrate. The liquid is 0.125M aqueous sodium chloride solution. The droplet radius is $R = 1.0$ mm.

both regimes, consistent with the scaling law, $t_a \sim \eta^{-0.6}$ reported previously [46].

5.5 Dependence of the transient dynamics on the outer fluid

In the previous sections, we present the transient dynamics of droplets in oil. It is reported that using oil as the outer fluid has many advantages such as reducing contact angle hysteresis, making substrates super-hydrophobic, or reducing interfacial tensions of droplets. However, in some applications, using oils as the outer fluids is not a good choice. For example, in tissue engineering applications using electrowetting actuation [14], due to the low surface energy of oil, the oil will stick to final products and cannot be removed. In those cases, using air as the outer environment is mandatory.

In Fig. 5.12, we show snapshots comparing the deformations of droplets actuated on a same substrate in air at 120 V (the upper panel) and in oil at 100 V (the lower panel).

We note that viscosity of air at the experimental temperature is $\mu_a = 1.8 \times 10^{-2}$ mPas which is about 50 times smaller than viscosity of water. Due to the low viscosity of the air phase, the deformation of the transient states of the droplet actuated in air is much stronger than that in oil. This effect is also facilitated by the higher surface tension of the droplet in air compared to that of the droplet in oil (see Table. 3.1). It is because high interfacial tensions cause stronger capillary waves at the droplet surface. As a result, the overshoots of the contact radius of droplets actuated in air are much higher than those in oil (Fig. 5.13). In some applications, e.g., droplet detachment using electrowetting [20], higher overshoot brings advantages, whereas most of other applications, high overshoots cause instability of droplet motions and, especially, reduction in actuation time of droplets as discussed in the previous part.

We now test the proposed characteristic timescales τ_u and τ_o for droplets actuated in air. In Fig. 5.14(a), we show the transient responses of contact radius r in the underdamped regime (the left subfigure) and overdamped regime (the right subfigure) for different viscosities of droplets actuated in air. The data of r versus t are well normalised by using the characteristic timescale τ_u and τ_o . The values of the non-dimensionless times, i.e., t/τ_u (see the left plots of Fig. 5.14(b)) and t/τ_o (see the right plots of Fig. 5.14(b)) are different from those in the case of droplets actuated in oil (Figs. 5.5 and 5.6). This maybe because the difference in the outer phases causes vertical shifts in the contact line friction coefficients (Fig. 4.4(a)). Anyway, due to the excellent collapse of r versus t by using the proposed timescales, we conclude that τ_u and τ_o also represent the dynamics of droplets under electrowetting in air. Nevertheless, it is necessary to have further investigations about the effects of the air phase on the prefactors of each timescale.

5.6 Effect of electrical conductivity of droplets on the transient dynamics

In most of studies about of electrowetting, we have an assumption that the liquid of droplets is ideally conductive. This assumption in fact reduces a lot of complications induced by the electrical phenomena appearing in the electrical double layer close to the solid surface. However, in an actual system, the liquid droplets are not totally conductive. When the electrical properties of the EWOD system are considered, one of the widely accepted models for the droplet-substrate system in an EWOD setup is the RC circuit model [109]. In this model, for a very short time after the voltage is applied to the system,

Figure 5.14: (a) Plots of r versus t of droplets actuated in air for underdamped regime (the left plot) and overdamped regime (the right plot). (b) Left plot: Plot of the normalised contact radius r/r_e versus the normalised time t/τ_u for droplets in the underdamped regime. (b) Right plot: Plot of the normalised contact radius r/r_e versus the normalised time t/τ_u for droplets in the overdamped regime. Other experimental parameters: $R = 1$ mm, $V = 120$ V.

the RC circuit is charging. It is reported that the electrical conductivity of the liquid strongly affects to the frequency response of AC electrowetting [91]. However, in this thesis, we assume that the electrical response of droplets due to the delay time of the RC circuit [109] is negligible. As a result, we only focus on the dependence of droplet behaviours on electrical conductivity of droplets in DC electrowetting and for hydrodynamical timescales.

In Fig. 5.15, we show the transient dynamics of 1 mm radius droplets having different electrical conductivities under EWOD in air. The voltage is kept fixed at 120 V. The both transient and steady states of the four samples are identical representing that electrical conductivity of droplets has insignificant effects on the hydrodynamical responses of droplets under electrowetting actuation. This observation is consistent with the prediction

Figure 5.15: Behaviours of 1 mm radius droplets having different electrical conductivity under 120 V electrowetting actuation in air.

when comparing the electrical response time and hydrodynamical response time of droplets actuated by electrowetting [11].

5.7 Summary

In summary, the transient dynamics of actuating droplets exhibit either underdamped or overdamped behaviour; the overdamped-to-underdamped (O-U) transition is insensitive to the applied voltage V , but is strongly dependent on the droplet size R and liquid viscosity μ . This results in a linear relation between the droplet size R and the critical viscosity μ_c at the O-U transition. The droplet actuation time t_a does not only depend on the system's control parameters, but also on the transient dynamics: it is minimised at the O-U transition. Interestingly, the applied voltage V considerably affects the actuation time ($t_a \sim V^{-1}$), although it hardly affects the O-U transition. We then compare the transient dynamics of droplet in air and in oil and find that the oil not only increases the electrowetting effect by reducing the interfacial tensions of droplets, but it also reduces the substrate's hysteresis and oscillations of droplets under actuation. Finally, not surprisingly, the electrical conductivity of liquid's droplets has a minus effect on the transient dynamics.

Chapter 6

The role of substrate properties on electrowetting effects

One of the motivations in designing innovating substrates is to reduce the actuating voltage as well as to maximise the energy efficiency of the actuation. In this chapter, we focus on the dependence of static and dynamical behaviours of electrowetting droplets on substrate's properties. We show that it is possible to achieve a very low actuating voltage, e.g., 10 V, while maintaining a fast actuation time by appropriately choosing the materials and thicknesses of the dielectric layer. To evaluate the effects of substrates on transient states of electrowetting droplets, we measure the contact line friction coefficients of the droplets on the substrates. We find that the contact line friction coefficients insignificantly depend on the dielectric layer properties of the substrates. This result can help in substrate's design of digital microfluidics chips.

6.1 Introduction

In an EWOD setup, the substrate plays an important role affecting to the electrowetting droplets' behaviours. In this chapter, we focus on effects of the dielectric layers of EWOD substrates on static and dynamical behaviours of actuated droplets. First, we aim to bring the applied voltage as low as 10 Volts while maintaining a sufficient change in contact angle. This is the voltage that can be used in fast control of droplets in digital microfluidics applications [11]. We then examine the dynamics responses of the actuated droplets on those substrates. We focus on evaluating the contact line friction coefficient λ , which is the most important parameter that affects significantly to the transient dynamics of electrowetting droplets.

We characterise various substrates with different materials and thicknesses in this

Figure 6.1: (a) Schematic of an EWOD experimental setup. (b) SEM images of the substrates in our experiment. (c) Changes in equilibrium contact angles θ_e versus the applied voltage V of the three substrates: Teflon (red circles), SU-8 (purple squares) and Silicon nitride (green diamonds). The solid lines represent the best fits of the quadrature relation between θ_e and V .

study (see Table. 3.2). As illustrated in Fig. 6.1(a), the substrates are made of indium tin oxide (ITO) glass slides covered by a dielectric layer of either fluoropolymer layer (Teflon AF-1600, DuPont), SU-8 2000 class or Silicon nitride. In order to fabricate these substrates, we used different techniques as listed in Table. 3.2. On top of the dielectric layer, we spin coat a 50 nm fluoropolymer layer. The contact angles of small water droplets on the substrates are close 180° in oil. The other properties of the substrates are given in Table. 3.2. Fig. 6.1(b) shows a SEM image of the surfaces of the substrates. The surfaces are considered smooth with characteristic roughness about 10 nm. Thus, we can ignore the effects of surface roughness in our analysis.

As similar as the previous experiments on transient dynamics, in order to generate droplets, we use aqueous glycerol solutions with properties listed in Table. 3.1. We immerse both the droplets and the substrates in silicone oils with viscosity $\mu_o = 1.8 \text{ mPas}$. The oils' temperature is kept at $20 \pm 0.5^\circ \text{C}$. To apply a potential difference between the droplets and

Figure 6.2: (a) Snapshots showing the deformations of $\mu = 1$ mPas droplets under a same electrowetting number actuation $\eta \approx 1.0$. (b) Snapshots showing the deformations of $\mu = 68.7$ mPas droplets under a same electrowetting number actuation $\eta \approx 1.0$.

the ITO layer, we immerse one end of a tungsten wire in the droplets and connect the other end to the positive electrode of a power supply (IT6723G, ITECH) via a solid-state relay (SSR). The ground electrode of the power supply is connected to the ITO layer. In each run of the experiment, we apply an electrical pulse in the form of a step function between the wire and the ITO layer and record the deformation of the droplet using a high-speed camera as same as in the transient dynamics experiments.

6.2 Dependence of steady states of electrowetting on substrate's properties

In this experiment, we investigate the change in equilibrium contact angles θ_e of droplets on different substrates. We slowly increase V and measure θ_e from the images captured by the high-speed camera. We determine θ_e when the droplets stabilise by keeping the applied voltage for a certain period which is typically 50 ms. In Fig. 6.1(c), we show a plot of θ_e versus V for the three substrates. For a same change in contact angle θ_e , the Teflon substrate is associated with the highest voltage applied. It is followed by the SU-8 and Silicon nitride, respectively. This is because dielectric layer of the Teflon substrate has the lowest dielectric constant and the highest thickness compared to the others. Best fits of our data to the equation $\cos \theta_e - \cos \theta_0 = \alpha V^2$ give fitting parameters $\alpha = (1.06 \pm 0.08) \times 10^{-4}$,

$(4.02 \pm 0.34) \times 10^{-4}$ and $(6.37 \pm 1.33) \times 10^{-3}$, respectively, for the Teflon, the SU-8, and the Silicon nitride substrates. The deviations are within 5% by comparing α with those of the theoretical values from the Young-Lippmann equation (Eq. 2.3), i.e. $\epsilon\epsilon_0/2d\sigma$. This shows that the changes in static contact angles is well-confirmed by the Young-Lippmann theory. Moreover, the Silicon nitride substrate can achieve a very low actuating voltage, i.e. 10 V, for θ_e to change from 165° to 90° . This actuating voltage is very suitable for many digital-microfluidics applications [11].

