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THERMOCAPILLARY ACTUATION AND DROPLET MANIPULATION IN MICROFLUIDICS

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Abstract

The researches on actuation and manipulation of micro-droplets in microchannels or on solid surfaces have been active in recent years. Based on thermocapillary effects, manipulations and temperature recycling of discrete droplets can be achieved in micro-devices, which can provide technical support for genomics, proteomics, drug delivery, etc., in biochemical and biomedical areas. It is of interests in both academic understandings and practical applications to investigate the thermal-driven actuation of liquid droplets inside capillaries and planar microchannels.

This thesis presents a study on the actuation and manipulations of discrete droplet in microchannels based on thermocapillary effect. The major objective of the study is to investigate the transient and periodic motions of thermal-driven liquid droplet in both one dimensional and two dimensional microchannels. This is achieved by modeling the temperature variations inside the channels, the coupling of the temperature fields to the liquid surface tensions, and the dynamics of the liquid plugs/droplets under the actuation. Experiments are conducted, not only to verify the predicted results from the modeling, but also to provide further information on thermocapillary effects in microchannels. The feasibility of using thermocapillary effect to control the discrete droplets in micro-scale devices is examined.

The research associated with this thesis has been carried out in three stages, and the results are accordingly documented in three parts. Firstly, the periodic thermocapillary actuation of a liquid plug in capillary is studied. An analytical model is developed to predict the temperature distributions along the capillary generated by alternated heating conditions. The temperature field is then coupled to the liquid plug through surface tensions at the plug ends. The motion of the liquid plug is predicted in terms of the displacement and velocity.

In the experiments, wire heaters were used to create alternate heat fluxes at two ends of the working portion along the capillary tube. Silicone oil was injected into the tube by a precise syringe to form a micro liquid plug with certain length. The actual temperature distributions along the capillary tube were captured by a thermal-tracer camera against time, and the reciprocating motion trajectory of the plug was recorded by a CCD camera. All the data were processed and plotted with Matlab programs. The agreement between the theoretical predictions and the experimental results showed that the thermocapillary model works well in this case, and the reciprocating plug motion can be achieved with right switching frequencies.

Secondly, a further study on the thermocapillary actuation of liquid plug has been conducted to investigate additional issues arisen from the first part, including the subsequent actuation by a heater array, the actuation of water droplet encapsulation in oil plug, and the chaotic phenomena occurred under high heating switching frequency are investigated.

In order to achieve further control on the liquid plug in thermocapillary actuation, a heater array is used to obtain a longer plug traveling distance in actuation. The array consists of three heaters, and the maximum traveling distance of the liquid plug in periodic reciprocating motion can be determined by the subsequently working heaters. Analytical models for actuation and spatial temperature cycling with three heaters are built based on the transient temperature distribution model. The heater array actuation concept presented in this study not only extends the actuation distance but also at the same time provides thermal cycling of the liquid plug. This concept has the potential applications in DNA amplification for droplet-based microfluidics.

Since in many applications, aqueous droplets encapsulated in an immiscible fluid are often kept in a glass capillary for storage and postprocessing, the present study also demonstrates

the periodic thermocapillary actuation of a silicone oil plug with a water droplet encapsulated inside. The effects and performance of the actuation in this case are examined by both simulations and experiments.

Furthermore, chaotic phenomena can be observed when the heaters switching frequency is high. By constructing the phase-space portraits, evaluating the largest Lyapunov exponent and calculating the fractal dimension, the chaotic characteristics of liquid plug under high-frequency thermocapillary actuation are identified and proved. The chaotic motion of the liquid plug under the thermocapillary actuation suggests the potential of using chaotic plug motion to improve mixing in capillary-based microfluidics.

Thirdly, the thermocapillary actuation of a silicon oil droplet in a planar microchannel is investigated to extend the one dimensional thermocapillary control of liquid plugs to droplets in a two dimensional space. Four heaters are located along the four edges of a square channel and the actuation or manipulations are achieved by controlling the heating strengths and schemes. Two operation modes, transient actuation and periodic actuation, are studied. In the transient actuation, the droplet can be driven to any position in the channel determined by a heating code according to the heating strength of the heaters. In the periodic actuation, the droplet can be driven to move in closed loops whose patterns are controlled by the periodic heating schemes and frequencies. All predicted results are verified by experimental observations, in terms of temperature distributions, droplet moving tracks, displacements and velocities. It shows that the droplet can be manipulated with great flexibility in planar microchannels for various applications.

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Nomenclature

C	Constant normalizing the initial separation , see equation (4.24), page 108
c	Heat capacity , see equation (3.1), page 44
$C(R)$	correlation dimension of an attractor , see equation (4.29), page 110
d	Diameter , see equation (2.3), page 11
$d(t)$	Average divergence of trajectories with nearby initial conditions on the attractor at time t , see equation (4.24), page 108
D_h	Heaters distance , see equation (3.2), page 45
G	Channel geometry constant , see equation (2.3), page 11
G	Nonlinear functions , see equation (4.20), page 104
h	Natural convection coefficient , see equation (3.1), page 44
J	Time delay , see equation (4.23), page 105
k_a	Thermal conductivity of air
L_{plug}	Liquid plug length , see equation (3.16), page 50
M	Number of the reconstructed vectors , see equation (4.29), page 110
m	Reconstructed phase portrait dimension , see equation (4.23), page 105
P	Pressure , see equation (2.0), page 9
q''	Heat flux , see equation (3.2), page 45
R	Meniscus curvature radius , see equation (2.0), page 9
r	Radius , see equation (2.3), page 11
R_i	Capillary pipette inner radius , see equation (3.1), page 44
R_o	Capillary pipette outer radius , see equation (3.1), page 44

R_c	Critical radius , see equation (2.1), page 9
T	Temperature , see equation (2.1), page 9
t	The area of the needle point , see equation (3.1), page 44
t^*	Dimensionless time , see equation (3.3), page 46
u	The area of the needle point , see equation (3.1), page 44
u^*	Dimensionless velocity , see equation (3.3), page 46
U_E	Velocity of the constant profile , see equation (2.6), page 34
x	Distance , see equation (3.1), page 44
$X(i)$	n-component vector in the phase space , see equation (4.20), page 104
x^*	Dimensionless distance , see equation (3.3), page 46
y_s	Height of the droplet profile , see equation (2.6), page 34
Gr	Grashof number
Nu	Nusselt number
Pe	Peclet number
Pr	Prandtl number
Ra	Rayleigh number
Re	Reynolds number
St	Strohal number

Abbreviations

1-D	One-dimensional
2-D	Two-dimensional
ACF	Autocorrelation Function
DNA	Deoxyribonucleic acid
fps	frames per second

IDT	Interdigital Transducer
MEMS	Micro electromechanical system
MLE	Maximal Lyapunov exponent
PCR	Polymerase chain reaction
SAW	Surface acoustic wave
SDIC	Sensitive Dependence on Initial Conditions
TCP	Thermocapillary pump
TTL	Transistor-Transistor Logic

Subscripts

0	Reference point
12	Interface of two phase
a	Advancing
c	Critical point
g	Gas phase
l	Liquid phase
r	Receding
s	Solid phase

Greek Letters

α	Thermal diffusivity , see equation (3.1), page 44
γ	Surface tension coefficient, see equation (3.15), page 50
γ_{12}	Mutual interfacial tension of two pahse , see equation (2.0), page 9
λ	Lyapunov exponent , see equation (4.24), page 108
μ	Viscosity , see equation (2.6), page 34

- ϕ Contact angle , see equation (3.16), page 50
- ρ Density , see equation (2.3), page 11
- σ_{lg} Surface tension of the gas-liquid interface , see equation (2.1), page 9
- $\theta_{A,R}$ Advancing/Receding contact angle , see equation (2.3), page 11
- θ Heaviside function , see equation (4.29), page 110
- θ Temperature difference relative to room temperature , see equation (3.1), page 44

Superscripts

- " Flux
- * Dimensionless

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Chapter 1

Introduction

1.1 Background

The interest in microfluidic devices for simultaneously actuating liquid through micro-channels has grown fast in the past decade (Thorsen et al 2003). This kind of micro-droplet manipulation promotes automated synthesis and analysis of small liquid samples, significantly reducing reagent volume and cost. Device fabrications have benefited from advancing silicon processing, MEMs technology and the widespread use of inexpensive polymers for surface patterning and encapsulation.

Droplet-based or digital microfluidics has been emerged as an alternative for continuous-flow microfluidics. Microdroplets formed in miniature channels can be used as a means for reagent transport and a platform for chemical reactions. Microdroplets whose lengths are larger than the channel width are considered here as microplugs. Manipulation of micro-droplets or microplugs promise a huge potential in this new field of digital microfluidics (Atencia & Beebe 2005). Darhuber and Troian(2005) recently summarizes the different microfluidic actuation concepts based on the modulation of surface stresses. For instance, Pollack et al.(2000) used electrowetting effect to manipulate surface tension and subsequently to transport a droplet. Ren et al.(2002) reported a theory on the dynamic behavior of droplet transport based on electrowetting. Beside electrowetting, the surface tension gradient can also be induced by a temperature gradient. Brozoska et al.(1993) investigated the movement of a droplet on a flat surface in a temperature field. Darhuber et al.(2003)

and Tseng et al.(2004) recently studied the dynamic behaviors of microdroplets in a temperature field of a flat plate. Sammarco and Burns (2000) investigated the heat transfer process inside a droplet. Yarin et al.(2004) studied the movement of droplets surrounding a thin fiber with a temperature gradient and a temperature jump as the initial condition.

The thermocapillary technology has been developed to achieve the actuation of liquid micro-plugs in microchannel by using thermocapillary effects, in which the actuation of the droplet is achieved by creating a temperature gradient along the desired movement direction of the droplet. The temperature difference of the two ends of the droplet can cause the surface tension force difference, which will actuate the liquid droplet.

Thermal gradients can be generated by means of substrate embedded microheaters or by radiative heating (Hitt & Smith 1993, Schatz et al. 2002). Darhuber et al. (2003) examined the horizontal thermocapillary spreading of Newtonian liquids emanating from a small reservoir pad onto a wettable microstripe subject to a linear temperature decrease. Nguyen and Huang (2005) reported a simple analytical model for the 1-D transient behavior of a liquid plug in a capillary. The plug was subjected to a temperature gradient field created by wire heater at one end of the glass capillary. This 1-D model agreed well with the measured results. The same problem was investigated later by Glockner and Naterer (2005) with a two-dimensional (2-D) numerical model and microchannels fabricated in silicon.

This thesis presents a research on droplet actuation based on thermocapillary effect. It is an attempt to achieve the micro-scale actuation and manipulation of discrete liquid plugs and droplets without mechanical driving components.

Figure 1.1: Demonstration for the liquid cohesion and surface Tension (<http://hyperphysics.phy-astr.gsu.edu/Hbase/surten.html>)

1.2 Basic knowledge

Surface tension

If there is another substance contacting with the liquid, such as air or other kind of liquid, the attractive forces at the interface is called interface tension. Molecules of liquid state experience strong intermolecular attractive forces. When those forces are between the same molecules, they are referred to as cohesive forces, which holds the molecules of a liquid droplet together. The imbalance cohesive forces at the interface constitute surface tension. From Figure 1.1 shows that the cohesive forces between molecules inside a liquid are shared with all neighboring atoms. Those on the interface have no same neighboring atoms above and exhibit different attractive forces upon their nearest neighbors on the surface. This enhancement of the intermolecular attractive forces at the surface causes surface tension.

Meniscus and Contact angle at liquid-solid interface

A meniscus (plural: menisci, from the Greek for "crescent") is a curve in the surface of a liquid which is produced in response to the surface of the container or another object. It can be either concave or convex. A convex meniscus occurs when the molecules of the liquid repel the molecules of the container or object. This may be seen between mercury

Figure 1.2: Meniscus and contact angles of the liquid drop in a channel. (Nguyen & Huang, 2005)

and glass in barometers. A concave meniscus occurs when the molecules of the liquid attract those of the container. This can be seen between water and glass surface. Contact angle is a quantitative measurement of the wettability of liquid on a solid surface, which is defined as the angle between the liquid-solid interface direction and the solid surface at the intersection point of the three phases. Figure 1.2 illustrates a liquid droplet in the channel horizontal with solid/liquid, gas/solid and liquid/gas interfaces that conjoin at a point.

Micro-scale fluidics

Effects of reducing a system to the micrometer scale are the reduction of length scale and the increase of ratio of surface area to volume, often by several orders of magnitude. The length scale determines the dominant force in the devices, and surface-to-volume ratio helps to create more efficient mass and heat transfer in microsystems, as more interfaces are available for transferring and less total mass or energy needs to be transferred to reach the final state. Therefore the generation and homogenization of solute or temperature gradient are faster as the system size is reduced. In micro-devices, the length scale and surface-to-volume ratio are two important parameters indicating the characteristics of the system mechanics. The large surface-to-volume ratio in a micro-device accentuates the role of surface force as well as other surface effects in general. In micro-channel flows, the Reynolds number, which shows the ratio between the viscous force and the inertial force, is typically small. However, in the case when gas is the working fluid, the size can be small enough to further modify the viscous effect when the device length scale is on the order of

the mean free path of the gas molecules.

Droplet-based microfluidics becomes increasingly popular with a number of interesting applications such as chemical analysis and protein crystallization (Song et al 2003). Encapsulation of nanoliter droplets can also be achieved with a double emulsion, where an intermediate fluid layer works as an additional barrier between the droplet and the carrier fluid (Okushima et al 2004; Utada et al 2005). In the applications mentioned above, microdroplets are often generated in a microfluidic device and stored as liquid plugs in a glass capillary for storage and postprocessing (Chen et al 2005). These liquid plugs stored inside a glass capillary can be manipulated and heated by external heaters to achieve one dimensional continuous movement. The technical implementation of such kind of actuation is relatively simple and does not need micro-fabrication. Thermocapillary technique can also be applied in two dimensional planar channel to achieve more complicated operations like merging, and mixing.

1.3 Objectives and Scope

The ultimate intension of this thesis is to study the mechanism and various operations of thermocapillary actuation in micro-scale. The major objectives are:

1. Study the transient and periodic dynamics of thermal driven discrete droplet in one dimensional and two dimensional micro-channels.
2. Investigate the mechanism of thermal fluidic interactions in microchannels.
3. Develop a controllable thermocapillary device for discrete droplets manipulation in microchannels.

The scope of this study encompasses the following aspects:

1. To develop analytical models for the temperature distribution and plug motions under periodic actuations in a 1-D capillary.

2. To carry out experimental studies on temperature measurement and liquid plug motion recording in capillaries.
3. To conduct the further studies on the thermocapillary actuation of liquid plug in capillary by different experimental approaches and analysis.
4. To develop analytical models for the temperature distribution and the thermal driven micro-droplet manipulations in a 2-D planar channel.
5. To conduct experimental studies on temperature measurement and droplet manipulations in 2-D microchannels.

1.4 Layout of thesis

The thesis consists of six chapters. In the current chapter one, the background and the introduction to the researches are given. A literature review of modern techniques for microscale actuation will be highlighted and discussed in chapter two. In chapter three, both modeling and experiments on periodic thermocapillary actuation in capillaries will be presented. In chapter four, further studies will be conducted on the thermocapillary actuation of liquid plug in capillaries, including the actuation of liquid plug by a heater array, the actuation of oil plug with water drop encapsulated inside and the chaotic motion of liquid plug under high frequency actuation, etc. Chapter five focuses on the droplet motion in a two dimensional planar channel, actuated by four embedded micro-heaters, in both transient and periodic temperature fields. In chapter six, the thesis concludes with a summary of the theoretical and experimental results obtained so far in this study. Some future work plans are also highlighted in this chapter, leading to the further research.

Chapter 2

Literature Review

2.1 Droplet actuation by curvature differences

In the presence of the non-uniformities in the liquid plug end surface curvature created by the non-uniform cross-section, a surface shear stress difference appears which drives the flow towards the direction of the end having higher interfacial tension force. The decreasing of contact angle increases the surface tension force component in the traveling direction. From the static capillary study it can be seen that, the active actuation of a certain length

Figure 2.1: A liquid plug with contact angle smaller than 90° moves toward the narrow gap region (Bico & Quere. 2002).

droplet can be achieved by establishing a difference in the surface contact angles at the ends of it, as the different contact angle can produce different surface tension force with the same surface tension. Hauksbee (1712) described the motion of a wetting droplet sandwiched in-between flat and nonparallel plates. Figure 2.1 demonstrates this experiment. In the experiment the liquid droplet moved towards the converging end, which had smaller contact angle, with increasing speed. In the same fashion, Bouasse (1924) found that a plug in an open conical tube migrates toward the cone tip for wetting liquids. Weislogel

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(1997) observed a similar effect in capillary tubes whose interior surfaces were partially coated to induce differences in contact angle.

Without energy input, this self propulsion method can be used in single-trip actuation manipulation, or to enhance the other method if the movement is too slow. It should be pointed out that this kind of actuation method is for one time single trip and is not reversible.

2.2 Droplet actuation by surface tension difference

In the presence of the non-uniformities in the surface temperature (thermocapillary flows), chemical composition (Marangoni flows), or charge density (electro-capillary flows) the gradients of the interfacial tension of a fluid-liquid interface can be produced. These give rise to a surface shear stress difference, which drags the flow towards the regions of higher interfacial tension.

2.2.1 Physical modification of surface tension

2.2.1.1 Bislug method

Figure 2.2: A self-propelled bislug ($\gamma_{12} = 18.0$ mN/m) of ethylene glycol ($\gamma_1 = 47.7$ mN/m) and silicone oil ($\gamma_2 = 20.3$ mN/m) in a 1 mm diameter glass capillary (Bico & Quere. 2002).

Basic mechanism A bislug consisting of two immiscible liquids of different surface tension within a capillary behaves analogously like the non-uniform cross-section channel method, where the liquid droplet is in self-propulsion. Marangoni (1871) reported the spontaneous motion of a water-carbon disulfide bislug in a glass capillary. Bico & Quere (2002) conducted an experimental study of liquid bi-slug in capillary tubes, taking into

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account of film entrainment. Bi-slug motion requires that one of the liquids be completely wetting. The difference in capillary pressure driving the motion for completely wetting menisci is $dP = 2(\gamma_1 - \gamma_{12} - \gamma_2)/R$, where γ_1 and γ_2 are the surface tension of the two different liquids in the slug and γ_{12} is the mutual interfacial tension and R is the meniscus curvature radius. The process is shown in Figure 2.2. The transparent slug (2) is water, while the dark slug (1) is carbon disulfide with larger surface tension. After release, the bislug traveled to the carbon disulfide side with self-propulsion.

Similar to non-uniform geometrical cross-section method, bislug self propulsion method is also a single trip method which is not reversible. The requirement of surface tension difference confines its application range as one of the liquids must be completely wetting, so that its self propulsion ability can only be used to special sample plugs or liquid plug carriers satisfying the requirements.

2.2.1.2 Thermocapillary stress method

The surface tension of a liquid depends on the temperature. At a higher temperature, the attracting force of the liquid surface reduces and subsequently the surface tension decrease. For a small temperature range, it is assumed a linear relation between surface tension and temperature,

$$\sigma_{lg}(T) = \sigma_{lg0} - \gamma(T - T_0). \quad (2.1)$$

In Equation (2.1) σ_{lg} is the surface tension of the gas-liquid interface, γ is a constant, T is the actual temperature, and σ_{lg0} is the surface tension at the reference temperature T_0 . The temperature dependency of surface tension is the fundamental mechanism of thermocapillary stress method.

In the experiments on Benard convection, Volkoviski (1935) first observed that liquid films

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tended to spread towards the cooler side of a substrate. Hershey (1939) discussed how variations in surface tension generated by evaporation of a volatile mixture caused similar liquid migration. He designed a controlled experiment to monitor the spatial variation in film height caused by a prescribed variation in temperature along a thin film. Within the lubrication limit and neglecting capillary pressure, he derived the velocity profile corresponding to the balance of thermocapillary and hydrostatic forces under steady conditions. Ludviksson & Lightfoot (1971) worked on the origin of so-called super-meniscus films, i.e., film climbing beyond the equilibrium capillary length. They examined the spontaneous spreading of thin and non-volatile liquid films on a vertical wettable substrate subject to a linear temperature decreasing.

Brochard (1989) was the first to formulate a theory on the movement of a liquid droplet on a solid with a horizontal thermal gradient. In his paper, he has revealed the reasons of the migration of the droplet under the temperature gradient: the surface tension was not uniform. He derived the function of velocity of the droplet depending on temperature gradient,

$$v = C \frac{h_0}{\eta} \left[\frac{\partial}{\partial x}(\sigma_{lg} - \sigma_{sl}) + \frac{\partial}{\partial x}(\sigma_{sg} - \sigma_{sl}) \frac{dT}{dx} + \frac{1}{2} \frac{\partial \sigma}{\partial T} \frac{dT}{dx} \right]. \quad (2.2)$$

In Equation (2.2) h_0 is the thickness of the droplet at the center, σ_{lg} , σ_{sl} and σ_{sg} are the surface tension of the liquid/gas, solid/liquid and solid/gas interfaces, respectively, C is a constant. Brzoska et al. (1993) experimentally investigated displacement of liquid droplets in a temperature gradient. This work focused on the different radii of the droplets. The results showed that the droplets moved only if its radius was above a critical radius R_c . The critical radius was strongly dependent on the contact angle hysteresis, but independent of the fluid viscosity. For small liquid droplets and radii above R_c , the velocity of the droplet was proportional to the temperature gradient and inversely proportional to the viscosity. Ford and Nadim (1994) determined the velocity and pressure fields within the droplet, which was modeled as an infinitely long strip of finite width and arbitrary height profile under the uniform temperature gradient. The effect of the boundary condition in the vicinity of contact line was highlighted.

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Sammarco and Burns (1999) studied thermocapillary pumping (TCP) of discrete droplets in micro fabricated analysis devices. The major factor limited the pumping velocity was the contact angle hysteresis, which is the difference between the maximum (advanced/advancing) and minimum (receded/receding) contact angle values. Contact angle hysteresis reduced the temperature induced driving force of TCP, thereby introduced a minimum temperature difference requirement for drop movement. This minimum temperature difference was a function of the hysteresis parameter $(1 - \cos\theta_A/\cos\theta_R)$, where θ_A and θ_R are the contact angles at the advancing and the receding edges of the droplet. The greater the degree of hysteresis, the higher the minimum temperature difference needed to initiate droplet movement. When contact angle hysteresis becomes so large that the droplet may boil before moving. Surface treatment can help to reduce the contact angle hysteresis. Further, converging micro-channels can offset the hysteresis and so does the externally applied pressure. Figure 2.3 shows a set up for measuring the contact angles of receding and advancing ends. Using the low-pressure air source and submerged in liquid, from the Yong-Laplace equation the contact angles can be derived,

$$\theta_{A,R} = \frac{1}{\cos [d (p - \rho gh) d / (G\sigma)]}, \quad (2.3)$$

while σ is the liquid surface tension, d is the channel diameter and G is a constant specific

Figure 2.3: Experimental setup for measuring the contact angle in a microchannel: (a) Receding; (b) advancing.

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to channel geometry ($G = 4$ for circular, $G = 2$ for slit-like, and $G = 2(1 + \text{height}/\text{width})$ for rectangular cross sections). ρ is the liquid density, while h is measure when the system is in stable as shown in Figure 2.3. When the pressure is supplied, the liquid plug in capillary moves to right and the final contact angle θ_R is the receding contact angle. When the vacuum is applied, liquid plug is sucked to the left side and now the contact angle is advancing contact angle θ_A .

Figure 2.4: Section of a bubble in a horizontal tube. Five regions are shown: the constant film thickness region (1), two capillary static's regions (3, 5), and two transition regions (2, 4). (Mazouchi & Homsy 2000)

Besides liquid droplets, bubbles can also be pumped in microfabricated channels. Mazouchi and Homsy (2000) investigated the migration of a long bubble in a tube with a prescribed axial temperature gradient. The resulting thermocapillary force moved the bubble towards the hotter region, which was opposite to the liquid droplets. The study focused on the determination of the bubble velocity. A simplified model was used. The model ignored the gravity in the horizontal tube, the viscosity and the thermal conductivity of the gas. At small Reynolds numbers and capillary numbers, a theory based on the lubrication approximation and matched expansions was presented to determine the shape and speed of the bubble. The assumption of small capillary numbers and long bubbles allows the division of the domain into five regions depicted in Figure 2.4. The long cylindrical region 1 of constant film thickness is connected to two constant curvature caps 3 and 5 through two transition regions 2 and 4.

