MICROTHERMAL DEVICES FOR FLUIDIC ACTUATION BY MODULATION OF SURFACE TENSION

by

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DEDICATION

To my loyal friends and extended family who have made life rich & fulfilling, and have been there for me through the years. To Dada, my source of wisdom and strength. To Ma, my emotional rock and supporter. And to Baba, my educator, who sacrificed his own doctoral studies so he could better teach to his two sons.
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ABSTRACT

Fluid manipulation at the micrometer scale has traditionally involved the use of batch-fabricated chips containing miniature channels, electrodes, pumps, and other integrated structures. This dissertation explores how liquids on non-patterned substrates can be manipulated using the Marangoni effect. By placing miniature heat sources above a liquid film, it is possible to generate micro-scale surface temperature gradients which results in controlled Marangoni flow. A variety of useful flow patterns can be designed by tailoring the geometry of the heat source.

As a surface tension-based phenomenon, the Marangoni effect is an efficient actuation mechanism at submillimeter dimensions. With optimized liquid carriers, flow velocities >10 mm/s can be generated with only small perturbations in surface temperature (<10 K). Thermally efficient microfabricated heat sources, such as polyimide thermal probes, can produce >1700 µm/s flow velocity in mineral oil while consuming <20 mW of power. In water films, the probes can generate surface doublets with linear velocities up to 5 mm/sec and rotational velocities up to 1300 rpm, making them potentially useful for active mixing.

The utility of Marangoni flows is demonstrated within the context of digital microfluidic systems. In contrast to conventional microfluidics, where samples are flowed through microchannels, digital microfluidic systems contain liquid samples in micro and nanoliter-sized droplets suspended in an immiscible oil layer. Marangoni
flows generated in the oil layer can manipulate droplets without any physical structures, thus avoiding surface contamination. By using point, linear, annular, and tapered heat source geometries, it is possible to engineer Marangoni flows which mimic the functionality of droplet channels, mixers, size-selective filters, and pumps. Arbitrary, two-dimensional actuation of droplets (Φ=400-1000 µm) can also be achieved using an array of heaters suspended above the oil layer. The 128-pixel heater array incorporates addressing logic and a software interface which allows it to programmatically transport and merge multiple droplets through the sequential activation of heaters.

The appendices outline other aspects of thermal probes, including i) the structure, fabrication, and operational characteristics of single probes and probe arrays, and ii) scanning thermal lithography, a technique for nanoscale patterning of thin films with heat.
CHAPTER 1:
INTRODUCTION

1. MICROFLUIDICS FOR MINIATURIZED CHEMICAL ASSAYS

Richard Feynmann, in his famous 1959 speech [Fey59], proclaimed that “there is plenty of room at the bottom”, encouraging leading scientists to explore a new field of science and engineering at micrometer and nanometer length scales. Among the several intriguing possibilities he described, Feynman noted “The Marvelous Biological System”, referring to microorganisms which move, interact, and store information at small length scales. He challenged scientists to build precision instruments that would be able to study and interact with these systems at the same length scales. Forty five years later, Feynman’s vision has now grown into one of the most promising areas of engineering and biomedical research.

One of the primary drivers behind the renewed interest is microfabrication technology, which allows us to manufacture micrometer scale, planar structures using the combined technologies of thin film deposition, photolithography, as well as chemical and plasma etching [Mad02]. These techniques, borrowed from the semiconductor industry, can be used to produce small microchips containing 1) various fluid channels, pumps, or valves for handling liquid samples of cells and molecules, and ii) sensors, heaters, and other instruments for performing sample analysis. The devices, collectively termed
micro total analysis systems (µTAS) or “lab-on-a-chip” (LOC), have revolutionized the way biological assays are performed, enabling massively parallel operation, analysis of miniscule sample volumes, integrated sample preparation, low power consumption, and portability. The first microfabricated DNA analysis system, incidentally, was developed here at the University of Michigan [Bur96].

Microfluidic systems will continue to play an increasingly significant role in the in vitro diagnostics (IVD) market, whose market size is expected to be ~$40 billion in 2008 [Ros04]. The market size for microchip technologies in general exceeded $1.7 billion in 2008, and is expected to grow at a 25% annual growth rate to $6 billion in 2017 [Kru07]. The major application categories in the microfluidics market include high throughput screening (HTS) and compound profiling, point of care (POC) diagnosis and testing, chemical analysis, drug delivery, genomics/proteomics, and homeland security [Ros04]. As of January 2008, numerous successful commercial µTAS devices have penetrated a number of areas within the IVD market. A few notable examples include the following:

- DNA microarrays have enabled massively parallel, high throughput profiling of gene expression (Affymetrix, Roche Diagnostics)

- Microfluidic cards for multiplexed Polymerase Chain Reaction (PCR) and electrophoretic separation of DNA. These cards can handle up to 380 simultaneous reactions and have reduced analysis time by 1 order of magnitude (Applied Biosystems)

- Miniature microfluidic systems for Reverse Transcriptase PCR and electrophoresis have enabled simple and portable genetic detection of
microorganisms (Handylab)

- Integrated, sample-to-answer genetic detection systems using microfluidic cards can perform sample preparation, PCR, electrophoretic separations, and molecular purification in portable, highly parallel format with low reagent consumption (Agilent Technologies, Caliper Life Sciences).

- Portable blood analyzers have enabled point of care (POC) testing of various biological markers (Honeywell, Siloam Biosciences)

- Microfabricated glucose monitors have provided a portable and less invasive option for diabetics to monitor their blood sugar (TheraSense)

2. USING THE MARANGONI EFFECT FOR MICROFLUIDIC ACTUATION

In his speech, Richard Feynman noted that the physics of nature changes at small lengths scales [Fey59]. In microfluidic systems, physical scaling laws enhance surface phenomena and diminish the importance of pressure, inertia, gravity, and other volumetric forces. As a result, many pumping techniques developed for conventional length scales become less effective. For example, microfluidic channels have a large hydraulic resistance due to their small cross sections, and require larger pressures from external pumps. At the same time, other physical phenomena, such as surface-based phenomena, tend to become more efficient at small length scales. One such example is the Marangoni effect, the topic of this thesis.

Marangoni flow, the movement of liquids due to surface tension gradients, is responsible for many common phenomena. These include, for example, the dispersion of oils in dishwater upon the addition of detergent [Her96], and the rotating flow of particles
below a candle wick \[\text{Adl70}\]. Nevertheless, at macroscopic length scales, the Marangoni effect is not a practical mechanism for fluidic actuation because surface forces are typically weak compared to pressure, inertial, and other body force mechanisms. However, like other surface phenomena, it scales favorably to the micrometer regime. If \( l \) is considered the length scale, surface tension forces are proportional to \( l \), pressure forces are proportional to \( l^2 \), and inertial forces are proportional to \( l^3 \). Thus, at small length scales, surface tension forces become increasingly significant compared to the other two. Furthermore, the high ratio of surface-area to volume present in microscale devices suggests that the Marangoni effect could be useful for microfluidic actuation.

The traditional, “macroscopic” approach for generating Marangoni flow is via isothermal heating (Fig 1.1a). A thin liquid layer is heated uniformly from below, and the resulting flow is a pattern of hexagonal convection cells (Fig. 1.1b) \[\text{Mar07, Kos93}\]. This multicellular flow, first observed by Henri Bénard in the late 1800’s \[\text{Bén00}\], was originally thought to be due to natural convection, and was later attributed to the Marangoni effect by Brock and Pearson in the 1950’s \[\text{Blo56, Pea58, Mar07}\]. Since then, it has been the subject of several efforts to mathematically analyze fluid stability \[\text{Kos93}\]. From a practical standpoint, however, the geometry and stability of the flow is very sensitive to the fluid container and the thermal boundary conditions. Therefore, \textit{isothermally-generated} Marangoni flows provide little opportunity for localized fluidic manipulation in the context of an automated system.
This dissertation focuses on a localized approach for generating Marangoni flow: by imposing micrometer scale temperature gradients on the surface [Bas07B]. This can be done by suspending small heat sources just above the liquid surface (Fig. 1.1c). The heat flux supplied to the surface causes localized variation in surface temperature. This, in turn, causes a corresponding surface tension gradient due to the inverse relation between surface tension and temperature that exists for most liquids. In the presence of a
surface tension gradient, a shear stress is generated at the liquid boundary which drives surface flow away from the heated regions (low surface tension) and towards the cool regions (higher surface tension). Cooling sources can generate Marangoni flow in the reverse direction. Thus, from a theoretical perspective, it would be possible to engineer arbitrary surface flows by superimposing multiple thermal sources as shown in Fig. 1.2.

This approach takes advantage of the favorable scaling of surface forces and could provide several important advantages in practicality and efficiency. The first potential benefit is flow localization: in contrast to isothermal heating, a point or linear heat flux favors the formation of a single Marangoni cell, which allows for precise control of the geometry and flow speeds of the cell.

The second benefit is efficiency. As will be shown in Chapter 2, Marangoni flow velocities are proportional to the surface temperature gradient. By using microscale heat
sources it is possible to achieve sharp temperature gradients which enable faster velocities while minimizing the absolute changes in surface temperature. An important aspect of this technique is that the heat sources used to generate flow are suspended above the oil. Benefiting from the low thermal conductivity of air, this approach creates sharp surface temperature gradients which would not be possible were the heat source embedded in the fluid. Embedded heaters would also cause significant heating in the bulk fluid which is undesirable for bio-analytical microsystems.

The third benefit is that it does not require a patterned fluidic substrate. Fig. 1.3A compares flow velocities and substrate complexity for various pumping methods. Substrate complexity is qualitative measure which considers the components, materials, and fabrication processes required to make the fluidic chip. The majority of popular techniques in microfluidic systems require patterned multilayer substrates containing electrodes, channels, and magnets, or mechanical components. Others require a special surface, such as a thermally insulative polystyrene [Kot04] or a photoresponsive layer [Chi03, Chi04] to function properly. Mechanical pumps, which generally require many components and multilayer fabrication steps, are not shown in the graph. From the perspective of substrate complexity, the Marangoni flow technique places no requirements on the fluidic substrate; all the complexity of generating flow is placed in the heat sources held above the fluid. Since this portion of the system is reusable, the present approach can potentially reduce the cost of repeated experiments.