We also observe that contact angle saturation varies with different substrates, i.e., $\theta_s = 60^\circ$, 70° and 85° , respectively, for the Teflon, the SU-8 and the Silicon nitride substrates. This might be because of the difference in electrical hysteresis among the substrates. Due to the reducing saturation voltages of the Silicon nitride substrate, to use this design for digital-microfluidic applications, more detail studies on contact angle saturation on this substrate are needed.

6.3 Dependence of the transient dynamics on substrate's properties

Let us now characterise the effects of the dielectric materials on the transient dynamics of electrowetting droplets. To observe the transient states of electrowetting actuated droplets, we fix the electrowetting number by choosing appropriate amplitudes of the applied voltages corresponding to each substrate. To keep $\eta \approx 1.0$, we choose $V = 100$ V, 50 V and 15 V, respectively, for the Teflon, SU-8 and Silicon nitride substrates. We applied the voltage as a pulse function, with the pulse width is typically 50 ms. We synchronized a high-speed camera (SAX2, Photron) with the applications of voltage to observe the deformation process of the droplets (Fig. 6.2). To investigate the dependence of different dynamical regimes on substrate's properties, we vary the viscosity of the droplets from 1 mPas to 615.0 mPas (see Table. 3.1). We observe droplets response mostly similarly on the three substrates (Fig. 6.2(a)) for both regimes underdamped and overdamped regime. It suggests that the effects of substrates on the dynamics is insignificant.

For more details, we consider the behaviours of contact radius r of the droplets. For each value of μ , we repeat the experiment three times and measure the spreading radius r and the dynamic contact angle θ_t as functions of time t . In Fig. 6.3, we show the temporal evolutions of the contact radius r and the dynamic contact angle θ_t extracted from

Figure 6.3: (a) Plots of contact radius r versus time t (upper panel) and dynamic contact angle θ_e versus time t (lower panel) for underdamped droplets having $\mu = 1.0$ mPas. (b) Plots of contact radius r versus time t (upper panel) and dynamic contact angle θ_e versus time t (lower panel) for underdamped droplets having $\mu = 68.7$ mPas. The radius of droplets in both sub-figures are $R = 1.0$ mm. The applied voltages are 100 V, 50 V and 15 V, respectively, for the Teflon, the SU-8 and the Silicon nitride substrates. These applied voltages are, respectively, translated to electrowetting numbers: $\eta_{\text{Teflon}} = 1.06$, $\eta_{\text{SU-8}} = 0.95$ and $\eta_{\text{SN}} = 0.98$.

experiments shown in Fig. 6.2. For $\mu = 1.0$ mPas, the contact lines and the contact angles oscillate significantly before reaching the new equilibrium (see Fig. 6.3a) indicating the dominance of inertia in underdamped regime. In contrast, with $\mu = 68.7$ mPas droplets, the both parameters reach equilibrium monotonically representing the overdamped behaviours. Comparing the transient behaviours between the different substrates, we confirm the previous qualitative observation that there is not a significant difference of r from both the low and high viscosity responses. The difference in θ_t can be accounted for the slightly difference in the electrowetting numbers η . With the applied voltages are 100 V, 50 V and 15 V, respectively, for the Teflon, SU-8 and Silicon nitride substrates, the corresponding η of the three actuations are $\eta_{\text{Teflon}} = 1.06$, $\eta_{\text{SU-8}} = 0.95$ and $\eta_{\text{SN}} = 0.98$. We note that due to the difference in the interfacial tensions between $\mu = 1.0$ mPas and $\mu = 68.7$ mPas (see Table. 3.1), the equilibrium contact angles of droplets with $\mu = 1.0$ mPas (Fig. 6.3(a)) are typically lower than those of droplets with $\mu = 68.7$ mPas (Fig. 6.3(b)). We come up with

Figure 6.4: Linear plot showing the linear dependence of the contact line force F on the contact line velocity u for different viscosities droplets on the SU-8 substrate. The other experimental parameters are: $R = 0.5$ mm, $V = 50$ V. The outer liquid is silicone oil having viscosity $\mu_o = 4.6$ mPas.

a conclusion that changing the dielectric material changes the applied voltage but does not significantly affect to the transient dynamics of droplets that is theoretically predicted by Vo et al.[51].

For more detail characterisation of those substrates, we investigate contact line friction coefficients of the substrates using the method suggested in Chapter 4. In Fig. 6.4, we show the dependence of F on u for different droplets having viscosity varied from 17.6 mPas to 615.0 mPas on the SU-8 substrate. The linear relations between F and u allow us to fit our data to equation $F = \lambda u$ (Eq. 4.2) to find the contact line friction coefficients λ [28, 51].

Similarly, we calculate λ for other experiments on the Teflon and Silicon nitride substrates. In Fig. 6.5(a), we show a log-log plot of the measured values of λ versus μ while keeping μ_o fixed at 4.6 mPas for the three investigating substrates. The data obtained in all substrates are consistent with the scaling law $\lambda \sim \mu^{1/2}$. The vertical shifts between datasets reflect variations in surface properties, i.e. the Silicon nitride substrate appears as the highest friction while SU-8 substrate has the lowest friction. In Fig. 6.5(b), we show a log-log plot of λ versus $\mu\mu_o$ for our datasets. Best fits to our data to Eq. 4.4 give $C_{\text{Teflon}} = 24.21 \pm 3.28$, $C_{\text{SU-8}} = 20.58 \pm 2.51$ and $C_{\text{SN}} = 27.68 \pm 3.89$, respectively, for data

Figure 6.5: (a) Log-log plot of λ versus viscosity μ for the different substrates. The solid line represents the scaling law $\lambda \sim \mu^{1/2}$. (b) Linear plot of λ versus $(\mu\mu_0)^{1/2}$. The solid lines represent the relations $\lambda = C(\mu\mu_0)^{1/2}$, where $C_{\text{Teflon}} = 24.21 \pm 3.28$, $C_{\text{SU-8}} = 20.58 \pm 2.51$ and $C_{\text{SN}} = 27.68 \pm 3.89$ are, respectively, the fitting parameters for data collected on the Teflon, SU-8 and Silicon nitride substrates.

collected on the Teflon, SU-8 and Silicon nitride substrates.

We close this section by giving some discussions on the effects of substrate's properties on the contact line friction coefficients. The insignificant difference among factor C in Fig. 6.5(b) shows the minus influence of the dielectric materials on contact line dynamics of electrowetting droplets. This is reasonable because the interactions between the contact line and substrates are considered short range interactions between liquid molecules and substrate's molecules [47, 110]. This means that the top layer of the electrowetting substrates, in this case are all Teflon, is the main factor affecting to the contact line dynamics. The effect of the top layer on the contact line friction coefficient of droplet spreading has been

studied carefully by Carlson et al. [42] showing that the contact line friction coefficients of spreading water droplets are significantly affected by the hydrophobicity of the surface. However, in this work, we only focus on characterising substrates for electrowetting-based droplet manipulation applications, which mostly used Teflon as the hydrophobic layer. Thus, more details in the effects of the top layer on droplet dynamics under electrowetting actuation merits another study.

The slight difference in the contact line friction coefficients between different substrates might be accounted for the difference in contact angle hysteresis resulted from the accumulation of charges on different type of dielectric materials. This cause pinning of the contact lines [64, 65] and subsequently increase the friction coefficients of the substrate. We observe that the pinning of contact line is strongest in the Silicon nitride substrate which results in the highest friction coefficient of this substrate. This might be because PE-CVD technique usually has pin holes effects when the Silicon nitride layer is too thin, e.g., 100 nm. This effect can be minimised by better controls of fabrication processes of the dielectric layers.

6.4 Summary

In summary, we have just characterised different substrates that are popularly used in electrowetting-based droplet manipulations. By properly choose dielectric layer's materials and thicknesses, we are able to bring the actuating voltage to as low as 10 V while maintaining large changes in contact angles. We also investigate the contact line friction of the substrates and find that the dielectric material has an insignificant effect on the contact line friction coefficients. We then conclude this chapter with a suggestion that Silicon nitride-Teflon is a good combination of materials for EWOD chips in droplet manipulating applications due to its strength in electrical breakdown voltage, considerable low in actuation voltage, and the acceptable friction of contact line dynamics compared to other studied substrates.

Chapter 7

Vertical actuation of droplets using electrowetting *

When a stretched droplet by electrowetting is released, the energy stored in droplet surface is converted into kinetic energy or dissipated by viscous effects. In the case the stored energy is enough, and the dissipation is small, the droplet is detached from the solid surface. Here, we investigate criteria for a sessile droplet to detach from a solid surface in ambient oil. Based on the energy conversion of the droplet through the detaching process and taking into account the effects of contact line elasticity, we develop a simple theoretical model capturing the transition between the detachable and non-detachable regimes. Our model is verified by our experimental data with various control parameters. We also investigate the detaching of droplets from maximum deformation with voltage varied over the contact angle saturation voltage. We show that the detachable regime is extended significantly by using over-saturation actuation. This gives a more powerful tool for droplet detachment technique in practices. Finally, we experimentally studied the detaching velocity of droplets. We propose a theoretical model based on the energy equation that can be used to collapse the data of the detaching velocity of droplets with the control parameters. The linear relation between the detaching velocity and the electrowetting number of droplets detaching from maximum deformation is also observed and investigated.

7.1 Introduction

As discussed in the last few chapters, empowered by electrowetting, a solid surface's wettability can be switched from hydrophobic to hydrophilic characters. This so-called spreading by electrowetting happens when a voltage is applied between a sessile

*Quoc Vo, and Tuan Tran, Critical conditions for jumping of droplets under electrowetting, submitted, (2018).