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Heating methods and manipulation Thermal gradients can be generated by means of substrate embedded micro-heaters or by radiative heating from above (Hitt & Smith 1993, Schatz et al. 2002). Darhuber et al. (2003) demonstrated active manipulation of nanoliter droplets on the surface of a glass or silicon substrate by combining chemical surface patterning (will be introduced in the later section of chemical non-uniform method) with electronically addressable micro-heater array. Hydrophilic lanes determine the possible routes for liquid migration, while the activation of a specific heater determines the trajectories. The induced temperature gradients spatially modulate the liquid surface tension by thermocapillary effect; thereby take over the control of the direction, timing, and flow rate of continuous streams or discrete drops. Temperature maps can be programmed to move, split, trap, and mix micro-scale volumes without mechanically moving parts. Figure 2.5 shows an example of droplet splitting by using thermocapillary forces. When the heater is on, the surface tension of the liquid in the middle part of the droplet reduces fast with the increasing of the temperature. A surface tension forces difference between two sides and the middle part drive the two ends traveling to different directions to split the droplet into two, while in this process the temperature spreading effect can not be so fast to heat up the two ends so that the splitting can be finished and then the two splitted droplets keep traveling apart from each other to a distance. This method of fluidic actuation allows direct accessibility to liquid samples for handling and diagnostic purposes and provides an attractive model for the thermocapillary pump.

Yarin et al. (2002) studied the movement of liquid droplets consisting of n-decane, n-undecane, n-dodecane, and n-hexadecane on a partially wettable cylindrical fiber. When the temperature gradient was created along the fiber, the droplets began to move along the fiber toward the cold region according to the phenomenon related to the thermocapillary motion. Their experimental data agreed reasonably well with the theoretical results. The model of the droplet motion reveals its potential importance for a number of applications, particularly for draining filters that coalesce liquid droplets from a gas stream.

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Figure 2.5: Process of droplet splitting by using thermocapillary forces.

Glockner and Naterer (2005) reported a new method of cyclic flow control with an external heat source for thermocapillary pumping of a microdroplet in a closed microchannel. The pumping concept involves a stationary cyclic heat source embedded within an adjoining silicon substrate. Lab-on-a-chip based on thermocapillary pumping can be realized with this concept. The internal and external motions of micro-droplet were examined numerically using the finite-volume method and analytically using slug-flow approximation. The solution of the full Navier-Stokes and energy equations within the droplet were considered. In addition, temperature boundary conditions for a stationary heat source were applied at the interface between the substrate and its surroundings, rather than along the microchannel wall.

Burns and Masterangelo (1996) reported the micro-fabricated structures for integrated DNA analysis based on photolithography silicon micromachining. The thermocapillary pump was able to move discrete nanoliter drops through enclosed channels using only local heating. The same actuation concept can accurately mix, measure, and divide drops by simple electronic control of the heater. In addition, they constructed thermal-cycling chambers, gel electrophoresis channels, and radio labeled DNA detectors that are compatible with the fabrication process. Since all of the components are made by conventional

photolithographic techniques, they can be integrated into a more complex system.

Debar and Liepmann (2002) reported a silicon-based thermocapillary pump with integrated micro-heaters. The devices were operated at a variety of heater settings to evaluate their performance over a range of flow rates and pressures. A minimum energy of 140 *mW* was required from the central heater to generate and maintain the vapor bubble, and the flow rate increased with input energy. The efficiency of the device increased with flow rate, since the overhead to create and maintain the bubble (140 *mW*) dwarfs the energy expended to generate the temperature gradient (15 – 50 *mW*). The devices generated a maximum pressure head of 44 Pa, and a maximum flow rate of 9.3 *nL/s*.

2.2.1.3 Marangoni Stress method

In contrast to thermocapillary propulsion, it is not quite efficient to manipulate droplet motion on a solid substrate by varying the surface composition of the surface or liquid droplet. Small droplets, however, can be "actively" propelled within a liquid film or bulk liquid phase deformation. Therefore Marangoni stress method is used. The kind of stress producing a shear stress on the surface acting upwards is called a Marangoni stress.

Quincke (1888) conducted experiments involving the migration and oscillation of air bubbles in a layer of distilled water held between two horizontal glass plates. Releasing a stream of alcohol with a flow rate of a few cm^3/hr near a large 2 cm gas bubble caused the bubble to move toward the alcohol source and to oscillate with a period of 1 – 3 s. Higher flow rates induced higher oscillation frequencies. By momentum conservation, the Marangoni stress that is directed toward the region of higher surface tension (less alcohol) causes the bubble to migrate toward the opposite end (alcohol enriched). Droplet propulsion can also be achieved by proximity to a film of lower surface tension. Figure 2.6 (a)-(d) shows an example of a droplet of hexadecane ($\gamma_{lv} = 27.0 \text{ mN/m}$) deposited near a miscible film of polydimethyl-siloxane (PDMS: $\gamma_{lv} = 20.0 \text{ mN/m}$) on a partially wettable silicon wafer, while γ_{lv} is the interfacial tension between liquid and vapor. As the spreading PDMS film approaches the hexadecane, the droplet is propelled forward by a Marangoni stress.

Figure 2.6: (a-d) Propulsion of a droplet of hexadecane (volatile, $\gamma_{lv} = 27.0$ mN/m, $\mu = 3.0$ mPas) by a spreading film of PDMS (nonvolatile, $\gamma_{lv} = 20.0$ mN/m, $\mu = 20$ mPas) on a dodecyltrichlorosilane-coated silicon wafer while μ is the viscosity. Optical interference images (width 2 mm) recorded at $t = 0, 8, 24, 60$ s (Darhuber & Troian, unpublished). (e) Schematic illustration of two substrate-immobilized lipid bilayer vesicles (diameter 5–25 μm) with surface tension $\sigma_a < \sigma_b$ connected by a lipid bilayer nanotube (diameter 100–300 nm). Two carbon fibers are used to deform vesicle 'b' into an ellipsoidal shape causing an increase in the vesicle's surface tension, which is presumed to induce Marangoni-driven flow of lipid restoring the system to equilibrium. (f-h) Image sequence showing transport of a small liposome (position denoted by black arrow) within a lipid bilayer nanotube of length 32 μm . (Karlsson et al. 2002.)

Karlsson et al. (2002) reported Marangoni-induced flow through a lipid bilayer nanotube (diameter 100–300 nm) connecting two surface-immobilized lipid bilayer vesicles (diameter 5 – 25 μm). Figure 2.6 (e) shows the two substrate-immobilized lipid bilayer vesicles with different surface tension connected by lipid bilayer nanotube. In the graph, v_a is the velocity of the substrate interface while v_p is the velocity of the droplet. In Figure 2.6 (f)-(h) mechanical deformation of one vesicle from a spherical to ellipsoidal shape induced flow of lipid molecules from the unreformed to the deformed vesicle through the nano-tube interior.

2.2.2 Chemical modification of surface tension

In order to achieve more complex movement of micro liquid, the direction and speed of droplets along a solid substrate should be controlled by modulating the interfacial energy between the solid and liquid phases by different means. The mechanism relies on the differ-

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ence in contact angle between the advancing and trailing ends, which is the most dissipative way for propulsion, in contrast to droplet migration on homogeneous surfaces. Greenspan (1978) developed a lubrication model for the motion of a small viscous droplet on either chemically homogeneous or heterogeneous surfaces. The calculations showed that the droplet migrates toward regions of smaller contact angle or equivalently regions of greater adhesion without obvious influence from the liquid viscosity. The droplet was only driven by virtue of the imposed contact line condition. The capability of guiding thermocapil-

Figure 2.7: Schematics of the setup used to introduce in-plane vibration to the drop. The output wave is obtained by connecting an accelerometer to the audio speaker. (Daniel & Chaudhury. 2002)

lary flow by chemical surface patterning provides a powerful method for controlled fluidic delivery. Chaudhury & Whitesides (1992) and Daniel & Chaudhury (2002) prepared surfaces with graduated surface energy by grafting a monolayer of decyltrichlorosilane with decreasing surface density on glass and silicon substrates. Then the water droplets deposited on these surfaces spontaneously move uphill against the force of gravity towards regions of lower contact angle. The contact angle decreased by about 60° over a distance of 1 cm. When a liquid drop was placed on a surface possessing a continuous gradient of wettability, it moved towards the more wettable part of the gradient with typical speeds of 1 – 2 mm/s. This low speed arisen due to surface tension reduced by contact angle

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Figure 2.8: (a) Indicates the drop at rest. (b), (c) Show drop movements only toward the right during both forward and reverse strokes of the vibration. The arrow indicates the plane of reflection of the drop when it rests on the glass slide. The net movement of the drop with time has a staircase shape, as shown in the above. (Daniel & Chaudhury. 2002)

hysteresis. The hysteresis force acting on a drop on a gradient surface is, however, spatially asymmetric magnitude against the gradient being larger than that along the gradient. Daniel and Chaudhury (2002) found that when a periodic force was applied to a droplet resting on such a gradient surface. The force against the gradient was rectified, whereas it was enhanced along the gradient. The rectified motion of a water drop is demonstrated in Figure 2.7 and Figure 2.8. Here the hysteresis of contact angle is so large ($> 20^\circ$). The capability of guiding thermocapillary flow by chemical surface patterning provides a powerful method for controlled fluidic delivery. Chaudhury & Whitesides (1992) and Daniel & Chaudhury (2002) prepared surfaces with graduated surface energy by grafting a monolayer of decyltrichlorosilane with decreasing surface density on glass and silicon substrates. Then the water droplets deposited on these surfaces spontaneously move uphill against the force of gravity towards regions of lower contact angle. The contact angle decreased by about 60° over a distance of 1 cm. When a liquid drop was placed on a surface possessing a continuous gradient of wettability, it moved towards the more wettable part of the gradient with typical speeds of 1 – 2 mm/s. This low speed arisen due to surface tension reduced by contact angle hysteresis. The hysteresis force acting on a drop on a gradient surface is,

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however, spatially asymmetric its magnitude against the gradient being larger than that along the gradient.

Daniel and Chaudhury (2002) found that when a periodic force was applied to a droplet resting on such a gradient surface. The force against the gradient was rectified, whereas it was enhanced along the gradient. Here the hysteresis of contact angle is so large ($> 20^\circ$) that the water drop of radius 1.6 mm does not move on the gradient surface. When the substrate is vibrated with a square wave of frequency=0.1 Hz, the drop moves in synchronization with the vibration pulse. This half-wave rectification of periodic force causes a droplet to move with enhanced speeds of 5 – 10 mm/s.) that the water drop of radius 1.6 mm does not move on the gradient surface. When the substrate is vibrated with a square wave of frequency=0.1 Hz, the drop moves in synchronization with the vibration pulse. This half-wave rectification of periodic force causes a droplet to move with enhanced speeds of 5 – 10 mm/s.

Besides long periodic force, ultrasonic wave has also been used by Rathgeber et al recently to pump micro-liquid based on energy gradient. They showed the results using a homogenous silanization of the surface with subsequent photolithographic lateral patterning. The confinement of the liquid to the circuits is achieved by lateral potential wells, which were defined by a controlled modification of the surface free energy. A momentum transfer from surface acoustic waves (SAW) propagating along the surface of the given substrate pumped the liquids along these fluidic circuits. Such waves were modes of elastic energy confined to a layer of about one acoustic wavelength measured from the surface of the chip. Typical displacement amplitudes of a SAW are in the nanometer regime, and can be externally controlled by adjusting the excitation signal.

The amplitude or the timing sequence of pulsed surface acoustic waves can adjust the speed of droplet motion. In their experiment, the speed was set to about 2.35 mm/s, which was rather slow. The droplet can be moved over large distances and then be brought to a stop

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Figure 2.9: Time series of an acoustically actuated single droplet (approx. 50 nl), moving along a fluidic track defined by a controlled lateral modulation of the surface free energy. (Rathgeber et al)

at a desired position on the chip. The nice side effect can be seen from the Figure 2.9.

2.2.3 Photosensitive surfactant method

Figure 2.10: An array of five pendant droplets formed at the tips of glass capillaries. After illumination with UV light, the surface tension of two drops becomes too low to support the drop weight (Shin & Abbott. 1999.).

Equally large changes in the dynamic surface tension of liquids are possible to be achieved by using UV exposure to the aqueous solutions containing photosensitive surfactant. Shin & Abbott. 1999 studied the light-activated capillary release of droplets of an aqueous (0.1 M NaCl, 0.16 mM SDS) solution of a photosensitive azobenzene surfactant.

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As shown in Figure 2.10, active release of droplets from a pendant array was triggered by selective exposure of droplets to UV light. This release was not caused by Marangoni effects but by the sharp reduction in surface tension upon UV exposure, which caused the Bond number, $\rho g R^2 / \gamma_{lv}$, to increase above the critical value for drop detachment. Spatial modulation of the illumination intensity, however, could provide actively tunable Marangoni stresses as a function of position and time.

Figure 2.11: (a) Image sequence ($\Delta t = 0.1$ s) of a reacting, self-propelled n-alkane droplet containing perfluorodecyltrichlorosilane on a 3 mm wide hydrophilic stripe. (DosSantos & Ondarcuhu. 1995.) (b-d) Schematic diagram and photographs of droplet propulsion (olive oil) caused by asymmetric irradiation of an azobenzene photo-isomerizable monolayer. UV (365 nm) light converts 90% of the monolayer to a cis conformation with a higher dipole moment; subsequent irradiation by blue light (436 nm) reverts the monolayer to the trans conformation. (Ichimura et al. 2000.)

Ichimura et al. (2000) coated a quartz substrate with a self-assembled monolayer containing photochromic azobenzene groups. By using UV irradiation, the molecules transformed from a planar trans-configuration, which exposes the hydrophobic backbone, to a twisted cis-configuration, in which the polar azo groups were exposed. The orientational change increased the value of interfacial energy, which produced a corresponding change in the liquid contact angle (Ishihara et al. 1982). Ichimura et al. (2000) also demonstrated that asymmetric irradiation of a substrate can be used to propel a droplet. Figure 2.11 (b) and (c). In Figure 2.11(d), if the droplet is under uniform lighting condition, the change of the liquid-solid interface surface tension is also uniform across the whole droplet, and the balance of force is always stable so that the droplet can not be actuated. When the light is adjusted to be non-uniform, the non-uniform photochemical reaction can result un-balance

surface tension force. The olive oil droplet travels to the right side as the left side surface tension has been reduced with the stronger photochemical reaction. A moving droplet containing a dissolved reagent that adsorbs to the substrate can also generate gradients in the interfacial energy dynamically. Bain et al. (1994) and Dos Santos & Ondarcuhu (1995) examined self-propulsion of alkane droplets containing a perfluorinated carboxylic acid or perfluorodecyltrichlorosilane, which adsorbed onto the glass during motion. The trailing monolayer renders the surface hydrophobic. Droplet speeds of a few centimeters per second were obtained in such (Hare & Zisman 1955) systems like Figure 2.11 (a).

2.2.4 Electro reaction method

2.2.4.1 Electrocapillary phenomena

Electrocapillarity refers to the modification of the interfacial tension at a fluid-fluid boundary by the presence of electrical charges. Lippmann (1875) constructed a capillary electrometer that contained a mercury-electrolyte (Hg-el) meniscus in a capillary tube subject to an externally applied voltage V to explore changes in the interfacial tension as a function of V . With increasing voltage, he observed that the curves were approximately parabolic in shape, first increasing toward a maximum and then decreasing. From thermodynamic considerations, Lippmann (1875) and Helmholtz (1882) derived the relation $(\partial\gamma_{\text{Hg,el}}/\partial V)_{\mu} = -\sigma$, where σ represents the surface charge density and the subscript μ denotes conditions of constant chemical potential. This relation essentially describes the reduction in surface tension due to coulombic repulsion of the surface charges. Assuming the differential capacitance of the electrical double layer, $C = \partial\gamma_{\text{Hg,el}}/\partial V$, is a constant, it follows that $\gamma_{\text{Hg,el}}(V) = \gamma_{\text{Hg,el}}^0 - C(V - V_{\text{pzc}})^2/2$. Here, $\gamma_{\text{Hg,el}}^0$ designates the maximum interfacial tension obtained for an uncharged interface and V_{pzc} is the applied voltage corresponding to the point of zero charge (pzc). Burdon & Oliphant (1927) reported that the spreading of electrolyte droplets on mercury was also affected by application of an external potential. Droplets can be made to spread further or contract to a given size by applying an external voltage. Moller (1908), Kabanov & Frumkin (1933), and Smolders (1961)

conducted contact angle measurements of gas bubbles at mercury-electrolyte interfaces and found that the curves of contact angle $\theta(V)$ resembled the electro-capillary curves for $\gamma_{Hg,el}$. They argued that a change in the interfacial energy proportional to $CV^2/2$ would be accompanied by a decrease in $\cos\theta$, according to the Young-Dupre equation. Fokkink & Ralston (1989) and Chatelier et al. (1995) presented theoretical models for contact angles of electrolytes on charged and ionizable surfaces using the Guoy-Chapman theory of electrical double layers. They calculated the change in γ_{ls} caused by a surface charge density for an infinite system, i.e., in the absence of a contact line. The Young-Dupre equation was then used to compute the modified contact angle assuming no change in γ_{lv} and γ_{sv} . Digilov (2000) and Chou (2001) concerned that the presence of a contact line at a charged surface might induce effects not accounted in Fokkink & Ralston's theory. Digilov concluded that the applied potential causes polarization of the interface and the three-phase contact line, which reduces both the interfacial tension and the line tension. Chou modeled a 2D electrolyte droplet embedded in an immiscible electrolyte medium and residing on a solid substrate. He assumed constant surface charge densities on the interior (σ_{1s}) and exterior (σ_{0s}) solid surfaces. From minimization of the total free energy with respect to the position of the contact line and the droplet shape, he derived the modification in contact angle due to charge effects, namely

$$\gamma_{01} \cos \theta = \gamma_{0s} - \gamma_{1s} + (\sigma_{0s} - \sigma_{1s})\varphi(\theta) \quad (2.4)$$

as well as the general equation describing the droplet shape. Here, γ_{ij} denotes the interfacial tension between phases 0 (gas), 1 (liquid), and s (solid) in the absence of electrostatic interactions, and $\varphi(\theta)$ is the electrical potential at the contact line.

2.2.4.2 Electrowetting on dielectrical substrate

Solid electrode surfaces are often rough and chemically heterogeneous due to oxide layers and contaminant residues from the fabrication process, which can compromise reproducibil-

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Figure 2.12: (a-c) 0.1 mM KNO_3 sessile droplet with Pt wire on substrate consisting of (1) a hydrophobic layer of Teflon AF1600, (2) an electrically insulating layer (Parylene Cor polyimide), and (3) an indium-tin-oxide counter-electrode. Applied voltage is (b) 0 and (c) 200 V. (Welters & Fokkink. 1998.). (d) Computed surface charge density of a perfectly conducting liquid wedge with contact angle of 60° . (Kang. 2002). (e) Side view of a droplet on a $50\mu\text{m}$ thick PTFE film at a voltage of 950 V (marker length 1 mm). The luminescence originating near the contact line is attributed to air ionization. Spectroscopic measurements show that the luminescence wavelength depends on the gas composition of the atmosphere and occurs in bursts of less than 100 ns duration. (Vallet et al. 1999.) (f-h) Splitting of a droplet sandwiched between an electrode array and a transparent cover plate by electrowetting (applied voltage 25 V, gap size $70\mu\text{m}$, drop volume $0.2\mu\text{l}$). (Cho et al. 2003.).

ity. If, however, an electrolyte solution is kept separated from the electrode surface by a thin, and electrically insulating (dielectric) layer like Figure 2.12 (a), electrochemical reactions and specific adsorption are largely suppressed. This is advantageous for microfluidic applications as a large number of different liquids, electrolytes, and electrode materials can be used to generate qualitatively similar behavior. In one of the first experiments of electrowetting on dielectric layers, Dahms (1969) measured the change in capillary rise of an electrolyte in a thin polyethylene tube as a function of the voltage applied across the tube wall. He showed that the presence of surface-active alcohols, which was adsorbed on the solid, greatly reduces the variation in h with the increasing voltage. Chudleigh (1976)

was interested in the charge transfer from an electrolyte droplet to a thin polymer foil under high electric fields as a means of information storage and measured a reduction in the contact angle with applied voltage for different electrolytes. Vallet et al. (1996, 1999) conducted a number of experiments with sessile droplets of water or aqueous polymer solutions on thin (12 – 50 nm) polymer films. A voltage was applied between a small wire inserted into the droplet and a counter electrode beneath the insulating layer, as sketched in Figure 2.12(a).

For low voltages it was found that

$$\cos \theta(V) = \cos(V = 0) + \varepsilon_0 \varepsilon_r V^2 / (2d\gamma_{lv}) \quad (2.5)$$

Where d is the insulator layer thickness, ε_0 is the permittivity of vacuum, and ε_r is the relative permittivity of the dielectric layer. Figure 2.12 (b) and (c) illustrates that an applied potential decreases the contact angle. Above a critical voltage, the contact angle saturated at a fixed value; further increases in V produced ionization phenomena manifest by light emission at the contact line Figure 2.12 (e)). Vallet et al. (1996) observed the ejection of fine droplets along the contact line of pure water at sufficiently high fields, and from a simplified linear stability analysis (Vallet et al. 1999) concluded that the maximally unstable wavelength is roughly proportional to the thickness of the dielectric layer. To our knowledge, there are no hydrodynamic models describing droplet propulsion by electrowetting. Several groups have attempted to explain the origin of the change in contact angle with applied potential using thermodynamic and electromechanical considerations. Following the derivation of Vallet et al. (1999), Kang (2002) considered a perfectly conducting droplet at constant potential V resting on a thin dielectric layer of thickness d deposited on a grounded electrode like Figure 2.12 (d) and (e). The corresponding divergence in the electric field is believed to cause air ionization and saturation of the contact angle at high fields. By using this theory simple manipulation of splitting a droplet by using electrode array was achieved by Cho et al (2003) in figure 2.12 (f)-(h). The droplet at the middle

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of the three electrode pairs was splitted gradually when the two side electrode pairs were on. The two ends of the droplet tended to spread to the high voltage electrodes and finally divided it into two smaller droplets. The similar manipulations like merging and mixing of droplets also can be achieved by this method.

Figure 2.13: Time-lapse image ($\Delta t = 2$ s) of a liquid crystal droplet convected by an aqueous film containing an electro active surfactant. A potential difference of $0.6V$ was applied to Pt electrodes at the south and east ends of the trajectory shown. (Gallardo et al. 1999.)

Instead of assuming that the droplet profile can be approximated by a solid wedge, Buehrle et al. (2003) balanced the electrical normal stress, $\epsilon_0 E^2/2$, at the air-liquid interface with the capillary pressure for a perfectly conducting droplet. They assumed that the surface slope far from the contact line was given by $\theta(V)$, as defined above. Numerical results based on energy minimization calculations show that the contact angle at the solid surface is equal to $\theta(V = 0)$, i.e. the Young-Dupre angle. Moreover, there develops a weak singularity in the droplet curvature at the contact line, which is reflected in the divergence of the surface charge density. Interestingly, Chou (2001) realized that a proper balance in the normal stress requires both the electrostatic and capillary contribution, but he concluded that the wedge approximation suffices on length scales smaller than the Debye screening length κ^{-1} . Kang et al. (2003) recently included double-layer effects and balanced the Maxwell stress and osmotic pressure in an electrolyte droplet disregarding the contribu-

tion from the capillary pressure. A complete description for an electrolyte droplet on an insulating layer subject to an external potential, including the effects of electrical double layers, Maxwell stresses, disjoining pressure, and capillary pressure, is still lacking. Such a description introduces at least two length scales, d and κ^{-1} , which can be of comparable magnitude. In microfluidic applications, surface tension gradients can spontaneously arise, for example, during droplet splitting or coalescence, mixing of samples, or chemical reactions. Typically, the gradients generated during contact of dissimilar liquids are much larger than corresponding thermocapillary variations. Deposition of biological liquids, which often contain surface-active material, onto a liquid film with higher γ_v will generate Marangoni stresses that can cause rapid film thinning and rupture. It is therefore important to understand the basic phenomena governing this class of flows. Levich (1941) outlined the thermodynamic basis for the shear stress condition at an interface containing surface-active molecules, which reduce the surface tension in proportion to the local concentration. Active control over the speed of droplets or solid particles convected within a thin liquid film can be enforced by electrochemical modulation. A voltage applied between two electrodes positioned near opposite ends of a thin aqueous film was used to modulate γ_v by tuning the active state of soluble surfactant with redox-active head groups Figure 2.13. A droplet of a nematic liquid crystal was convected along a 1 mm deep aqueous film of $Fc(CH_2)_{11} - N^+(CH_3)_3Br^-$ by applying a voltage difference of 0.6 V (Gallardo et al. 1999). Speeds of 4 mm/s were achieved with $\Delta\gamma_v = 22$ mN/m.