Compared to other pumping techniques, Marangoni flow also offers low drive voltages (Fig. 1.3B). For example, electrical field-based techniques such as electro-osmotic (EO) and electro hydrodynamic (EHD) pumping, requires high voltages up to 1
Figure 1.3: Comparison of non-mechanical microfluidic pumping methods. (a) Flow velocities (in continuous flow systems) or droplet velocities (in discrete fluidic systems) as a function of substrate complexity for various pumping methods. (b) Flow/droplet velocities versus the required drive voltage for the same pumping methods. Abbreviations and references for each pumping method are as follows: Ma, Marangoni flow (this work) [Bas05A, Bas05B]; OT, Optical Tweezers [Kat01, Sas92]; ET, Electrostatic tip [Kats99]; Th-Ma, Thermal Marangoni effect on droplet interfaces using lasers [Kot04]; OEW, Optoelectrowetting [Chi03]; OET, Optoelectrostatic tweezers [Chi04]; AC-EW, AC Electrowetting [Cho02]; DC-EW, DC Electrowetting [Cho03]; EHD, Electrohydrodynamic pumping [Fuh92, Ahn98]; EO, Electroosmotic pumps, [Har91, Che02]; and MHD, Magnetohydrodynamic [Lem00].
kV, although newer methods like electrowetting-on-dielectric (EWOD) have reduced this requirement to 20 V. The presence of high electric fields, particularly DC fields, can lead to electrolysis which degrades electrodes and also causes bubble formation in channels.

As a thermal actuation technique, Marangoni flows are generated by electrically heating a source. By using an efficient microfabricated heat source with $<40 \ \Omega$ resistance, flow velocities up to $>5 \ mm/s$ can be achieved with voltages $<2 \ V$ and input powers $<25 \ mW$. This is due not only to the efficient design of the heat source, but also the efficient conversion of heat to mechanical energy at small length scales. Thus, this technique has potential for enabling low power, reconfigurable microfluidic systems.

A fifth benefit is the lack of physical contact between the heat source and the liquid sample, which eliminates contamination of the device and cross-contamination between samples. A previous approach to using Marangoni flow for fluidic actuation requires electrochemically generated surfactants [Gal99], which causes ionic contamination of the sample. Temperature gradients generated by substrate heaters [Dar03] or external lasers [Kot04] have also been used to initiate Marangoni flow and move a liquid droplet or film on a substrate. Both these approaches, however, require that the liquid sample be in contact with the substrate.

In this approach, aqueous samples are contained in droplets which are suspended in a high-density, immiscible oil layer. Due to the high density of the oil, the droplets float near the surface, away from the actuator and the substrate below, and they can manipulated using Marangoni flows generated by the heat sources from above. This approach to fluidic manipulation is less prone to contamination than those mentioned
above, as well as other popular techniques for droplet manipulation, such as electrowetting [Cho03, Yoo03].

The last benefit is the central theme of this dissertation: the ability to engineer Marangoni flows. Using microscale heat sources of various geometries, it is possible to shape the surface temperature gradient and the resulting Marangoni flow. These flows can be used to manipulate liquids, particles, and droplets without any physical structures in the liquid film. Microdroplets, in particular, have potential applications in microfluidic biochemical assays.

3. CONTINUOUS FLOW MICROFLUIDIC SYSTEMS

In general, microfluidic sample handling can be categorized into two broad categories. The early generations of microfluidic chips have been primarily “continuous flow” systems. In other words, reagents and samples are flowed through microchannels formed on the fluidic substrate. These channels can be formed in a number of ways, including bulk micromachining of silicon [Che97], chemical etching of glass [Har92, Sei93], parylene deposition with a sacrificial photoresist layer [Man97], and micromolding with a silicone elastomer [Xia98]. Due to the small cross section and length of the fluidic channels, small amounts of liquids are consumed, and flows are primarily laminar in nature [Tak01], resulting in predictable flow and mixing profiles.

Mechanical actuators, similar to conventional pumps, can be used to generate pressure and flow of liquids through microchannels. The most common implementation is a peristaltic membrane pump, driven by integrated thermopneumatic, electrostatic, and piezoelectric actuators, or by off-chip pressure driven sources [Gro99, Xie04, Ung00].
Since these devices often require moving parts with out of plane deflection, device reliability and fabrication complexity is often a concern for mechanical pumps.

Several non-mechanical methods, which take advantage of surface and capillary effects in small channels, are also effective in controlling fluids without moving parts. These include electro-osmotic [Har91, Che02], electrohydrodynamic [Fuh92, Ahn98], thermocapillary [Sam99A, Sam99B], and magnetohydrodynamic pumps [Lem00], along with many more. These pumps generally rely on the interaction of electromagnetic fields with mobile charges in the fluid, and often require large field strengths in order to function. However, they are more amenable to integration because their fabrication complexity tends to be simpler. For example, electro-osmotic pumps require only two electrodes aligned in the channel [Har91]. For a review of micropump technologies, the reader is referred to [Ngu02].

Although the continuous flow systems are appropriate for many assays, users seek several areas of improvement. First of all, due to the high hydraulic resistances of the microchannels, pumps must generate large pressure heads in order to achieve reasonable flow rates. The presence of moving parts is a concern for mechanical pumps, and in nonmechanical pumps, high field strengths can cause undesirable effects such as electrolysis.

Another issue is reconfigurability. Early in the years of digital electronics, application specific IC’s (ASICs) were designed to perform specific computing tasks. ASICs were eventually replaced by a more versatile microprocessor chip which could be reprogrammed to perform a wide range of general computations. Similarly, the first generation of fluid handling chips have been designed with fixed geometries for use in a
specific assay. While this is sufficient if the fluid handling protocol is fixed, it does present a problem if flexibility in the handling of reagents is required [Gas04, Cho03]. With a fixed geometry, each assay requires its own chip design and fabrication, resulting in non-recurring engineering (NRE) costs and effort.

Still another issue with continuous flow systems, arguably the most significant, is the problem of surface adsorption. Hydrophobic proteins and DNA have low surface hydration energies [Gas04], making it likely that any contact to a solid surface will result in nonspecific adsorption; thus, any degree of contact or wetting between a liquid sample and the channels walls can result in surface adsorption. Most channel materials, particularly hydrophobic materials such as Teflon, Parylene, and Polydimethylsiloxane (PDMS) are particularly susceptible to such adsorption [Yoo03, Sia03, Son03]. In microchannels, the adsorption of proteins and cellular debris leads not only to contamination, but can also cause channel blockages [McC03]. More importantly, contamination eliminates the possibility of reusing the device, and the sample loss due to adsorption can make it difficult to detect low concentration samples [Lin06].

4. MICRODROPLET-BASED “DIGITAL” MICROFLUIDICS

Digital microfluidic systems offer an elegant alternative to continuous flow microfluidics (Fig 1.4). In these systems, liquid samples are handled in the form of compartmentalized droplets. Specifically, aqueous microdroplets immersed in an immiscible phase serve to encapsulate reagents and to function as microscale reaction containers. Precise, user-defined chemical reactions may be achieved by transporting and merging droplets containing the appropriate samples and reagents [Son03]. Some of
these systems rely on microchannels to move the droplets; others rely upon interactions between the droplets and a two dimensional grid of microstructures which can generate arbitrary movements. The details of these techniques will be given below.

Compared to continuous flow microfluidic systems, droplet systems offer a number of important advantages. First, reagent consumption can be drastically reduced because droplet volumes are on the order of nanoliters, picoliters, and even femtoliters. With low droplet volumes, it is possible to detect low concentrations and even single molecules of DNA due to the increase in effective concentration at small volumes [Nak03]. Second is an inherent ability to store and isolate a large number of reagents. For example, if 3 µm droplets are used, nearly $10^{10}$ individual containers can be stored in a 1 mL volume. The liquid-liquid interface between the droplet and the immiscible phase serves as a skin to prevent cross contamination between droplets [Son03]. Surfactant chemistries can be used to prevent adsorption to this interface, which adds an additional safeguard against cross contamination or loss of function. Third is the possibility of elegantly managing thousands of samples simultaneously in a scalable manner [Cho03, Chi03, Cha06], allowing for a high throughput, parallel processing. By contrast,

![Figure 1.4: Comparison of continuous flow microfluidic systems and droplet systems.](image)

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continuous flow systems require complex valving for isolating multiple reagent streams [Tho03].

From an application standpoint, microdroplet-based systems have been successfully employed in a number of biochemical assays. The low volumes and fast diffusive mixing rates allow the study of enzyme kinetic reactions in real time [Son03]. The ability to screen a large number of droplets, each with a different composition, has been shown to be indispensable in optimizing protein crystallization conditions [Zhe03]. PCR amplification in droplets allows the detection of single molecules of DNA [Nak03]. Droplets can be used to preconcentrate and isolate solutes [He04], and they also offer a controlled, low-volume microenvironment of droplets for the culture and study of single cells [He05]. The absence of dilution in the encapsulated environment enables quantitative measurements of intra and extracellular secretions [Iri04]. Given the large number of applications and the advancement of droplet system technology, it is likely that the use of droplets in biochemical assays will grow rapidly in the next several years.

In order to mirror the complete set of fluidic operations that would be conducted on a laboratory benchtop, the ideal digital microfluidic device should be able to perform the following droplet functions (Fig. 1.5):

- **Storing** reagents in precisely metered quantities in an isolated manner
- **Transporting droplets** from one location to another
- **Mixing** droplets together in precise quantities.
- **Splitting** droplets into aliquots for use in multiple downstream reactions

The broad range of approaches for performing microdroplet unit operations are summarized in Fig. 1.6 and Table 1.1. In the most basic approach, droplets are
transported through microchannels in the form of plugs. Various channel structures such as T-junctions can be used to generate, mix, split, and merge droplets [Son03]. The disadvantage of this approach is that it requires external pumps to generate flow in channels. A somewhat surprising advantage to using droplet channels is that there is no contact between the droplet and the channel walls. The hydrophobic carrier fluid surrounding the droplets forms a thin boundary which separates and isolates the droplet from the wall [Son03]. Therefore, this technique avoids surface adsorption. However, the drawback is its lack of programmability because the channel geometries are fixed.