Figure 7.1: (a) Snapshots of droplet retracting and jumping from the solid substrates at different voltage V causing different initial contact angles θ_e . (b) Left axis: plot showing the dependence of θ_e on the applied voltage V . Contact angle saturation occurs at $V = 120$ V. Right axis: plot showing the dependence of the jumping height h on the applied voltage V . The liquid for generating droplets is a solution deionized water and 0.125 M sodium chloride.

droplet and an electrode beneath the solid surface [5]. Another direction of changing the surface's energy, i.e. from hydrophilic to hydrophobic, occurs when the applied voltage to a droplet equilibrated by electrowetting is released. This reverse stage of electrowetting has recently been exploited to detach sessile droplets from solid surfaces. As reviewed in Chapter 2, the detaching method can be either steady state actuation [72], or maximum deformation actuation [20]. These methods of controlling the detachment of droplets on solid surfaces are the core techniques in vertical actuation of droplets in three-dimensional microfluidics applications.

In this chapter, we will systematically give possible solutions for some remaining

problems of droplet detachment using electrowetting actuation. We first investigate the droplet detachment from steady state actuation. We take into account the most important parameters including viscosity of the droplet, viscosity of the outer phase, droplet size, and magnitude of the applied voltage altogether. We explore the condition for a droplet to detach from the solid surface by examining the energy conversion of the actuated droplet. Based on this analysis, we propose a theoretical model to determine the critical condition for a droplet to detach. Our analysis is then verified by our experimental data of the whole considered parameter's space. We also investigate droplet detachment from maximum deformation actuation and compare the behaviours of the actuated droplets with the case of detaching droplet from steady state. Finally, we study the detaching velocity of droplets in both detaching methods.

7.2 Experimental methods

In our experiment, the substrate is an indium tin oxide (ITO) coated glass electrode covered with a amorphous polymers layer (Teflon AF 1600, DuPont) of thickness $d = 2.2\mu\text{m}$ and dielectric constant $\epsilon = 1.93$. To induce the electrowetting effect for a droplet on the substrate, a $18\mu\text{m}$ diameter tungsten wire, is dipped into the bulk of the droplet. The wire and the electrode are connected to a power supply through a solid-state relay (SSR) to close the circuit. The liquid used to generate droplets is an aqueous glycerin solution consisting of glycerol, DI water, and 0.125 M sodium chloride. By adjusting the glycerol concentration, we vary the viscosity μ of the solution from 1.0 mPas to 68.7 mPas (see Table.3.1). The volume of dispensed solution is adjusted to control the droplet radius R from 0.25 mm to 1.25 mm. We immerse droplets and the electrode in a pool of silicone oil with viscosity $\mu_o = 1.8\text{ mPas}$. The temperature of the pool is kept fixed at $20 \pm 0.5^\circ\text{C}$ to maintain consistent experimental conditions.

7.3 Critical conditions for droplets to detach

7.3.1 Experimental method

In this experiment, we use a typical electrowetting setup and materials as described in Chapter 3. The EWOD substrate is an electrode covered with an amorphous polymers layer (TEFLON AF1600) of thickness $d = 2.2\mu\text{m}$ and permittivity $\epsilon = 1.93$. The working fluid used to generate droplets is an aqueous glycerol solution consisting of glyc-

erol, DI water, and 0.125 M sodium chloride. By adjusting the glycerol concentration, we vary the viscosity μ of the solution from 1.0 mPas to 68.7 mPas. The volume of dispensed solution is adjusted to control the droplet radius R from 0.25 mm to 1.25 mm. We immerse tested droplets and the electrode in a pool of silicone oil with viscosity $\mu_o = 1.8$ mPas and a fixed temperature 20 ± 0.5 °C to maintain consistent experimental conditions.

First, we apply a voltage V to the tungsten wire dipping into the bulk of a droplet resting on the EWOD substrate by closing the solid-state relay (SSR) (see Chapter 3 for the details of the setup). This application of voltage induces the electrowetting effect and forces the droplet spread to its equilibrium having contact angle θ_e . When the droplet is at the equilibrium we release the voltage by suddenly opening the SSR letting the droplet freely retract. θ_e now plays as the initial condition of the retracting stage of the droplet. In Fig. 7.1(a), we show several representative snapshots of droplet actuation after the voltage difference is turned off. We use a high-speed camera (Photron, SAX2), typically running at 5000 frames per second, to record the droplet dynamics. We observe that for a fixed droplet radius, detachment occurs when V is higher than a threshold value. For instance, a 1 mm diameter water droplet detaches for $V > 90$ V, or equivalently $\theta_e < 74^\circ$ (Fig. 7.1b). Without contact angle saturation [5], θ_e is directly related to the applied voltage V following the Young-Lippmann equation (Eq. 2.3) $\epsilon\epsilon_0 V^2 / 2\sigma d = \cos \theta_e - \cos \theta_0 = \eta$. We use the so-called electrowetting number η as the control parameter of the spreading state of droplets instead of θ_e or V . By keeping θ_0 fixed at 164 degrees and vary the voltage in the range $50 \text{ V} \leq V \leq 110 \text{ V}$, we vary η between 0.26 and 1.27 for droplets with viscosity $\mu = 1.0$ mPas. The upper limit of V ensures that all of our experiments are carried out without contact angle saturation, which occurs at $V_s = 120$ V, correspondingly, $\eta_s = 1.51$ for all the droplet size and viscosity.

For each set of the control parameters (R, μ, η) , we repeat the droplet actuation experiment several times to determine the characteristic behaviour as detachable or non-detachable (Fig. 7.1(b)). The transitions between the two regimes are shown in Fig. 7.2. On one hand, for a fixed viscosity ($\mu = 1.0$ mPa.s), the required value of η for detachment to occur reduces with increasing droplet radius (Fig. 7.2), implying that smaller droplets require higher excessive surface energy to detach. On the other hand, for droplets with $R = 0.5$ mm, η at the transition increases with μ and is limited at $\mu = 17.6$ mPa.s, i.e., it is not possible to induce detachment for $\mu \geq 17.6$ mPa.s

Figure 7.2: (a) Phase diagram of detachable actuation (blue open diamonds) and non-detachable actuation (green solid squares) of 1.0 mPa.s droplets with different radius R . (b) Phase diagram of detachable actuation (blue open diamonds) and non-detachable actuation (green solid squares) of 1.0 mm diameter droplets with different viscosity μ . The dash lines in both figures are achieved by balancing two sides of Eq. 7.12 with $\ln(L/\gamma) = 8$.

7.3.2 Surface energy difference of a detaching droplet

To examine the transition between the two regimes, we consider conversion of energy between two stages of actuation: the initial stage, shortly after the applied voltage is released so that no hydrodynamical response occurs (Fig. 7.1(a), $t = 0$), and the final stage at which detachment takes place. The difference in surface energy between the two states, assuming sphericity of the droplet under actuation at the final stage, is $\Delta E_s = \sigma(A_1 - A_2) + \pi r_e^2(\sigma_{sl} - \sigma_{so})$, where A_1 and A_2 respectively are areas of liquid-oil interface at the initial and final stages, r_e is the contact radius at the initial state. Here σ_{so} and σ_{sl} are interfacial tensions of the solid-oil and solid-liquid interfaces, respectively. Using the Young's relation $\sigma_{so} - \sigma_{sl} = \sigma \cos \theta_0$ and noting that $A_1 - A_2$ can be expressed as a function of θ_e and r_e

$$A_1 - A_2 = \pi r_e^2 \left[\left(\frac{1 - \cos \theta_e}{\sin \theta_e} \right)^2 + 1 - \frac{4R^2}{r_e^2} \right] \quad (7.1)$$

Figure 7.3: (a) Snapshots showing the velocity field of a $R = 0.5 \text{ mm}$ droplet having viscosity $\mu = 4.8 \text{ mPa.s}$ when $V = 100 \text{ V}$ is released. The droplet detaches at $t = 11 \text{ ms}$. (b) Velocity distributions along the r -direction at $\zeta = 96 \mu\text{m}$. The linear relation between $u(r, t)$ and $r(t)$ confirms that the internal flows at $\zeta \geq 96 \mu\text{m}$ can be approximated to potential flows. (c) Velocity distributions along the r -direction at $\zeta = 32 \mu\text{m}$. For small distance from the substrate, the relation between $u(r, t)$ and $r(t)$ is not linear meaning that the flows in this region cannot be considered potential flows. (d) Plot of k versus droplet viscosity μ . It is observed that k is a constant with $\mu \leq 17.6 \text{ mPa.s}$ and $k \sim \mu^{-1/2}$ with $\mu \geq 17.6 \text{ mPa.s}$.

we obtain

$$\Delta E_s = \left[\left(\frac{1 - \cos \theta_e}{\sin \theta_e} \right)^2 + 1 - \frac{4}{\beta^2} - \cos \theta_0 \right] \sigma \pi r_e^2 = \alpha (\sigma \pi r_e^2). \quad (7.2)$$

Here, since $\beta = r_e/R$ is a function of θ_e [51], α is also a function of θ_e , which is directly related to η following the Young-Lippmann equation. If we denote W_d the viscous dissipation during actuation and E_{cl} as the stored energy by contact line elasticity [40, 64], the condition for the droplet to detach is

$$\Delta E_s \geq W_d + E_{cl}. \quad (7.3)$$

7.3.3 Viscous dissipation of a detaching droplet

Let us first examine the viscous dissipation W_d . For droplets spreading or retracting on solid surfaces, W_d consists of viscous dissipation in the bulk of the droplet T_b , contact line dissipation T_c and dissipation due to shear stress near the surface T_s [42, 43].

For such droplets, we assume potential flow for vertical distance z far from the surface, i.e., $z > \zeta$, where $\zeta \approx 0.665[\nu r(t)/u(r, t)]^{1/2}$ is the Blasius boundary layer thickness. Here, ν is the kinematic viscosity of the working liquid.

In Fig. 7.3(a), we show internal flows of a 0.5 mm radius droplet having viscosity $\mu = 4.8$ mPas retracting and detaching in 1.9 mPas silicone oil of a Particle image velocimetry (PIV) experiment analysed by using PIVlab MATLAB package [92] that is described in Chapter 3. From the PIV data, we respectively calculate the horizontal velocity $u_r(t)$ distributed along the horizontal axis at distances $\delta = 96 \mu\text{m}$ and $\delta = 32 \mu\text{m}$ above the solid surface (Figs. 7.3(b), (c)). We observe that, at $\delta = 96 \mu\text{m}$, which is far from the surface, the horizontal velocity linearly decreases with the position $r(t)$ (Fig. 7.3(b)). At $\delta = 32 \mu\text{m}$, which is close to the substrate, $u(r, t)$ is no longer conserves the linear relation to the position $r(t)$. This result indeed confirms that the flows far from the surface is potential.