2.2.5 Electrocapillary and Electrochemical Marangoni Flows

Chemical reactions at interfaces can generate variations in interfacial tension although these phenomena are still difficult to control. Paalzow (1858) and Bernstein (1900) described the irregular motion and oscillations of a mercury droplet in an acidic electrolyte in proximity to a dissolving potassium dichromate crystal. In one experiment Bernstein (1900) centered a small mercury droplet inside a glass capillary filled with dilute sulfuric acid, when the diffusing front of $Cr_2O_7^{2-}$ ions from a small $Cr_2O_7K_2$ crystal positioned at one end of the

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capillary reached the center of the tube, the mercury drop moved towards the crystal. The motion was attributed to the reduction and spatial inhomogeneity in Hg_{el} due to oxidation of the mercury by the diffusing ions. Homogenizing the ion concentration by stirring caused any motion or oscillation of the mercury drop to cease. Bernstein's interest in this system was fueled by what he thought was a striking analogy between the drop migration in a concentration gradient and the locomotion of primitive organisms. He presented a simple theoretical model for motion caused by variations in the capillary pressure and contact angles of mercury on the glass surface but neglected Marangoni stresses. Propulsion methods such as these, however, remain largely unexplored for fluidic applications.

Figure 2.14: Experimental setup for electrocapillary propulsion of Hg droplets. Copper clamps (C) are used to suspend two platinum electrodes (B) into 45 cm³ of a 10 mM KNO_3 solution in a 10 cm long glass container (A). A watch glass (E) contains the droplet of mercury of initial diameter 11 mm. (e) Droplet shapes corresponding to electric currents of 0, 10, and 20 mA (Christiansen 1903).

Figure 2.14 shows Christiansen's experimental setup and the significant distortion in droplet shape observed with increasing electrical current. Levich (1962) presented a first-order model for the migration velocity of an ideally polarizable, spherical liquid metal droplet of radius R in a weak electric field E . The droplet speed was estimated to be $U = \sigma ER / (2\mu_{\text{el}} + 3\mu_{\text{Hg}} + \sigma^2/k_{\text{el}})$, where el and Hg are the viscosities of the electrolyte and liquid metal and k_{el} is the electrolyte conductivity. This velocity is orders of magnitude

larger than typical speeds for electrophoretic actuation of solid particles. For a solid particle, the viscous motion of the liquid decays within the electrical double layer of thickness, d , whereas for a liquid metal droplet, the velocity field persists over a distance comparable to the droplet radius R , leading to a mobility increase by a factor of R/d . This propulsion method is not limited to mercury droplets in electrolytes. The speed of an emulsion droplet of conductivity κ_{em} can be derived in similar fashion, where the approximation holds for a small emulsion conductivity κ_{em} . Beni et al. (1982) constructed a ("continuous electrowetting") system based on mercury/electrolyte actuation capable of generating droplet speeds on the order of 10 cm/s using only 1 V.

2.3 Droplet actuation by surface acoustic wave

A SAW is propagating from left to right along the x -axis. At $x = 0$, it reaches the boundary of a liquid at the surface of the substrate. A SAW with non-vanishing amplitude in the z -direction, i.e. normal to the surface of the substrate, is then strongly absorbed by the fluid, as indicated by the decaying amplitude for positive x values. Moreover, it creates a small but finite pressure difference in the fluid between the ridges and the wells of the wave, which transforms into a small but finite difference in the liquid density in the direction of the sound propagation in the fluid. This leads to an internal streaming in a closed volume like a droplet. Droplet can be actuated on surface by using SAW because the driving force behind this interaction and the resulting acoustically driven flow is under an effect of acoustic streaming.

Beyssen et al (2006), have demonstrated that SAW can be used to actuate small amounts of liquids of viscosities extending over a large range (from 1 to 1000 mPa.s) (Figure 2.15) based on the contact angles changing. In order to improve the droplet displacements, an hydrophobic film was deposited on the LiNbO₃ substrate. It is deposited by plasma enhanced chemical vapor deposition a-CFX film. He measured the evolution of the advancing

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Figure 2.15: (a) Experimental set-up with the RF power supply and the RF amplifier (Mini Circuits ZHL-SW-1) connected to the LiNbO₃ Wafer. (b) Sketch of the acoustic streaming acting on a small droplet on the surface of a piezoelectric substrate. The acoustic energy is radiated into the fluid under an angle θ_R , leading to internal streaming in the small fluid volume. (Beyssen et al. 2006)

contact angle θ_a and the receding contact angle θ_r during the motion of the water droplet on the PVDF surface (Figure 2.16). Firstly, absorbed energy by the droplet is transformed in vibration energy (Figure 2.16b). Secondly the droplet was deformed by the acoustic pressure (Figure 2.16c) and began to move (Figure 2.16d). The figure 2.16e shows the measured values of those angles in each steps (a, b, c, d). He also clearly measured the three-step motion of the droplet for water and during its displacement (Figure 2.17), the water droplet get out of shape with a cyclical way at a frequency of 120 Hz. The periodicity or frequency of the droplet behavior was determined with a high-speed acquisition camera FTA (360 frames per second equivalent to 1 frame per 0.0028 s) and is shown in Figure 2.17. Strobl et al (2002) built the simplest microfluidic device for droplet actuations based on the theory (Figure 2.18). They used a SAW device with a split 4 Interdigital Transducer (IDT) on a 128° rot LiNbO₃ substrate. The IDT consisted of twelve pair split 4 fingers with 600 μ m aperture. The resonant frequencies are 114, 340, 567 and 800 MHz. It is realized to actuate the smallest amounts of liquid without the need for sophisticated pumps and tubes. The device was produced by using cheap surface processes similar to those of

Figure 2.16: Evolution of advancing and receding contact angle, θ_a and θ_r , during motion of droplet ($5\mu l$). (Beyssen et al. 2006)

semiconductor technology. This enables us to implement all known biological assays that are developed on glass, on the chip and combine it with the presented technology.

2.4 Microfluidic dynamics

There are two important aspects in the investigations of microfluidic dynamics. In the process of the actuation of microscopic droplet in micro-devices, the droplet itself can be treated as a particle being propelled by surface stress caused by different kinds of energy field. Besides the dynamical movement of the whole droplet particle, the dynamics of the spreading and deformation of the liquid on solid substrate is also an important problem with technically significant influence on the actuation effect of the micro-device. In this section we will go through the dynamics of both the spreading and macro- movement of the micro-scale actuated droplet.

Figure 2.17: Periodical distortion of droplet: step a: droplet adopts a spherical shape on our hydrophobic coating ($t=0$ s), step b: the droplet stand up and the solid/liquid interface decrease ($t=0.0028$ s), step c: the droplet top bend to the side, in the direction of SAW propagation ($t=0.0056$ s), step d: the three-phase contact line advances and the droplet adopts a spherical shape again ($t=0.0084$ s). (Beyssen et al. 2006)

Figure 2.18: A droplet is moving from the right to the left, the cross shows the starting position. The droplet consists of a aqueous 1% Bromophenol Blue solution. (Strobl et al. 2002)

2.4.1 Dynamics of micro-droplet spreading

In the paper of Tanner (1978), the use of optical methods was described to study the shape of oil droplets falling slowly down a vertical surface. This showed that there is an interaction between the shape of the drop and the surface tension forces acting on it, and that the drop is supported against gravity partly by surface tension and partly by viscous forces. Next year, Tanner (1978) did a study of the spreading of silicone oil drops on horizontal surface, with particular attention to the dominant effect of the conditions near the edge and the surface tension forces acting there. It is shown that the drop profiles can be predicted and that this leads to a relation between the edge velocity and the maximum slope, which occurs at an inflection point close to the edge.

$$y_s^2 \frac{d^3 y_s}{dx^3} = \frac{3\mu U_E x}{\sigma L} = -\frac{kx}{L} \quad (2.6)$$

In the above equation, y_s is the height of the droplet profile where $du/dy = 0$. U_E is the velocity of the constant profile part. μ , L and σ are the viscosity, droplet radius and surface tension respect. This relation can lead to others governing the variation of drop size and slope with time. The predictions were then compared with experiment, using silicone oils, and good agreement obtained. But the lubrication approximation theory gives no solution for thicknesses below a value varying from 2 to 9×10^{-8} m at the drop edge. At thicknesses of this order, or possibly even larger, other effects become important, and some other observations on edge behavior are included.

Abraham et al (1989) proposed a solid-on-solid-model description of the dynamics of wetting, using langevin equation. In his research, the Gaussian version, appropriate to partial wetting, was solved exactly. The general version was solved using local equilibrium and scaling arguments. The dynamical contact angle, the shape of the profile near the sub-

Figure 2.19: The horizontal model of a wedge in computer simulation (Abraham 1992)

Figure 2.20: Example snapshots of the three-dimensional wedge profiles for three different cutoff values and time instants in the wetting region. (Abraham 1992)

strate, and, for dry spreading, the occurrence, speed and possible laying of a precursor film were all obtained like Figure 2.19. Abraham, Heinio and Kaski (1992) did computer simulation of the dynamics of a microscopic droplet on a solid surface based on the Langevin theory for the two-dimensional case, and used the Monte Carlo method for the two- and three-dimensional cases. They described the substrate interaction with droplet, first with one-monolayer-range chemical potential and second with a long-range van der Waals-type potential. The dynamical droplet profile, spreading speed, contact angle and characteristic time behaviors were investigated by both partial and complete wetting regimes. In the theory, the thickness and speed of the precursor film depend on the value and range of the substrate potential. The wedge advancing was divided into $n(j = 0, 1, 2, n)$ sub layers for analyzing like Figure 2.19. Figure 2.20 gives out two examples for the computer simulation results with different cutoff values of the layer number j . As the van der Waals substrate potential has a discrete cutoff value j_c , which is zero for $j < j_c$ and unit for $j \geq j_c$.

Figure 2.21: Time evolution of complete terraced wetting sample (Yang & Koplik. 1991)

Above langevin method is successful in the films much thicker than the size of their constituent molecules, which can be treated hydrodynamically. However, different behavior

was seen in ultra-thin films, whose thickness is only several molecular diameters. Instead of a smoothly varying continuum, experiments found that the spreading of the liquid consists of distinct monomolecular layers which advance of millimeters. These films are too thin to be described by lubrication equations and alternative models based on langevin dynamics. Yang and Koplik (1991) therefore conducted molecular-dynamics (MD) simulations of spreading, like Figure 2.21, restricted to small droplets with radius about 10 atomic sizes. They considered a molecular system described by interaction potentials, but in the system studied, the substantial molecular diffusion is observed throughout the layers so that the theory is not applicable and a theoretical understanding of terraced spreading remains to be fully understood.

2.4.2 Dynamics of propulsion for microscopic droplet

Most of the actuation methods are based on surface tension differences created by external energy gradient. So far, little researches were done on the dynamics of the propulsion movement for the microscopic droplet. Here we choose thermal stress actuation method to be the example to demonstrate the dynamics of the microscopic droplet movement in energy potential gradient

Yarin and Reneker (2002) conducted an experiment with small n-decane droplets deposited on a partially wettable cylindrical fiber, which are axis-symmetric. In the experiments it was found that when a temperature gradient was created along a thin horizontal fiber, droplets moved toward the cold region. Figure 2.22 (a) and (b) describe the experimental models and the velocity field of the internal liquid with different reference points.

Based on the simple model and temperature dependent surface tension and viscosity, Figure 2.23 shows the comparison between the theoretical and experimental results of the movement position plots, while we can observe that there are acceleration and stable, two stages. Nguyen and Huang (2005) presented a novel concept for transport of aqueous sample in capillaries. The concept was based on the thermocapillary effect, which utilized the

Figure 2.22: Sketch of a spherical droplet on a fiber. (a) The flow field as perceived by an observer attached to the fiber. (b) The flow field as perceived by an observer moving with the center of the droplet. (Yarin & Reneker. 2002)

Figure 2.23: Position of large and small n-decane droplets as a function of time (Yarin & Reneker. 2002)

temperature dependency of surface tension to drive a sample droplet. The temperature distribution function and boundary conditions are shown in equation (2.7), while q'' is the energy inputs and R_o, R_i are the outer and inner diameters respectively.

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} - \frac{2hR_o}{\rho c(R_o^2 - R_i^2)} T \quad (2.7)$$

while

$$\begin{aligned} t = 0 : & \quad T(x) = 0 \\ t > 0 : & \quad \begin{cases} x = 0, \quad \frac{\partial T}{\partial x} \big|_{x=0} = -\frac{q''}{k} \\ x = L, \quad T = 0 \end{cases} \end{aligned}$$

Figure 2.24: Dimensionless temperature and temperature gradient distributions against time and position. (Nguyen & Huang, 2005)

From Figure 2.24 it is seen that the temperature difference of a certain length droplet in this field decreases very fast with the position increasing and increases fast at the initial position near the heater. From this observation, a prediction can be made that the droplet surface have an acceleration stage at first and then goes to stable stage soon, because the spreading of heat along the capillary should be slower than the velocity of the droplet accelerated by the initial high temperature difference.

Figure 2.25 (b) depicts the measurement results of position and velocity of droplets with

Figure 2.25: (a) Theoretical and (b) measured position versus time and velocity versus position of a droplet in a transient field with different viscosities. (Nguyen & Huang, 2005)

different viscosities. The experimental results agree relatively well with the theoretical results shown in Figure 2.25 (a). The droplet first accelerates in a short time, but most of the distance is traveled in this period. Initially, the temperature at the heater rises quickly, but temperature spreading along the capillary needs more time. Thus, the initial acceleration is controlled by the heat flux, while the later motion depends on the spreading process of the temperature. During this process, the liquid droplet moves to the cooler region because of the initially high velocity. In this region, the temperature gradient decreases significantly leading to slow-down of the motion.

2.5 Conclusions

The technologies and research activities associated with droplet-based digital microfluidics are reviewed in this chapter. Among the actuation methods introduced, chemically non-uniform surface stress method, marangoni stress method and electro reaction method have been studied for a rather long period and have already been applied in lab-on-chip devices. Thermocapillary stress method and photosensitive surfactant method, however, are still in developing stages. For the thermocapillary stress method, simple implementation of the micro heaters array can be used to achieve controllable continuous movements of the discrete droplets. Despite its simplicity in implementation, the thermocapillary pumping technique is still not fully exploited in microfluidics research community. Apart from the droplet transport, the thermocapillary force can also be used for other droplet manipulation functions, such as splitting, merging and dispensing. The integration of multiple actuation methods in a single system can help to overcome weak points of individual method. Along with decreasing the size of microfluidic systems, smaller and cheaper lab-on-chip devices can be produced, even in nano-scales.

Chapter 3

Reciprocating thermocapillary plug motion in an externally heated capillary

3.1 Introduction

In this chapter, a study on generating reciprocating plug motion in an externally heated capillary is presented, which is an extension of thermocapillary actuation of a silicone oil plug in a transient temperature field (Nguyen & Huang 2005). The actuation is based on thermocapillary effect generated by alternately activating two heaters. The actuation technique in this case has a potential in manipulating not only the plug motion but also the flow field inside the plug. Firstly, the actuation process is analytically modeled, including the temperature field and plug motion. The effects of some liquid parameters on the plug motions is discussed in terms of the plug peak-to-peak maximum traveling distance. Next, details on the experimental setup are described. Measurement results, such as plug positions and maximum traveling distance, are then compared to the simulation results. Comments and discussions are presented, in terms of switching frequency, liquid viscosity and plug length.

Figure 3.1: Modeling of the thermocapillary actuation concept: (a) micro capillary with liquid oil droplet and heaters arrangement, (b) capillary cross-section, (c) alternating heating schemes.

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3.2.1 Analytical modeling of temperature distribution

Figure 3.1 depicts the model of this actuation concept. A liquid plug is positioned in a capillary between two external heaters. The capillary with two open ends is considered to be very long compared to the distance between the two heaters. The rest of the capillary is filled with air link to the atmosphere. The actuation concept is modeled according to the following steps. First, the periodic temperature change with time along the capillary is described. With the known temperature as a function of position and time, the temperature difference across the liquid plug and consequently the thermocapillary force are determined. The balance equation of forces acting on the liquid plug is then used for calculating its velocity and position.

Since the silicone oil, which is used as the plug liquid in this study, is of a thermal con-

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ductivity one order less than that of glass (Table 3.2), it can be assumed that the liquid plug and the glass capillary has weak thermal interactions. Because of the thin glass capillary wall, the temperature is assumed to be uniform through the capillary cross-section. Heat transferred by radiation here is assumed to be negligible due to the relatively low temperature, while the radiation heat loss takes only 20% of the natural convection loss (Details can be found in Appendix A). The liquid plug in capillary can be treated as a particle driven by surface tension difference which is assumed to have constant volume, density and specific heat. The glass properties are also assumed to be uniform throughout the temperature distribution field. Heat loss to the air is by natural convection. Thus, the temperature distribution is assumed to be determined only by the heater and the glass capillary by the following function,

$$\frac{\partial \theta}{\partial t} = \alpha \frac{\partial^2 \theta}{\partial x^2} - \frac{2hR_o}{\rho c(R_o^2 - R_i^2)} \theta, \quad (3.1)$$

where θ is the temperature difference relative to the ambient temperature, R_o and R_i are the outer and inner radii of the capillary, α , ρ , and c are the thermal diffusivity, density and specific heat capacity of the capillary material, respectively, and their values can be found in Table 3.2. Lateral cooling of the capillary is due to the natural convection in air. For a capillary of $R_o = 0.7$ mm, $R_i = 0.45$ mm, because of the non-uniform temperature distributions along the tube outer surface, an average outer surface temperature about 50° C is chosen based on the measurement value which will be introduced in the later experimental section. Based on the average temperature, an effective heat loss coefficient h is defined, including both convection conduction effects, in Appendix A. According to Figure 3.1(c), the periodic boundary conditions at the two heaters are,

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$$\begin{aligned}
\left. \frac{\partial \theta}{\partial x} \right|_{x=0} &= \begin{cases} -\frac{q_0''}{k}, & 0 \leq t < T_h/2; \\ 0, & T_h/2 \leq t < T_h, \end{cases} \\
\left. \frac{\partial \theta}{\partial x} \right|_{x=D_h} &= \begin{cases} 0, & T_h/2 \leq t < T_h; \\ \frac{q_0''}{k}, & 0 \leq t < T_h/2, \end{cases}
\end{aligned} \tag{3.2}$$

where D_h is the distance between the two heaters, T_h is the heating period, k is the thermal conductivity of the capillary material and q_0'' is the heat flux through the capillary cross-section. In order to get a reasonable estimation of the heating flux value in the later simulations, the value of heating flux will be adjusted until the simulated heater position point temperature equals to the measurement value of the temperature at the heater position by using infra camera which will be introduced in the experimental section.

For the convenience of calculations in the analytical analysis, the dimensionless variables are introduced,

$$t^* = t/T_h, \quad x^* = x/D_h, \quad \theta^* = \theta k / (q_0'' D_h),$$

so that,

$$t = t^* T_h, \quad x = x^* D_h, \quad \theta = \theta^* (q_0'' D_h / k).$$

Equation (3.1) can thus be non-dimensionlized as,

$$\frac{\partial[\theta^*(q_0'' D_h / k)]}{\partial(t^* T_h)} = \alpha \frac{\partial^2[\theta^*(q_0'' D_h / k)]}{\partial(x^* D_h)^2} - \frac{2hR_0}{\rho c(R_0^2 - R_i^2)}[\theta^*(q_0'' D_h / k)],$$

and the final form is ,

$$\eta \frac{\partial \theta^*}{\partial t^*} = \frac{\partial^2 \theta^*}{\partial x^{*2}} - \beta^2 \theta^* \tag{3.3}$$

with

$$\begin{cases} \beta^2 = 2hD_h^2 R_o / [k(R_o^2 - R_i^2)] \\ \eta = D_h^2 / (\alpha T_h) \end{cases},$$

The corresponding dimensionless boundary conditions are,

$$\begin{aligned} \frac{\partial \theta^*}{\partial x^*} \Big|_{x^*=0} = f_1(t^*) &= \begin{cases} -1, & 0 < t^* \leq 1/2; \\ 0, & 1/2 < t^* \leq 1, \end{cases} \\ \frac{\partial \theta^*}{\partial x^*} \Big|_{x^*=1} = f_2(t^*) &= \begin{cases} 0, & 0 < t^* \leq 1/2; \\ 1, & 1/2 < t^* \leq 1, \end{cases} \end{aligned} \quad (3.4)$$

where $f_1(t^*)$ and $f_2(t^*)$ are the functions of heating scheme according to Figure 3.1. Based on the periodic boundary conditions in equation (3.4), the dimensionless relative temperature θ^* can be expanded by the Fourier series,

$$\theta^* = \sum_{n=-\infty}^{\infty} A_n(x^*) e^{i2\pi n t^*}, \quad (3.5)$$

where $A_n(x^*)$ is a function to be determined. By substituting equation (3.5) into equation (3.3), it yields,

$$(i2\pi n \eta) A_n(x^*) = A_n''(x^*) - \beta A_n(x^*),$$

or,

$$A_n''(x^*) - (\beta^2 + i2\pi n \eta) A_n(x^*) = 0. \quad (3.6)$$

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The solution of equation (3.6) is

$$A_n(x^*) = E_n e^{\lambda_n x^*} + G_n e^{-\lambda_n x^*},$$

where E_n, G_n are two constants to be determined, and

$$\lambda_n = \sqrt{\beta^2 + i2\pi n\eta}.$$

So that

$$\theta^* = \sum_{n=-\infty}^{\infty} (E_n e^{\lambda_n x^*} + G_n e^{-\lambda_n x^*}) e^{i2\pi t^*}, \quad (3.7)$$

$$\frac{\partial \theta^*}{\partial x^*} = \sum_{n=-\infty}^{\infty} (E_n e^{\lambda_n x^*} - G_n e^{-\lambda_n x^*}) \lambda_n e^{i2\pi t^*}. \quad (3.8)$$

According to the boundary conditions (3.4),

$$\left\{ \begin{array}{l} \frac{\partial \theta^*}{\partial x^*} \Big|_{x^*=0} = \sum_{n=-\infty}^{\infty} (E_n - G_n) \lambda_n e^{i2\pi t^*} = f_1(t^*) = \sum_{n=-\infty}^{\infty} F_{1n} e^{i2\pi t^*} \\ \frac{\partial \theta^*}{\partial x^*} \Big|_{x^*=1} = \sum_{n=-\infty}^{\infty} (E_n e^{\lambda_n} - G_n e^{-\lambda_n}) \lambda_n e^{i2\pi t^*} = f_2(t^*) = \sum_{n=-\infty}^{\infty} F_{2n} e^{i2\pi t^*} \end{array} \right., \quad (3.9)$$

and equations for E_n and G_n are therefore,

$$\left\{ \begin{array}{l} F_{1n} = (E_n - G_n) \lambda_n \\ F_{2n} = (E_n e^{\lambda_n} - G_n e^{-\lambda_n}) \lambda_n \end{array} \right. . \quad (3.10)$$

By solving equations (3.10) E_n and G_n can be obtained,

$$\left\{ \begin{array}{l} E_n = \frac{F_{2n} e^{\lambda_n} - F_{1n}}{\lambda_n (e^{2\lambda_n} - 1)} \\ G_n = \frac{F_{2n} e^{\lambda_n} - F_{1n}}{\lambda_n (e^{2\lambda_n} - 1)} - \frac{F_{1n}}{\lambda_n} \end{array} \right. . \quad (3.11)$$

In equation (3.9) F_{1n} and F_{2n} are the Fourier series coefficients of the time functions $f_1(t^*)$ and $f_2(t^*)$, i.e.,

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for $n \neq 0$

$$\begin{cases} F_{1n} = \int_0^1 f_1(t^*) e^{-i2\pi n t^*} dt^* = - \int_0^{0.5} e^{-i2\pi n t^*} dt^* = \frac{i}{2n\pi} [1 - (-1)^n] \\ F_{2n} = \int_0^1 f_2(t^*) e^{-i2\pi n t^*} dt^* = \int_{0.5}^1 e^{-i2\pi n t^*} dt^* = \frac{i}{2n\pi} [1 - (-1)^n] \end{cases} \quad (3.12)$$

For $n = 0$

$$\begin{aligned} F_{1n} &= F_{10} = -0.5 \\ F_{2n} &= F_{20} = 0.5 \end{aligned} \quad (3.13)$$

The solution of equation (3.3) with boundary conditions in equation (3.4) gives in the dimensionless relative temperature,

$$\begin{aligned} \theta^*(x^*, t^*) &= \Re \left\langle \sum_{n=-\infty}^{\infty} \frac{1}{\lambda_n} \left\{ \frac{F_{2n} \exp(\lambda_n) - F_{1n}}{\exp(2\lambda_n) - 1} \exp(\lambda_n x^*) + \right. \right. \\ &\quad \left. \left. + \left[\frac{F_{2n} \exp(\lambda_n) - F_{1n}}{\exp(2\lambda_n) - 1} - F_{1n} \right] \exp(-\lambda_n x^*) \right\} \exp(i2\pi n t^*) \right\rangle \end{aligned} \quad (3.14)$$

where $\Re$ denotes the real part of a complex number, i is the imaginary unit, and

$$\begin{aligned} n = 0 : & \quad \begin{cases} F_{1n} = -0.5 \\ F_{2n} = 0.5 \end{cases} \\ n \neq 0 : & \quad F_{1n} = F_{2n} = \frac{i}{2\pi n} [1 - (-1)^n] \\ \lambda_n &= \sqrt{\beta^2 + i2\pi n \eta} \end{aligned}$$

The theoretical dimensionless temperature distributions between the two heaters, as a function of dimensionless time t^* and traveling distance x^* , can then be predicted for different heating periods. According to the definition of the dimensionless temperature, $\theta = \theta^*(g_0'' D_h / k)$, it is easy to calculate the actual value of the relative temperature field θ .