Electrowetting on dielectric (EWOD), perhaps the most popular technique for droplet manipulation, uses voltages on a two dimensional grid of electrodes to control the movement of droplets [Pol02]. An aqueous droplet is sandwiched between an upper and lower surface. The lower surface contains a grid of control electrodes coated with a hydrophobic surface, while the upper surface contains one large electrode which serves as the ground plane. When a voltage is applied to one of the control electrodes, the surface becomes hydrophilic, and the droplet is attracted to the surface. By activating adjacent electrodes in a sequential manner, it is possible to create surface energy gradients which can move droplets from one electrode to the next. Other activation patterns can split, cut, merge, and dispense droplets via electronic control [Cho03].
Optoelectrowetting, a similar technique, also relies on switching surface energies of electrodes, but the switching is done via optical means, thus avoiding the need to electronically address each electrode [Chi03].

Although both electro and optoelectrowetting can perform a wide range of operations, perhaps the most fundamental limitation with these techniques is that they require the droplet to wet the surface. The avoidance of surface contact cannot be under-emphasized, and it is a serious concern if the system is to be reusable or able to detect small amounts of reagents. Due to its high hydrophobicity, Teflon is particularly susceptible to adsorption. It is possible to reduce adsorption by maintaining an acidic pH in the droplet, reducing the duration of inactive time, or by the use of plasma deposited fluoropolymer coatings [Bay07, Yoo03]. It has also been suggested that if silicone oil is used as the encapsulating medium, the droplet may be separated from the Teflon surface by a thin film of oil [Sri04]; however, the effectiveness of the technique depends significantly on the interfacial tension between the oil and the protein concentration in the droplet. None of these techniques for avoiding adsorption are 100% effective, as would be required for a robust, reusable device. Adsorption can also render hydrophobic surfaces hydrophilic, which results in contact angle hysteresis and interferes with the EWOD actuation [Yoo03].

Optical tweezers (lasers) rely on radiation pressure which acts on the liquid-liquid interface of the droplets [Ash80, Kat01, Sas92, Chi07]. Since the typical forces are fairly small, optical traps work with small droplets with volumes on the order of femtoliters. Unfortunately, optical tweezers can only attract particles which have a higher refractive index than the surrounding media. The index of refraction in aqueous droplets ($n = 1.33$),
is always lower than that of the surrounding oil; therefore, the laser spot repels droplets.

**Figure 1.6:** Illustration of various techniques used from droplet manipulation, including the Marangoni flow technique to be presented in this thesis.
rather than attracts them. To overcome this issue, the laser beam must be scanned to
create a cage-like optical profile, requiring a more complex setup.

Dielectrophoresis (DEP) is a promising approach which uses non-uniform AC
electric fields acting on the liquid-liquid interface of a droplet. Positive DEP forces can
attract a droplet, avoiding the problem of having to create cages as with optical traps.
Moreover, greater forces are possible with DEP, allowing the manipulation of droplets up
to 100 nL [Gas04]. Using a two dimensional grid of electrodes, droplets can be
manipulated and merged arbitrarily. Although DEP devices do not rely on surface
contact, in most cases droplets sit on the substrate. It is not clear whether this technique
will result in contamination.

DC and pulsed electric fields acting on the liquid-liquid interface can also be used
to perform a wide range of operations. Weitz et al. demonstrated the use of both DC and
pulsed fields to dispense and split droplets inside microchannels [Lin06]. A DC electric field at a channel bifurcation can be used to split a droplet into two
daughter droplets with a positive and negative charge, respectively. The existence of
charge allows further electrical manipulation by electric fields; however, the droplets lose
charge over time and must be recharged. This approach allows some degree of
programmatic control, but due to fixed channel geometries it cannot perform arbitrary
routing in a 2D grid. It does, however, avoid surface adsorption since it does not rely on
surface wetting.

Magnetic fields, generated by a two dimensional array of coils, can be used to
manipulate droplets in a programmable manner. Superparamagnetic beads or
nanoparticles are embedded in each of the droplets, and the local magnetic fields induced
by the coils can transport and split droplets [Leh07]. In addition to having large forces and long throw, an advantage of this approach is that the beads can be functionalized for capturing DNA, viral RNA [Pip07], or for other solid phase extraction. The concern with magnetic beads and fields is whether or not they are scalable and reusable. In these systems, the droplets also contact the surface, which results in adsorption.

A final technique reviewed is thermocapillary flow, which is related, but not identical, to the approach mentioned in this thesis. The thermocapillary approach uses microheaters patterned on a substrate [Dar03]. When a finger shaped-film of liquid is placed near an active heater, the boundary of the liquid tends to move away from the heater (towards the cooler region) due to thermocapillary stresses in the liquid film. This technique can be used to transport and split liquid films and droplets; however, in order to localize the liquids on the substrate, hydrophilic strips must be patterned on the substrate, which causes surface wetting and can result in contamination. A variant of this technique uses an external laser [Kot04] for heating, which simplifies the fluidic substrate, but still requires droplet/surface contact.

The technique that will be discussed in this dissertation is the use of Marangoni flows for manipulating droplets suspended in oil [Bas07A-C]. As mentioned earlier, surface Marangoni flows at small length scales can be created by placing small heat sources above the fluid surface. Droplets suspended near the surface of the oil layer can be manipulated using these flows. Although this technique does not offer the ability to split droplets, it avoids all surface contact between the droplets and the system. Having the heaters above the fluid surface allows the formation of sharp temperature gradients of various shapes, which can generate a number of useful flow patterns for advanced droplet
control.

**Table 1.1:** Techniques for microdroplet manipulation. An ‘X’ is placed in the column if the technique offers the feature indicated on the top of the respective column.

<table>
<thead>
<tr>
<th>Techniques for Microdroplet Manipulation</th>
<th>Programmable Transport</th>
<th>Merging (Mixing)</th>
<th>Splitting (Metering)</th>
<th>Simultaneous control (High Throughput)</th>
<th>Avoids surface contact (Reusable)</th>
<th>Droplet Volumes</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluidic channels</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>pL-nL</td>
<td>[Son03]</td>
</tr>
<tr>
<td>Electrowetting</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>200 nL</td>
<td>[Cho03]</td>
</tr>
<tr>
<td>Optoelectrowetting</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>200 nL</td>
<td>[Chi03]</td>
</tr>
<tr>
<td>Magnetic beads</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>100 nL</td>
<td>[Pip07]</td>
</tr>
<tr>
<td>Optical trap</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td>fL-pL</td>
<td>[Chi07]</td>
</tr>
<tr>
<td>Dielectrophoresis</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>.1-100nL</td>
<td></td>
<td>[Gas04]</td>
</tr>
<tr>
<td>Marangoni flow</td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td>500nL</td>
<td>[Bas07]</td>
</tr>
<tr>
<td>Thermocapillary</td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
<td>nL</td>
<td></td>
<td>[Dar03]</td>
</tr>
<tr>
<td>Electric Fields</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td>fL-pL</td>
<td>[Lin06]</td>
</tr>
</tbody>
</table>

A summary of the capabilities of each technique is summarized in Table 1.1. It is clear that no technology to date can perform all the droplet functions in a programmable manner without surface contact. It is important, therefore, to continue developing technologies for droplet control, including the Marangoni effect shown in this dissertation. Eventually, a combination of the technologies developed will contribute to the development of a reusable, reprogrammable system for generalized droplet manipulation.
5. ORGANIZATION OF DISSERTATION

Chapter 2 of this thesis explores the effect of the heat source geometry on Marangoni flow. It is shown that a number of useful flow patterns can be obtained in thin layers of oil using simple geometries such as point heat sources, lines, rings, and tapered shapes. These flows can emulate droplet traps, channels, filters, and pumps, all accomplishing their functionality without physical structures. Chapter 3 focuses on a specific pattern called the doublet, which occurs if a sharp linear gradient is imposed on a low viscosity liquid such as water. This flow can be used for microfluidic mixing. Chapter 4 demonstrates a complete system for droplet manipulation using the Marangoni effect. This system can achieve arbitrary two dimensional control of droplets using a grid of heaters suspended above the oil layer. This system demonstrates simultaneous control of multiple droplets, as well as droplet merging. In all of the cases, it is shown that droplet velocity can be controlled by adjusting the power to the heat source. In addition to experimental results, this dissertation presents a supporting simulation model which reveals the mechanism of operation, and also gives a methodology for predicting behavior of Marangoni flow at other geometries and length scales.

The three appendices in this thesis describe the microfabricated thermal probes and probe arrays which were used as heat sources in this work. In addition to their use in fluidic actuation, these probes are useful in several other areas as well, including nanoscale imaging and lithography. These were part of early research efforts which are not in the scope of this thesis, but nevertheless showcase the versatility of the devices which were designed and fabricated as part of this effort. Appendix 1 describes the probe [Li03], including its structure, fabrication, and integrated features which allow it to
perform a wide variety of thermal functions. An array of thermal probes [McN04A, McN04B], fabricated in the same process, is also described. Appendix 2 presents simulations which show the thermal interactions between the probe and the liquid surface, included as supplementary material to the simulations in Chapters 2-4. Appendix 3 describes a new technique to pattern thin films with high resolution using heat [Bas04A, Bas04B]. Here, the probe acts as a localized heat source, causing an irreversible chemical reaction on the surfaces which comes in contact with the heated tip. This technique is the first demonstration of thermochemical patterning with a heat source, and it has potential application in maskless lithography.
CHAPTER 2: VIRTUAL MICROFLUIDIC TRAPS, FILTERS, CHANNELS, AND PUMPS USING MARANGONI FLOWS

This chapter describes several microfluidic components, including traps, channels, filters, and pumps, for manipulating aqueous droplets suspended in a film of oil on blank, unpatterned substrates. These are “virtual” devices because they have no physical structure; they accomplish their function entirely by localized variations in surface tension (Marangoni flows) created in a non-contact manner by heat sources suspended just above the liquid surface. Various flow patterns can be engineered through the geometric design of the heat sources on size scales ranging from 10-1,000 µm. A point source generates toroidal flows which can be used for droplet merging and mixing. Virtual channels and traps, emulated by linear and annular heat fluxes respectively, demonstrate nearly 100% size selectivity for droplets ranging from 300-1,000 µm. A source of heat flux that is parallel to the surface and is triangular with a 10° taper, serves as a linear pump, translating droplets of about the same size at speeds up to 200 µm/s. The chapter includes simulations that illuminate the working principle of the devices. Models show that Marangoni flows scale favorably to small length scales. By using microscale thermal devices delivering sharp temperature gradients, it is possible to generate mm/s flow velocities with small increases (<10°) in liquid temperature.
1. INTRODUCTION

The primary topic of this thesis is the ability to engineer Marangoni flows to perform various fluidic manipulations. Using microscale heat sources of different geometries, it is possible to shape the surface temperature gradient and the resulting Marangoni flow. This chapter shows that a number of useful flow patterns can be obtained in thin layers of oil using simple geometries such as point heat sources, lines, rings, and tapered shapes.