For the potential flows outside the boundary layer, the velocity field on r direction can be described by $u(r, t) = kr(t)$, where k is a constant. As a result, the momentum layer thickness now can be estimated as $\zeta = 0.665(\nu/k)^{1/2}$. From the PIV data, we observed that the relation between velocity $u(r, t)$ and the position $r(t)$ of a small volume inside the droplet is well normalised by using contact line velocity $u_{\text{ct}}(t)$ and contact line radius $r_{\text{ct}}(t)$ (Figs. 7.3(b) and 7.3(c)). As a result, we can simply estimate k as: $k \sim u_{\text{ct}}(t)/r_{\text{ct}}(t)$. Now, k can be considered as the retracting rates [100]. When the viscosity of liquid is varied, we found that k is a constant with $\mu \leq 17.6$ mPas and $k \sim \mu^{-1/2}$ with $\mu \geq 17.6$ mPas (Fig. 7.3(d)). In our experiments, $k \approx 215 \text{ s}^{-1}$ (see Fig. 7.3(d)) leading in $\zeta \approx 96 \mu\text{m}$.

To calculate the dissipation of viscous effects in the two regions, we use a cylindrical coordinate system as described in Fig. 7.3(a). We denote $\Phi = 2\mu((\partial_r u_r)^2 + (u_r/r)^2 + (\partial_z u_z)^2) + \mu(\partial_r u_z + \partial_z u_r)^2$ the dissipation term in the cylindrical coordinate system. Therefore, T_b and T_s can be calculated as

$$\dot{T}_b = \int_{\Omega_1} \Phi d\Omega_1, \text{ and } \dot{T}_s = \int_{\Omega_2} \Phi d\Omega_2, \quad (7.4)$$

where Ω_1, Ω_2 is respectively the volumes of the regions that $z > \zeta$ and $z \leq \zeta$.

In contrast to the dissipation by the viscosity of the bulk and the shear stress at the surface, the contact line dissipation is localized at contact line vicinity. A simple estimation gives

$$\dot{T}_c \sim 2\pi\lambda r_{\text{ct}} u_{\text{ct}}^2 \quad (7.5)$$

Figure 7.4: Rates of different dissipation sources, i.e., viscous dissipation caused by the shear stress at the solid surface due to the non-slip boundary condition $\dot{T}_s$, viscous dissipation in the liquid bulk $\dot{T}_b$ and viscous dissipation due to contact line friction $\dot{T}_c$. It is observed that $\dot{T}_c$ dominates over $\dot{T}_s$ and $\dot{T}_b$ in fast dynamics of the contact line, e.g., $t < 6$ ms in this case.

Figure 7.5: Plot of the apparent receding contact angle θ_{ar} versus contact radius r . It is observed that θ_{ar} is mostly independent from r . This allows us to calculate the contact line dissipation by using Eq. 7.7.

where λ is the contact line friction coefficient [42, 43]. Moreover, λ can be estimated from the viscosities μ and μ_o using Eq. 4.4 as: $\lambda = C(\mu\mu_o)^{1/2}$ [28, 51], where C is a constant depending on substrate's properties. Here, we use the same substrate with the previous work on transient dynamics of electrowetting droplets having $C = 32.9 \pm 3.2$ [51].

In Fig. 7.4(d) we show a comparison between the dissipation rates using $\zeta = 96 \mu\text{m}$

for a representative case in which $R = 0.5 \text{ mm}$, $\mu = 4.8 \text{ mPas}$, and $\eta = 1.28$. The contact line dissipation rate $\dot{T}_c$ is calculated using Eq. 7.5 with measured values of $u_{ct}(t)$, $r_{ct}(t)$, and the contact line friction coefficient λ in Eq. 4.4 [28, 51]. We note that $\dot{T}_c$ dominates over $\dot{T}_b$ and $\dot{T}_s$. Integrating the individual rates gives $T_b \approx 2.65 \times 10^{-9} \text{ Nm}$, $T_s \approx 4.24 \times 10^{-9} \text{ Nm}$, and $T_c \approx 1.84 \times 10^{-8} \text{ Nm}$, which correspondingly contribute to 10.5 % and 16.8 % and 72.7 % of the viscous dissipation W_d . Similar calculations for other actuation conditions give similar result, i.e., contact line dissipation dominates over the total dissipation. We note that the dominance of contact line dissipation over the viscous dissipation of rapid dynamics of wetting was also previously reported both theoretically and experimentally [41, 42]. As a result, the energy dissipation W_d can be estimated as the contact line dissipation: $W_d \sim T_c$.

When the droplet retracts, W_d can be calculated by taking integration of $\dot{T}_c$ from Eq. 7.5 over time t :

$$W_d \sim \int \dot{T}_c dt = 2\pi\lambda \int r_{ct} u_{ct} (dr_{ct}/dt) dt = 2\pi\lambda \int r_{ct} u_{ct} dr_{ct} \quad (7.6)$$

If we denote U the characteristic velocity of the contact line meaning $u_{ct} \sim U$, Eq. 7.6 can be rewritten:

$$W_d \sim 2\pi\lambda U \int_0^{r_e} r_{ct} dr_{ct} = \lambda U \pi r_e^2 \quad (7.7)$$

To estimate the contact line velocity U , we note that in the situation whereby the contact line dynamics is overwhelmed by viscous effect, i.e., in the overdamped regimes [51], the characteristic timescale of the retracting dynamics is $\tau_o = r_e/U \sim \lambda r_e/\eta\sigma$. The resulting contact line velocity is $U \sim r_e/\tau_o$, which leads to $W_d \sim \lambda r_e/\tau_o \pi r_e^2 = \eta\sigma\pi r_e^2$. Combining this expression for W_d and ΔE_s (Eq. 7.2), the condition in Eq. 7.3 is only satisfied if $\alpha = \eta$, i.e., $\theta_e = 0$, or $E_{cl} < 0$, both of which are not practical. This implies that in the overdamped regime, the contact line friction dissipates all the stored surface energy ΔE_s , preventing the droplet from reaching the detaching point. As a result, we conclude that droplet detachment is not possible in the overdamped regime.

Similarly, in the underdamped regime, i.e., the retracting dynamics is dominated by inertia, the characteristic velocity is $U \sim r_e/\tau_u$, where $\tau_u = \pi(\rho R^3/\eta\sigma)^{1/2}$ [51] is the characteristic timescale in this regime, and ρ is the density of the working liquid. The contact line dissipation therefore can be rewritten as

$$W_d \approx \lambda \frac{r_e}{\tau_u} \pi r_e^2 = \eta\sigma \frac{\tau_o}{\tau_u} \pi r_e^2 = \eta\xi\sigma\pi r_e^2. \quad (7.8)$$

Here $\xi = \tau_o/\tau_u$ is the damping ratio representing the dynamics, i.e., $\xi \geq 1$ for the underdamped regime and $\xi \leq 1$ for the overdamped regime [51]. Neglecting the effect of the

Figure 7.6: Phase diagram of detachable (blue diamonds) and non-detachable (green squares) droplets presented by the initial condition $\alpha - \pi \sin^2 \theta_e / \ln(L/\gamma)$ in the vertical axis versus the system's properties $\xi = \tau_o/\tau_u$ in the horizontal axis. Here, the values of the both quantities are calculated based on the data presented in Fig. 7.2 and $\ln(L/\gamma) = 8$. The solid line represents the relation $\alpha - \pi \sin^2 \theta_e / \ln(L/\gamma) = \xi$ which is the transition between detachable and non-detachable regimes. The shaded area shows the extent of the transitional regime when $\ln(L/\gamma)$ varies from 8.5 and 7.5 corresponding to the upper and lower bounds, respectively.

energy barrier caused by surface's imperfection, i.e., $E_{cl} = 0$, the condition for droplet to detach, Eq. 7.3, now become $\Delta E_s - W_d > 0$ which results in

$$\alpha - \eta\xi > 0 \quad (7.9)$$

for droplets in underdamped regime. Since we always have $\alpha < \eta$, Eq. 7.9 is equivalent to $\xi < \alpha/\eta < 1$ which is possible in the underdamped regime. As a result, it is possible for the surface energy difference $\Delta E_s = \alpha\sigma\pi r_e^2$ to be larger than the contact line dissipation $W_d \approx \eta\xi\sigma\pi r_e^2$. The dynamics of a droplet in the underdamped regime therefore becomes the necessary condition for its detachment from the surface.

7.3.4 Effects of contact line pinning on the detachment of a droplet

To find the sufficient condition for droplets to detach, we investigate the effect of the substrate's imperfection. When the droplet moves from the initial state to the detaching point, a common assumption that at the detaching point the droplet is a sphere is usually made. This assumption in facts is not correct in practices since the droplet deform

significantly before detaching (see Fig. 7.1(a)). Instead, the deformation of the droplet can be accounted for contact line pinning force by chemical contamination or roughness of the solid surface [40, 64].

Giving a Gaussian distribution of weak heterogeneities over the solid surface, an estimation of the elastic force per unit length imposing on the contact line gives [64, 111]

$$f \sim \frac{\pi\sigma \sin^2 \theta_r}{\ln(L/\gamma)}. \quad (7.10)$$

Here L is the macroscopic cut-off length; γ is the defect's size varying from order of molecular size to order of ten micrometres; θ_r is the receding contact angle. In order to overcome the elastic force to move the contact line over surface's heterogeneities, a certain amount of energy is required. A simple dimensional analysis of this energy when the contact line sweeps an area πr_e^2 in the retracting stage gives

$$E_{cl} \sim f\pi r_e^2 \sim \frac{\pi \sin^2 \theta_r}{\ln(L/\gamma)} (\sigma\pi r_e^2). \quad (7.11)$$

Here, we expect that the receding contact angle θ_r is constant and independent from the radius r when the contact line is moving.