3.2.2 Coupling of temperature distribution and the plug motion

The time for the heat transfer through the capillary wall is in an order of $(R_o - R_i)^2/\alpha \approx 0.083$ s, which is much shorter than the heating time in one period. It is therefore assumed that the temperature is uniform across the glass capillary cross-section. The surface tension σ of the liquid then depends on the temperature along the capillary. For a small temperature range, a linear relation can be assumed,

$$\sigma_{lg}(\theta) = \sigma_{lg0} - \gamma(\theta - \theta_0), \quad (3.15)$$

where σ_{lg0} is the surface tension at the reference temperature difference when $\theta_0 = 0$. The temperature field resulting from equation (3.1) is in turn a function of the traveling distance x and time t . Since the silicone oil completely wets the inner capillary wall, and the surface tension force is mainly caused by the thin wetting film contacting with the inner wall of the glass capillary, it is assumed that there is a weak thermal interaction between the glass surface and the thin oil film. The surface tension can be expressed as a function of the plug traveling distance x and time t .

$$\sigma_{lg}(\theta) = f[\theta(x, t)] = g(x, t) = \sigma_{lg}(x, t). \quad (3.16)$$

The velocity u then can be determined through the force balance equation,

$$\rho\pi R_i^2 L_{\text{plug}} \frac{du}{dt} = -8\pi\mu L_{\text{plug}} u + 2\pi R_i [\sigma_{lg}(x + L_{\text{plug}}, t) \cos \phi_r - \sigma_{lg}(x, t) \cos \phi_a],$$

which can be arranged as,

$$\frac{du}{dt} + \left(\frac{8\nu}{R_i^2} \right) u + \frac{2}{\rho R_i L_{\text{plug}}} [\sigma_{lg}(x, t) \cos \phi_a - \sigma_{lg}(x + L_{\text{plug}}, t) \cos \phi_r] = 0, \quad (3.17)$$

where L_{plug} is the length of the plug, R_i is the inner radius of the capillary, and ν is the kinetic viscosity of the plug liquid. The receding and advancing contact angles are denoted

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with ϕ_r and ϕ_a , which are always settled as 0° (around 10° by image measurement) because of complete wetting of silicone oil on glass and the surface pre-coated by silicone oil. The small discrepancy between zero contact angles and the actual values can be compensated by the estimation of heating flux according to the linear relationship between temperature and liquid surface tension. The three terms in equation (3.17) represent the acceleration, the friction and the thermocapillary force, respectively. In the simulations of the traveling displacement and velocity, a numerical method was used to solve equation (3.17) with,

$$\begin{cases} A = \frac{8\nu}{R_i^2} \\ B = \frac{2}{\rho R_i L_{\text{plug}}} [\sigma_{\text{lg}}(x, t) - \sigma_{\text{lg}}(x + L_{\text{plug}}, t)] \end{cases}.$$

In the simulation of droplet movement, every period of the heating scheme was divided into 1000 time intervals. During each short time interval (0.001 s), the change of the liquid surface tension and viscosity were so little that A and B can be treated as constants and they were updated for every numerical iteration based on the average temperature and position results of the previous iteration. The solution of equation (3.17) with A and B being constants, i.e.,

$$u = -\frac{B}{A} + \left(\frac{B}{A} + u_0\right) \exp(-At), \quad (3.18)$$

where u_0 is the initial velocity for current iteration and equals to the velocity calculated in previous iteration. The temperature dependence of the liquid viscosity will be discussed and presented in the next section. From equation (3.18), the traveling distance of the left side of the plug can also be simulated by iterations based on the following formula,

$$x = \int_0^t u dt = x_0 + \frac{B}{A}t - \left(\frac{B}{A^2} + \frac{u_0}{A}\right) \exp(-At). \quad (3.19)$$

3.2.3 Results and discussion

Figure 3.2 illustrates the temperature distribution as function of the dimensionless time

Figure 3.2: Dimensionless temperature distribution between the two heaters as a function of dimensionless time t^* (capillary with inner radius $R_i = 0.475$ mm and outer radius $R_o = 0.69$ mm): (a) $T_h = 100$ sec or $f_h = 0.01$ Hz, (b) $T_h = 10$ sec or $f_h = 0.1$ Hz, (c) $T_h = 1$ sec or $f_h = 1$ Hz.

$t^* = t/T_h$. The “temperature surface” represents a thermal potential surface, while the plug always move to the lower potential direction. According to equation (3.18), the higher temperature differences and lower friction forces lead to a larger velocity and thus a more effective reciprocating movement. As shown in Figure 3.2, a lower actuation frequency produces a higher temperature difference potential field, which leads to a larger driving force and a higher traveling velocity. Besides the switching frequency, the length of the plug and the dynamic viscosity of the liquid are also important in determining the traveling velocity through the friction force.

In the following discussions, the liquid plug is assumed to have constant surface tension properties and the capillary geometry is fixed (e. g. constant inner and outer radii). The simulation results are presented and discussed in terms of three parameters: the switching frequency, plug length and liquid viscosity.

3.2.3.1 Switching frequency

Figure 3.3 shows the typical theoretical predictions of plug movement under different heating switching frequencies. The curves of the traveling distance and velocity of a liquid

Figure 3.3: Theoretical traveling distance and velocity of a plug as functions of time at different switching frequencies (capillary with inner radius $R_i = 0.475$ mm and outer radius $R_o = 0.69$ mm, kinematic viscosity $\nu = 10$ cSt, heat flux $q'' = 2 \times 10^4$ W/m², plug length $L_{\text{plug}} = 1$ mm): (a) $T_h = 100$ sec or $f_h = 0.01$ Hz, (b) $T_h = 10$ sec or $f_h = 0.1$ Hz, (c) $T_h = 1$ sec or $f_h = 1$ Hz

plug are plotted as a function of time at three frequencies $f = 0.05$ Hz, $f = 0.1$ Hz and $f = 0.5$ Hz. From the simulation results, it is seen that switching frequency is a quite important parameter in the controlling of liquid plug movements. There is a frequency interval with upper and lower limits, in which the plug can be actuated effectively. At a high frequency the temperature can not spread fast enough to generate a big temperature gradient, as indicated in Figure 3.2(c) for $T_h = 1$ s and $f = 1$ Hz. Consequently, the plug can not move a large distance due to the lack of thermocapillary force. At this situation, the thermal interactions at the interface of capillary inner wall with the oil plug and other unknown factors could not be ignored, and may cause unpredictable chaotic movement in a small length scale. This phenomena will be discussed in chapter 4. The upper limit of

Figure 3.4: The maximum traveling distance versus switching frequency (inner radius $R_i = 0.475$ mm, outer radius $R_o = 0.69$ mm, heating power $q = 4.38$ W, plug length $L_{\text{plug}} = 1$ mm).

switching frequency is associated with the second term on the right side of equation (3.1), which is determined by the thermal capacity of the capillary and the thermal resistance of free convection,

$$f_{\text{cr,u}} = \frac{2hR_o}{\rho c(R_o^2 - R_i^2)} \approx 1.95 \text{ Hz}. \quad (3.20)$$

It's seen from equation (3.20), that for a given capillary the upper limit of switching frequency can be increased by improving the heat transfer coefficient h , using forced convection for instance. The lower limit of the switching frequency is determined by the plug motion. The frequency should not be too low, so that the plug is traveling out of the region of interest between the two heaters. By setting $x = D_h$ in equation (3.19), we have an equation for the lower limit switching frequency $f_{\text{cr,l}}$,

$$\frac{B}{A} \frac{1}{f_{\text{cr,l}}} + \frac{B}{A^2} \exp(-A/f_{\text{cr,l}}) - D_h = 0. \quad (3.21)$$

The above equation is nonlinear and can only be solved numerically. The result gives the lower limit switching frequency to be $f_{\text{cr,l}} \approx 0.025$ Hz. The switching frequency has also ef-

fect on the maximum peak-to-peak traveling distance of the plug, which is shown in Figure 3.4. This figure will be mentioned again later in section 3.3.3 for the experimental results and discussion. It is seen that at frequency of 0.5 Hz and above, no significant motion can be observed. Based on this result, the actual upper critical frequency is about one quarter of the value estimated purely from the thermal condition in equation (3.20).

3.2.3.2 Plug length

A longer liquid plug experiences a higher temperature difference across its ends and thus a higher thermocapillary force. However, a longer liquid plug also causes more viscous friction. These two effects may compensate each other, which leads to a less sensitivity of velocity and maximum traveling distance to the plug length. Figure 3.5 depicts the pre-

Figure 3.5: The maximum traveling distance versus plug length (inner radius $R_i = 0.475$ mm, outer radius $R_o = 0.69$ mm, measured data were taken for $\nu = 10$ cSt and $f_h = 0.05$ Hz).

dicted traveling distance and velocity of a plug as functions of plug length under certain power input. The amplitude of plug reciprocating movement and velocity are not significantly changed with the increasing of plug length. The result can be explained that a longer liquid plug experience a larger thermocapillary force and also a larger friction force.

These two effects cancel each other on certain level and finally result in a nearly constant maximum peak-to-peak traveling distance in reciprocating movement. This figure will be mentioned again later in section 3.3.3 for the experimental results and discussion.

3.2.3.3 Liquid viscosity

Figure 3.6: The maximum traveling distance versus kinematic viscosity (inner radius $R_i = 0.475$ mm, outer radius $R_o = 0.69$ mm, heating power $q = 4.38$ W, plug length $L_{plug} = 1$ mm).

According to equation (3.17), the damping friction force acting on the plug is proportional to its viscosity. A higher viscosity leads to a smaller peak-to-peak traveling distance. Figure 3.6 shows that with the increasing of liquid viscosity, the reciprocating movement was damped and the maximum peak-to-peak traveling distance have a typical exponential reducing form following increase of viscosity. The effect that a larger viscosity leads to a smaller peak-to-peak traveling distance can also be observed in both Figure 3.4 and Figure 3.5, where the effects of switching frequency and plug length on the maximum traveling distance were simulated with different liquid viscosities. The liquid viscosity is actually dependent on the liquid temperature and the analytical model presented here can take this into account. If the plug has the same temperature as the glass capillary, the viscosity

Figure 3.7: The effect of temperature dependence of viscosity on the traveling distance and velocity of the plug (switching frequency $f_h = 0.05$ Hz, inner radius $R_i = 0.475$ mm, outer radius $R_o = 0.69$ mm, heat flux $q'' = 2 \times 10^4$ W/m², plug length $L_{\text{plug}} = 1$ mm, kinematic viscosity at 25 °C $\nu_0 = 10$ cSt.)

values can be updated for every iteration round in the numerical simulation according to the following equation (Darhuber 2003),

$$\nu = \nu_0(10^{-4}T^2 - 2.62 \times 10^{-2}T + 1.57) \quad (3.22)$$

where ν_0 is kinematic viscosity at 25 °C, T is temperature. Figure 3.7 shows the effect of temperature dependency comparing with the constant viscosity by plotting traveling distance and velocity of a plug as functions of time. Constant viscosity is proved to cause some discrepancies in the movement displacement and velocity at the position nearest to the heaters, comparing to the temperature dependent viscosity model. This difference is presented because at the position near to the heaters temperature gradient is rather larger across the plug comparing to the middle section position of the capillary. Friction force caused by liquid viscosity is not uniform along the plug axis at this moment comparing to constant viscosity assumption modeling. The discrepancies are presented to be in only a very short distance in the reciprocating process and the temperature dependent viscosity influences on the maximum traveling distance and velocity are so small that it is valid to make the assumption of constant viscosity for the liquid plug.

3.3 Experiments

Figure 3.8: Experimental setup for characterization of the plug movement.

3.3.1 Experimental setup and materials

Figure 3.8 depicts the measurement setup used for the characterization of the plug motion. There are a few units contained in this setup, including an actuation unit, a signal and power control unit and an image capture unit. The details of the experimental setup are described in the following sections. The corresponding measurement errors are discussed in Appendix B.

3.3.1.1 Actuation unit

Figure 3.9 shows the capillary actuation unit. A glass capillary tube was held by two aluminium brackets on a PMMA supporting base. Alloy wires were used to heat the two ends of the capillary with a length of D_h based on the PC controlling signals. A oil plug was

Figure 3.9: Actuation unit composed by a capillary, heaters and a supporting base.

injected into the capillary by precise syringe. The details of all the materials are introduced bellowing.

Capillary pipettes The microcapillary pipettes used in the experiments were product from Sigma-Aldrich company, as shown in Figure 3.10. The corresponding size information of the pipettes is shown in Table 3.1. In this experiment, the capillary pipettes (yellow code, 40 μL) was used. The capillaries were 127 mm long. The inner diameter and outer diameter were 0.95 mm and 1.39 mm, respectively. All capillary pipettes were made of glass, and the corresponding glass properties can be found in Table 3.2.

Wire heater The heaters were made simply by using a section of nickel/chromium alloy wire with length 10 cm, as shown in Figure 3.11. The wire was made by nickel/chromium alloy (Ni80/Cr20), produced by Goodfellow Cambridge Limited Company, UK. The wire had a diameter of 125 μm and was insulated by a 8- μm -thin polyimide layer. The electric current and voltage across the heaters were monitored by multimeters during the experiments.

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Figure 3.10: Four calibrated size microcapillary pipettes.

Figure 3.11: Nickel/chromium alloy wire and wire heater

Table 3.1: Microcapillary pipettes calibrated size

Capillary Pipettes	Outer diameter (mm)	Inner diameter (mm)	Tube Volume (μL)
Yellow label	1.39	0.95	40
Black label	1.36	0.6	20
Orange label	1.1	0.5	10
White label	1.1	0.37	5

Table 3.2: Material properties used in this work.

Materials	Glass	Silicone oil 10 cSt	Silicone oil 100 cSt	Silicone oil 1000 cSt	Air
Density $\rho(\text{kg/m}^3)$	2500	930	960	970	1.1614
Specific heat $c_p(\text{J/kgK})$	750	1150	1150	1150	1007
Thermal conductivity $k(\text{W/mK})$	1.4	0.14	0.14	0.14	2.63×10^{-2}
Thermal diffusivity $\alpha(\text{m}^2/\text{s})$	7.47×10^{-7}	1.31×10^{-7}	1.27×10^{-7}	1.26×10^{-7}	2.25×10^{-7}
Surface tension at 25°C $\sigma_0(\text{N/m})$	–	2.345×10^{-2}	2.345×10^{-2}	2.345×10^{-2}	–
Kinematic viscosity $\nu(\text{m}^2/\text{s})$	–	10^{-5}	10^{-4}	10^{-3}	2.09×10^{-5}

Silicone oil Silicone oils PDMS (polydimethylsiloxane), made by Sigma Aldrich Company, of different viscosities were used in the experiments as the working liquids. The oils $[-\text{Si}(\text{CH}_3)_2\text{O}-, -\text{C}_7\text{H}_8\text{OSi}-, -\text{Si}(\text{CH}_3)_2\text{O}-]$ have different viscosities and densities but the same surface tension (Table 3.2).

3.3.1.2 Signal and power control unit

The signal control unit is composed by a signal generator and an amplifier.

Timing Diagrams

Figure 3.12: Typical signal system behavior.

Signal generator The heating scheme depicted in Figures 3.1(c) were achieved by signals generated by a multifunction cards (Adventech PCI-1710), which was fabricated as an external card in PC. By using MATLAB, customized program was written for different signal profiles. In this research work, the different heat flux profiles was needed and they were created through the multi-function card by a customized MATLAB program using logical pulse-width modulated signals.

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Figure 3.12 generally describes the timing diagrams of the controlling signals. Different power output profiles were controlled by using different percent of on(1) and off(0) time in a period of the pulse-width modulated signals. Constant 5 V signals generated by the PC card was transferred to high frequency logical pulse signals. In every period, a pulse signal had a periodic pulse-width length ranged from 0 sec to $1/f_{PC}$ sec, and the amplitude was 5 V, while f_{PC} was the PC default frequency. Corresponding power ranged from 0 to 100% of the maximum power output was produced respectively. These signals were then amplified by a micro-chip L298N (Figure 3.14) driven by power supplier (Figure 3.13), and work on the heaters finally. The chip L298N worked as high frequency relay and transistor group, two logical input signals can be amplified to the power supplier voltage at the same time. The time percent of on and off status inside the chip then can create different power output by using fixed voltage input.

Figure 3.13: Power supply.

Power supply The power supply, as shown in Figure 3.13, was a Triple Output Power Supplies, (Model GPC3030D, GW company, USA). In the triple outputs, 5V fixed (3A) (In addition to dual variable outputs) output was used to drive the logical circuit inside chip L289N. One of the outputs was used to drive the heaters via the chip L289N, amplifying the logical pulse signals.

Signal amplifier The L298N, shown in Figure 3.14, is an integrated monolithic circuit in a 15-lead Multi-watt and PowerSO20 packages. It is a high voltage, high current dual

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Figure 3.14: Micro chip L298N.

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full-bridge driver designed to accept standard TTL logic levels, and drive inductive loads such as relays, solenoids, DC and stepping motors. Two enable inputs are provided to enable or disable the device independently. An additional supply input is provided so that the logic works at a lower voltage (5 V).

3.3.1.3 Image capture unit

A CCD camera (Figure 3.15, Model, TM-6701AN Pulnix, USA) was used in the experiments. The frame rate of the camera can be selected according to the plug velocity

Figure 3.15: CCD camera.

(1 – 20 fps). The resolution of the camera was 640 pixels $\times$ 480 pixels. The photos captured were analyzed by MATLAB, and the tracks of the plug movement were extracted from the photos by using background filter. The traveling distance and velocity can then be plotted against the time based on the frame rate. Relevant MATLAB programs can be found in Appendix C.

3.3.1.4 Temperature measurement unit

For the temperature measurement, a thermal tracer camera (NEC TH9100PMVI) was used in order to prove the correctness of the temperature distribution model. The temperature

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Figure 3.16: (a) Thermal tracer and typical images captured by the thermal tracer camera. (b) Experimental temperature distributions against space position and time caused by two heaters according to the schematics in Figure 3.1 (c).

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data of positions along the capillary can be recorded as a function of time in the video frames. The relatively long switching period allows the measurement with a sampling rate corresponding to the frame rate of the camera. According to its specifications, the thermo tracer camera has a 2% measurement accuracy. The camera can only measure the outer surface temperature of the capillary while the capillary inner surface temperature distribution actually drives the liquid plug, so that in the initial calculations, it is assumed that the temperature is distributed uniformly throughout the capillary cross-section due to the thin glass wall. The only drawback of the thermo tracer camera is the lack of triggering capability. Figure 3.16 (a) shows the photo, typical thermal images captured by this thermal tracer camera and the measured temperature distribution plot against time. In Figure

Figure 3.17: Time-dependent temperature distribution along the capillary: (a) theoretical, (b) experimental. The inserts shows the corresponding temperature distribution in space-time coordinate system.

3.17, the measured temperature distribution plot with switching frequency $f_h = 0.05$ Hz is compared to the theoretical predictions under different time points. The comparison shows that the temperature model describes reasonably well the temperature distribution along the capillary with two heaters heating alternately.

3.3.2 Experimental procedure

The experiment was conducted following a procedure which is described bellow.

1. Inject the oil plug of certain length into the capillary pipette by using precision syringe, put the capillary tube across the heater wire helix and fix them on the base of the actuation unit setup to make sure the good contact between glass capillary and the wire.
2. Accomplish the connections of the circuit for both control system and actuating system. Check the connections and make sure there is no shortcut before the power is turned on.
3. Run the computer program on MATLAB to start generating the control signals. Turn on the power supply and adjust the voltage to about 7 V, record the working currents for both of the heaters.
4. After a few minutes, until the thermal system has reached a quasi-steady-state condition, start the CCD camera to record images for three periods time(60 s).
5. Save the images as AVI video format, and then analyze them by MATLAB program to track the plug traveling distance and velocity of the liquid plug ends with shining meniscus. Plot the corresponding curves against time.

3.3.3 Experimental results and discussion

In all the experiments, the heating power of both heaters were kept at 4.38 W by monitoring and adjusting the voltage applied. Traveling distance measurement was started when the whole system was thermally in a quasi-steady-state condition. The distance between the two heaters was $D_h = 8$ mm in all experiments. The same rate of one frame per second was kept for the CCD camera throughout all experiments. Figure 3.18 shows the typical images of a plug during its passage between the two heaters. The traveling distance of the left side of the plug was measured in pixels and converted into millimeters. The velocity can be evaluated using results of two subsequent frames $u = \Delta x / \Delta t$, where $\Delta t = 1$ s determined by the frame rate.

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Figure 3.18: Images of the silicon oil plug at different time instances ($\nu = 10$ cSt, plug length $L_{\text{plug}} = 2$ mm).

Figure 3.19: Measured results of plug traveling distance x and velocity u as functions of time at different switching frequencies (inner radius $R_i = 0.475$ mm, outer radius $R_o = 0.69$ mm, heating power $q = 4.38$ W, plug length $L_{\text{plug}} = 1$ mm, kinematic viscosity $\nu = 10$ cSt): (a) $f_h = 0.05$ Hz, (b) $f_h = 0.1$ Hz, and (c) $f_h = 0.5$ Hz.

Figure 3.19 shows the measured results of the traveling distance and velocity of a 1 mm plug at different switching frequencies, corresponding to the predictions in Figure 3.3. The silicone oil used in the experiment has a kinematic viscosity of 10 cSt. The results show that the lower frequency leads to further traveling distance of the plug. The experimental reciprocating tracks agree well with the predicted results described in Figure 3.3. Certain discrepancies between the theoretical predictions and the experimental results come from some experiment errors which are discussed in Appendix B. Figure 3.4, which has been mentioned and presented in section 3.2, shows the relationship between the maximum peak-to-peak traveling distance and the switching frequency, comparing the experimental results and predicted curves. The heat flux in the analytical model was used to fit the measured data at $f_h = 0.05$ Hz and the simulations were conducted for three viscosities: $\nu = 10$ cSt, $\nu = 100$ cSt and $\nu = 1000$ cSt. Both measured and predicted results show that the maximum traveling distance decreases almost exponentially with the increasing switching frequency. Figure 3.5, which has also been mentioned and presented in section 3.2, shows the relationship between the maximum peak-to-peak traveling distance and the plug length. The measured data were taken under viscosity $\nu = 10$ cSt and the plug was actuated at 0.05 Hz. The difference between the simulated and the experimental result is probably caused by the temperature-depending properties of both viscosity and surface tension, which could be different from what assumed in the analytical model. When the oil of viscosity $\nu = 100$ cSt and $\nu = 1000$ cSt were used in the experiments, the plug was not actuated at all. The results show that plug length does not affect the motion significantly. However, the trend of the measured data shows that the viscous friction may dominate the thermocapillary force for longer plugs. In that case, both the viscosity and the Hagen-Poiseuille friction model in equation (3.5) may need to be modified. The same data used in Figure 3.4 are plotted in Figure 3.6 to show the relationship between the maximum peak-to-peak traveling distance and the kinematic viscosity. The results show a discrepancy between the theoretical model and the measured data. Viscous damping effect seems to be smaller as assumed in the analytical model. The effect of temperature

dependency of viscosity and surface tension may play important roles here. Furthermore, the current Hagen-Poiseuille model of viscous force may overestimate the actual friction force. Besides, the internal flow of the liquid plug may dissipate certain amount of the energy which will influence the reciprocating movement of the entire plug.