With respect to lab-on-a-chip systems, the purpose of these flows is to enable the manipulation of microdroplets in an oil layer. The flows demonstrated are capable of emulating the function of droplet traps, channels, filters, and pumps. It is envisioned that these virtual components could be integrated into a noncontact microfluidic system driven only by heat fluxes (Fig 2.1).

Section 2 outlines general theoretical models of Marangoni flow. Section 3 gives simulation results focusing on each geometry of flow: a point heat source, which generates toroidal flows useful for trapping particles and droplets; linear heat sources emulating virtual channels and filters; ring heat sources acting as single droplet traps; and tapered heat sources emulating a pump. Section 4 presents experimental data for each type of flow, and Section 5 discusses design and experimental considerations.
2. THEORETICAL MODEL OF MARANGONI FLOWS

Marangoni flows occur on a liquid-gas interface on which there exists a gradient in surface tension. The difference in interfacial shear stress drives flow tangential to the surface, directed from regions of low surface tension to high surface tension [Kos93]. In this work, the surface tension gradient is created by imposing a temperature profile upon the interface. For most liquids, and for small temperature perturbations, surface tension decreases linearly with increasing temperature. The temperature coefficient of surface

Figure 2.1: Concept of a contactless microdroplet manipulator based upon Marangoni flows. The flow is driven by heat sources of various geometries suspended above the oil layer. The projected temperature gradient (shown in red) generates flows which emulate droplet channels, reservoirs, and mixers.
tension $\sigma_T$ can be calculated using the Eötvös law, $\sigma_T = k_T \sqrt{V_m^{2/3}}$, where $V_m$ is the molar volume of the liquid and $k_T = 2.1 \times 10^{-7}$ J/K for nearly all liquids [Pil51, Eöt86].

Thus, if a spatial temperature profile is imposed on the liquid surface, it is accompanied by a corresponding surface tension gradient, and the resulting interfacial shear stress ($\tau_s$) is proportional to the temperature gradient $\nabla T_s$. For a Newtonian fluid, the shear stress also determines the surface velocity gradient, resulting in a surface stress boundary condition which is the basis of Marangoni flows [Hig00]:

$$\tau_s = \mu \frac{\partial \vec{u}_s}{\partial \vec{N}} = -\sigma_T \nabla T_s \quad (2.1)$$

In this equation, $\mu$ is the dynamic viscosity of the fluid, $\vec{u}_s$ is the tangential surface velocity vector, and $\vec{N}$ is the surface normal vector (Fig 2.2). The shear stress and flow vector is oriented from regions of low surface tension to high surface tension, opposite to the temperature gradient. The surface Marangoni flow, therefore, is directed away from

![Figure 2.2](image)

**Figure 2.2**: Theoretical formulation of Marangoni flow driven by a surface temperature gradient. In this figure showing the liquid cross section, it is assumed that the left side of the fluid layer is heated, forming a temperature gradient oriented towards the left. $\nabla T_s$ is the surface temperature gradient, $\vec{u}_s$ is the tangential surface velocity of the Marangoni flow, and $\vec{N}$ is the surface normal vector. The parallel flow vectors illustrate the typical profile of surface and subsurface flow.
the heat source. It is accompanied by subsurface flow, oriented in the opposite direction, which provides the return path needed to maintain fluid continuity. The depth at which the subsurface flow reaches maximum velocity, defined as the inversion depth, depends on the length scale of the flow and the depth of the liquid. Together, the surface and subsurface flows create a recirculating cell which is the basis for all the microfluidic components to be discussed in this chapter.

To determine the specific geometry and velocity of flow requires a model which couples the basic fluid mechanics and the temperature gradients. Higuera [Hig00], Taslim [Tas89], and Lai [Lai86] have formulated the problem of Marangoni flow in a thin fluid layer resulting from a surface heat flux. The problem is posed in either planar or cylindrical coordinates, where \( x \) represents the radial distance from the heat source, and \( y \) the vertical position in the fluid of depth \( h \). The two-dimensional, incompressible flow is governed by the continuity equation (2.2), the Navier-Stokes equations (2.3-2.4), and the energy equation (2.5):

\[
\left( \frac{1}{x} \right)^{j} \frac{\partial}{\partial x} (x'u) + \frac{\partial v}{\partial y} = 0 \tag{2.2}
\]

\[
\rho \left( u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right) = -\frac{\partial p}{\partial x} + \mu \nabla^2 u \tag{2.3}
\]

\[
\rho \left( u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} \right) = -\frac{\partial p}{\partial y} - \rho g + \mu \nabla^2 v \tag{2.4}
\]

\[
u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = \frac{\kappa}{\rho C_p} \nabla^2 T \tag{2.5}
\]

The horizontal velocity, vertical velocity, and temperature are denoted by \( u, v, \) and \( T \) respectively. Liquid properties include the density \( \rho \), viscosity \( \mu \), thermal conductivity \( \kappa \), and specific heat \( C_p \). The constant \( g \) is the acceleration due to gravity. The constant \( j \) is
set to 0 if cylindrical coordinates are used, or 1 in a planar coordinate system. In low
Reynolds number flows, which can be assumed at submillimeter length scales, the inertial
terms in the momentum equations are typically small compared to the viscous terms, so
the left hand side of eq. (2.3-2.4) can usually be ignored. The gravitational term in eq.
(2.4), which represents natural convection, is also insignificant as it is known that
Marangoni effect dominates natural convection by one to two orders of magnitude in thin
(<1 mm) films of liquid [Kos93]. Finally, it can be assumed that there is negligible
curvature at the liquid interface, which is valid for small values of capillary number
[Hig00].

Dimensional analysis can be useful for gaining intuition and predicting general
trends in the behavior of convective flows without the need for simulations. Convective
flow in thin liquid layers, driven by buoyancy and surface tension, can be reformulated
using the Boussinesq approximation [Hig00], a slight variation to the conventional form
of the constitutive fluid equations. The dimensionless forms of the equations (in planar
coordinates) are as follows:

\[
\frac{1}{x} \frac{\partial}{\partial x} (xu) + \frac{\partial v}{\partial y} = 0 \tag{2.6}
\]

\[
\frac{\text{Ma}}{\text{Pr}} \left( u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right) = -\frac{\partial p}{\partial x} + \nabla^2 u \tag{2.7}
\]

\[
\frac{\text{Ma}}{\text{Pr}} \left( u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} \right) = -\frac{\partial p}{\partial y} + \nabla^2 v + \frac{\text{Ra}}{\text{Ma}} \theta \tag{2.8}
\]

\[
\text{Ma} \left( u \frac{\partial \theta}{\partial x} + v \frac{\partial \theta}{\partial y} \right) = \nabla^2 \theta \tag{2.9}
\]

The physical parameters and their dimensionless counterparts are listed below.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Characteristic Value</th>
<th>Dimensionless Variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>$\Delta T_0 = \frac{q_0 h}{k}$</td>
<td>$\theta = \frac{(T_{\text{ABSOLUTE}} - T_A)}{T_0}$</td>
</tr>
<tr>
<td>Velocity</td>
<td>$u_0 = \frac{\partial \sigma / \partial T \Delta T_0}{\mu}$</td>
<td>$u = \frac{u_{\text{ABSOLUTE}}}{u_0}$, $v = \frac{v_{\text{ABSOLUTE}}}{v_0}$</td>
</tr>
<tr>
<td>Pressure</td>
<td>$p_0 = \frac{\mu v c}{h}$</td>
<td>$p = \frac{p_{\text{ABSOLUTE}}}{p_0}$</td>
</tr>
<tr>
<td>Position</td>
<td>$d$</td>
<td>$x = \frac{x_{\text{ABSOLUTE}}}{d}$, $y = \frac{y_{\text{ABSOLUTE}}}{d}$</td>
</tr>
</tbody>
</table>

The four dimensionless numbers which govern the geometry and onset of flow include the Marangoni number, the Rayleigh number, dynamic Bond number, the Prandtl number, and the Reynolds number.

\[
\text{Ma} = \frac{\rho |\partial \sigma / \partial T| q_0 h^2}{\mu k^2 / c} \quad (2.10)
\]

\[
\text{Pr} = \frac{\mu}{k / c} \quad (2.11)
\]

\[
\text{Ra} = \frac{\rho^2 g \beta q_0 h^4}{\mu k^2 / c} \quad (2.12)
\]

\[
\text{Bo} = \frac{\text{Ra}}{\text{Ma}} = \frac{\rho g \beta h^2}{|\partial \sigma / \partial T|} \quad (2.13)
\]

\[
\text{Re} = \frac{\text{Ma}}{\text{Pr}} \quad (2.14)
\]

The Marangoni number (Ma) indicates the relative strength of surface tension driven flow, whereas the Rayleigh (Ra) number is an indicator of buoyancy driven flow. The ratio of the Rayleigh and Marangoni numbers, the dynamic Bond number (Bo), tells
which of the two forces is dominant. The Reynolds number (Re), equal to Ma/Pr, indicates the relative strength of the inertial terms in the Navier-Stokes equations. In microfluidic laminar flows, where Re is low, inertial terms can typically be ignored. In this set of experiments, where heat fluxes on the order of $10^4$ W/m$^2$ are applied to mineral oil layers approximately 100 µm thick, the typical values for the Marangoni, Rayleigh, Bond, Prandtl, and Reynolds numbers are, respectively, 88, 0.028, $3 \times 10^{-4}$, and 370, and 0.24. This indicates that, under typical experimental conditions, 1) Marangoni convection (surface tension driven force) largely supercedes buoyancy driven effects, and 2) the flow is laminar.