The elastic energy E_{cl} is accumulated when the contact line moves and will eventually be converted to liquid-oil surface energy by deforming the liquid-oil interface at the vicinity of the contact line. As a result, the more heterogeneities of the surface, the more deformation of the liquid-oil interface at the detaching point (see Fig. 7.1(a)). Although this amount of elastic surface energy is in the form of surface energy, it does not assist the motion of the contact line. Once the droplet detaches from the solid surface it will be converted back to kinetic energy and eventually dissipated by viscous effects. Thus, if the droplet is detached, it has some minimum kinetic energies resulting in some minimum jumping heights that is well agreed with experimental observations [20].

By substituting Eqs. (7.2), (7.8) and (7.11) into Eq. (7.3), we have the condition for the droplet to detach: $\alpha - \eta\xi \geq \pi \sin^2 \theta_r / \ln(L/\gamma)$ that can be rearranged to the form

$$\frac{\alpha - \pi \sin^2 \theta_r / \ln(L/\gamma)}{\eta} \geq \xi. \quad (7.12)$$

We note that although η appear in the description of ξ , changing η has an insignificant influence on ξ [51].

It is reasonable when using the receding contact angle instead of the static contact angle in this case because we only deal with the receding contact line [66]. Unfortunately,

the microscopic receding contact angle θ_r is not a practical parameter making it hard to experimentally compute the condition for droplet to detach. Thus, for a practical estimation of the transition between the two regimes, we use the apparent receding contact angle denoted by θ_{ar} which is measured at some distance from the vicinity of the contact line. We observe that, during the dewetting stage, θ_{ar} is mostly constant with the spreading radius r (Fig. 7.5). These values are independent from the initial state contact angle θ_e and liquid's viscosity meaning that it only depends on the properties of the substrate. Thus, for a rough estimation, ones can take the average value of $\bar{\theta}_{ar} \approx 121^\circ$ for the analysis.

Fig. 7.6 shows the phase diagram of actuated droplets rearranged by two parameters: the initial condition $\alpha - \pi \sin^2 \theta_e / \ln(L/\gamma)$ in the vertical axis and the system's properties ξ in the horizontal axis. The detachable behaviours only occur in the underdamped regimes, i.e., $\xi \leq 1$. When ξ increases, the detaching dynamics changes from detachable regime to non-detachable regime. The transition between the two regimes is represented by the solid line which is the relation $[\alpha - \pi \sin^2 \theta_r / \ln(L/\gamma)] / \eta = \xi$, with $\ln(L/\gamma) = 8$. The shaded area represents the extent of the transitional regime when $\ln(L/\gamma)$ varies from 7.5 to 8.5 corresponding to the lower and upper bounds of this area (Fig. 7.6, two dash lines). We note that, in most practical cases of moving contact line problems, the logarithmic factor $\ln(L/\gamma)$ varies from 2 to 15 [66]. The data presented in Fig. 7.6 is calculated using $\ln(L/\gamma) = 8$ which is appropriate for normal surfaces. If we choose $L \sim R$ [40], $\ln(L/\gamma) = 8$ results in the defect's size $\gamma \sim 100$ nm which is reasonable for Teflon surfaces fabricated by the spin coating technique [93, 94].

In the case of inviscid liquid is used, i.e. $\xi = 0$, the Eq. (7.12) reduces to

$$\alpha \geq \pi \sin^2 \theta_r / \ln(L/\gamma) \quad (7.13)$$

which only depends on the initial contact angle θ_e and substrate smoothness and chemical homogeneity.

7.4 Enhancement of droplet detachments under electrowetting actuation

In the previous sections, we have just investigated the transition between detachable and non-detachable regimes of a droplet under electrowetting actuation when the droplet is released from its equilibrium. In practices, one of the methods to maximise the efficiency of a detaching droplet, is releasing the voltage V when the droplet reaches its

Figure 7.7: (a) Snapshots showing spreading, retracting and detaching of a $R = 0.5$ mm water droplet when $V = 100$ V is applied for $\tau_p = 6.1$ ms. The experiment is done in 2 cSt silicone oil. (b) Schematic of the applying and releasing of the voltage in order to detach the droplet in (a) from maximum deformation actuation.

maximum spreading [20]. By using this method, the additional surface energy difference by overshoots of droplets is taken advantages. In this section, we will show technical details of detaching droplets from maximum deformation. We also extend the ability of this method by using over-saturation voltage to detach droplets. We note that in the overdamped regime because there is no overshoot of the spreading radius, the maximum deformation actuation method is not efficient. Thus, the rest of this section will discuss the detachment of droplets only in the underdamped regime where droplet overshoots occur.

7.4.1 Droplet detaching from maximum deformation actuation

First of all, the time for droplet to reach maximum deformation can be related to the system properties by the underdamped characteristic timescale [51]:

$$\tau_p = \pi \left(\frac{\rho R^3}{\eta \sigma} \right)^{1/2}. \quad (7.14)$$

In this experiment, we use τ_p as the characteristic actuation period meaning that we apply a voltage V with a period $T_p = \tau_p$ to force the droplet to spread to maximum deformation, then release the voltage to let the droplet to retract freely (Fig. 7.7(b)). For example, as shown in Fig. 7.7(a), with a $R = 0.5$ mm water droplet the time for the droplet to reach maximum deformation under an application of $V = 100$ V is $\tau_p = 6.1$ ms. Thus, we close the SSR to apply the voltage to the system for 6.1 ms then release it. The droplet detaches from the surface at $t = 13$ ms resulting in time for the droplet to detach after releasing the voltage is 6.9 ms. If we compare these snapshots with the case of droplet detaching from

Figure 7.8: Snapshots showing detachments of a $R = 0.5$ mm water droplet when V is increased over the saturation voltage $V_s = 120$ V. The periods of the applied voltages are calculated using Eq. 7.14 and are presented by the time in the second snapshots of each row. The experiment is done in 2cSt silicone oil. The jumping heights represented by the last snapshots are still increasing after $V \geq V_s = 120$ V showing that over-saturation voltages still have effects on jumping droplets.

equilibrium state (Fig. 7.1(a), third panel), we can see that by using maximum deformation method, the droplet not only detach from the substrate in a shorter time, but it also reaches a higher height after the detachment. This proves that detaching from maximum deformation method is more efficient than detaching from steady state method.

7.4.2 Droplet detachment by over-saturation actuation

As introduced in Chapter 2, when the applied voltage is higher than the saturation voltage, the steady state contact angles saturates. However, for the transient states of droplets under EWOD, we observe that the maximum deformation of droplets when the applied voltage is higher than the saturation voltage is still increasing with the voltage applied (Fig. 7.8, second snapshots). Therefore, although the contact angle saturation limits the steady states of electrowetting droplets, it does not affect to the transient states. Thus, it is possible to use this interesting effect to improve the detachment of droplets under electrowetting actuation.

It is reported that contact angle saturation of electrowetting droplets is related to the electrical properties of the dielectric layers that allows how much energy can be stored inside this layer [32]. As a result, overshoot in the energy that charged to the dielectric layer in transient states of the charging process may cause overshoots in the net forces pulling the droplet contact lines. These overshoots happen at a very short time after the voltage is applied. This net force can be achieved by integrating the horizontal component of the Maxwell stress tensor [5, 29, 101]:

$$F_e = \frac{\epsilon\epsilon_0 V^2}{2d} = \sigma\eta_e. \quad (7.15)$$

Here, we use the electrical electrowetting number, termed as η_e , to denote for the effect of the over-saturation voltage to distinguish with the hydrodynamical electrowetting number η . The overshoot of the net force F_e causes increasing in the maximum deformation of droplets in the transient states (Fig. 7.8, second column of snapshots). Unfortunately, due to the current limit in understanding of electrowetting contact angle saturation, an exact explanation for this effect is out of scope of this thesis.

7.4.3 Phase diagram of droplet detachment under maximum deformation actuation

The maximum deformation of droplets and the over-saturation actuation provide additional surface energies to droplets. As a result, it is possible to extend the detachable regimes of droplets using this actuation method. In Fig. 7.9, we show a phase diagram of droplets under maximum deformation actuation. Compare this phase diagram with the phase diagram of detaching droplets under steady electrowetting actuation (Fig. 7.2), we can see that the detachable behaviours typically occur at lower electrowetting numbers. Moreover, smaller droplets, i.e., $R \leq 0.125$ mm now can be detached from the substrate with $\eta_e \geq \eta_s = 1.51$ (Fig. 7.9(a)). The phase diagram of detachable regimes has been expanded.

We explore this extension of the phase diagram by applying the analysis of detaching droplets from steady state into the maximum deformation case. However, due to the non-spherical shape of droplets at maximum deformation states, we are not able to estimate the surface energy of the droplets. Fortunately, by comparing the values of α (given in Eq. 5.11) and η for $\eta \leq \eta_s = 1.51$, we can roughly scale $\alpha \approx 0.5\eta$. The error of this approximation is less than 4%. We note that this approximation is only valid for non-saturation actuation cases, i.e., $\eta \leq \eta_s = 1.51$. As a result, Eq. 7.12 reduces to

Figure 7.9: (a) Phase diagram of detachable actuation (blue open diamonds) and non-detachable actuation (green solid squares) of 1.0 mPa.s droplets with different radius R . (b) Phase diagram of detachable actuation (blue open diamonds) and non-detachable actuation (green solid squares) of 1.0 mm diameter droplets with different viscosity μ . All the data here are collected from the experiment of maximum spreading actuation.

$(0.5\eta - \pi \sin^2 \theta_r / \ln(L/\gamma)) / \eta \geq \xi$, which can be rearranged in the form

$$\eta \geq \frac{\pi \sin^2 \theta_r}{\ln(L/\gamma)} \frac{1}{0.5 - \xi}. \quad (7.16)$$

Interestingly, the LHS of Eq. 7.16 represents the initial condition of droplets while the RHS shows the properties of the system including properties of the droplets, the outer phase and the substrate.

In Fig. 7.10, we show the phase diagram (Fig. 7.9) rearranged with η on the vertical axis and $0.5 - \xi$ on the horizontal axis for non-saturation voltage only. The extended detachable regime is observed proving the higher efficiency of maximum deformation actuation method.