3.4 Conclusions

The reciprocating motion of a liquid plug under thermocapillary actuation has been investigated both analytically and experimentally. The analytical model considers the coupling effect between heat transfer in the capillary wall and the liquid surface of the plug. The transient temperature distribution determines the surface tension difference across the plug and thus driving force. In the experiments, two heating-wire heaters were activated alternatively. The silicone oil plug was positioned between the two heaters. The periodic temperature gradients generated by the two heaters drove the liquid plug to move back and forth. The traveling distance of the plugs was captured and evaluated using a CCD camera. The results are presented and discussed with different switching frequencies, viscosities and plug lengths. It shows that the maximum traveling distance and velocity decreases with the increasing of switching frequency as well as viscosity. The plug length did not have significant influences on the reciprocating movements. The analytical model generally works well in comparing with the plug behaviors observed in the experiments. The actuation concept has potential applications in postprocessing stages for droplet-based microfluidics.

Chapter 4

Further studies on thermocapillary actuation effect in capillaries

4.1 Introduction

Based on the analytical model for temperature and liquid plug dynamics established in chapter 3, as well as the experiment set up, the study on the thermocapillary actuation is extended further in this chapter to other issues. These include the actuation of liquid plug by heater arrays and water droplet encapsulation in an oil plug. Besides, the chaotic motions of droplet under high heating switching frequencies are also studied.

4.2 Thermocapillary actuation of oil plugs with an array of heaters

4.2.1 Introduction

Special reciprocating motion style and temperature cycling could be realized spatially by multiple heaters or temporally by two heaters with different heating profiles. In this section, three heaters in an array are activated sequentially to propel a liquid plug through three temperature zones to achieve longer actuation distance. Repeating this process in the reverse direction would allow a long distance thermal cycling and mixing inside the liquid plug. The motivation of this work is associated with the polymerase chain reaction (PCR) of deoxyribonucleic acid (DNA) in plug-based capillary platforms. The performance of the heater array is studied both analytically and experimentally. The observed of plug

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traveling distance and plug velocities driven by the heater array are compared with the theoretical predictions.

Figure 4.1: Model of the concept with thermocapillary actuation and spatial cycling, (a) heater arrangement, (b) capillary cross section, (c) heating schemes of the three heaters. Heater 1 starts working at $t = 0$. Heater 2 starts working at $t = T_1$, when liquid plug just pass heater 2. Heater 3 starts working at $t = T_2$, when liquid plug just reaches heater 3.

4.2.2 Modeling of transient temperature distribution

Figures 4.1 (a) and (b) show the schematics of the spatial cycling with an array of three heaters, with a distance of L for adjacent two heaters. Figure 4.1 (c) shows the working scheme of the three heaters, while the individual heater works subsequently. The plug is actuated by the heater 1 firstly, and the heater 2 starts working once the plug passes through it. The heater 3 starts working once the right end of the plug reaches the heater position, and the plug is driven back. The basic actuation concept can be described by a transient model for each heater with corresponding boundary conditions and initial conditions. The transient temperature distribution generated by a single heater in a capillary

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can be predicted by the following equation [the details are given in Appendix D, equations (D.12) and (D.12),

Figure 4.2: Typical dimensionless temperature distribution caused by three heaters as a function of dimensionless space position and dimensionless time.

$$\theta^* = \frac{1}{\beta} \left[\frac{\sinh(\beta)}{\cosh(\beta)} \cosh(\beta x^*) - \sinh(\beta x^*) \right] + \sum_{n=1}^{\infty} D_n \exp \left\{ - \left[\left(n - \frac{1}{2} \right)^2 \pi^2 + \beta^2 \right] t^* \right\} \cos \left[\left(n - \frac{1}{2} \right) \pi x^* \right], \quad (4.1)$$

with

$$D_n = 2 \int_0^1 \left\{ \theta_0 - \frac{1}{\beta} \left[\frac{\sinh(\beta)}{\cosh(\beta)} \cosh(\beta x^*) - \sinh(\beta x^*) \right] \right\} \cos \left[\left(n - \frac{1}{2} \right) \pi x^* \right] dx^*. \quad (4.2)$$

The temperature distributions generated by the three heaters activated according to the heating scheme shown in figure 4.1(c) are shown in Figure 4.2.

By using the coupling equation(3.18) between the temperature distribution and plug motion introduced in chapter 3, the predictions of the plug actuation track with both traveling

Figure 4.3: Theoretical results of actuation with three heaters: (a) traveling distance, (b) velocity, according to the heating scheme depicted in Figure 4.1 (c).

distance and velocity are plotted in Figure 4.3. Similar to the concept introduced in chapter 3, the plug is seen to be accelerated initially by the large temperature gradient near the first heater. When the plug passes through the second heater, the plug is accelerated again by the second heater. The third heater is switched on when the plug just arrives at it to create a reverse driving force to send the plug back with a negative acceleration. According to the simulations, it is seen that the effective thermocapillary actuation distance has been extended, comparing the the maximum traveling distance obtained in a single heater shown in chapter 3.

4.2.3 Experiments

4.2.3.1 Experimental setup and materials

In the experiment of thermocapillary actuation cycling with three heaters, all the materials were the same as those described in chapter 3. The heating power of each heater was kept equally at 4 W by monitoring and adjusting the applied voltage. The traveling distance measurement was started when the first heater was triggered on. The frame rate of the CCD camera was kept at 2 frames per second throughout experiments. The distances between the first and the second heater and between the second and the third heater were $L = 8$ mm, which was less than the maximum actuation distance by individual heater.

Figure 4.4: Images of the silicon oil plug at different time instances ($\nu = 10$ cSt, plug length = 1 mm).

Figure 4.4 shows the typical images of a plug during its passage through the capillary.

Figure 4.5: Experimental results of actuation with three heaters: (a) traveling distance, (b) velocity, according to the heating scheme depicted in Figure 4.1 (c)

4.2.3.2 Experimental results and discussions

Figure 4.5 shows the measured traveling distance and velocity of a 1 mm long plug propelled by three heaters. By comparing with the predictions plotted in Figure 4.3, except

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some noise, both of the experimental and analytical results agree well with each other. In order to send the plug back to its initial position at the first heater, the active time of the third heater should be chosen accordingly before the plug passes through the third heater. If the third heater is activated after the plug has passed itself, the plug can be delivered to a further position, and if more heaters are used in the array, a rather far distance transportation of the plug can be achieved step by step to overcome the limited traveling distance of thermocapillary actuation. In summary, the actuation of the oil plug can be controlled by adjusting the heater working time to achieve further delivery or being trapped between any two heaters by alternately switching the heaters under certain frequency as described in chapter 3. In applications of PCR, the transport of DNA molecules may be achieved by using an array with certain number of heaters.

4.3 Thermocapillary actuations of water droplet encapsulated in oil plug

4.3.1 Introduction

Deoxyribonucleic acid (DNA) processing system based on liquid plugs in glass capillary was reported previously by Friedman and Meldrum (Friedman et al 1998), while DNAs and most of the other bio molecules would require an aqueous environment. The thermocapillary actuation may be used in this type of operations with some modifications. On the one hand, the rate of water evaporation increases with elevated temperature. Thus the actuation temperature is required to be kept at a low level. If the system requires higher temperatures, such as that needed for thermal cycling for polymerase chain reaction (PCR) of DNA, it is extremely difficult to avoid evaporation of the aqueous micro droplets. The higher surface to volume ratio in micro-scale makes the matter even worse. On the other hand, the temperature dependency of surface tension of water is much less sensitive than that of silicone oil, making thermocapillary actuation of a water plug ineffective. A technique is presented in this section to achieve thermocapillary manipulation of aqueous droplets. The aqueous droplet is encapsulated in an immiscible fluid-silicone oil plug in capillary. The surrounding oil protects the aqueous droplet from evaporation, and in the meanwhile, effective thermocapillary manipulations can be achieved because of the higher temperature sensitivity of silicone oil's surface tension. Details of the modeling and experiment are described in this section.

4.3.2 Modeling of actuation of the two-phase system with water droplet encapsulated in an oil plug

The actuation concept is shown in Figures 4.6 (a)-(d). The design of the device and the fabrications are the same as that described in chapter 3. The oil plug is injected into the capillary by syringe first, another precise syringe is then used to inject water droplet into the oil plug to form a two phase system. Figure 4.6(d) shows the model of the two-phase plug system. It is assumed that the oil plug encapsulates the entire water plug. There

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Figure 4.6: Model of the thermocapillary actuation concept: (a) heater arrangement, (b) capillary cross section, (c) heating schemes, (d) geometry parameters of the two-phase liquid plug.

exists a thin oil film between the water plug and the capillary wall. Thus, the friction force is assumed to be determined only by the viscosity of oil μ_o . The lengths of the oil plug and water droplet are defined to be L_o and L_w , respectively. The temperature distribution can be predicted by the analytical modeling introduced in chapter 3, equation (3.14). The solution of the temperature is the real part of the following expression,

$$\theta = \frac{k}{q'' D_h} \sum_{n=-\infty}^{\infty} \left\{ \frac{F_{2n} e^{\lambda_n} - F_{1n}}{\lambda_n (e^{2\lambda_n} - 1)} e^{\lambda_n x^*} + \left[\frac{F_{2n} e^{\lambda_n} - F_{1n}}{\lambda_n (e^{2\lambda_n} - 1)} - \frac{F_{1n}}{\lambda_n} \right] e^{-\lambda_n x^*} \right\} e^{i2\pi n t^*} \quad (4.3)$$

with,

$$n = 0 : \begin{cases} F_{1n} = -0.5 \\ F_{2n} = 0.5 \end{cases} \quad n \neq 0 : \begin{cases} F_{1n} = \frac{i}{2\pi n} [1 - (-1)^n] \\ F_{2n} = F_{1n} \end{cases} \quad (4.4)$$

where $\lambda_n = \sqrt{\frac{2hD_h^2 R_o}{k(R_o^2 - R_i^2)} + i2\pi n D_h^2 / (\alpha T_h)}$ and k is glass conductivity. The dimensionless

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variables are defined as $x^* = x/D_h$, $t^* = t/T_h$. D_h and T_h are the distance between the two heaters and the switching period, respectively. Based on the fitting curves of the measured data, shown in Figure 4.7, the coefficients in the following relations can be calculated to decide the temperature dependance of surface tension σ_o of silicone oil and the interfacial tension σ_{ow} between oil and water,

$$\sigma_o(\theta) = \sigma_{o0} - \beta_o \theta, \quad (4.5)$$

$$\sigma_{ow}(\theta) = \sigma_{ow0} + \beta_{ow} \theta + \alpha_{ow} \theta^2, \quad (4.6)$$

where σ_{o0} and σ_{ow0} are the surface tension at the room temperature of $25^\circ C$. Through the temperature, the surface tension is in turn a function of the traveling distance x . So that the surface tension can be described as a function of traveling distance x ,

$$\sigma(\theta) = f[\theta(x)] = g(x) = \sigma(x).$$

In the model of the plug dynamics, it is assumed that the shear stress at the inner wall remains constant throughout the length of the composite plug. The model is used for the friction between the liquid plug and the capillary wall to estimate the total shear force in capillary based on relatively low traveling velocity (Mazouchi et al 2000). The velocity u can then be determined through the force balance equation,

$$\begin{aligned} \pi R_i^2 (\rho_o L_o + \rho_w L_w) \frac{du}{dt} = & -8\pi \mu_o (L_o + L_w) u + 2\pi R_i [-\sigma_o(x) \cos \phi_{o,r} + \\ & \sigma_{ow} \left(x + \frac{L_o}{2}\right) \cos \phi_{ow,r} - \sigma_{ow} \left(x + \frac{L_o}{2} + L_w\right) \cos \phi_{ow,a} + \\ & \sigma_o(x + L_o + L_w) \cos \phi_{o,a}] \end{aligned} \quad (4.7)$$

or

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$$\frac{du}{dt} + \frac{8\mu_o(L_o + L_w)}{R_i^2(\rho_o L_o + \rho_w L_w)}u + 2 \left[\sigma_o(x) \cos \phi_{o,r} - \sigma_{ow} \left(x + \frac{L_o}{2} \right) \cos \phi_{ow,r} + \sigma_{ow} \left(x + \frac{L_o}{2} + L_w \right) \cos \phi_{ow,a} - \sigma_o(x + L_o + L_w) \cos \phi_{o,a} \right] / [R_i(\rho_o L_o + \rho_w L_w)] = 0 \quad (4.8)$$

where L_w is the length of the water droplet, L_o is the length of the oil plug on each side of the system, R_i is the inner radius of the capillary, and ν is the kinematic viscosity of silicone oil. The receding and advancing contact angles are denoted with the subscripts “r” and “a” for oil and water-oil interface respectively. There are three terms in equation (4.7), $\pi R_i^2(\rho_o L_o + \rho_w L_w) \frac{du}{dt}$ represent the acceleration, $-8\pi\mu_o(L_o + L_w)u$ represents the friction dissipation and the rest term represents the thermocapillary force.

A model of the small dynamic contact angles are introduced. Balancing the non-compensated capillary force with the viscous force close to the contact line leads to (Gennes et al 1985),

$$\phi = (6\Gamma \frac{\mu u}{\sigma})^{1/3}, \quad (4.9)$$

where σ is the interfacial tension, and μ is the fluid viscosity. ϕ is the dynamic contact angle and the factor Γ is related to the tube radius R and the molecular length a , as shown in equation (4.10). In this work, with $R_i = 9.5 \times 10^{-4}$ m, $a \approx 3 \times 10^{-10}$ m, the value of Γ is about 15.

$$\Gamma = \ln(R_i/a). \quad (4.10)$$

The value of σ can be calculated by using equation (4.5) and equation (4.6), based on the temperature at both ends of the liquid system. The solution of the above ordinary differential equation leads to the velocity of the system (similar to equation (3.18)),

$$u = -\frac{B}{A} + \left(\frac{B}{A} + u_0 \right) e^{-At}, \quad (4.11)$$

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with

$$A = \frac{8\mu_o(L_o + L_w)}{R_i^2(\rho_o L_o + \rho_w L_w)}$$

$$B = 2 \left[\sigma_o(x) \cos \phi_{o,r} - \sigma_{ow} \left(x + \frac{L_o}{2} \right) \cos \phi_{ow,r} + \sigma_{ow} \left(x + \frac{L_o}{2} + L_w \right) \cos \phi_{ow,a} - \sigma_o(x + L_o + L_w) \cos \phi_{o,a} \right] / [R_i(\rho_o L_o + \rho_w L_w)] \quad (4.12)$$

The plug velocity will be predicted approximately following the same approach described in Chapter 3.

4.3.3 Experiments

4.3.3.1 Experimental setup and materials

Figure 4.7: Interfacial tension and surface tension as function of temperature measured by pendant drop method: (a) water in silicone oil with 0.13wt% span80, (b) silicone oil with 0.13wt% span80 in air.

The experimental setup and materials used were the same as those introduced in chapter 3. Silicone oil ($\nu_o = 10$ cSt) with 0.13wt% surfactant span80 and de-ionized (DI) water were used in the experiments. The surfactant was used to reduce the interfacial tension

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between oil and water, allowing the easy encapsulation of the water droplet by the oil plug. Without surfactant, the interfacial tension force between the water and oil may dominate over the oil surface tension, preventing the system from being driven by the thermocapillary forces.

The fluid properties used in the analytical model were characterized experimentally. The surface tension σ_o of 10 cSt silicone oil and its interfacial tension to water σ_{ow} were measured as functions of temperature. The surface tension and interfacial tension were characterized with a commercial tensiometer (FTA200, First Ten Angstroms) based on the pendant drop method. The temperature was controlled by a customized system consisting of a heater and a temperature sensor. Figure 4.7 shows the measured interfacial tension and surface tension as functions of temperature difference relative to the room temperature of 25°C. The oil/water interfacial tension increases with increasing temperature. Paik et al reported a similar trend of 1 cSt silicone oil in DI water (Paik et al 2004). In this experiment, the coefficients in equation (4.5) and equation (4.6) were determined as $\beta_o = 0.031 \text{ mN}/(\text{mK})$, $\beta_{ow} = 0.0097 \text{ mN}/(\text{mK})$ and $\alpha_{ow} = 0.0025 \text{ mN}/(\text{mK}^2)$, from the fitting functions of the experimental data which is shown in Figure 4.7. Figure 4.8 shows the effects of liquid/liquid interactions and water droplet length on the oil plug motions. These theoretical results indicate that the temperature-dependent liquid/liquid interfacial tension force and the size of the water droplet have little effect on the motion of the oil plug encapsulated with a water droplet, as long as the water droplet is completely encapsulated inside the oil plug.

4.3.3.2 Experimental results and discussions

Before filling with the oil plug, the capillary was flushed with silicone oil to coat the inner wall with a thin oil film. A needle with a diameter of 0.33 mm was used to fill the capillary with the liquid plugs. The length of the liquid plug can be adjusted by using precision syringes. Another needle was then inserted into the middle of the oil plug for injecting water drop. Any air bubbles appear in the process can be removed by slightly shaking of the capillary. In all the experiments, the heating power of both heaters were kept at

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Figure 4.8: Theoretically predicted traveling distances and velocities as function of time. Solid line is the model without considering about water/oil interfacial tension, dashed line is the model with considering about water/oil interfacial tension ($L_o = 3$ mm, $T_h = 20$ s).

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3 W by monitoring and adjusting the applied voltage. The traveling distance measurement only started when the whole system was thermally in a quasi-steady-state condition. The distance between the two heaters was fixed at $D_h = 10$ mm in all experiments. The frame rate of the CCD camera was kept at 2 frames per second. Figure 4.6(d) shows the basic configuration of the two-phase system consisting of an oil plug with an encapsulated water droplet. Under the alternate heating conditions of the two heaters, the following phenomena was observed: water droplet completely wets capillary inner wall, water droplet partially wets the capillary inner wall, water droplet rotating inside the oil plug, and encapsulated water droplet traveled with the oil plug. Details on the motions are discussed bellowing.

Water droplet completely wets capillary inner wall At room temperature, a large water droplet was able to be encapsulated inside the oil plug, because the interfacial tension was effectively reduced by the surfactant. Figure 4.7(a) shows that the interfacial tension between water and silicone oil with surfactant increases with temperature. The increase of the interfacial tension causes the capsule to break when the system was heated for a certain time. Subsequently, water droplet completely wetted the capillary inner wall, as shown in Figure 4.9. Figures 4.9(b) and (c) show the images of a plug system heated on a single side.

Figure 4.9: Images of water completely wetting the capillary inner wall: (a) heated on both sides, (b) heated on the right side, (c) heated on the left side ($L_w = 1.5$ mm $L_o = 3$ mm).

The deformation of the meniscus was caused by unbalanced thermocapillary force created

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by temperature difference between two oil plug ends. However, the thermocapillary force was not strong enough to move the two-phase liquid system.

Figure 4.10: Water droplet partially wets capillary inner wall: (a) images of the liquid system, (b) theoretical traveling distance and velocity of the system, (c) experimental traveling distance and velocity of the liquid system ($L_w = 0.5$ mm, $L_o = 3$ mm, $T_h = 20$ s).

Water droplet partially wets the capillary inner wall When the water droplet size was reduced to a critical value, the interactions between water and the capillary inner wall can be partially broken by the Laplace pressure generated by the interfacial tension. A tunnel formed across the water droplet, where silicone oil can flow through freely. The reciprocating actuation of oil plug was achieved, while the water droplet did not move. Figure 4.10(a) shows the typical images of oil plug passing the immobile water droplet. The shear stress between oil flow and water droplet resulted in its deformation. If the water droplet did not touch ends of the oil plug during its motion, the analytical model described in earlier can predict well the behavior of the motion, as shown in Figure 4.10(b) and (c).

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The small velocity peaks detected at the oil/water interface represent the deformations of the water droplet, when the liquid system reversed its moving direction.

Figure 4.11: Water droplet partially wets the capillary inner wall and limits the motion of the system: (a) images of the liquid system (the motion is blocked by the water-oil interface at a longer heating period), (b) theoretical traveling distance and velocity of the liquid system, (c) experimental traveling distance and velocity of the liquid system ($L_w = 0.5$ mm, $L_o = 3$ mm, $T_h = 30$ s).

When the heating period was increased to 30 seconds, the periodic motion would not be established properly if one end of the oil plug touched the end of the water droplet. The measurement shows the cut-off characteristics in the traveling distance curve (Figure 4.11(c)), although the model still predicts the continuation of the motion (Figure 4.11(b)). In fact, the analytical model should stop working in this case. The slight changes in the traveling distance was caused by the deformation of meniscus. The stored elastic energy

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was released when the temperature gradient reverses its direction causing a detectable velocity peak, as shown in Fig. 4.11(c).

Figure 4.12: Reciprocating motion of an oil plug with a rotating water droplet inside: (a) images of the liquid system, (b) theoretical traveling distance and velocity of the liquid system, (c) experimental traveling distance and velocity of the liquid system ($L_w = 0.3$ mm, $L_o = 3$ mm, $T_h = 20$ s).

Water droplet rotating inside the oil plug Further reducing of the water droplet size would levitate it completely inside the oil plug without any contact with the capillary inner wall. Figure 4.12(a) shows the images of a moving oil plug with a small water droplet rotating inside. The asymmetric shear forces around the water droplet driven it to rotate around an axis. There was no deformation of the water droplet. The motion of the system can be predicted relatively well with the analytical model Figure 4.12(b) and (c). Since the energy dissipated in the rotation of the water droplet is not considered in the model,

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the agreement between the analytical model and the measurement results indicates that this assumption may be valid.

Encapsulated water droplet travels with the oil plug The concentration of surfactant in silicone oil was relatively low to make oil completely wet the capillary wall. In this case, water completely or partially wetted the capillary inner wall, which prevented the two-phase system from moving under thermocapillary actuation (Figure 4.11). In order to increase the concentration of surfactant at the wall to keep water droplet being encapsulated under higher temperature conditions, mineral oil with 1wt% span80 was used to pre-coat the capillary inner wall, and the experiment was repeated. Figure 4.13(a) shows the images of oil plugs with water droplets of different lengths encapsulated completed. Figure 4.13(b) shows the measured results of two-phase systems with different water droplet lengths, with oil plug length fixed at $L_o = 3$ mm. It is apparent that the water droplet length as well as the total length of the system does not affect the motion of the system obviously. This fact is important for practical applications. The same amount of silicone oil can cater to different amounts of aqueous sample. The water droplet moved along with the encapsulating oil plug. No deformation of the water droplet was observed. The results shown in Figures 4.14(a) and (b) show the theoretical and experimental traveling distances and velocities of the two phase system with $L_w = 1$ mm, $L_o = 3$ mm, for example, which proves that there was no relative movement between oil and water and the analytical model can describe well the motion of the system. The slight difference in velocity peaks may be caused by the fact, that the induced temperature field of the two heaters in reality may not be perfectly identical as assumed in the analytical model.

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Figure 4.13: (a) Images of oil plugs with water droplets of different lengths completely encapsulated. (b) Experimental reciprocating motions of an oil plug with encapsulated water droplets of different lengths ($L_o = 3$ mm, $T_h = 20$ s).

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Figure 4.14: Reciprocating motion of an oil plug with water droplet encapsulated completely inside oil plug: (a) theoretical traveling distance and velocity of the liquid system, (b) experimental traveling distance and velocity of the liquid system ($L_w = 1$ mm, $L_o = 3$ mm, $T_h = 20$ s).

4.4 Chaotic motion of micro plugs under high frequency

4.4.1 Introduction

Since early 1980s, research on nonlinear dynamics of physical systems has been matured. A number of techniques and methods for detecting chaotic dynamic behaviors have been developed. One of the important features of chaos is the sensitive dependence on initial conditions (SDIC). Small changes in the initial state of a system can grow at an exponential rate and then dominates the behavior of the system. SDIC can be quantified with Lyapunov exponents, which are the longtime average exponential rates of divergence of nearby states. The Lyapunov exponent or Lyapunov characteristic exponent of a dynamical system is a quantity that characterizes the rate of separation of infinitesimally close trajectories. Quantitatively, two trajectories in phase space with initial separation diverge. If a system has at least one positive Lyapunov exponent, the system is chaotic. The larger the positive exponent, the more chaotic the system will be. In a system there might be any number of Lyapunov exponents, however, we only need to find out that the largest one is positive to confirm chaos. Hence, estimation of the dominant exponent is especially important. Recently many experiments in different fields have demonstrated that chaos is common in non-equilibrium systems. In these experiments the systems have totally different physical mechanisms and levels of complexity, but the chaotic behaviors are often mathematically similar. A study is conducted in this research to examine if chaotic motions exist in the periodic thermocapillary actuation of liquid plug at high frequencies. In order to identify chaotic motions from experimentally measured time series, the most often used methods are phase portraits, Lyapunov exponents, and fractal dimensions. All these three methods are applied in this study and are presented in the following parts.