In addition to the well known parameters for dimensional analysis, Lai [Lai86] determined the following relations for estimating the radial extent of the flow region ($L$) and the change in surface temperature ($\Delta T_0$).

$$L \sim (A^2 Ma)^{1/4} \propto h \sqrt{L_R q_0^{1/4}} \quad (2.15)$$

$$\Delta T_0 \sim (A^2 Ma)^{-1/4} \Delta T_R \propto \sqrt{L_R q_0^{3/4}} \quad (2.16)$$

Here, $h$ is the fluid depth, $q_o$ is the peak value of the gaussian heat flux, and $L_R$ is its characteristic radius. The radial extent of the flow is a strong function of the liquid depth, and a weak function of the temperature and diameter ($\sim L_R$) of the heat source. The surface temperature increase, meanwhile, depends a combination of the heat flux amplitude and its width. Both are confirmed in simulations and experimental data.
3. SIMULATION RESULTS

In general, the Marangoni flow resulting from a given geometry and magnitude of heat flux can be computed numerically using a thermal computational fluid dynamics solver (FLUENT6, Fluent Corp., Lebanon, NH). The simulation model is planar or axisymmetric as described above, or a full 3 dimensional model as necessitated by the symmetry of the input heat flux. The software determines the Marangoni flows from a given heat flux using an iterative procedure which includes the following steps: 1) calculation of the surface temperature profile gradient using a heat conduction simulation, 2) equating the surface temperature gradient to surface shear stress, and 3) solving the Navier Stokes and continuity equations with the shear stress as a boundary condition. The alteration in the temperature profile as a result of the convective flow is reflected in the following iteration. The process repeats until the both sets of equations converge.

To model the heat transfer from the suspended heat source, a heat flux is applied at the fluid surface. For example, in a 2D simulation, a heat flux \( q(x) \) is applied to the surface \( y = h \), forcing a vertical temperature gradient \( dT / dy = -q(x) / \kappa \) at the interface. The lateral temperature gradient resulting from the heating is equated to a surface stress boundary condition using eq. (2.1). Next, according to the kinematic boundary condition, the normal velocity at the interface is set to zero. At the bottom surface of the fluid layer, an isothermal ambient temperature \( T_d = 300 \text{K} \) is specified, along with a no-slip boundary condition. The same condition is applied in the lateral far field boundaries. If an axisymmetric, planar, or 3D symmetric model is used to model the fluid, then symmetry boundary conditions apply at plane of symmetry. These conditions nullify the orthogonal
flow velocities as well as the orthogonal field gradients. For example, in the case of a 2D simulation, \( u = dv/dx = dT/dx = 0 \).

Mineral oils are chosen as the carrier fluids due to their low thermal conductivity and low volatility. Material properties used in the simulations are as follows [Ber03, Lai86]: \( \rho = 886 \text{ kg/m}^3, \mu = 0.026 \text{ Pa-s}, k = 0.12 \text{ W/K}, C_p = 1700 \text{ J/kg-K}, \text{ and } \sigma/\partial T = 16 \times 10^{-5} \text{ N/m-K} \).

Simulations were carried out for each of the four heat flux geometries explored in this effort, including 1) a point heat source, 2) a parallel, linear heat source, 3) a ring-shaped heat source, and 4) a tapered heat source. Each geometry represents a specific microfluidic component, and each is discussed in turn.

The point heat source, the most basic geometry, serves as a fluidic trap. The point source generates radial surface temperature gradients and Marangoni flow directed outward on the surface, and inward below. In three dimensions, the combined flow resembles a toroid (Fig. 2.3) which can trap particles and droplets. Due to the axial symmetry, the point heat source is modeled in a 2-D geometry as shown in Fig. 2.3a. The fluid layer is meshed with 5 \( \mu \text{m} \) square elements, with refinements at the surface thermal boundary layer, and the symmetry axis. A Gaussian heat flux \( q(x) = q_o \exp\left( -x^2/r_o^2 \right) \) is applied to the upper surface to represent the heating from the point heat source. The heat flux is given a peak amplitude \( q_o = 6 \text{ mW/mm}^2 \) and a characteristic radius \( r_o = 40 \mu \text{m} \), corresponding to 20 \( \mu \text{W} \) total power at the surface. These values are chosen to model flow velocities obtained in experiments. The liquid film is assumed to be 140 \( \mu \text{m} \) thick mineral oil with the properties indicated above.
Simulation results are shown in Fig. 2.3 and Fig. 2.4. Contours of the stream function (Fig. 2.3b), which represent the flow pathlines, convey the unicellular nature of the flow. If a particle or droplet is trapped in the flow, it continues to travel along the

**Figure 2.3:** A microfluidic trap generated by a point heat source. (a) schematic showing the suspended heat source, the projected Gaussian heat flux profile, and the toroidal flow region in the oil layer. (b-c) Thermal CFD simulation results showing flow resulting from a Gaussian heat flux with amplitude $q_0 = 6 \text{ mW/mm}^2$ and $r_0 = 40 \mu\text{m}$ applied to a 140 $\mu\text{m}$-thick layer of mineral oil with surface tension coefficient $-0.16 \text{ mN/m-K}$. (b) Contours of stream function, illustrating pathlines in the oil layer. The 20 contours are equally spaced between 0 and $1.5 \times 10^{-9} \text{ kg/s}$. (c) Temperature profile in the oil layer, again with 20 equally spaced contours between 300K and 301.4K.
streamline unless upset by an external factor. The maximum surface temperature increase (Fig. 2.3d) is $\Delta T_{MAX} = 1.5$ K at the center, and it drops off as a Gaussian function of the radius. This is consistent with the dominance of conduction as the main heat transfer mechanism. (In contrast, the dominance of convection would lead to a wider spread in the temperature profiles.) The flow velocity profile at the surface and at several depths below the surface is shown in Fig. 2.4. It is notable that 1.7 mm/s maximum flow velocity is obtained with only a 1.5 K increase in surface temperature. The maximum velocity occurs about 40 µm from the center of the heat source, corresponding to the location of the maximum temperature gradient. The radial velocity is positive at the liquid surface, reverses direction at approximately 30 µm depth, attains a maximum negative velocity at 70 µm depth, and eventually diminishes to zero at the interface with the solid substrate. Simulations at various heat flux amplitudes show a linear dependence of surface velocity on heat flux - about 1.1 mm/s flow velocity is attained for every 1
degree increase in surface temperature. The slope of this function is determined by the surface tension coefficient $\partial \sigma / \partial T$ and the surface temperature gradient $\partial T / \partial x$, the latter of which depends inversely on the thermal conductivity $\kappa$.

In experiments, a microfabricated thermal probe serves as the point heat source. To model the interaction of the probe with the fluid surface, a full three dimensional thermal fluid simulation is performed, which includes a 360 x 120 x 3 µm thin film cantilever probe suspended in air, 15 µm above a layer of mineral oil with thickness 200 µm. A heat generation condition of 1.5 mW is applied to a volume at the tip of the probe.

![Figure 2.5](image)

**Figure 2.5:** (a) Three dimensional thermal fluid simulation showing the interaction of a microfabricated thermal probe held above a layer of mineral oil. The numerical value of the temperature contours depends on the applied power as shown in part (b); however, the shapes of the contours do not change. Inset shows the qualitative surface heat flux resulting from the probe held at a 30° angle. (b) Maximum temperature increase on the liquid surface ($\Delta T_{MAX}$) vs. separation between the probe and the liquid surface. (c) Maximum surface temperature gradient vs. gap. In (b,c), the diamonds represent simulation results. The lines are a 1/x best fit.
to emulate joule heating, resulting in a tip temperature of ~320K. The resulting
temperature contours (Fig. 2.5) show a sharp vertical gradient between the probe and the
liquid surface, and a sharp lateral heat flux gradient due to the length scale. The surface
heat flux results in a lateral temperature gradient that approximately resembles a point
source, although the gradient across the probe is also reflected in the contours. Figures
2.5b-c show a sharp decrease in surface temperature perturbation and surface temperature
gradient as the probe is moved away from the liquid surface. Both fall off as a function
1/g, where g is the gap between the probe and the surface. This is due to the high thermal
resistance of air, and it underscores the importance of maintaining a small air gap for
maximum efficiency. The shear stress corresponding to a surface temperature gradient
can be found by multiplying the temperature gradient by the surface tension coefficient
∂σ/∂T. At a 15 µm gap, the maximum shear stress is 1.6 N/m², assuming ∂σ/∂T = -
0.16 mN/m. Another important aspect of this model is to investigate whether the
convective air flow around the probe affects the Marangoni flow in the liquid.
Simulation results show that flow velocities in air are several orders of magnitude less
than the liquid Marangoni flow; thus, it is concluded that air flow has negligible impact.

One level of complexity above the point heat sources are the linear heat sources,
which emulate virtual microfluidic channels. Virtual channels collect droplets within a
specific size range and confine them within their boundaries. One way to form a virtual
channel is by using two parallel heat sources separated by a spacing s. When placed
above a layer of oil, the sources project two linear heat fluxes on the liquid surface which
define the boundaries of the channel (Fig. 2.6). The range of droplets captured within the
channel is a function of the spacing, $s$. Target-sized droplets are pulled into the channel, while smaller droplets are pushed out by the surface flows.