Figure 7.10: Plot of η versus $0.5 - \xi$ by a rearrangement of the data from Fig. 7.9. The dash line represents the detachable to nondetachable (D-N) transition in the case of droplets detaching from steady state (Eq. 7.12 with $\ln(L/\gamma) = 8$).

7.5 Detaching velocity of droplets

We now examine the detaching velocity of droplets under both steady state and maximum spreading actuations. We define detaching velocity as the velocity of the centre of mass of a droplet at the moment when the detachment takes place. Considering the energy conservation, the kinetic energy of a droplet at the detaching moment is

$$E_k = E_s - E_{cl} - W_d. \quad (7.17)$$

We note that the amount of kinetic energy resulted from E_{cl} is excluded from the calculation of the detaching velocity (Eq. 7.17), since we are considering the detaching velocity at the moment when the droplet just detaches. We now assume that the kinetic energy of the internal flows inside the droplet is negligible and the droplet maintains its spherical shape at the detaching moment. As a result, the kinetic energy E_k can be calculated as: $E_k = (2/3)\rho\pi R^3 u_d^2$. In other words,

$$u_d \sim \left(\frac{3}{2}\right)^{1/2} \left(\frac{r_e}{\tau_u}\right) \left(\frac{\alpha - \pi \sin \theta_r / \ln(L/\gamma)}{\eta} - \xi\right)^{1/2}. \quad (7.18)$$

If we denote $U_r = r_e/\tau_u$ as the characteristic velocity of the retracting motion of the droplet, Eq. 7.18 can be rewrite in the dimensionless form as

$$\frac{u_d}{U_r} \sim \left(\frac{3}{2}\right)^{1/2} \left(\frac{\alpha - \pi \sin \theta_r / \ln(L/\gamma)}{\eta} - \xi\right)^{1/2}. \quad (7.19)$$

Figure 7.11: (a) Plot showing detaching velocity u_d for steady actuation with non-saturation voltages. The data are collected from the detached droplets in Fig. 7.2. The numbers in square brackets represent the actuated electrowetting number η . (b) Data in (a) rearranged to reveal the linear relation between u_d/U_r and $[(\alpha - \pi \sin \theta_r / \ln(L/\gamma)) / \eta - \xi]^{1/2}$. A best fit of this data to Eq. 7.18 gives the slope of the solid line 2.17 ± 0.76 which is very close to the coefficient $(3/2)^{1/2}$ in the Eq. 7.18.

Fig. 7.11(a) shows the experimental detaching velocity u_d versus μ of detached droplets from steady state actuation for different droplet radius. The numbers in the square brackets represent the electrowetting number. We observe that when μ increases, the detaching velocity decreases due to the greater dissipation in the system. For a fix value of μ , increasing η causes droplets to detach with higher velocity. For instance, for $R = 0.5$ mm droplets (red dots) having $\mu = 1.0$ mPas, when η increases from 1.06 to 1.52, the detaching velocity increases from 10 mm/s to 65 mm/s. In Fig. 7.11(b), we rearrange the

Figure 7.12: (a) Plot of detaching velocity u_d versus electrical electrowetting number η_e for different droplet radius R . (b) Plot of detaching velocity u_d versus electrical electrowetting number η_e for different droplet viscosity μ . The experiments are done in 2 cSt silicone oil.

data in Fig. 7.11(a) to reveal the dependence of u_d/U_r on $((\alpha - \pi \sin \theta_r / \ln(L/\gamma)) / \eta - \xi)^{1/2}$ which are the two sides of Eq. 7.19. Interestingly, all our data collapse into a single line confirming the validation of Eq. 7.18 in describing the detaching velocity of droplets under steady actuation. Best fit to Eq. 7.18 gives the slope of the solid line 2.17 ± 0.76 which is very similar to the coefficient $(3/2)^{1/2}$ in the Eq. 7.18. The shift of the fitting line over the origin may be caused from the assumption that the internal kinetic energy of droplets at the detaching moment is ignored.

In the case of detaching from maximum deformation with non-saturation voltage, ones can think that the expression for u_d is the same as Eq. 7.18 but replacing r_e by $r_{\max}$:

$$u'_d \sim \left(\frac{3}{2}\right)^{1/2} \left(\frac{r_{\max}}{\tau_u}\right) \left(\frac{\alpha - \pi \sin \theta_r / \ln(L/\gamma)}{\eta} - \xi\right)^{1/2}. \quad (7.20)$$

The characteristic retracting velocity now can be calculated by $U_r = r_{\max} / \tau_u$ giving a suggestion that U_r can also be used as the characteristic velocity of the detaching dynamics.

Unfortunately, in the case of droplets detaching from maximum deformation, we have no exact description for α since the initial state is no longer a spherical cap. As a result, experimentally verification of Eq. 7.20 cannot be done within the scope of this work.

Fig. 7.12 shows the detaching velocities of droplets under maximum deformation with η_e is varied over the saturation voltages. We observe that when $\eta_e \leq 2$, the detaching velocity has a linear relation with η_e . However, when $\eta_e \geq 2$, the detaching velocity saturates. This result is observed for droplets either with different radius R (Fig. 7.12(a)), or with different viscosity μ (Fig. 7.12(b)). The linear relation between u'_d and η_e for $\eta_e \leq 2$ can be explained by Eq. 7.20. We can see that if we approximate $\beta_e \sim \eta^{1/2}$ [51], $r_e = \beta_e R \sim \eta^{1/2} R$. In addition, $\tau_u \sim \eta^{-1/2}$ leading in $U_r \sim \eta$ resulting in $u_d \sim \eta$. The linear relation between the detaching velocity and the electrowetting number is observed for both detaching methods (Figs. 7.11 and 7.12). The saturation of u'_d when $\eta_e \geq 2$ can be considered as the maximum detaching velocity of a droplet using electrowetting actuation. This is reasonable because the maximum force pulling the contact line horizontally is $F_{\max} = \cos 0 - \cos \pi = 2\sigma$. As a result, this is the limit of hydrodynamical responses of any droplet under electrowetting actuation.

7.6 Summary

In summary, we systematically investigate the dynamics of the detachment of droplets under electrowetting actuation. By conducting a PIV experiment, we are able to study different sources of the energy dissipation by viscous effects and confirm that contact line dissipation contributes mostly to the energy dissipation. We also examine the effects of contact line elasticity on the detachment of droplets using electrowetting. Based on energy conversion of actuated droplets, we develop a simple theoretical model capturing the transition between the detachable and non-detachable behaviours of the droplets. Our model is verified by our experimental data with various control parameters. We also extend the detachable regime of droplets under electrowetting actuation by using maximum deformation actuation and voltages varied over the contact angle saturation limits. This gives a more powerful technique for detaching of droplets in practical applications. Finally, we experimentally study the detaching velocity of droplets. We also propose a theoretical model based on the energy equation that can be used to normalise the detaching velocity of droplets with different η , μ and R . The linear relation between the detaching velocity and electrowetting number is observed for both methods of actuation.

Chapter 8

Spreading and retracting dynamics of droplets upon impact on dielectrowetting substrates

In this chapter, we investigate spreading and retracting dynamics of droplets upon impact on dielectrowetting substrates. We find that the dielectrowetting effects facilitates the spreading of droplets on solid substrates, whereas it restricts the retracting of the droplets. More interestingly, the retracting dynamics are asymmetrical. We propose and verify a timescale characterising the retracting dynamics of droplets. By using dielectrowetting effects, we are able to control the retracting dynamics of droplets and subsequently provide a basic understanding for actuating droplet applications with EWOD without the top-electrode.

8.1 Introduction

Currently, dielectrowetting has been used efficiently in assisting liquid spreading and super-spreading on solid substrates [86, 87] by changing the substrate's wettability. In this chapter, we investigate spreading and retracting dynamics of droplets on solid substrates under dielectrowetting effects caused by applications of an electric field to electrodes beneath the substrates. We spread a droplet on the solid substrates by falling the droplet from a distance above the substrate. We then characterise the influence of the voltage amplitude on both spreading and retracting stages. We consider the dynamics of the droplets in both directions, i.e., along and perpendicular to the electrodes. We then discuss theoretical models related to the dynamics of the both stages focusing on the dependence of the maximum spreading factor and the retracting dynamics on the applied voltage. We finally test the proposed theoretical models by our experimental data with a sufficiently varied

Figure 8.1: (a) Schematic of the experimental setup for the droplet impact on dielectrowetting substrates experiment. (b) Plot of equilibrium contact angle θ_e observed on the longitudinal direction versus the applied voltage V_p . The upper snapshots are the deformations of the droplet in the transverse direction D_T showing that the contact angle does not change regardless to the applied voltage. The lower snapshots show the deformation of the droplet in the longitudinal direction D_L . (c) Linear plot of $\eta = \cos \theta_e - \cos \theta_0$ versus V_p^2 . The solid line shows the best fit of the equation $\eta = m_{\text{exp}} V_p^2$ to the experimental data. Here, $m_{\text{exp}} = (1.01 \pm 0.02) \times 10^{-5}$ is a fitting parameter. (d) Snapshots showing the temporal evolutions of droplets upon impacting, spreading and retracting for the D_L directions with different applied voltages.

range of the voltage. Our study aims to understand the dynamics of droplets in order to provide a physical background for vertical actuation of droplets using top-electrode-free EWOD configuration.

8.2 Experimental method and material

Fig. 8.1a illustrates the schematic of our experimental substrate. We deposit gold electrodes on glass wafers by sputtering vaporised gold onto photo-lithographed wafers. The

Figure 8.2: (a) Linear plot of contact length D_L (red circles) and contact width D_T (green diamonds) of an impact droplet versus time t for two voltage levels, i.e. $V_p = 0$ V (solid markers) and $V_p = 240$ V (open markers).

width of each electrode and the gap between the electrodes are $\Phi = 50 \mu\text{m}$ (see Fig. 8.1a). We then cover the electrodes with a silicon nitride layer (Si_3N_4) having thickness $d = 500$ nm using the plasma-enhanced chemical vapor deposition (PECVD) technique. On top of the Silicon nitride layer, we spin coat a 50 nm fluoropolymer layer [60] to make the surface hydrophobic. Contact angles of glycerol-water droplets without the applied voltage is as high as $\theta_0 \approx 110^\circ$ (see Fig. 8.1(b) snapshots). We use AC voltage with frequency $f = 10$ kHz and amplitudes varied in the range $0 \text{ V} \geq V_p \geq 295 \text{ V}$ by using a high voltage amplifier to amplify sine wave signals generated from a function generator (see Chapter 3 for more information about the experimental setup).