The periodic thermocapillary actuation concept has been described in chapter 3. A liquid plug is placed between the two heaters. The temperature gradient across the liquid plug drives it back and forth, following the periodic change of the temperature field. The dynamic system of the experiment is described by two coupled differential equations, one

is for the spreading of temperature in the capillary wall and another one is for the plug motion. This system with coupled partial differential equations indicates the possibility of a chaotic phenomena. In fact, it has been observed in this study that the motion of the plug becomes irregular when the switching frequency is high. At lower frequencies ($f_h < 0.1$ Hz), the plug follows the change of temperature and the plug motion is periodic. In the experiment, the traveling distance of the plug was automatically captured and converted into a time series using a customized image-processing programme in MATLAB. The times series of the traveling distance can be analyzed to detect the chaotic characteristics of the motion. The experiment was conducted to investigate the nonlinear behavior of plug movement under high switching frequency ($0.1 \leq f_h \leq 1$). After getting the time series of the plug traveling distance, nonlinear dynamical analysis methods, such as phase portraits, Lyapunov exponents, and fractal dimensions, were then applied to the measured time series, from which the chaotic behavior of the system was examined.

4.4.2 Experiments

The experimental setup and materials have been described in chapter 3. The experiments were carried out within the yellow label glass capillary, which had an outer diameter of $D_o = 1.39$ mm, an inner diameter of $D_i = 0.95$ mm and a length of $L_c = 127$ mm. The working liquid is silicone oil with dynamic viscosity of $\nu = 10$ Cst, surface tension of $\sigma = 20.1$ mN/m, density of $\rho = 930$ kg/m³. The distance between the two heaters was $D_h = 8$ mm. In all the experiments, heating power of both heaters were kept at about 2 W by monitoring and adjusting the applied voltage and current. Traveling distance tracking started only when the whole system was thermally in a quasi-steady-state condition. The frame rate of the charge coupled device (CCD) camera was kept at 10 frames per second in switching period throughout the whole experiment. The resolution of the CCD camera used in experiments was $16.7 \mu\text{m}$, and the minimum traveling distance in Figure 4.15 was about $200 \mu\text{m}$. The relative error of the experiment was controlled under 10%.

Figure 4.15: Time signal of plug traveling distance at (a) $f_h = 0.1$ Hz, (b) $f_h = 0.4$ Hz, (c) $f_h = 0.8$ Hz and (d) $f_h = 1$ Hz

Figure 4.15 shows the recorded time function of the traveling distance of a 1 mm long plug at a switching frequencies f_h of 0.1 Hz, 0.4 Hz, 0.8 Hz and 1 Hz. The results show that the traveling distances obviously have an irregular behavior under high frequencies. The plug did not follow the switching frequency of the temperature field. At high frequencies, unstable behavior was dominant due to the small movement magnitudes, the relatively small driving force and the short switching period. Uncertainties in forces such as the damping viscous force become dominant at high-frequency, low-magnitude actuation. According to the bellowing function, autocorrelation functions of the time series depicted in Figure 4.15 were calculated to show if the data series have periodic characteristic,

Figure 4.16: Autocorrelation function of the time series depicted in Figure 4.15 (the two dashed lines in each diagram indicate the approximate upper and lower confidence bounds): (a) $f_h = 0.1$ Hz, (b) $f_h = 0.4$ Hz, (c) $f_h = 0.8$ Hz and (d) $f_h = 1$ Hz

$$A(\tau) = \frac{\sum_{i=1}^N (x_{i+\tau} - \bar{x})(x_i - \bar{x})}{\sum_{i=1}^N (x_i - \bar{x})^2}. \quad (4.13)$$

Figure 4.16 shows the corresponding autocorrelation functions of the time series depicted in Figure 4.15. Autocorrelation function (ACF) is a basic technique used in analyzing of time series. ACF helps to determine how quickly signals or processes change with respect to the time and whether a process has a periodic component. The autocorrelation function will have its largest value $A = 1$ at $\tau = 0$. This peak can appear again, if the time

series is periodic. The signal in Figure 4.16(a) is obviously periodic. ACF is used later for determining the time delay for constructing the phase portrait and determining the Lyapunov exponent as well as the fractal dimension.

4.4.3 Phase portrait from time series

The dynamical equations of a physical system can often be written in the following form,

$$\frac{dX(i)}{dt} = G[X(i)], \quad (4.14)$$

where $X(i)$ is the n -component vector in the phase space of the system, and G stands for n nonlinear functions of these components. It is well-known that much could be learned about dynamical behavior of a system from analyzing the trajectories in the phase space. For a practical physical system, the phase space often has a large number of components, i.e., the dimension of the phase space is very large. However, most dynamical systems involve only a small number of important degrees of freedom. In practice, the study can often be restricted to a low-dimensional phase space which only includes these important degrees of freedom. Such a phase space is usually called embedded phase space. In most experimental investigations, only time series of a single variable of the system can be measured. The time-delay technique is used to reconstruct multidimensional phase portraits from this time series, in order to examine the dynamic properties of the whole system. Take a N -point traveling distance time series $x(i)$ as the example; the reconstructed trajectory, X , can be expressed as a matrix,

$$X = (X_1, X_2, X_3, \dots, X_M)^T, \quad (4.15)$$

where X_k , $k = 1, 2, \dots, M$, is the state of the system at discrete time k , and is given by

$$X_k = (X_k, X_{k+J}, \dots, X_{k+(m-1)J}), k = 1, 2, \dots, M, \quad (4.16)$$

where J is the time delay on reconstruction delay, and m is the embedding dimension. The integers M , N , m , and J satisfy the following equation,

$$M = N - (m - 1)J. \quad (4.17)$$

Thus, an m -dimension phase portrait can be reconstructed from the time series of traveling distance $x(i)$. The embedding dimension m is usually estimated in accordance with Taken's theorem, i.e., $m > 2n$, where n is the dimension of the attractor. It has been shown that if the embedding dimension m is sufficiently large, the pseudo-phase portrait constructed by the method of time delays will in principle have the same properties as a phase portrait constructed from the independent variables. For visualization of the reconstructed phase portrait, $m = 2$ or $m = 3$ is often used, while higher m is used for the further study to determine the largest Lyapunov exponent and fractal dimension of the attractor. The choice of the time delay J is almost but not completely arbitrary. A good approximation of J is equal to the discrete time lag where the autocorrelation function of the time series drops to $(1 - 1/e)$ of its initial value.

In the present study, the embedding dimension $m = 2$ and the time delays $J = 4$ are used to obtain the phase portraits. According to the ACF shown in Figure (4.16), the value of J is equal to the discrete time lag τ where the autocorrelation function drops to $1 - 1/e$ (Rosenstein 1993) of its initial value. Due to the small number of data points in our experiment, the value for the time delay is chosen as $J = 4$. In our customized Matlab programme, the positive integer of discrete values, beyond which the theoretical ACF is effectively 0, was chosen to be 40. The two dashed lines in each diagram of figure 4.16 indicate the approximate upper and lower confidence bounds. As the time series has 120 data points, the other 80 ACF values confidently lie between these two dashed lines.

Two-dimensional vectors $X_k = (x_k, x_{k+J})$, $k = 1, 2, \dots, M$, are constructed from the time series data $x(i)$. Figure 4.17 shows the two-dimensional phase portraits obtained by plotting $x(i + J)$ versus $x(i)$ for $J = 4$. The time series data were measured at $f_h = 0.1$ Hz,

Figure 4.17: Phase portrait constructed from the traveling distance measured at a time lag of $J = 4$: (a) $f = 0.1 \text{ Hz}$, (b) $f = 0.4 \text{ Hz}$, (c) $f = 0.8 \text{ Hz}$ and (d) $f = 1 \text{ Hz}$.

$f_h = 0.4 \text{ Hz}$, $f_h = 0.8 \text{ Hz}$ and $f_h = 1 \text{ Hz}$. In these phase portraits, it can be seen that the trajectories lie on a limit set in the embedded phase space for each time delay, which demonstrates that these phase portraits are attractors. Following, Lyapunov exponents and fractal dimensions are determined to prove that these attractors are strange or chaotic.

4.4.4 Lyapunov exponents and fractal dimensions

The most widely used criteria to quantify chaos in a system are the Lyapunov exponents and the fractal dimensions. Positive Lyapunov exponents indicate the sensitive depen-

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dence on initial conditions. If a system has at least one positive Lyapunov exponent, the system is chaotic. A system may possess many Lyapunov exponents, but only the largest Lyapunov exponent needs to be checked in order to confirm chaos.

The fractal dimension is a non-integer dimension which is a hallmark of a chaotic attractor. There are many types of definitions and measures of fractal dimensions, of which the correlation dimension is the commonly used one. There are many algorithms that are applicable to estimate the largest Lyapunov exponent from time series (Rosenstein 1993, Wales 1991). The method used here was developed by Rosenstein (1993). This method is fast, easy to implement, and robust to changes in parameters such as the embedding dimension, the size of data set, the reconstruction delay, and the noise level. Furthermore, the correlation dimension can also be calculated simultaneously.

The largest Lyapunov exponent of a chaotic attractor is defined in the following equation,

$$d(t) = Ce^{\lambda_1 t}, \quad (4.18)$$

where $d(t)$ is the average divergence of trajectories with nearby initial conditions on the attractor at time t , C is a constant that normalizes the initial separation, and λ_1 is the largest Lyapunov exponent.

The first step of Rosenstein's algorithm involves reconstructing the attractor dynamics from a single time series by using the method described above. The algorithm then locates the nearest neighbor of each point on the trajectories. The nearest neighbor, U_j is found by searching for the point that minimizes the distance to the particular reference point $\hat{j}$. This can be expressed as

$$d_j(0) = \min \|X_j - X_{\hat{j}}\|, j = 1, 2, 3 \dots M, \quad (4.19)$$

where $d_j(0)$ is the initial distance from the j -th point to its nearest neighbor, $\|\cdot\|$ denotes the Euclidean norm, and M is the number of reconstructed vectors in the phase space. The largest Lyapunov exponent is then estimated as the mean rate of separation of the nearest neighbors (Packard N.H et al 1980).

Figure 4.18: $\ln d_j(i)$ versus time ($m = 10$, $J = 4$, the dashed lines are the fitting functions) for (a) $f_h = 0.1$ Hz; (b) $f_h = 0.4$ Hz; (c) $f_h = 0.8$ Hz; (d) $f_h = 1$ Hz.

Let the nearest neighbors evolve with time along the trajectories and assume that the j -th pair of nearest neighbors diverges approximately at a rate given by the largest Lyapunov exponent,

$$d_j(t) = C_j e^{\lambda_1(i\Delta t)}, j = 1, 2, 3 \dots M, \quad (4.20)$$

where C_j is the initial separation, i is the discrete time with which the nearest neighbors evolve, and Δt is the time interval between samples. Taking the logarithm of both sides of (4.20) yields,

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$$\ln d_j(i) = \ln C_j + \lambda_1(i\Delta t), j = 1, 2, 3 \dots M. \quad (4.21)$$

Equation (4.21) represents a set of approximately parallel lines for $j = 1, 2, \dots, M$, with a slope proportional to λ_1 . Taking the average of $\ln d_j(i)$ over all values of j , the largest Lyapunov exponent λ_1 then equals to the slope of a line defined by,

$$\langle \ln d_j(i) \rangle = \lambda_1(i\Delta t), j = 1, 2, 3 \dots M, \quad (4.22)$$

where $\langle \rangle$ denotes the average over all values of j .

Figure 4.18 shows the plots of $\langle \ln d_j(i) \rangle$ versus the time $t = (i\Delta t)$. The solid lines are the calculated results, and the dashed lines are the fitting functions based on the least-square method. The largest Lyapunov exponent λ_1 is equal to the slope of the dashed lines. The analyzed time series $x(i)$ is the same as presented in the previous sections. The embedding dimension remains constant at $m = 10$. The calculated largest Lyapunov exponents is $\lambda_1 = 0.01$ when the switching frequency is $f = 1$ Hz. The positive largest Lyapunov exponents indicate that the attractors are chaotic. With increasing positive Lyapunov exponents from 0.0032 at 0.1 Hz to 0.026 at 1Hz. the results prove the existence of chaos in the plug motion at high switching frequencies.

The next important quantitative measure of an attractor is the correlation dimension. The correlation dimension estimates the complexity of a system, which can be determined from the correlation function $C(R)$. Let R denote a small positive value; for a reconstructed attractor X , the two-point correlation function is defined as, (Abarbanel et al)

$$C(R) = \frac{1}{M(M-1)} \sum_{i=1}^M \sum_{j \neq 1}^M \theta[R - d(X_i - X_j)], \quad (4.23)$$

where M is the number of the reconstructed vectors, θ is the Heaviside function, and $d(X_i - X_j)$ represents the distance between two m -dimensional vectors. The Euclidean

Figure 4.19: $\log C(R)$ versus $\log R$ ($m = 10$, $J = 4$, the dashed lines are the fitting functions) for: (a) $f_h = 0.1$ Hz, (b) $f_h = 0.4$ Hz, (c) $f_h = 0.8$ Hz, and (d) $f_h = 1$ Hz.

norm can be used to measure the distance between two vectors. $C(R)$ is interpreted as the fraction of pairs of points that is separated by a distance less than or equal to R . The correlation dimension of an attractor is defined in the following equation,

$$C(R) = \lim_{R \rightarrow 0} aR^{D_c}, \quad (4.24)$$

where a is a constant value, D_c is the correlation dimension, and J is the time delay. The correlation dimension can now be estimated from the slope of the linear part of the $\log C(R)$ versus $\log(R)$ curve according to

$$D_c = \frac{d \log[C(R)]}{d \log(R)} \quad (4.25)$$

Figure 4.19 shows the curves of $\log[C(R)]$ versus $\log(R)$ for the different switching frequencies. The solid lines are the calculated results. The dashed lines are the fitting functions. The correlation dimension is determined by the slope of the dashed line. Embedding dimension m is taken equal to 10. The results show that the system has non-integer dimensions, which means that the attractors depicted in Figure 4.17 are chaotic.

4.5 Conclusions

In this chapter, further control of the plug motion driven by thermocapillary effect are studied based on both analytical models and experiments. Analytical models and experimental verifications are presented for the actuation and spatial temperature cycling of a liquid plug under an array consisting of three heaters. Although the same heat flux is assumed for the three heaters in the present study, the actuation concept can be formulated for three heaters with different heat fluxes in the case of PCR application. In order to achieve aqueous based requirements, water droplet encapsulation in oil plug is also studied based on different phenomena. Surfactant was used to achieve completely encapsulation of water droplet inside oil plug. The chaotic motion of a liquid plug under high-frequency thermocapillary actuation was also investigated. The measured time series data of the traveling distance were analyzed by constructing the phase-space portraits, evaluating the largest Lyapunov exponent and calculating the fractal dimension. The results show that the phase-space trajectories define a limit set in the phase space that is an attractor. This attracting set is chaotic, because nearby trajectories separate exponentially. Moreover, the fractal dimension of the attractor has also been calculated, which gives the degree of the system complexity. The results indicate the potential use of chaotic plug motion to improve mixing in capillary-based microfluidics.

Chapter 5

Thermocapillary actuation and manipulation of droplet in a planar microchannel

5.1 Introduction

In this chapter, the 1-D model for the thermocapillary actuation in capillary tube is extended to a two dimensional (2-D) planar microchannel. A liquid droplet is positioned inside the planar channel formed between a square substrate and a top layer, and four heaters are embedded along the four edges. The square channel area is much larger than the droplet size. Temperature distributions in the square region are realized spatially by four controllable heaters. Through the coupling between the temperature field and the surface tension dependency, the droplet motion can be manipulated. It is demonstrated that a complete manipulation of the droplet in a 2-D channel can be achieved by various heating schemes at the boundaries, including both transient and periodic manipulations.

5.2 Modeling of temperature distribution

5.2.1 Modeling of transient temperature distribution

Figure 5.1 shows the concept of thermocapillary actuation of a single droplet in a planar microchannel formed between a substrate and a top layer. Four heaters are located on the

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Figure 5.1: Schematic illustration of the actuation of droplet in a two dimensional channel. (a)The channel and heaters. (c)The droplet configuration

bottom substrate at boundaries. In order to simplify the model, a square region is used in the present study. The transient actuation is to switch on the heaters whose heating powers are fixed according to the operation requirement. The temperature distribution induced by the boundary heating on the substrate surface can be described by the following governing equation,

$$\frac{\partial \theta}{\partial t} = \alpha \left(\frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} \right) - \frac{h}{H \rho c} \theta, \quad (5.1)$$

where θ is the temperature difference relative to the environmental temperature, H is the thickness of the substrate plane, α , ρ , h and c are the thermal diffusivity, density, convection coefficient and specific heat capacity of the substrate material, respectively. Heat radiation is neglected in this model because of the relatively low temperature of the substrate surface. The boundary conditions for the temperature are,

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$$\left\{ \begin{array}{l} \frac{\partial \theta}{\partial x}|_{x=0} = -f_1 \frac{q_0''}{k} \\ \frac{\partial \theta}{\partial x}|_{x=a} = f_2 \frac{q_0''}{k} \end{array} \right\}, \left\{ \begin{array}{l} \frac{\partial \theta}{\partial y}|_{y=0} = -f_3 \frac{q_0''}{k} \\ \frac{\partial \theta}{\partial y}|_{y=a} = f_4 \frac{q_0''}{k} \end{array} \right\}, \quad (5.2)$$

where q_0'' is the maximum heat flux that can be supplied by individual heater, k is the conductivity of the substrate material and a is the length of the square region edge. f_1, f_2, f_3 and f_4 are strength factors controlling heater operations, which are four constants between 0 and 1, corresponding to minimum and maximum heat flux for the four heaters respectively. By introducing dimensionless variables $\theta^* = \theta k / (q_0'' a)$, $x^* = x/a$, $t^* = t/(a^2/\alpha)$ and $\xi = ha^2/Hk$ in equations 5.1 and 5.2, we have the dimensionless heat transfer equation and boundary conditions,

$$\frac{\partial \theta^*}{\partial t^*} = \left(\frac{\partial^2 \theta^*}{\partial x^{*2}} + \frac{\partial^2 \theta^*}{\partial y^{*2}} \right) - \xi \theta^*$$

$$\left\{ \begin{array}{l} \frac{\partial \theta^*}{\partial x^*}|_{x^*=0} = -f_1 \\ \frac{\partial \theta^*}{\partial x^*}|_{x^*=1} = f_2 \end{array} \right\}, \left\{ \begin{array}{l} \frac{\partial \theta^*}{\partial y^*}|_{y^*=0} = -f_3 \\ \frac{\partial \theta^*}{\partial y^*}|_{y^*=1} = f_4 \end{array} \right\}. \quad (5.3)$$

In order to homogenize the boundary conditions, an auxiliary function is introduced,

$$\psi(x^*, y^*) = -f_1 x^* + \frac{x^{*2}}{2} (f_1 + f_2) - f_3 y^* + \frac{y^{*2}}{2} (f_3 + f_4), \quad (5.4)$$

such that it meets the boundary conditions,

$$\left\{ \begin{array}{l} \frac{\partial \psi}{\partial x^*}|_{x^*=0} = -f_1 \\ \frac{\partial \psi}{\partial x^*}|_{x^*=1} = f_2 \end{array} \right\}, \left\{ \begin{array}{l} \frac{\partial \psi}{\partial y^*}|_{y^*=0} = -f_3 \\ \frac{\partial \psi}{\partial y^*}|_{y^*=1} = f_4 \end{array} \right\}. \quad (5.5)$$

By setting

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$$\theta^*(x^*, y^*, t^*) = g(x^*, y^*, t^*) + \psi(x^*, y^*), \quad (5.6)$$

and substituting equation (5.6) into equation (5.3), we obtain the equation and boundary conditions for the new function $g(x^*, y^*, t^*)$,

$$\frac{dg}{dt^*} = \left(\frac{d^2g}{dx^{*2}} + \frac{d^2g}{dy^{*2}} \right) - \xi g + (f_1 + f_2 + f_3 + f_4) - \xi \psi, \quad (5.7)$$

and

$$\left\{ \begin{array}{l} \frac{\partial g}{\partial x^*} \big|_{x^*=0} = 0 \\ \frac{\partial g}{\partial x^*} \big|_{x^*=1} = 0 \end{array} \right\}, \left\{ \begin{array}{l} \frac{\partial g}{\partial y^*} \big|_{y^*=0} = 0 \\ \frac{\partial g}{\partial y^*} \big|_{y^*=1} = 0 \end{array} \right\}. \quad (5.8)$$

Equation (5.7) is solved by the Fourier series which meets the boundary condition (5.8). Let

$$\begin{aligned} g = & g_{00}(t^*) + \sum_{m=1}^{\infty} g_{m0}(t^*) \cos(m\pi x^*) + \sum_{n=1}^{\infty} g_{0n}(t^*) \cos(n\pi y^*) \\ & + \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} g_{mn}(t^*) \cos(m\pi x^*) \cos(n\pi y^*) \end{aligned}, \quad (5.9)$$

where g_{00}, g_{m0}, g_{0n} and g_{mn} are the coefficients to be determined, and

$$\begin{aligned} \psi(x^*, y^*) = & \psi_{00} + \sum_{m=1}^{\infty} \psi_{m0} \cos(m\pi x^*) + \sum_{n=1}^{\infty} \psi_{0n} \cos(n\pi y^*) \\ & + \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \psi_{mn} \cos(m\pi x^*) \cos(n\pi y^*) \end{aligned}, \quad (5.10)$$

where

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$$\left\{ \begin{array}{l} \psi_{00} = \int_0^1 \int_0^1 \psi dx^* dy^* \\ \psi_{m0} = 2 \int_0^1 \psi \cos(m\pi x^*) dx^* dy^* \\ \psi_{0n} = 2 \int_0^1 \psi \cos(n\pi y^*) dx^* dy^* \\ \psi_{mn} = 4 \int_0^1 \int_0^1 \psi \cos(m\pi x^*) \cos(n\pi y^*) dx^* dy^* \end{array} \right. \quad (5.11)$$

Substituting equations (5.9)-(5.11) into (5.7), taking the initial condition $\theta(x^*, y^*, 0) = 0$, the final result is obtained,

$$\begin{aligned} \theta^*(x^*, y^*, t^*) &= g(x^*, y^*, t^*) + \psi(x^*, y^*) \\ &= g_{00}(t^*) + \sum_{m=1}^{\infty} g_{m0}(t^*) \cos(m\pi x^*) + \sum_{n=1}^{\infty} g_{0n}(t^*) \cos(n\pi y^*) , \\ &\quad -f_1 x^* + \frac{x^{*2}}{2} (f_1 + f_2) - f_3 y^* + \frac{y^{*2}}{2} (f_3 + f_4) \end{aligned} \quad (5.12)$$

where

$$\left\{ \begin{array}{l} g_{00} = -d_{00} - \psi_{00} + d_{00}e^{-\xi t^*} \\ g_{m0} = \frac{\xi}{\beta} \psi_{m0} + d_{m0}e^{-\beta t^*} \\ g_{0n} = \frac{\xi}{\gamma} \psi_{0n} + d_{0n}e^{-\gamma t^*} \end{array} \right. , \left\{ \begin{array}{l} d_{00} = -\frac{1}{\xi} (f_1 + f_2 + f_3 + f_4) \\ d_{m0} = -\left(1 + \frac{\xi}{\beta}\right) \psi_{m0} \\ d_{0n} = -\left(1 + \frac{\xi}{\gamma}\right) \psi_{0n} \end{array} \right. , \quad (5.13)$$

and $\beta = (m\pi)^2 + \xi$, $\gamma = (n\pi)^2 + \xi$. The cross terms, $\cos(m\pi x^*) \cos(n\pi y^*)$, do not appear in the solution because $\psi_{mn} = g_{mn} = 0$.