The mechanism of operation is shown using three-dimensional CFD simulations (Fig. 2.7). In the simulation, a $5 \times 5 \times 0.2$ mm fluid layer is meshed with $10 \ \mu$m square elements. The heat flux applied to fluid surface consists of a pair of one-dimensional Gaussian functions along the horizontal axis, with amplitude $q_0 = 6$ mW/mm$^2$, characteristic radius $r_0 = 40 \ \mu$m, and a spacing of $900 \ \mu$m between the peaks. This results in two parallel peaks in surface temperature (Fig. 2.7a,c) as would be expected from two linear sources. The resulting Marangoni flow is comprised of two circulating cells on opposite sides of the heat sources, and a relatively still region between them. Surface flows are directed away from the virtual channel, and subsurface flows are directed toward it. A droplet of appropriate size is pulled into the channel by the subsurface flows, which apply a lateral force to the center of mass of the droplet. The
surface flows, meanwhile, apply only a tangential force on the top side of the droplet and, therefore, do not cause lateral movement. In contrast, a smaller droplet, whose center of mass is closer to the surface, is pushed out of the channel by the surface flows and is, therefore, excluded. The distinction between ‘large’ and ‘small’ droplets is a function of $s$.

Another way to create a virtual channel is with a single line heat source instead of two parallel sources (Fig. 2.7b,d). In this case, the channel size and the droplet size-selectivity are defined by the width of the heat source ($w$) rather than the spacing $s$. Simulation conditions are identical to the previous, except that the applied surface heat...
flux includes only a single peak, and the characteristic radius is increased \( (r_o = 175 \, \mu m) \) to represent a wider heat source. Simulation results illustrate the differences in flow patterns of the double and single line heat sources. The recirculating flows present inside the double line channel do not appear in the single line version; however, these internal flows do not affect the trapping capability of the channel. The double line heat source offers some flexibility in that the virtual channel region can be easily tuned wider than the single line channel for trapping larger droplets. It is notable that in both cases, up to 4 mm/s surface velocities can be obtained with \(<6 \, ^\circ C\) change in surface temperature, again illustrating the potential efficiency of Marangoni flows. The subsurface flows are only about \(1/3^{rd}\) the velocity of the surface flows, but they are sufficient to pull in selected droplets. Experimental results will be discussed in the following section.

A single droplet trap can be implemented using an annular heat source (Fig. 2.17). Compared to the parallel heat sources, the cross section of the flow vectors are identical; however, when viewed from above, the flow pattern is axially-symmetric about the heat source. With respect to droplet manipulation, the primary difference between this component and the channel is that the droplet can be confined in both lateral dimensions. The trap is useful as a reservoir for holding single droplets, and for moving droplets if the heat source is translated laterally. On a broader note, a particularly interesting aspect of this flow pattern is the isolation of the fluid region within the confines of the ring. Simulations and experimental results show that the fluid within the ring boundary circulates independently and does not flow into the outer bulk fluid. In a sense, the inner and bulk fluid are doubly separated by two walls of co-rotating flows. This suggests that a ring heat source may have potential use as a fluid isolator outside the context of droplet
In the simulation model, the heat flux profile is an axisymmetric ring shape, the cross section of which consists of Gaussian peaks at a radius of 300 µm. The amplitude and characteristic width of the Gaussian profile is maintained at the same values as prior simulations \((q_0 = 6 \text{ mW/mm}^2 \text{ and } r_o = 40 \text{ µm})\). Figure 2.17b shows the surface temperature profile \((\Delta T_{MAX} = 6^\circ \text{C})\) and flow resulting from a ring-shaped heat source in a 200 µm-thick layer of mineral oil. For clarity, the arrows show only the subsurface flows (140 µm beneath the surface) since they are the ones for droplet trapping. The flow can be divided into two distinct regions. Flow vectors outside the perimeter of the ring are oriented inward, and these flows push the droplet to the center. The maximum flow velocity in this region is 1.3 mm/s. Inside the perimeter of the ring, the subsurface flows are oriented outward, reaching a peak velocity of 0.8 mm/s; however, these flows do not affect the trapped droplet because the lateral forces they impart on a trapped droplet are symmetric and therefore cancel each other. Target-sized droplets, therefore, remain stable at the center of the ring. Like the earlier geometries, smaller droplets are rejected from the trap by the surface flows (not shown), which are oriented opposite the subsurface flows. Thus, the size exclusion capability applies to the annular geometry as well.

A fundamental component of any fluidic system is a pump. With noncontact Marangoni flows, pumping or actuation of droplets can be accomplished by two methods. The first is simply a consequence of the trapping: the heat source projecting a channel or a trap can be translated physically with respect to the substrate, and the trapped droplets follow it. However, droplet actuation can be also accomplished by steady-state,
motionless heating provided by a tapered shape and angled spacing (Fig. 2.18). The tapered geometry provides a triangular heat flux on the fluid surface and a temperature gradient oriented in the direction of increasing width. It can be simulated by applying a triangular heat flux with amplitude 6 mW/mm² and a 10° tip angle on a 500 µm square, 140 µm-thick layer of mineral oil. This results in a triangular temperature profile with a maximum temperature increase of \( \Delta T_{MAX} = 5^\circ C \) on the fluid surface. The resulting subsurface flows (Fig. 2.18b) are biased in the direction of increasing taper, and can pull appropriately sized droplets along the length of the guidewire. The maximum subsurface flow velocity of 1.5 mm/s can be found near the tip of the guidewire. The surface flows (not shown) have velocities roughly 3x larger than the subsurface flows and are biased in the opposite direction. As before, the surface flows affect only the small droplets, rejecting them from the guidewire.

4. EXPERIMENTAL RESULTS

Marangoni flows from point heat sources were obtained with a micromachined polyimide-shank thermal probe [Li03] which provides high thermal efficiency, sharp temperature gradients, and controllable temperatures. The probe consists of a 40 x 360 x 3.5 µm polyimide cantilever with a thin film heater near the tip which provides control of the probe power and temperature. The probe was mounted on a motorized micromanipulator stage (MP-285, Sutter Instruments, Novato, CA) and suspended above a 140 µm thick layer of mineral oil (Mineral Oil USP, Rite Aid Corp., Harrisburg, PA). The thickness of the oil was measured optically. Flow velocities were measured at input powers ranging from 5-20 mW and at air gaps ranging from 20-320 µm. Weed pollen
(25 µm diameter, Sigma-Aldrich, St. Louis, MO), was immersed in mineral oil to serve as tracer particles in characterizing the flow, and also for demonstrating particle collection. Particle displacements were tracked using a CCD video camera (DVC-107, Sony USA, Culver City, CA) mounted on a stereomicroscope (SZX12, Olympus Corp, Center Valley, PA). Video clips were analyzed frame by frame to determine the position of a selected particle at 1/30 second intervals. Velocities were obtained by dividing the displacement over the time interval.

**Figure 2.8:** Experimental velocity profile of a toroidal flow cell in 140 µm-thick mineral oil obtained with a thermal probe and the experimental conditions shown in the figure. (a) Radial displacement of a selected particle from the toroid center graphed as function of time over two oscillation cycles (b) Particle velocity graphed as a function of the radial position for two cycles, obtained by taking the time derivative of the displacement data. The particle follows a clockwise path; outbound velocities are positive; inbound velocities are negative.
Experimental flow velocities from a point heat source are shown in Fig. 2.8. The spatial velocity profile, obtained by differentiating the displacement data in time, closely resembles the simulation results which used Gaussian heat fluxes with $q_0 = 6 \text{ mW/mm}^2$ heat fluxes and $r_0 = 40 \text{ µm}$. The probe width itself is about 40 µm, showing reasonable correlation with the simulation. Flow velocities reach a maximum of 1.7 mm/s. Although it is not feasible to accurately measure the temperature profile, the 1.5K surface

![Graph](image)

**Figure 2.9:** Control of flow velocities with toroidal flows generated by a microfabricated point heat source. (a) Flow velocity vs. input power to the thermal probe plotted for three different separation distances. Also shown are simulated flow velocities as a function of input power. In the simulation, a Gaussian heat flux of increasing amplitude was applied to a 2D, axisymmetric fluid layer. (b) Experimental flow velocity vs. separation with experimental conditions as shown. A 140 µm layer of mineral oil was used in all experiments and simulations.
temperature elevation found in simulations suggests that Marangoni actuation requires only small increases in surface temperature in order to function.

Figure 2.9a demonstrates the linear relationship between heat flux and flow velocity found in both simulations and experimental results. The linear offset in the experimental data was the result of an inadvertent photothermal effect: due to the high thermal isolation provided by the polyimide cantilevers, the microscope lamp heated the probe tip enough to create a non-zero velocity even when no electrical current was applied to the probe. Nevertheless, it can be seen that velocities scale approximately linearly with increasing power, and decreases exponentially with increasing separation between the probe and the liquid surface.

Marangoni flow in the reverse orientation can be generated by using a cooling point source rather than a heating source. The point cooling source is made using a

Figure 2.10: (a) Cold probe experimental setup. (b) Collection of particles using reverse Marangoni flow
plastic syringe tube filled with dry ice. Styrofoam is wrapped around the syringe to provide thermal insulation. A metal wire protruding from the syringe acts as the tip; this wire is also wound along the inside of the syringe to maximize the heat transfer between the wire and the ice. Typical temperatures on the metal tip are between -10 and -20°C. Fig. 2.10 shows the experimental setup where the syringe is held above the glass slide on which the sample is placed. Reverse flow is demonstrated using Φ=25µm pollen particles immersed in a 300 µm-thick layer of mineral oil (Fig. 2.10b). The probe is held

FIGURE 2.11: Effect of fluid depth. a) Radius of the convective region as a function of fluid depth. b) Peak radial velocity as a function of fluid depth. In both graphs, experimental conditions are as follows: probe type (R01, 35 Ω), input power=18 mW, air gap=100 µm, and the liquid is mineral oil. Simulation conditions: \( q_0 = 6000 \text{ W/m}^2 \), \( r_0 = 50 \text{ µm} \), and mineral oil properties are used.
above the fluid layer for 10s, after which the aggregation of particles can be seen. The aggregation is the result of surface Marangoni flow directed towards the cooling source. Due to condensation and ice formation, the cooling source is not practical for general use, and therefore the remainder of the chapter returns to heating sources.