We first characterise our experimental setup by conducting a static experiment of dielectrowetting. The reduction of static contact angle θ_e upon the applied voltage V_p is shown in Fig. 8.1(b). Here, V_p is the zero-to-peak amplitude of the applied AC voltage. The penetration depth of the electric field to the dielectric liquid is $\delta = 4\Phi/\pi \sim 64 \mu\text{m}$ [86] (see Chapter 2 for more information on the physical principle of this phenomenon). The quadratic relation between θ_e and V_p leads in the linear relation between η and V_p^2 as shown in Fig. 8.1(c). The fitting line in Fig. 8.1(c) has a slope $m_{\text{exp}} = (1.01 \pm 0.02) \times 10^{-5}$. The predicted slope of Eq. 2.7 after corrected using the voltage reduction factor (Eq. 2.8) caused by the dielectric layer [86] is $m_p = 3.03 \times 10^{-5}$ that is in order of m_{exp} .

For the experiment of spreading and retracting of droplets upon impact to the substrate, we use aqueous glycerol solutions consisting of 70 %wt glycerol and 30 %wt DI water as working liquids for generating droplets. The solution is a dielectric liquid having

dielectric constant $\epsilon_1 = 55.6$ [112]. At the recorded temperature of the experiment, typically 25°C , the working liquid has surface tension $\sigma = 65 \text{ mN.m}^{-1}$, density $\rho = 1.18 \text{ g.cm}^{-3}$ and dynamic viscosity $\mu = 20 \text{ mPas}$ which are all measured experimentally. We generate droplets by dispensing liquid from a needle and let it fall from 25 cm above the substrate. The diameters of the generated droplets are kept fixed at $D_0 = 2.2 \pm 0.01 \text{ mm}$. The measured velocities of the droplets before impact are $v = 2.18 \pm 0.05 \text{ m.s}^{-1}$. This gives Weber number $We = \rho v^2 D_0 / 2\sigma = 88.1$, Reynolds number $Re = \rho v D_0 / 2\mu = 136.3$ showing the dominance of inertia and kinetic energy in the spreading stages. The Ohnesorge number $Oh = \mu / (\rho \sigma D_0 / 2)^{1/2} = 6.9 \times 10^{-2}$ representing that the influence of viscosity is significant. Therefore, upon impact, the droplets spread without splashing or bouncing [113] and consequently retract slowly without the contact line oscillation (see Fig. 8.1(d)). To observe the spreading and retracting processes, we use two high-speed cameras, (SA5 and SAX, Photron) placed at the two sides of the substrate. All the cameras run at 40,000 frame-per-second giving time resolution 25 microseconds/frame. One of them captures the deformation on the longitudinal direction D_L , the same direction with the electrodes; the other one observes the deformation in the transverse direction D_T which is perpendicular to the electrodes (see Fig. 8.1(a)). Typical changes of D_L are shown by the snapshots in Fig. 8.1(d). When V_p increased, the impacting dynamics change significantly. In the spreading stages ($t \leq 2.5 \text{ ms}$), although the maximum spreading time is mostly constant, the maximum spreading length increases. In the retracting stages ($t \geq 2.5 \text{ ms}$), the droplets retract slower when the voltage is higher. We will quantitatively study both stages experimentally and analytically in the next sections of the chapter.

8.3 Asymmetrical spreading and retracting dynamics

By using image processing technique, we extract the spreading lengths on both directions, i.e., D_L and D_T , from the recorded images. In Fig. 8.2, we show the temporal evolutions of D_L (red circles) and D_T (green diamonds) for two voltage levels, i.e., $V_p = 0 \text{ V}$ (solid markers) and $V_p = 240 \text{ V}$ (open markers). We observe that, when no voltage is applied, the spreading and retracting of D_L and D_T are mostly the same representing that the spreading and retracting are symmetrical on both sides. When $V_p = 240 \text{ V}$ is applied, in the spreading stages, the maximum spreading radius increases in both directions, but it increases more on the D_L compared to the D_T direction. In the retracting stages, asymmetrical motions of the contact line are observed. The D_L retracts slower compared

Figure 8.3: (a) Linear plot of normalised contact length D_L/D_{Lmax} versus time t of impact droplets for different applied voltages. (b) Linear plot of normalised contact width D_T/D_{Tmax} versus time t of impact droplets for different applied voltages. (c) Linear plot of the maximum longitudinal spreading factor $\beta_{Lmax} = D_{Lmax}/D_0$ versus the applied voltage V_p (red circles), and the maximum transverse spreading factor $\beta_{Tmax} = D_{Tmax}/D_0$ versus the applied voltage V_p (green diamonds).

to the D_T . We note that the current theory on dielectrowetting is only applied for the D_L direction. The dynamics of spreading and retracting on the D_T direction is still unknown [86, 87].

8.4 Spreading dynamics

We investigate this phenomenon more detail by changing the voltage from 0 V to 290 V (Fig. 8.3) with steps of 50 V. In Figs. 8.3(a) and (b), we normalise D_L and D_T , respectively, by $D_{L\max}$ and $D_{T\max}$ which are the maximum spreading lengths on the two directions. By carrying out this normalisation, we observe that the spreading stages on both directions collapse very well representing that the dynamics of the spreading stages are self-similar and can be represented by the maximum spreading lengths. Thus, we define maximum spreading factors $\beta_{L\max} = D_{L\max}/D_0$ for the longitudinal direction and $\beta_{T\max} = D_{T\max}/D_0$ for the transverse direction. In Fig. 8.3(c), we show the dependence of these maximum spreading factors on the applied voltage V_p . We observe that both the maximum spreading factors have linear dependencies on the applied voltage. However, $\beta_{L\max}$ increases faster than $\beta_{T\max}$ when the voltage is increased. This means that the spreading is facilitated by the applied voltage and it favors the longitudinal direction.

We argue that while the spreading dynamics on the two directions are different due to the asymmetrical arrangement of the electric field generated by the electrodes, the change of the liquid-solid contact area should be according to the change of the liquid-solid surface energy, which is resulted from the dielectrowetting effect, in order to form the new equilibrium having minimum surface energies. To examine the change in the contact area, we assume that the contact line has an elliptic shape. As a result, the contact area can be calculated by $S = (\pi/4)D_LD_T$. We define the general maximum spreading factor as $\beta_{S\max} = (D_{L\max}D_{T\max})^{1/2}/D_0$, or $\beta_{S\max} = (\beta_{L\max}\beta_{T\max})^{1/2}$. We also argue that the change in surface energies contributes to the maximum spreading factors via the spreading by capillary, i.e., the spreading when the impacting velocity is vanished. This zero-velocity spreading factor can be calculated by $\beta_e = (D_{Le}D_{Te})^{1/2}/D_0$ [114]. Here, D_{Le} and D_{Te} are, respectively, the longitudinal and transverse contact lengths of the droplet at the final equilibrium, i.e., the equilibrium after the retracting stages. By balancing the kinetic energy and surface free energy in the spreading stages and taking into account the zero-velocity spreading factor, ones achieve [114]:

$$(\beta_{S\max}^2 - \beta_e^2)^{1/2} \sim \frac{We^{1/2}}{Re^{1/5}(A + We^{1/2})} = \text{const.} \quad (8.1)$$

In Fig. 8.4(a), we show the dependence of $\beta_{S\max}$ on V_p . The insignificant influence of V_p on $(\beta_{S\max}^2 - \beta_e^2)^{1/2}$ is shown in the inset of Fig. 8.4(a). When the voltage increases, $(\beta_{S\max}^2 - \beta_e^2)^{1/2} = 2.27 \pm 0.05$ is constant showing that the wettability of the solid surface

Figure 8.4: (a) Linear plot of spreading factor of the contact area $\beta_{Lmax}\beta_{Tmax}$ versus V_p . Inset: plot of $(\beta_{Lmax}\beta_{Tmax} - \beta_e^2)^{1/2}$ versus the applied voltage. We observe that $(\beta_{Lmax}\beta_{Tmax} - \beta_e^2)^{1/2} = 2.27 \pm 0.05$ is constant regardless to the applied voltage. (b) Linear plot of the normalised spreading factor of contact area β_S/β_{Smax} versus time t . The data in the spreading stages collapse very well whereas those in the retracting stages do not. (c) Linear plot of the normalised spreading factors of contact area in the spreading stages versus the dimensionless time $\tau \ln(\gamma/L)$. The data excellently collapse showing that τ is indeed the characteristic timescale of the retracting dynamics. Inset: plot of $\tau \ln(\gamma/L)$ versus applied voltage V_p .

contributes to the spreading factor β_{Smax} of droplet impact through β_e (inset of Fig. 8.4(a)). Best fit the data in the inset of Fig. 8.4(a) to Eq. 8.1 gives $A = -7.83 \pm 0.04$ for all values of V_p .

8.5 Retracting dynamics

It is reasonable that when the applied voltage facilitates the spreading stage, it resists the motions of the contact line in the retracting stage. In contrast to the spreading stage which is driven by the kinetic energy, in the retracting stage, the change in the solid-liquid free energy drives the motion of the contact line. To calculate the driving force, we need to calculate the contact line length which is the perimeter of the contact area. Since there is no exact solution for the perimeter of the elliptic contact area, we assume that it approximates to a circle with radius $R = [(D_L^2 + D_T^2)/8]^{1/2}$. As a result, the capillary force acting at the contact line can be estimated by

$$F_{ct} = 2\pi R(t)\sigma(\cos \theta_t - \cos \theta_e), \quad (8.2)$$

where θ_t is the instantaneous contact angle. This force depends on the wettability of the solid substrate represented by the static contact angle. When a voltage is applied, dielectrowetting effect makes the static contact angle drops reducing the capillary force.