5.2.2 Modeling of periodic temperature distribution

For the periodic actuation, the governing equation for the temperature is the same as equation (5.1),

$$\frac{\partial \theta}{\partial t} = \alpha \left(\frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} \right) - \frac{h}{H\rho c} \theta. \quad (5.14)$$

The periodic boundary conditions are controlled by the periodic heating scheme functions $f_1(t)$, $f_2(t)$, $f_3(t)$, $f_4(t)$ with the same period T_h , i.e.,

$$\left\{ \begin{array}{l} \frac{\partial \theta}{\partial x}|_{x=0} = -f_1(t) \frac{q_0''}{k} \\ \frac{\partial \theta}{\partial x}|_{x=a} = f_2(t) \frac{q_0''}{k} \end{array} \right\}, \quad \left\{ \begin{array}{l} \frac{\partial \theta}{\partial y}|_{y=0} = -f_3(t) \frac{q_0''}{k} \\ \frac{\partial \theta}{\partial y}|_{y=b} = f_4(t) \frac{q_0''}{k} \end{array} \right\}. \quad (5.15)$$

By introducing the new dimensionless variables $\theta^* = \theta k / q_0'' a$, $x^* = x/a$, $t^* = t/T_h$, we have the dimensionless heat transfer equation and boundary conditions,

$$\eta \frac{\partial \theta^*}{\partial t^*} = \left(\frac{\partial^2 \theta^*}{\partial x^{*2}} + \frac{\partial^2 \theta^*}{\partial y^{*2}} \right) - \xi \theta^* \\ \left\{ \begin{array}{l} \frac{\partial \theta^*}{\partial x^*}|_{x^*=0} = -f_1(t^*) \\ \frac{\partial \theta^*}{\partial x^*}|_{x^*=1} = f_2(t^*) \end{array} \right\}, \quad \left\{ \begin{array}{l} \frac{\partial \theta^*}{\partial y^*}|_{y^*=0} = -f_3(t^*) \\ \frac{\partial \theta^*}{\partial y^*}|_{y^*=1} = f_4(t^*) \end{array} \right\}, \quad (5.16)$$

where $\eta = a^2 / (\alpha T_h)$ and $\xi = ha^2 / Hk$. In order to homogenize the time dependent boundary conditions, we introduce a similar function used in the transient actuation case,

$$\psi = -f_1(t^*)x^* + \frac{x^{*2}}{2} [f_1(t^*) + f_2(t^*)] - f_3(t^*)y^* + \frac{y^{*2}}{2} [f_3(t^*) + f_4(t^*)], \quad (5.17)$$

such that

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$$\left\{ \begin{array}{l} \frac{\partial \psi}{\partial x^*}|_{x^*=0} = -f_1(t^*) \\ \frac{\partial \psi}{\partial x^*}|_{x^*=1} = f_2(t^*) \end{array} \right\}, \left\{ \begin{array}{l} \frac{\partial \psi}{\partial y^*}|_{y^*=0} = -f_3(t^*) \\ \frac{\partial \psi}{\partial y^*}|_{y^*=1} = f_4(t^*) \end{array} \right\}. \quad (5.18)$$

By setting

$$\theta^*(x^*, y^*, t^*) = g(x^*, y^*, t^*) + \psi(x^*, y^*, t^*), \quad (5.19)$$

and substituting equations (5.17) and (5.19) into equation (5.14), it is obtained that

$$\frac{dg}{dt^*} = \left(\frac{d^2 g}{d^2 x^*} + \frac{d^2 g}{d^2 y^*} \right) - \xi g + [f_1(t^*) + f_2(t^*) + f_3(t^*) + f_4(t^*)] - \xi, \quad (5.20)$$

and

$$\left\{ \begin{array}{l} \frac{\partial g}{\partial x^*}|_{x^*=0} = 0 \\ \frac{\partial g}{\partial x^*}|_{x^*=1} = 0 \end{array} \right\}, \left\{ \begin{array}{l} \frac{\partial g}{\partial y^*}|_{y^*=0} = 0 \\ \frac{\partial g}{\partial y^*}|_{y^*=1} = 0 \end{array} \right\}. \quad (5.21)$$

The function $g(x^*, y^*, t^*)$ can be expanded and solved from equation (5.21) by the Fourier series method according to the homogeneous boundary conditions and periodic characteristic, and the final temperature is obtained as

$$\begin{aligned} \theta^*(x^*, y^*, t^*) &= g(x^*, y^*, t^*) + \psi(x^*, y^*, t^*) \\ &= \sum_{N=-\infty}^{\infty} g_{00N} e^{i2\pi N t^*} + \sum_{m=1}^{\infty} \sum_{N=-\infty}^{\infty} g_{m0N} \cos(m\pi x^*) e^{i2\pi N t^*} \\ &\quad + \sum_{n=1}^{\infty} \sum_{N=-\infty}^{\infty} g_{0nN} \cos(n\pi y^*) e^{i2\pi N t^*}, \quad (5.22) \\ &\quad - f_1(t^*)x^* + \frac{x^{*2}}{2} [f_1(t^*) + f_2(t^*)] - f_3(t^*)y^* + \frac{y^{*2}}{2} [f_3(t^*) + f_4(t^*)] \end{aligned}$$

where

$$\begin{cases} g_{00N} = \frac{d_{00N} - (i2\eta\pi N + \xi)\psi_{00N}}{i2\eta\pi N + \xi} \\ g_{m0N} = \frac{-(i2\eta\pi N + \xi)\psi_{m0N}}{i2\eta\pi N + \xi + m^2\pi^2} \\ g_{0nN} = \frac{-(i2\eta\pi N + \xi)\psi_{0nN}}{i2\eta\pi N + \xi + n^2\pi^2} \end{cases} \quad (5.23)$$

and

$$d_{00N} = \int_0^1 [f_1(t^*) + f_2(t^*) + f_3(t^*) + f_4(t^*)] e^{-i2\pi N t^*} dt^*. \quad (5.24)$$

ψ_{00N} , ψ_{m0N} , ψ_{0nN} are evaluated from the following integrals,

$$\begin{cases} \psi_{00N} = \int_0^1 \int_0^1 \int_0^1 \psi e^{-i2\pi N t^*} dx^* dy^* dt^* \\ \psi_{m0N} = 2 \int_0^1 \int_0^1 \psi \cos(m\pi x^*) e^{-i2\pi N t^*} dx^* dy^* dt^* \\ \psi_{0nN} = 2 \int_0^1 \int_0^1 \psi \cos(n\pi y^*) e^{-i2\pi N t^*} dx^* dy^* dt^* \end{cases} \quad (5.25)$$

5.3 Coupling of the temperature distribution and droplet motion

The temperature distributions in the channel are coupled to the droplet through surface tensions. The unbalanced surface tensions forces on the droplet, due to the temperature gradients and temperature dependent surface tension, drive the droplet moving inside the channel. For a small temperature range, a linear relation can be assumed,

$$\sigma_{lg}(\theta) = \sigma_{lg0} - \varepsilon(\theta - \theta_0), \quad (5.26)$$

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where σ_{lg0} is the liquid-gas surface tension at the reference temperature θ_0 and ε is the temperature coefficient of surface tension. The temperature fields resulting from equations (5.1) and (5.14) are in turn functions of the position (x, y) and time t . Assuming a weak thermal interaction between the droplet and the substrate surface, the surface tension can be described as a function of the position (x, y) and time t through the temperature distributions,

$$\sigma_{lg}(\theta) = f[\theta(x, y, t)] = \sigma_{lg}(x, y, t) \quad (5.27)$$

The droplet is driven by the unbalanced surface tension force which depends on the

Figure 5.2: Side view of the profile of traveling droplet actuated in the temperature gradient field created by left side heater, showing that the curvature radius and contact angle between the droplet and the channel do not change much during the actuation process.

temperature of the liquid film contacting the glass surface only. The weak coupling thus results the negligible heat capacity of the droplet, which means that the temperature profile on the glass surface is unaltered. Since the droplet diameter $2R \approx 1$ mm is normally less than the Laplace length $\kappa^{-1} \approx 1.64$ mm ($\kappa^2 = \rho g / \sigma_{lg}$), the droplet profile can be

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assumed to be circular, the curvature radius be constant and the dynamic contact angle be uniform along the contact line, which can be proved by the experiment shown in Figure 5.2. For the flat surface in the case, the dominant viscous dissipation occurs in the bulk, and the dissipation at the solid-liquid-gas contact line is negligible. With the lubrication approximation model of ridge with a free liquid-air surface, the viscous drag force generated within the liquid is $D = 3\mu u \int_M^N \frac{dx}{\lambda(x)}$ (Daniel et al 2002), where $\lambda(x)$ is the droplet height profile function, μ is the liquid viscosity, R is the the droplet base radius and u is the velocity. In this problem, the droplet is formed in between the two glass plates, the middle of the droplet presents zero shear stress due to the symmetric configuration. So that the drag forces on the droplet are calculated by treating the two contacting surfaces as two separated droplets on a flat surface. The droplet height profile is then $\lambda(x) = h_g/2$, and h_g is the channel height, and the viscous drag forces are

$$\begin{cases} D_x = 12\pi\mu Ru \int_M^N \frac{dx}{\lambda(x)} = \frac{12\mu\pi u R^2}{h_g}, \\ D_y = 12\pi\mu Rv \int_P^Q \frac{dy}{\lambda(y)} (2\pi R) = \frac{12\mu\pi u R^2}{h_g}, \end{cases} \quad (5.28)$$

where u, v are the velocity magnitudes in x and y directions respectively. The liquid viscosity, based on the work of Yarin, is dependent on temperature at the droplet center (Yarin et al 2002),

$$\mu = \mu_0 \exp \left[3.8T_b \left(\frac{1}{T_{\text{center}}} - \frac{1}{T_0} \right) \right], \quad (5.29)$$

where μ_0 is the viscosity at some reference temperature T_0 (normally 293K), and T_b is the liquid boiling temperature. In order to make the droplet evaporate with an imperceptible amount and make hysteretic effects not prominent, silicone oil is chosen to be the droplet liquid. In this case, the capillary number $Ca = \frac{\mu |\vec{U}|}{\sigma_{lg}} < 1 \times 10^{-3}$, when the droplet velocity magnitude $|\vec{U}|$ is less than 1 mm/s (here $\vec{U} = u\hat{x} + v\hat{y}$). The low capillary number ensures that the moving droplet has nearly a constant circular profile, and the dynamic contact

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angles are assumed to be constant for simplification. The circular profile is divided into n sectors, the resultant force on both x , and y directions can be calculated by combining all the surface tension forces acting on individual sector,

$$\begin{cases} F_x = 2 \sum_{i=1}^n \frac{2\pi R}{n} \cos \left[\frac{(2i+1)\pi}{n} \right] \sigma_{lg}(x_i, y_i, t) \\ F_y = 2 \sum_{i=1}^n \frac{2\pi R}{n} \sin \left[\frac{(2i+1)\pi}{n} \right] \sigma_{lg}(x_i, y_i, t) \end{cases}, \quad (5.30)$$

where $\sigma(x_i, y_i, t) = \sigma \left(x_0 + R \cos\left(\frac{\pi(2i+1)}{n}\right), y_0 + R \sin\left(\frac{\pi(2i+1)}{n}\right), t \right)$, (x_0, y_0) is the droplet initial center point position. A larger n leads to more accurate result, and we set $n = 8$ in this study. The velocity $\vec{U}$ can be determined by the force balance between the acceleration, friction and thermocapillary force, i.e.,

$$\begin{cases} \rho V \frac{du}{dt} = -\frac{12\pi\mu R^2}{h_g} u + F_x \\ \rho V \frac{dv}{dt} = -\frac{12\pi\mu R^2}{h_g} v + F_y \end{cases}. \quad (5.31)$$

V is the volume of the droplet ($V \approx \pi R^2 h_g$). Because of the completely wetting of silicone oil on glass surface, the dynamic contact angle along the contact line was quite small, about 10° , which is measured in Figure 5.2. By setting $A = \frac{12\mu}{\rho h_g^2}$, $B_x = -\frac{F_x}{\rho V}$ and $B_y = -\frac{F_y}{\rho V}$, the velocity of the droplet can be solved by using the same numerical method introduced in chapter 3. In each time iteration step, A and B are treated as constants and the velocities are obtained by the following equation

$$\begin{cases} u = -\frac{B_x}{A} + \frac{B_x}{A} e^{-At} \\ v = -\frac{B_y}{A} + \frac{B_y}{A} e^{-At} \end{cases}. \quad (5.32)$$

In the numerical calculation, the heat flux value was estimated based on the dimensionless temperature calibrated by the actual temperature values measured in experiments.

5.4 Experiments setup and materials

The experimental setup is illustrated in Figure 5.3. The planar channel was formed be-

Figure 5.3: Experimental setup

tween a glass wafer as the bottom plate and a glass plate on top. The channel had a height of 0.5 mm and area of $10 \times 10 \text{ mm}^2$. A four-inches Pyrex glass wafer with $500 \mu\text{m}$ thickness was used to fabricate the glass plate with integrated microheaters. The wafer was first cleaned in a piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ at 3 : 1), rinsed in deionized (DI) water and dried with nitrogen. After the drying step at 120°C for 30 mins, a $3\text{-}\mu\text{m}$ thick layer of lift-off resist (LOR30B, Microchem, USA) and subsequently a $3\text{-}\mu\text{m}$ thick layer of photo resist (AZ1512, Clariant, Singapore) were spin-coated onto the wafer. The photoresist was then baked and subsequently exposed to UV light using the photo lithography mask to define the heater structure. After a short oxygen plasma treatment to remove the organic residues and to improve the adhesion to the glass surface, 30 nm of titanium and subsequently 300 nm of platinum were deposited by e-beam evaporation (BOC Edwards, UK). Finally, the resist was lift-off in acetone in an ultrasonic bath. The glass plate was diced into square chips ready for mounting on the casing. The casing was fabricated in polymethyl methacrylate (PMMA) using laser machining. The top glass plate was positioned and secured at a distance of 0.5 mm on top of the plate with the four integrated heaters.

The droplet was actuated within the square region. The control and power supply system were the same as that introduced in chapter 3. Silicone oils PDMS (polydimethylsiloxane, Sigma Aldrich) of viscosity 10 cSt was used in the experiments as the working liquid for the droplets. The droplet was injected into the planar channel and droplet radius was controlled around 0.5 mm by precise syringe.

5.5 Results and discussions

Figure 5.4: The transient temperature distributions at different time: (a) $t^* = 0.0075$; (b) $t^* = 0.075$; (c) $t^* = 0.375$; (d) $t^* = 0.75$. The heating code is $(f_1, f_2, f_3, f_4) = (1, 1, 1, 1)$.

5.5.1 Simulation results

5.5.1.1 Simulation results of transient manipulations

The transient actuation in the present study is to switch on the heaters and keep the heating fluxes constant. Under this operation mode, the temperature field can be established in a transient time period and the final temperature distribution depends on the heating code

Figure 5.5: (a) The track of droplet movement under transient actuation with the heating code $(f_1, f_2, f_3, f_4) = (1, 1, 1, 1)$. (b) Displacement of droplet against time in both x and y directions. (c) Velocity magnitude of droplet against time. (d) Temperature gradient magnitude at the droplet center against time.

formed by (f_1, f_2, f_3, f_4) . Figure 5.4 shows the dimensionless temperature distributions at different times after switch-on of the heaters. The four heaters have equal heat flux in this case and the heating code is therefore $(1, 1, 1, 1)$. It is seen that the temperature is increased from the heater sides and stabilized in a symmetric distribution with the lowest temperature point at the center of the region.

The motions of a droplet actuated by the symmetric heating process is shown in Figure 5.5. The droplet moves from its initially location towards the center and stays there, as illustrated in Figure 5.5(a). The displacement and velocity of the droplet, together with the temperature gradient at the droplet position, are shown in Figures 5.5(b)(c)(d). It is seen that the droplet is accelerated by a large temperature gradient following switching on of the heaters, reaching to a maximum velocity before slowing down, and finally stops at the channel center point $(0.5, 0.5)$, where the temperature gradient is zero. Because $\frac{\partial \theta}{\partial x} = \frac{q_0''}{k} \frac{\partial \theta^*}{\partial x^*}$ and the span of the droplet is 1 mm, the maximum temperature difference across the droplet is $\Delta \theta < 2R \frac{q_0''}{k} \left| \frac{\partial \theta^*}{\partial x^*} \right|_{\max} \approx 21.4^\circ \text{C}$. The final stable temperature distributions associated with four different heating codes are plotted in Figure 5.6, three of them are not symmetric. Figure 5.7 shows the tracks of the droplet movement corresponding to the heating codes and temperature distributions shown in Figure 5.6. By starting the droplet movement from different positions, it is seen that the end positions of the droplet are independent of the initial positions. Comparing to the dimensionless temperature fields in Figure 5.6, it shows that the ending position of the droplet movement is always the lowest temperature point in each case, where the temperature gradient is zero so that the actuation force is zero. Once the droplet reaches the lowest temperature point, it is trapped there. Theoretically, the droplet can be driven to any positions from any initial position by using different heating codes combined from four heaters. Lowing down one of the heat fluxes, relative to others, leads to the end position being closer to it.

Figure 5.6: The final temperature distributions generated by different heating codes: (a) $(f_1, f_2, f_3, f_4) = (1, 1, 1, 1)$, (b) $(f_1, f_2, f_3, f_4) = (1, 0.3, 1, 1)$, (c) $(f_1, f_2, f_3, f_4) = (1, 0.3, 0.3, 1)$, (d) $(f_1, f_2, f_3, f_4) = (1, 0.3, 1, 0.3)$.

Figure 5.7: (a)-(d) The corresponding tracks of the droplet movements, with different initial positions, driven by the transient temperature fields described in Figures 5.5(a)-(d).

5.5.1.2 Simulation results of periodic actuation

In the periodic actuation, the heaters are assumed to be switched on for a long time and the periodic temperature distributions have been established inside the square glass plate. The temperature variations depend on the heating scheme within one period. Figure 5.8

Figure 5.8: (a) Periodic heating schemes of the four heaters in one period. (c)-(e) Temperature distributions in four quarters of period corresponding to the heating scheme in (a).

shows a typical case, in which one period is divided into four quarters and each heater works only in one quarter period, as shown in Figure 5.8(a). The corresponding temperature distributions in each quarter period are plotted in Figures 5.8(b)-(e). In this case, a droplet introduced into the channel will be driven to move in a loop as illustrated in Figure 5.9(a). The periodic motion of the droplet is better observed by plotting its displacement and temperature in Figures 5.9(b) and (c) respectively. It is interesting to note that the droplet experiences a quick change from low temperature to high temperature in each period, which is depicted in Figure 5.9(d). The predicted highest temperature that the droplet center experiences is $T_{\max} < 0.9 \frac{q_0'' a}{k} \approx 96.4^\circ\text{C}$. Three different periodic heating

Figure 5.9: (a) The track of droplet movement under the periodic heating schemes described in Figure 3 (a). (b) Dimensionless displacement against dimensionless time in both x and y directions. (c) Dimensionless relative temperature at droplet center against dimensionless time. (d) Details of the temperature increase in (c).

Figure 5.10: (a)-(c) Different periodic heating schemes and the corresponding droplet tracks.

schemes and the corresponding droplet moving patterns are illustrated in Figure 5.10. A variety of loop patterns for the droplet moving inside the platform can be generated by different periodic heating schemes.

5.5.2 Experimental characterization

Figure 5.11: The experimental results of transient temperature distributions at different time: (a) $t = 1\text{ s}$; (b) $t = 5\text{ s}$; (c) $t = 10\text{ s}$; (d) $t = 50\text{ s}$. The heating code is $(f_1, f_2, f_3, f_4) = (1, 1, 1, 1)$.

5.5.2.1 Experimental characterization of transient actuation

The experimental characterization of the droplet movement actuated in the planar channel are conducted to verify the simulation results and demonstrate that the concept is achievable. Figure 5.11 shows the transient temperature distributions captured by the thermal tracer at different time when four heater are switched on with the same power, which is the case corresponding to the heating code $(1, -1, 1, -1)$. By comparing to the predicted temperature distributions presented in Figure 5.4, it is seen that the experimental results agree well with the modeling, except for the low temperatures at four corners. This is because

the nonuniform heat flux along the individual micro heater, especially at the corners where two heaters are not really joined as the boundary conditions assumed in the simulation.

Figure 5.12: (a) Images of the silicon oil droplet at different time instances (Droplet radius $R = 0.5$ mm). (b) The displacements of the droplet center versus time. (c) Variations of velocity of the droplet center versus time. The heating code is $(f_1, f_2, f_3, f_4) = (1, 1, 1, 1)$

With the symmetric heating $(1, 1, 1, 1)$, Figure 5.12(a) shows selected images of a silicon oil droplet moving from a corner of the planar channel towards the center at different time instances. The process and track have been predicted by the simulation. Figures 5.12(b) and (c) show the displacements and velocity of the droplet center point versus time, based on the recorded images. The velocity was evaluated by using the results of two subsequent

Figure 5.13: Images of the silicon oil droplet at different time instances. (a) The heating code is $(f_1, f_2, f_3, f_4) = (1, 0.3, 1, 0.3)$; (b) The heating code is $(f_1, f_2, f_3, f_4) = (1, 0.3, 0.3, 1)$.

frames to get the displacement difference Δx and Δy , so that $u = \Delta x / \Delta t$, $v = \Delta y / \Delta t$, and $\Delta t = 0.5$ sec determined by the frame rate. The results show clearly that the droplet is accelerated initially, reaching to a maximum velocity, then is decelerated, and is finally trapped at the center of the square region, where the temperature is the lowest. The results agree with the predicted process shown in Figures 5.5(b) and (c).

In order to further verify the modeling results, the silicon droplet was actuated with another two heating codes, $(f_1, f_2, f_3, f_4) = (1, 0.3, 1, 0.3)$ and $(f_1, f_2, f_3, f_4) = (1, 0.3, 0.3, 1)$. The results are shown in Figure 5.13, which are selected images of the droplet motion at different time instances. It is seen that, in these cases, the droplet has been driven from the lower-left corner to the upper-right and down-right corners respectively, which also agrees with the simulation described in Figure 5.7 (c)(d).

5.5.2.2 Experimental characterization of periodic actuation

The experimental characterizations of the droplet under periodic thermocapillary actuation were conducted to verify the simulation results, and also to demonstrate the possibility of achieving periodic droplet manipulation. Figure 5.14 shows the measured periodic temperature distributions in four quarters of a single period, captured by the thermal tracer camera. Except for the low temperatures at the four corners, experimental results (Figure 5.14) agree relatively well with the theoretical results (Figure 5.8). The discrepancy is caused by the lack of heat generation at the corners. Under this heating scheme, Figure 5.15 shows the captured images of the silicon oil droplet at different time instances, the corresponding trajectory and the displacements versus time. In comparison to the results depicted in Figures 5.9(a) and 5.9(b), we can see a qualitative agreement between the simulation and experimental results in terms of trajectories and time-dependent position of the droplet. Three other heating schemes, as shown and theoretically predicted in Figure 5.10, were tested in the experiment with the same period $T_h = 80$ s. The results are presented in Figure 5.16, illustrated by selected images in one period and trajectories obtained from the recorded images. It is seen that the trajectories recorded from the experiment are similar

Figure 5.14: (a)-(d) Experimental temperature distributions in four quarters of one period corresponding to the heating scheme described in Figure 5.4 (a)

Figure 5.15: (a) Real images of droplet motion. (b) Droplet track under the periodic heating schemes described in Figure 5.8 (a). (c) Droplet displacement against time on both x and y directions.

Figure 5.16: (a)-(c) The experimental motion tracks of droplet corresponding to the periodic heating schemes described Figure 5.10 (a)-(c).

Figure 5.17: The experimental motion tracks of droplet under heating schemes described Figure 5.8 (a) with different periods.

to those closed loop trajectories theoretically predicted in Figure 5.10. The effect of the heating period on droplet motions was studied in the experiment by actuating a droplet with the same heating scheme but in different periods. The results are shown in figure 5.17. The main differences are in the loop sizes and the corner shapes. The longer period leads to a larger loop with sharp corners, while a shorter period results in a smaller loop with rounded perimeters, indicating that the actuation period or the frequency is a parameter to control the trajectory shapes.

5.6 Conclusions

The thermocapillary actuation of a silicon oil droplet in a planar micro-channel has been investigated by both simulations and experimental verifications. Under transient heating codes, the droplet can be driven to any position in the square region. The results also show that, the droplet can be driven to move in a closed loop whose pattern was controlled by periodic heating schemes and actuation frequencies. Good agreements have been obtained between the predictions and the experimental characterization, in terms of temperature

distributions, droplet moving tracks, displacements and velocities. The results show that the droplet can be manipulated with a great flexibility in terms of positions and moving tracks. The droplet can be delivered to any point in the channel, while the tracks can also be controlled with desired pattern. The application of this kind of manipulation has the potential to be used in bio-analysis processes, as the maximum temperature that the droplet experiences can be kept to be less than one hundred degree and the maximum temperature difference across the droplet is also very small. With the internal mixing effect caused by shear force in the process of droplet actuation, this temperature difference can be reduced further.

Chapter 6

Conclusions and Outlook

6.1 Conclusions

The actuation and manipulation of a liquid droplet by thermocapillary forces in microchannels have been investigated in both simulations and experiments. Following conclusions can be drawn from the studies.