Localization of the flow cell is an important parameter needed to selectively trap particles. Figure 2.8b shows that the flow cell is confined to an approximately 300 µm radius from the center of the heat source. The radial extent of the flow can be made smaller by using a thinner fluid layer; however, it should be noted that flow velocities

![Figure 2.12](image)

**Figure 2.12:** Applications of the toroidal flow pattern in particle and droplet collection. (a) Schematic showing the heat source, XY scanning stage, toroidal flow patterns, and particles trapped within the collection area. Collection of (b) weed pollen in 125 µm mineral oil, and (c) 1 second exposure fluorescent image illustrating the movement of water microdroplets containing fluorescent dye.
diminish in a thinner layer due to increased viscous forces between the flow layers (data not shown). Simulations and experimental results of the radial extent of flow versus fluid thickness show reasonable agreement (Fig. 2.11). In the simulation, an axisymmetric Gaussian heat flux with $q_0 = 6 \text{ mW/mm}^2$ and radius $r_0 = 50 \text{ µm}$ was applied to a mineral oil layer. In the experimental data, a 40 x 360 x 3.5 µm probe with 18 mW applied power was placed approximately 100 µm above the mineral oil layer.

Highly localized Marangoni flows can be useful for trapping and manipulating particles (Fig. 2.12). For example, the thermal probe can be suspended above the liquid sample on an XY scanning stage so that the collection region can be shifted laterally. In one demonstration (Fig. 2.13), a thin fluid layer (80 µm) is used to minimize the radius of the collection region and a low viscosity dielectric liquid (EDM-185, Commonwealth Oil, Harrow ON) is chosen to help offset the increased shear that occurs in thin liquid

![Figure 2.13: Collection of 25 µm weed pollen using local toroidal flows. (1) The heat source is first advanced towards the particles. (2) When the heat source reaches the area above the particles, the particles are swept into the vortex and trapped. (3-4) The trapped particles are moved to a new location and released by turning off the heater.](image-url)
layers. Figure 2.13(b-d) illustrates the harvesting of 25 µm diameter weed pollen with a localized collection region of 50 µm radius. In this experiment, the pollen particles were immersed in the 80 µm-thick dielectric oil, and an 18 mW heat source was held 50 µm above the oil surface and scanned as indicated. The micrographs show that as the heat source is scanned laterally, the particles are swept into the flow cell and transported with it. Particles are released by turning off the heat source. The notable aspect of this approach is that the heat source does not physically contact the liquid or the particles.

**Figure 2.14:** Droplet merging of four droplets with (φ = 200-400 µm). (0s) The droplets are trapped in the self-circulating convective flow. (2s-9s) The droplets merge together, one by one, eventually forming a single, φ = 600 µm droplet.
By using the same approach, it is possible to collect and merge microdroplets with radii ranging from 5-100 µm. The ability to merge discrete droplets is important in microdroplet systems, as it allows reagents to be mixed at millisecond time scales, fast enough to study chemical kinetics [Son03]. When brought in contact with one another, aqueous droplets spontaneously merge unless treated with a stabilizing surfactant. To demonstrate droplet collection and merging, a 650 µm diameter, 80°C wire tip was suspended < 100 µm above mineral oil which contained droplets with diameters 200-400 µm. The heat source collects droplets in the regions over which it is scanned. Droplets trapped in the flow eventually collide and merge with one another (Fig. 2.14). By scanning the heat source over a large area, many droplets can be collected and merged in this manner.

A third interesting capability of a point heat source is the ability to rotate and mix individual droplets. In general, when the particles and/or droplets immersed in the oil are small compared to the cross-sectional height of the convective flow region, they follow the toroidal streamlines. However, when the height of the flow region is approximately the same as the droplet diameter, the recirculating currents can rotate and mix the droplet in various patterns depending on the size of the heated tip (Fig. 2.15). In the case where the tip diameter is approximately the same size as the droplet, the Marangoni flows can rotate the droplet at high speeds. For example, if a 650 µm-diameter heated tip (T≈40°C) is placed near a droplet of the same size (Fig. 2.15b) in an 800 µm-thick mineral oil layer, single axis rotation is observed at rates up to 300 rpm. In the case where the tip diameter (50 µm) is smaller than the droplet (1000 µm), the flow pattern is instead composed of two vortices within the droplet (Fig. 2.15b). Both of these manifestations can be useful
for micro mixing within a single droplet.

Figure 2.15: Droplet rotation and mixing. (a) Schematic showing Marangoni flows around a suspended droplet which can rotate the droplet. (b) Experimental results showing single axis rotation up to 300 µm/s obtained when a 650 µm diameter tip is placed near a droplet of approx. the same dimensions. The tip temperature was ≈40°C. Flow patterns are visualized using immersed fluorescein particles and a 0.5 second CCD exposure with 490 nm/500 nm excitation/emission filters.

With the intent of demonstrating the simplicity and generality of droplet manipulation methods, the demonstrations of droplet merging, rotation, and mixing were carried out simply with a heated metal tip rather than the microfabricated thermal probe. Although not as thermally efficient or as small as the microfabricated heat source, the use of simple metal structures demonstrates the versatility of this technique. In the same spirit, simple metal structures are used to represent the ring, linear, and tapered heat sources discussed in the remainder of this chapter.
Virtual droplet channels, generated by linear heat sources, were experimentally verified by placing two parallel, cylindrical metal structures above a thin layer of phenylmethyl polysiloxane oil (Corning 550 Fluid, Dow Corning, Midland, MI). This particular oil was chosen for its high density (specific gravity = 1.07), which causes the aqueous droplets to float on the oil surface. The suspension of the droplets is critical because droplet manipulations depend on the surface Marangoni flows. It also prevents contact between the droplet and the glass slide below. Droplets with diameters ranging from 20-2,000 µm were generated by pipetting 5 µL of deionized water into the oil and stirring vigorously. The metal structures, with spacing $s = 600$ µm and $s = 900$ µm, were located 200-400 µm above the oil surface and heated to approximately 110 °C. The size

![Image](image_url)

**Figure 2.16**: Size selective filtration of droplets in virtual channels. (a) Micrographs showing two 500 µm-diameter droplets (circle) entering the channel while a smaller one (square) is rejected. (b) Histogram showing the size selectivity of two droplet channels with 600 µm and 970 µm spacing. Droplet statistics were compiled over video clips spanning 40 minutes. Bins are in 100 µm increments.
selectivity is demonstrated by time-lapse images in Fig. 2.16, which show that droplets within a specific size range move into the channel, while smaller droplets are actively removed by the Marangoni flows. Very large droplets are unaffected by the flows, and therefore are not actively recruited into the channel.

The ability to tailor the size selectivity of the channels is quantitatively shown in Fig. 2.16b. A histogram of droplet capture vs. droplet size is shown for the two channels with different spacings \( s \). When \( s = 600 \) µm, the minimum diameter for entry into the channel is 250 µm, and when \( s = 970 \) µm, the minimum diameter is 350 µm. A sharp transition can be seen in both cases, and nearly 100% exclusion of off-sized droplets is shown. Therefore, these channels inherently provide a size-based filtration capability.

Figure 2.17c shows experimental results for the annular heat source functioning as a droplet trap. A rectangular ring-shaped metal pin \( (T \approx 120^\circ C, s = 600 \) µm) was suspended 200-400 µm above the oil layer to approximate an annular heat flux. The micrographs show that a 700 µm-diameter droplet is actively pulled into the trap, driven by the subsurface flows directed into the center of the trap. If the trap boundary is moved (by the translation of the substrate or heat source), the droplet follows it. The process is repeatable, and the droplet velocity, as it enters the trap, is approximately 200 µm/s.

Experimental confirmation of the guidewire pump (tapered heat source) is shown in Fig. 2.18c. To create the surface heat flux, a steel needle \( (T\approx130^\circ C) \) with 10° lateral taper, and a 5° taper in vertical spacing was placed \( \approx200 \) µm above the fluid surface. Time lapse images show a 523 µm-diameter droplet pulled along the axis by virtue of the Marangoni flows. The droplet moves quickly when first approaching the tip of the heat flux and continues to move in the direction of increasing taper, achieving a maximum
velocity of 196 µm/sec at the tip end of the guidewire (i.e., the location of greatest axial temperature gradient).

**Figure 2.17**: Single droplet trapping with an annular heat flux. (a) Schematic illustrating the annular heat flux projected on the surface, the trapped droplet, and the exclusion of larger or smaller droplets. (b) CFD Simulation. The shaded contours represent the surface temperature gradient, with evenly spaced contours and a maximum temperature increase $\Delta T_{\text{MAX}} = 6^\circ\text{C}$. White arrows represent the subsurface flow at 140 µm depth beneath the surface. The two regions of flow are marked with dashed lines. (c) Micrographs showing strong affinity of a 1 mm droplet to the annular heat source ($T\approx120^\circ\text{C}$). Gap is $\approx200$ µm.
5. DISCUSSION

It is clear that the Marangoni technique relies on the ability to produce sharp and accurate temperature profiles on the liquid surface. Given the relatively high thermal conductivity of most liquids, it is difficult to achieve sharp surface temperature gradients.

Figure 2.18: Guidewire pump emulated by a tapered heat source. (a) Schematic showing the orientation of the triangular heat flux projected on the fluid surface, and a droplet being pulled in along its longitudinal axis. (b) CFD Simulation. Shaded contours represent the surface temperature gradient, and white arrows represent the subsurface flow (140 µm depth) which pushes the droplet from left to right. (c) Micrographs illustrating movement of a droplet at 196 µm/s driven by a suspended heat source (T≈130°C) with 10° lateral taper and a 5° taper in vertical spacing. Gap is ≈200 µm.
if the heaters are embedded within the fluid. By contrast, placing the heat sources above
the liquid benefits from the low thermal conductivity of air, which is nearly an order of
magnitude less than oil. This limits lateral heat conduction and allows the formation of
sharp surface temperature gradients at the resolution needed to obtain shaped temperature
profiles at the sub-millimeter scale. An added benefit is that the heaters do not contact
the sample, obviating contamination concerns.

With regards to reconfigurability, one of the projected advantages of this type of
approach is that the substrate itself remains unpatterned. The complexity and burden of
the fluid actuation is essentially placed to the suspended heating structures rather than the
fluidic substrate. Since the heating structure can be reused and reconfigured, this can
lower the overall cost of repeated experiments.