On the other hand, due to the dominance of the viscous effects in the retracting stage, viscous dissipation plays an important role in resisting the motion. One of the possible methods to examine the dissipation of a retracting droplet in air uses the approach of de Gennes[40] for dissipation by viscous effects inside the wedge at the vicinity of the contact line:

$$T = \frac{3\mu\dot{R}(t)^2}{\theta_t} \ln\left(\frac{L}{\gamma}\right), \quad (8.3)$$

where $L \sim D_0/2$ is the macroscopic cut-off length, $\gamma \sim \Gamma/\theta_t^2$ is the microscopic cut-off length, with Γ is molecular size. This dissipation can be seen by the work of friction per unit length of the contact line $W = -F_f\dot{R}(t)/2\pi R(t)$. By balancing this work and the dissipation in Eq. 8.3 we get the equivalent friction force acting at the vicinity of the contact line

$$F_f = -\frac{6\pi\mu}{\theta_t} \ln\left(\frac{L}{\gamma}\right) R(t)\dot{R}(t). \quad (8.4)$$

We note that due to the fast dynamics of the whole spreading and retracting stages, i.e., in order of milliseconds, evaporation of droplets can be ignored leading in conservation of droplet volume which is $\pi D_0^3/6 \sim (\pi/4)\theta_t R(t)^3$. Eqs. (8.2), (8.4) and the volume conservation result in the description for a characteristic timescale of the retraction dynamics of droplet impact [100]

$$\tau \sim \varepsilon^{-1} \approx \left(\frac{25}{3}\right)^{1/3} \frac{5\ln(L/\gamma)}{(1 - \cos\theta_e)^{5/3}} \tau_v. \quad (8.5)$$

Here, $\tau_v = \mu D_0/2\sigma$ is the viscous timescale; $\varepsilon = \max\left[\dot{R}(t)/R(t)\right]$ is the retraction rate [100]. In Fig. 8.4(c), we show the collapse data using the timescale $\tau/\ln(L/\gamma) = \tau \ln(\gamma/L)$ of the data for the retracting stage shown in Fig. 8.4(b). Here we define the spreading factor of the contact area $\beta_S = (D_L D_T)^{1/2}/D_0$. The data is excellent collapsed showing that the dependence $\tau \sim (1 - \cos\theta_e)^{-5/3}$ extracted from Eq. 8.5 is valid. We also show the values of $\tau \ln(\gamma/L)$ versus the applied voltage V_p in the inset of Fig. 8.4(c). When V_p is increased making θ_e drops (Eq. 2.7), the characteristic timescale τ increases representing the slower retraction dynamics.

8.6 Summary

In conclusion, this chapter shows a new effect of electric field on retracting dynamics of droplets upon impact to solid surfaces. We find that, by increasing the strength of the field, the maximum spreading factor increase linearly in the spreading stages. This is due to the increasing of spreading factor by pure capillary, i.e., the spreading factor when the impacting velocity is zero. In the retracting stages, we observe that the retraction dynamics are asymmetrical. We also find that the dynamics become slower when the voltage is increased. By balancing the driving force and friction at the contact line, we establish a characteristic timescale that characterise the dynamics. The timescale works well with our experimental data by excellently collapsing all the data of the retracting stages in our experiment. However, this study just gives a very basic understanding on this new and interesting effect. Further studies are needed in the future in order to achieve a full knowledge of the phenomenon and to look towards its applications.

Chapter 9

Conclusions and outlook

9.1 Conclusions

In this thesis, we present the contact line dynamics of droplets under electrowetting actuation. We focus on various contact line phenomena including spreading, retracting and impacting of droplets on solid substrates with a presence of electric fields that cause electrowetting or dielectrowetting effects. In Chapter 4, we find that viscosity of droplets μ and viscosity of outer fluids μ_o contribute equally to the contact line friction coefficients in high viscosity regime. As a result, the contact line friction coefficients can be described by the geometric mean of the two viscosities. Based on this result, we derive a characteristic timescale that describes the spreading and retracting dynamics of viscous droplets on solid substrates. The timescale is tested and confirmed for different μ , μ_o in both the spreading and the retracting stages. We also find that, in this regime, the spreading and retracting rates have an inversely proportional relation to the characteristic timescale.

In Chapter 5, we investigate the transient dynamics of droplets spreading under electrowetting actuation. We determine two transient dynamical regimes of droplet behaviours, i.e., underdamped and overdamped regimes. In underdamped regime, the inertia of the whole actuated droplet resists to the electrical driving force resulting in overshoots of the contact line in the droplets' behaviours. We then derive the characteristic timescale for this behaviour based on the inertial timescale. In the overdamped regime, the contact line friction is the dominant factor among the resisting forces. Droplets in this regime response to the actuation slowly and monotonically. We base on the analysis from Chapter 4 to establish the characteristic timescale that describes the dynamics of this regime. By comparing the two characteristic timescales, we derive the condition for the transition between the two dynamical regimes. The two timescales as well as the transition are consistent with our experimental data having about three order-of-magnitude of the varying control

parameters. Also, we study the actuation time of droplets under electrowetting actuation. We find that the actuation time not only depends on the system parameters, but it is also affected by the hydrodynamical behaviours of the actuated droplets, i.e., it is minimised at the transition between the two hydrodynamical regimes. We also derive mathematical descriptions for this minimum actuation time and the dependencies of the actuation time on system parameters such as the applied voltage and the droplet radius.

In Chapter 6, we investigate the dependence of the droplet behaviours on substrate's properties, particularly, the dielectric materials. By properly choosing the materials and thicknesses of the dielectric layers, we are able to bring the actuating voltage to as low as 10 V while maintaining large changes in contact angles. We then investigate the contact line friction of the substrates and find that the dielectric material has an insignificant effect on the contact line friction coefficients. We suggest that Silicon nitride - Teflon is a suitable combination of materials for designing EWOD chips for droplet manipulating applications due to its strength in electrical breakdown voltage, considerable low in actuating voltage, and acceptable friction coefficients of contact line dynamics.

Next, in Chapter 7, we investigate the conditions for vertical actuation of droplets under electrowetting actuation. By conducting a PIV experiment, we are able to determine different sources of the energy dissipation during the actuation. We confirm that contact line dissipation contributes the most significantly to the energy dissipation. We also find that the contact line pinning has a significant effect on the detachment of the actuated droplets. Based on these findings, we develop a theoretical model capturing the transition between the detachable and non-detachable behaviours of droplets. Our model is consistent with our experimental data for various control parameters. We also extend our study on droplet detachment to maximum deformation method with high applied voltage. We find that although the static contact angles saturate when the voltage applied is higher than the saturation voltage, the over-saturation voltage still facilitates the deformation of droplets in the transient states. We take advantage of this interesting effect to extend the detachable regime of droplet detachment under the electrowetting actuation. We show that it is possible to detach droplets with smaller size and higher viscosity compared to the non-saturation detaching methods. The initial velocities of the detached droplets in all the actuation methods, i.e., detachment from steady state methods, detachment from maximum deformation with and without over-saturation voltage methods, are also investigated in detail.

Finally, the contact line dynamics of droplets impacting on substrates with a presence of a non-uniform electric field is investigated in Chapter 8. The interplay of the kinetic energy in impacting phenomenon, and the capillarity in spreading and retracting dynamics, makes the dynamics of droplets impinging on dielectrowetting substrates very special. We find that, by increasing the strength of the electric field, the maximum spreading factors increase linearly in the spreading stages due to the assistance of the dielectrowetting effect. In the retracting stages, the dynamics become slower when the voltage increase. We also find that due to the difference in the dielectrowetting effects between the two directions, i.e., the longitudinal and transverse directions, the retraction dynamics becomes asymmetrical. By balancing the driving forces and the frictions at the contact line using P.G. de Gennes theory on contact line dissipation, we derive a characteristic timescale describing the retracting dynamics. The timescale works well with our experimental data as it excellently collapses all the data of the retracting stages in our experiment.

9.2 Outlooks

Beside the various aspects investigated in this thesis, the fascinating process of the contact line dynamics under electrowetting and dielectrowetting effects still holds a large number of mostly unexplored phenomena related to droplet manipulation using electric field, which seem worth studying.

It is an intriguing question how the over-saturation voltage affects to the transient dynamics of droplets under electrowetting actuation. To understand this effect, we might need to take a closer look into the electrical responses of the electrowetting process. In which, one of the most important factors is the properties of the dielectric material which is also known as the most crucial factor affecting to the contact angle saturation phenomenon. The electrical charging process of the dielectric layer causes overshoots in the electrical force acting on the contact line of the droplets. This also suggests that the behaviours of droplets for over-saturation voltage may depend on the frequency of the applied voltage. It would be very interesting to see what extent the dependence of the hydrodynamic behaviours of droplets on different dielectric layers under over-saturation voltage, especially when the voltage is at high frequency.

Another interesting aspect that is also related to Chapter 7 is the condition for droplet to detach under maximum deformation actuation. Due to the undefined surface

energy at the maximum deformation state, it is difficult to investigate this condition experimentally. Therefore, a numerical study based on the analysis of the energy conversion given in this thesis can give more information on the surface energy, therefore, provide a better understanding on this problem. Once the surface energy at the maximum deformation state is determined, the detaching velocity would also be calculated.

Taking one further step towards the vertical actuation of droplets using dielectrowetting effect, one could think of the effects of the geometry of the electrodes on detaching characteristics of the actuated droplets. The spatial distribution of the electric field on the solid surface is determined by this geometry. As a result, different arrangements of electrodes, e.g., rectangular or circular electrodes, would have different effects on the spreading and retracting dynamics of the actuated droplets, and eventually, affect to the detachment of the droplets differently. The geometry of the electrodes also plays a crucial role in determining the energy barrier of droplet detachment. As discussed in Chapter 7, it will also affect to the condition for droplet to detach. These effects will be of interests in both fundamental and industrial aspects.

In short, our findings, presented in this thesis, not only strengthen the current knowledge on contact line dynamics of droplets under electrowetting actuation, but also provide important technical guidelines in design, control and optimisation of droplet-manipulations using electrowetting as the core technology. Besides, our results also help in understanding other surface tension phenomena such as wetting, droplet impact, droplet evaporation due to the common physical essence of contact line dynamics. However, our investigations in this thesis are not enough to give a full understanding of the phenomena. Further studies are needed in the future in order to achieve a full knowledge of the phenomena and to look towards applications.

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