1. The periodic temperature distributions along the capillary tube can be used to achieve the continuous reciprocating movements of the liquid plug formed inside a microcapillary, which is based on the mechanism that surface tension of the liquid plug depends on the temperature. The liquid plug motion can be simulated by calculating temperature distributions along the capillary between the actuation heaters, and then coupling the temperature field to the dynamic equations of the liquid plug through the temperature-sensitive surface tensions at the liquid-air interfaces. The displacement and velocity of the liquid plug can be obtained by solving the dynamic equations for the plug. The model and simulations are verified by the experiments, in which silicone oil (as the working liquid) was injected into a glass capillary to form the liquid plug of certain length. Two wire heaters at the two ends of the tube section were switched alternately to create periodic heat fluxes to drive the plug moving reciprocating in between the two heaters. The good agreement between the simulations and experimental results proves that the model developed for the thermocapillary actuation of the liquid plug works well. For the periodic actuation of oil plug in capillary, both the theoretical predictions and experimental measurements

show that the maximum traveling distance of periodic motion decreases when the switching frequency is increased, or the liquid viscosity increases. The plug length does not have significant effect on the maximum traveling distance.

2. The maximum traveling of the liquid plug can be increased by using multiple heaters, or heater array. This is achieved by activating the individual heater subsequently at the right timing according to the plug positions related to the heaters. The actuation of the liquid plug by the heater array can also be used to achieve different droplet thermal cycling for polymerase chain reaction (PCR) of DNA.
3. For DNAs and most of the other bio-chemical samples, it would require an aqueous environment for the carrier liquid in the lab-on-a-chip applications. The thermocapillary actuation may also be used in this type of operations by encapsulating aqueous micro droplets into an oil plug. In the experiment, a water droplet was encapsulated in an immiscible fluid-silicone oil plug in capillary. The surrounding oil protects the aqueous droplet from evaporation, and in the meanwhile, effective thermocapillary manipulations can be achieved because of the higher temperature sensitivity of silicone oil's surface tension. The results show that a complete encapsulation of the water droplet inside the oil plug is necessary for an effective actuation. This is realized in the present study by adding surfactant into the oil plug to reduce the water-oil interfacial tension, so that the water droplet can be encapsulated completely into the oil plug.
4. In the reciprocating actuation of the liquid plug, the motion of the liquid plug cannot follow the desired oscillations when the switching frequencies of the two heaters are increased to certain high values. Instead, the motion of the plug will be developed into chaotic patterns. By constructing the phase-space portraits, evaluating the largest Lyapunov exponent and calculating the fractal dimension, the chaotic characteristics of liquid plug under high-frequency thermocapillary actuation are identified and proved. The chaotic motion of the liquid plug under the thermocapillary actuation may be used to improve mixing in capillary-based microfluidics.

5. The periodic thermocapillary actuation of a liquid plug can be extended in a two dimensional planar channel to achieve more complex manipulations on a liquid droplet. Under transient actuation, the droplet can be driven continuously to any position in the channel according to a heating code determined by the heater strengths. And also, the droplet can be driven to move in a closed loop whose pattern is controlled by the periodic heating schemes and periodic actuation frequencies. Good agreement has been obtained between the modeling results and the experimental characterization, in terms of temperature distributions, droplet moving tracks, displacements and velocities.

6.2 Outlook

As mentioned in Chapter 2, the researches on the actuation of discrete droplet in micro-scale is developing fast in the past decade. It is recognized that the pumping effect without mechanical components in micro-scale has a growing importance in the microfluidics researches. The development of various techniques is still in the early stage, a lot of problems need to be solved before the technique have a big impact on microfluidics field. For the research on thermocapillary actuation in the future, the studies will focus on the following issues,

1. The influence of the capillary geometries ,such as the inner radius, on the plug motion will be studied, while the dimension of the capillary tube can be reduced further to nano-scale, for example. The current actuation analytical modeling may need to be modified under the new scale.
2. The model of the friction force could also be revised. A lubrication model may give a better explanation for the lower friction force observed in the experiments.
3. The research of the internal flow field and mixing pattern inside the liquid plug can be studied. The current experimental results indicate the potential of the use of chaotic plug motion to improve mixing or merging in capillary-based microfluidics. Relevant numerical calculation can be induced into the simulation of mixing process.

4. In order to avoid the damages caused by the high temperature induced by micro-heaters, different fluids can be used for higher temperature dependent surface tension coefficient. Heat sink source can also be integrated into the actuation system to enhance the temperature gradients with lower temperature at the heaters.
5. Different manipulations, such as transportation, mixing, merging and so on, can be achieved in planar channel by using more complex system design.

As an ultimate target, a complete DNA processing system using glass capillaries, or planar channels, can be designed and fabricated entirely based on thermocapillary actuation and control. The heating and actuation concepts documented in the thesis can be used in this system to realize polymerase chain reactions (PCR) of DNA as reported before by Friedman and Meldrum (1998).

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Appendix A

Heat transfer analysis

A.1 Natural convection

The cooling of the capillary is mainly decided by the natural convection by air. For a capillary of 1.4 mm outer diameter and the average temperature around 70°C, the corresponding product of the Grashof and Prandtl numbers is needed to calculate the Nusselt number and then the convection heat transfer coefficient.

With $T_f = 323$ K, $\beta = 1/T_f = 3.1 \times 10^{-3}$ K⁻¹, $\alpha = 26.2 \times 10^{-6}$ m²/s, $\nu = 18.4 \times 10^{-6}$ m²/s, $Pr = 0.7035$, $k_a = 26.3 \times 10^{-3}$ W/m·K, $D_o = 1.4$ mm

$$Ra = GrPr = \frac{8g\beta\theta D_o^3}{\nu\alpha} = 65.12 \quad (\text{A.1})$$

$$Nu = \left\{ 0.6 + \frac{0.387Ra^{1/6}}{[1 + (0.559/Pr)^{9/16}]^{8/27}} \right\} = 1.55 \quad (\text{A.2})$$

so that the average convection coefficient $h_0 = 1.55k_a/(2R_o) \approx 28$ W/m²·K

A.2 Radiation loss

It is known that radiation emissivity of smooth glass is $\varepsilon = 0.9$ and Stefan-Boltzmann constant $\sigma = 5.670 \times 10^{-8}$ W/m²·K⁴. From the experiment, it is shown that the average glass surface temperature difference relative to the environment is about 50°C, the total

heat loss flux by radiation emissive power is,

$$E = \varepsilon E_b = \varepsilon \sigma [(\theta + T_0)^4 - T_0^4] = 0.94(5.670 \times 10^{-8})(343^4 - 293^4) \approx 187.3 \text{ W/m}^2. \quad (\text{A.3})$$

$T_0 = 293$ K is the environment temperature, the power of each heater is kept at 2 W and the distance between two heaters is D_h . The total energy lost by radiation is,

$$Q = EA = 2\pi E D_h R_o = 2\pi \times 187.3 \times 0.01 \times 0.7 \times 10^{-3} \approx 0.0082 \text{ W} \ll 2 \text{ W}, \quad (\text{A.4})$$

while the radiation loss can be neglected comparing to heater power input. The original governing equation including both convection and radiation loss is,

$$\frac{\partial \theta}{\partial t} = \alpha \frac{\partial^2 \theta}{\partial x^2} - \frac{2hR_o}{\rho c(R_o^2 - R_i^2)}\theta - \varepsilon \sigma \frac{2R_o}{\rho c(R_o^2 - R_i^2)}[(\theta + T_0)^4 - T_0^4]. \quad (\text{A.5})$$

The ratio of the heat lost between the radiation and the convection at $\theta \approx 50$ K, γ , is then,

$$\gamma = \frac{\varepsilon \sigma [(\theta + T_0)^4 - T_0^4]}{h\theta} \approx 0.2, \quad (\text{A.6})$$

while the total energy loss by radiation can be neglected comparing to natural convection in our quantitative simulation.

A.3 Effective heat loss coefficient h

Because some of the parameters like the emissivity of the capillary material and the average temperature can not be decided precisely in the experimental measurement, finally, the author proposes an effective heat loss coefficient $h \approx 33.6 \text{ W/m}^2 \cdot \text{K}$, which was calculated based on the estimation of average temperature and the glass capillary emissivity to simulate the problem qualitatively based on equation (3.1).

Appendix B

Experimental measurements errors

B.1 Temperature measurement errors

In the experiments, a thermal tracer camera was used to measure the temperature distributions. The NEC TH9100PMVI camera had a 2% measurement accuracy. The camera can only measure the outer surface temperature of the capillary while the capillary inner surface temperature distribution actually drives the liquid plug. In equation (3.1), it is assumed that the temperature is distributed uniformly throughout the capillary cross-section due to the thin glass wall. The actually inner wall surface temperature is proportional to the outer wall surface temperature, so that it can be used to estimate the inner wall temperature with qualitative errors.

B.2 Movement tracking errors

The CCD camera was used to track the displacement of the traveling plug. All the pictures captured were processed by MATLAB to track the shining meniscus. The positions of the central point of the meniscus were recorded as the plug positions. The maximum width of the shining meniscus was about 0.2 mm and the plug traveling distance was about 4 mm, which made the traveling displacement measurement accuracy to be $\frac{0.1}{4} = 2.5\%$.

The frame rate of the camera in the experiments was set according to the actual heating period. Also, because of the limitation of frames number, only 144 frames can be used in the recording, normally for 3 periods. The accuracy of the CCD camera frame rate is

0.01 s, which leads to a velocity measurement accuracy in a range of 0.025% – 1%.

B.3 Heating source errors

In actual experiments, heat fluxes generated by the heaters can not be measured precisely, because of the unknown heat loss by conduction and convection situation. Besides, the two heaters used in experiments were not identical. the asymmetric heating also caused little error. The value of heat fluxes used in the simulation program was chosen based on the actual power input of the heater timing a fraction coefficient. In conclusion, the comparisons between modeling and experimental results are qualitative.

Appendix C

MATLAB programs

C.1 Image processing program

```
timeinterval=0.5;%time between two frames;
aviname='E:video';
thresh=0.95;
movl = aviread(aviname); mov = aviread(aviname,1);
imshow(mov.cdata); [x1 y1]=getpts; [x2 y2]=getpts;
framelist=length(movl); ratio=10/abs(x1-x2);
u=[];time=[];ax=[];x=[]; start=1;
for index=start:framelist mov = aviread(aviname,index);
time(index)=(index-start)*timeinterval;
bw=threshold(mov.cdata,index,thresh,x1,x2,y1,y2);
imshow(bw);
L=bwlabel(bw); % 'particle' assignment
stats=regionprops(L,'centroid'); % retrieve some of the 'particle' properties
Lstats=length(stats);
if index==start
u(index)=0;
ax(index,1)=stats(1).Centroid(1);
x(index)=ratio*ax(index,1);
else
```

C.2. Analytical results plotting program

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```

if Lstats==0
ax(index,1)=2*ax(index-1,1)-ax(index-2,1);
else
for i=1:Lstats
ax(index,i)=stats(i).Centroid(1);
end
ax(index,1)=max(ax(index,:));
end
x(index)=ratio*ax(index,1);
u(index)=(x(index)-x(index-1))/timeinterval;
end
end
meanx=mean(x(5:framelist));
figure
plot(time(2:framelist),x(2:framelist)-meanx);
xlabel('time t (s)');
ylabel('Position x (mm/s)');
figure
plot(time(2:framelist),u(2:framelist));
xlabel('time t (s)');
ylabel('Velocity u (mm/s)'); save name u x time

```

C.2 Analytical results plotting program

```

N=400;
x0=0.005;
y0=0.005;
a=0.01; b=0.01; H=0.0005; Th=80; r=0.0005; q=1.5e2;
kGlass=1.4;%conductivity of glass

```


C.2. Analytical results plotting program

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```

kAir=0.0263; %conductivity of air
rhoGlass=2500;%density of glass
rho=930;%density of liquid
cGlass=750;
%heat capacity of glass
V=H * pi * r^2; m=rho * V; phi=10; Deltat = 2 * Th/N;
alphaGlass=kGlass/rhoGlass/cGlass;
t=[];x=[];y=[];ux=[];uy=[];T0=[];U=[];
for k=1:N
t(k)=(k-1)*Deltat;
if k==1
x(k)=x0; y(k)=y0;
ux(1)=0; uy(1)=0;
else
[muBxBYdeltaT(k)] = rectforce(x(k-1),y(k-1),r,t(k),a,H,Th,q);
Bx=2*Bx/m;
By=2*By/m;
A = 12 * mu * pi * r^2/m/H;
ux(k)=Bx/A-Bx/A*exp(-A*t(k));
uy(k)=By/A-By/A*exp(-A*t(k));
x(k)=x(k-1)+ux(k)*Deltat;
y(k)=y(k-1)+uy(k)*Deltat;
U(k) = (ux(k)^2 + uy(k)^2)^0.5;
end
end
figure subplot(2,2,1)
h=plot(1/a*x(1:400),1/a*y(1:400),'LineWidth',1);axis square;hold on
xlabel('x*');ylabel('y*'); axis([0 1 0 1]);
plot(1/a*x(1),1/a*y(1),'o','LineWidth',1);plot(1/a*x(N),1/a*y(N),'o','LineWidth',1);

```

Appendix D

Modeling of one dimensional transient heat transfer in capillary

D.1 Governing equation and boundary conditions

The governing equation for the temperature is,

$$\frac{\partial \theta}{\partial t} = \alpha \frac{\partial^2 \theta}{\partial x^2} - \frac{2hR_o}{\rho c(R_o^2 - R_i^2)} \theta \quad (\text{D.1})$$

where θ is the temperature difference relative to the ambient temperature, R_o and R_i are the outer diameter of the capillary, α , ρ , and c are the thermal diffusivity, density and specific heat capacity of the capillary material, respectively. Heat radiation is neglected in this model because of the relatively low temperature of the outer capillary surface. The transient boundary conditions for the individual heater are,

$$\begin{aligned} t = 0 : \theta(x) &= \theta_0(x) \\ t > 0 : \begin{cases} \frac{\partial \theta}{\partial x}|_{x=0} = -q''/k \\ \theta|_{x=L_c} = 0 \end{cases} \end{aligned} \quad (\text{D.2})$$

where L_c is the length of the capillary, k is the thermal conductivity of the capillary material and q'' is the heat flux inside the capillary and $\theta_0(x)$ is the initial temperature. For simplicity, we assume the same heat flux for all three heaters in both the analytical analysis

and the later experimental investigation.

D.2 Analytical solution

Introducing the dimensionless variables,

$$t^* = t/(L_c^2/\alpha), \quad x^* = x/L_c, \quad \theta^* = \theta k/(q'' L_c).$$

and substitute them into equation (D.2), which means,

$$t = t^*(L_c^2/\alpha), \quad x = x^* L_c, \quad \theta = \theta^*(q'' L_c/k).$$

Substitute them into equation (D.1),

$$\frac{\partial[\theta^*(q'' L_c/k)]}{\partial[t^*(L_c^2/\alpha)]} = \alpha \frac{\partial^2[\theta^*(q'' L_c/k)]}{d(x^* L_c)^2} - \frac{2hR_o}{\rho c(R_o^2 - R_i^2)}[\theta^*(q'' L_c/k)],$$

leads to the dimensionless heat transfer equation,

$$\frac{\partial \theta^*}{\partial t^*} = \frac{\partial^2 \theta^*}{\partial x^{*2}} - \beta^2 \theta^*, \quad (D.3)$$

with

$$\beta = \sqrt{hL_c^2 R_o/k(R_o^2 - R_{in}^2)}.$$

The corresponding dimensionless initial conditions and boundary conditions are,

$$\begin{aligned}
t^* = 0 : \theta^*(x^*) &= \theta_0^*(x^*) \\
t^* > 0 : \begin{cases} \frac{\partial \theta^*}{\partial x^*} \big|_{x^*=0} = -1 \\ \theta^* \big|_{x^*=1} = 0 \end{cases}
\end{aligned} \quad (D.4)$$

Because of the transient process, when the time goes to infinite the temperature becomes stable, the dimensionless relative temperature can be divided into two parts, transient and stable parts, let

$$\theta^* = u(x^*) + v(x^*, t^*), \quad (D.5)$$

if $t^* \rightarrow \infty$ then $v = 0$, and substitute u into the equation (D.3)

$$\frac{\partial^2 u}{\partial x^{*2}} - \beta^2 u = 0. \quad (D.6)$$

Solving equation (D.6):,

$$u = A \sinh(\beta x^*) + B \cosh(\beta x^*),$$

and

$$\frac{\partial u}{\partial x^*} = A\beta \cosh(\beta x^*) - B\beta \sinh(\beta x^*),$$

while A, B are two unknown constants, with the dimensionless boundary conditions when $t^* \rightarrow \infty$,

$$\begin{cases} \frac{\partial T^*}{\partial x^*} \big|_{x^*=0} = -1 \\ T^* \big|_{x^*=1} = 0 \end{cases},$$

which can be transferred to,

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$$\begin{cases} \frac{\partial u}{\partial x^*}|_{x^*=0} = -1 \\ u|_{x^*=1} = 0 \end{cases}, \quad (\text{D.7})$$

or

$$\begin{cases} A \sinh(\beta) + B \cosh(\beta) = 0 \\ A\beta \cosh(0) - B\beta \sinh(0) = -1 \end{cases}. \quad (\text{D.8})$$

Equation group (D.8) can be solved,

$$\begin{cases} A = -\frac{1}{\beta} \\ B = \frac{1 \sinh(\beta)}{\beta \cosh(\beta)} \end{cases},$$

and then

$$u = \frac{1}{\beta} \left[\frac{\sinh(\beta)}{\cosh(\beta)} \cosh(\beta x^*) - \sinh(\beta x^*) \right].$$

For v it also satisfies the partial differential equation,

$$\frac{\partial v}{\partial t^*} = \frac{\partial^2 v}{\partial x^{*2}} - \beta^2 v \quad (\text{D.9})$$

Using cosine fourier series method, v can be expanded to

$$v = \sum_{n=1}^{\infty} G(t^*) \cos \left[\left(n - \frac{1}{2} \right) \pi x^* \right].$$

Here $\cos[(n - \frac{1}{2})\pi]$ is used because when $x^* = 1$, $\theta^* = 0$.

Substitute v into equation (D.9)

$$\begin{aligned} \sum_{n=1}^{\infty} \frac{\partial [G(t^*)]}{\partial t^*} \cos \left[\left(n - \frac{1}{2} \right) \pi x^* \right] &= - \left(n - \frac{1}{2} \right)^2 \pi^2 \sum_{n=1}^{\infty} G(t^*) \cos \left[\left(n - \frac{1}{2} \right) \pi x^* \right] \\ &\quad - \beta^2 \sum_{n=1}^{\infty} G(t^*) \cos \left[\left(n - \frac{1}{2} \right) \pi x^* \right] \end{aligned}$$

which is

$$\frac{\partial[G(t^*)]}{\partial t^*} = \left[-\left(n - \frac{1}{2}\right)^2 \pi^2 - \beta^2 \right] G(t^*), \quad (\text{D.10})$$

and $G(t^*)$ is solved with a constant D_n

$$G(t^*) = D_n \exp \left\{ - \left[\left(n - \frac{1}{2}\right)^2 \pi^2 + \beta^2 \right] t^* \right\},$$

so that v is solved,

$$v = \sum_{n=1}^{\infty} D_n \exp \left\{ - \left[\left(n - \frac{1}{2}\right)^2 \pi^2 + \beta^2 \right] t^* \right\} \cos \left[\left(n - \frac{1}{2}\right) \pi x^* \right]. \quad (\text{D.11})$$

The resulting dimensionless temperature is the real part of the following expression,

$$\begin{aligned} \theta^* = & \frac{1}{\beta} \left[\frac{\sinh(\beta)}{\cosh(\beta)} \cosh(\beta x^*) - \sinh(\beta x^*) \right] + \\ & \sum_{n=1}^{\infty} D_n \exp \left\{ - \left[\left(n - \frac{1}{2}\right)^2 \pi^2 + \beta^2 \right] t^* \right\} \cos \left[\left(n - \frac{1}{2}\right) \pi x^* \right]. \end{aligned} \quad (\text{D.12})$$

And the corresponding dimensionless temperature gradient is,

$$\begin{aligned} \frac{\partial \theta^*}{\partial x^*} = & \left[\frac{\sinh(\beta)}{\cosh(\beta)} \sinh(\beta x^*) - \cosh(\beta x^*) \right] - \\ & \sum_{n=1}^{\infty} \left(n - \frac{1}{2}\right) D_n \exp \left\{ - \left[\left(n - \frac{1}{2}\right)^2 \pi^2 + \beta^2 \right] t^* \right\} \sin \left[\left(n - \frac{1}{2}\right) \pi x^* \right]. \end{aligned} \quad (\text{D.13})$$

As the initial condition is $t^* = 0 \rightarrow \theta^* = \theta_0^* = 0$

$$\frac{1}{\beta} \left[\frac{\sinh(\beta)}{\cosh(\beta)} \cosh(\beta x^*) - \sinh(\beta x^*) \right] + \sum_{n=1}^{\infty} D_n \cos \left[\left(n - \frac{1}{2}\right) \pi x^* \right] = 0,$$

so that by using cosine fourier transform we can solve D_n ,

$$D_n = 2 \int_0^1 \left\{ \theta_0 - \frac{1}{\beta} \left[\frac{\sinh(\beta)}{\cosh(\beta)} \cosh(\beta x^*) - \sinh(\beta x^*) \right] \right\} \cos \left[\left(n - \frac{1}{2} \right) \pi x^* \right] dx^*, \quad (\text{D.14})$$

where θ_0 is the initial dimensionless relative temperature at the position of x^* . If there are more than one heater in the system, we can use the final state of the last heater temperature distribution as the initial condition of the current heater.

Appendix E

Publication list

E.1 Journal papers

1. S.S.Wang, Z. Jiao, X. Huang, N. T. Nguyen, Acoustically induced bubbles in a microfluidic channel for mixing enhancement, *Microfluidics and Nanofluidics*, accepted, 2008.
2. Z. Jiao, X. Huang, N. T. Nguyen, Scattering and attenuation of surface acoustic waves in droplet actuation, *Journal of Physics A: Mathematical and Theoretical*, Vol. 41, pp. 355502, 2008.
3. Z. Jiao, X. Huang, N. T. Nguyen, Manipulation of droplet in a planar channel by periodic thermocapillary actuation, *Journal of Micromechanics and Microengineering*, vol. 18, No. 4, pp. 045027, 2008.
4. Z. Jiao, X. Huang, N. T. Nguyen, P. Abgrall, Thermocapillary Actuation of Droplet in a Planar Microchannel, *Microfluidics and Nanofluidics*, accepted, 2007.
5. Z. Jiao, N. T. Nguyen, X. Huang, Thermocapillary Actuation of a Water Droplet Encapsulated in an Oil Plug, *Journal of Micromechanics and Microengineering*, Vol. 17, No. 9, pp. 1843-1852, 2007.
6. Z. Jiao, N. T. Nguyen, X. Huang, Thermocapillary Actuation of Liquid Plugs Using a Heater Array. *Sensors and Actuators A*, Vol. 140, No. 2, pp. 145-155, 2007.

7. X. Huang, N. T. Nguyen, Z. Jiao, Nonlinear standing waves in a resonator with feedback control, The Journal of the Acoustical Society of America, Vol. 122, No. 1, pp. 38-41, 2007.
8. Z. Jiao, N. T. Nguyen, X. Huang, Chaotic motion of micro plugs under high-frequency thermocapillary actuation, Journal of Micromechanics and Microengineering, Vol. 17, pp. 180-185, 2007.
9. Z. Jiao, N. T. Nguyen, X. Huang, Y. Z. Ang, Reciprocating Thermocapillary Plug Motion in an Externally Heated Capillary, Microfluidics and Nanofluidics, Vol 3, No.1, pp. 39-46, 2006.

E.2 Conference papers

1. Z. Jiao, N. T. Nguyen, X. Huang, Thermocapillary Actuation and Cycling of Liquid Plugs, The first ASME Micro/Nanoscale Heat Transfer International Conference (MNHT2008-52145), Tainan, Taiwan, 2008. [Top five article]
2. Z. Jiao, N. T. Nguyen, X. Huang, Thermocapillary Programmable Manipulation of a Droplet in a Planar Microchannel, The Sixth International Conference on Nanochannels, Microchannels, and Minichannels (ICNMM2008-52145), Darmstadt, Germany, June 23-25, 2008
3. Nguyen, N. T., Jiao, Z.J, Huang, X.Y., Thermocapillary Effect of a Water/Oil System, ASME Micro/Nanoscale Heat Transfer International Conference, Tainan, Taiwan, MNHT2008-52061, 2008.
4. Nguyen N.T., Jiao Z, Huang X, 2006, Thermocapillary Actuation of Microplugs, International Conference on Bio-Nanotechnology ICBN, Al Ain, UAE, pp 205-209, 2006. .