To achieve the sharpest temperature gradients on the liquid surface, it is important
to place the heat sources as close to the surface as possible, since heat spreads
isotropically in the air gap. Typical gaps on the order of 100-400 µm can be obtained by
visual estimation during the approach of the heat source to the sample surface. An
automated technique which would allow for small air gaps would greatly benefit
efficiency, as simulations indicate that when the gap is less than 100 µm, both the surface
temperature gradient and resulting velocity sharply increases.

Another benefit of placing the probes close to the surface is lower power
operation. Although the low thermal conductivity of air helps achieve a sharp lateral
gradient, it also reduces the heat transfer from the heat source to the liquid surface.
Experimental results with the microfabricated thermal probe show that approximately 10
mW of heat power must be dissipated in order to generate 1 mm/s flow velocity.
Simulations, however, indicate that <0.2 mW of surface heat flux is needed to generate the same flow velocity. The discrepancy between the two arises due to the poor heat transfer between the probe and the liquid surface. Three dimensional heat conduction simulations of the probe above the liquid surface show that at a 100 µm separation, the surface temperature rise is only 1.3% that of the probe. This figure drops to only 0.3% if the gap is 300 µm. As shown earlier (Fig. 2.5), there is an approximate 1/x dependence on the surface temperature rise vs. the probe-liquid separation.

An equally important way to improve efficiency is by optimizing the heat source. Microfabricated heaters with well-designed thermal isolation can achieve thermal resistances in the range of 10,000 K/W [Li03], and thermal masses of only $10^{-9}$ J/K. This enables temperatures of 100 °C with <10 mW of input power, and dynamic heating times on the order of 10 ms. In these probes, the relatively small thermal losses are due to conduction through the probe shank. Thus, the efficiency can be further improved by using a thinner cantilever or lower thermal conductivity materials in its fabrication. With the existing devices, the best power efficiency, obtained experimentally at a 30 µm gap, is about 1 mm/s per milliwatt input power, reaching a maximum liquid velocity of 1700 µm/s with < 20 mW input power to the probe.

The ability to localize flow is an important aspect as well. Fig. 2.11 shows that the radius of the collection region scales with the thickness of the liquid layer, and intuitively, it would also scale with the size of the heat source. The former approach is simpler, but the latter offers the ability to accommodate a larger range of droplet sizes. The smallest flow cell observed was a 50 µm diameter toroidal flow, obtained using a thermal probe above 80 µm thick low viscosity oil.
Another purpose of this effort was to show that even simple metal tools can be used to generate Marangoni flow which can emulate microfluidic components. Because these components are larger in size (a few mm) than the microfabricated probe (< 100 µm), they cannot generate as sharp a gradient. Thus, a larger absolute increase in temperature is needed to drive flows at the same rate. In the case of the tapered, ring, and linear geometries, the heat source temperatures are between 80-120°C, and the liquid surface temperatures are measured to be 10-40° above ambient. This temperature requirement can be reduced by scaling the heat sources to smaller sizes.

Overall, scaling down to smaller length scales can potentially provide significant performance benefits. For example, the microfabricated thermal probe used in this work obtains temperature gradients of up to 1 K/µm (10^6 K/m) along a 200 µm-long cantilever. Experimental and simulation data using this probe show that on the liquid surface, the typical temperature gradient ranges from 1-10 K/mm, resulting in shear stresses between 0.1-1 N/m^2 and velocities between 1-10 mm/s on a 200 µm thick oil layer. Hypothetically, if the thermal gradients on the microfabricated probe (up to 10^6 K/m) could be directly transferred to the fluid surface without loss, this could result in shear stresses up to 100 N/m^2, and theoretical velocities above 10 cm/s (if viscous resistance can be minimized). Although this is not possible in the existing setup, it does illustrate the favorable scaling of this technique, and the potential to achieve high speed flow.

6. SUMMARY

This chapter has shown that microfluidic Marangoni flows can be engineered through the geometric design of the heat flux. A surprising number of microdroplet
operations, including mixing, confining, filtering, trapping, and pumping, can be emulated through the creative use of surface and subsurface flows. As a noncontact technique, these virtual components avoid many of the contamination issues which limit many microfluidic technologies. The future direction of this research is to integrate several of these components into a usable system for droplet manipulation. A system with programmable heat fluxes may also be useful for research applications which require flexibility and reusability over portability.
CHAPTER 3: HIGH SPEED DOUBLET FLOW

The toroidal flows described in Chapter 2 are consistent with flow patterns driven from thermal monopoles, \textit{i.e.} a point heat source. Doublets, in contrast, are consistent with thermal dipoles. This chapter describes doublet flow patterns, which have potential utility in microfluidic mixing. Section 1 begins with a background on microfluidic mixers. Section 2 introduces basic concepts and describes how doublets may be driven by thermal probes. Section 3 gives a theoretical model, presenting two theories for doublet formation. Section 4 gives experimental results of a typical doublet, and also describes how i) flow can be reversed by changing the angle of the cantilever, and ii) how multiple heat sources (i.e., the thermal probe array) can be superimposed to generate uniform flow.

1. BACKGROUND

The ability to generate high speed micro-flow patterns plays a critical role in the mixing, pumping, and pre-concentration of particle solutions, particularly for cellular and biomolecular manipulations. It is well known that microfluidic mixing is difficult at the micro-scale due to laminar flow, which causes conjoined fluid streams to remain separate rather than intermix. Active mixing via chaotic advection [Mel96, Aref84] requires that the fluid is folded or turned, but the planar nature of microfabricated devices makes the
fabrication of mechanical mixing components difficult and exceedingly costly. For this reason, alternative mixing techniques have been sought, many of which focus on generating in-plane vortex flow without mechanical components. An opto-electrostatically driven vortex pattern generated by a focused 50 mW laser spot in combination with a 2 kV/cm electric field was shown to have a maximum particle velocity of 120 µm/s in conductive liquids [Miz93]. Vortices driven by electrokinetic instability formed in polymer channels with patterned surface charges [Odd01] operate on a smaller electric field (100 V/cm), but produce slower velocities and require ionic solutions [Hau03]. Pressure differentials and dielectrophoresis [Lee01] are other active methods for generating vortices for active mixing.

Figure 3.1: Schematic of doublet flow generation. The heated thermal probe, when suspended above a liquid, induces a high-speed doublet flow pattern at the surface.
Combining a fluidic source and sink in a planar liquid layer forms the well known doublet flow pattern, which contains two adjacent vortices useful for mixing. Although rarely observed in nature, doublet flows can be realized by placing a drain in a fluid layer and pumping the drained fluid into an adjacent region. Such extraction/injection well pairs have been implemented at very large scales because their mixing characteristics efficiently purify groundwater [Luo04, Gan02]. Evans [Eva93] and Cola [Col06] implemented source-sink pairs in microfabricated devices to facilitate advective mixing. A mixing chamber was flanked by channels which either pumped fluid away or into the chamber in a pulsatile fashion. Efficient mixing was demonstrated; however, the devices did require mechanical actuation, provided by either integrated [Eva93] or provided by off chip components [Col06].

Here, we show that a high speed fluidic doublet, with rotational velocities of up to 1200 rpm and linear velocities of 5 mm/sec, can be realized on a thin aqueous layer placed on a glass slide, without a fluidic chip or pumps. The doublet is driven by the thermal probe suspended above the liquid surface (Fig. 3.1). Since the probe has no moving parts and makes no contact with the liquid, common problems of mechanical wear, electrode contamination, and bubble generation, can be avoided. The technique does not require ionic or conductive liquids.

2. TEMPERATURE GRADIENT THEORY

A doublet, the fluidic analog of a magnetic or electric dipole, is a two dimensional planar flow pattern consisting of two adjacent vortices of opposing rotational directions, and resulting linear streamlines between them (Fig. 3.1). This chapter presents two
Theories on how doublets can be formed.

The first theory considers the sharp temperature gradient formed across the length of the thermal probe. When the probe is placed near the liquid surface, this gradient is mirrored on the surface as shown in Fig. 3.1a. A simple point heat source would create axially symmetric temperature gradients, which does not generate doublet flow. However, a linear gradient imposed on a small region on the fluid surface can create a local pumping effect similar to the tapered heat source geometry discussed in Chapter 2. Through the Marangoni effect, this local gradient results in the application of stress and mass flow to the fluid layer.

The local pumping effect can be simulated using commercial CFD software (Fluent 6.0, Fluent Corp.). A two dimensional fluid layer with dimensions 300µm x 300µm is meshed with 2 µm square elements, and a linear momentum of $10^{18}$
kg-m/s per m² is applied to a 20x20µm region in the center of the fluid layer to model the local velocity due to the thermal gradient. Simulation results (Fig. 3.2) demonstrates doublet flow matching in scale and geometry to experimental observations.

3. SOURCE/SINK THEORY

Another way a doublet can be generated is if a fluidic source and fluidic sink are placed next to one another. The source/sink model is particularly useful for deriving analytical relations because the source, sink, and doublet are all 2 dimensional planar potential flows which can be described by their respective stream functions $\psi$. The fluidic source is a point from which fluid flows radially outward, and a sink is a point to which fluid flows inward (Fig 3.2a). For a source or sink located at the origin, the respective stream functions in polar coordinates are:

$$\psi_{\text{SOURCE}}(r, \theta) = \frac{m}{2\pi} \theta,$$  \hspace{1cm} (3.1) \\
$$\psi_{\text{SINK}}(r, \theta) = -\frac{m}{2\pi} \theta$$  \hspace{1cm} (3.2)

The constant $m$ is the volumetric flow rate, and is related to the radial velocity through the relation $m = 2\pi r V_r$. Flow resulting from the combination of a source and sink can be found by adding the contributions respective stream functions, using the principle of superposition. If a sink and source of equal strength $m$ are placed at $(-a,0)$ and $(a,0)$ in a Cartesian plane, the resulting doublet flow can be expressed as

$$\psi_D(x, y) = \psi_{\text{SOURCE}} + \psi_{\text{SINK}} = -\frac{m}{2\pi} \tan^{-1}\left(\frac{2ar\sin\theta}{r^2 - a^2}\right)$$  \hspace{1cm} (3.3)

where $x = r\cos(\theta)$ and $y = r\sin(\theta)$. If the separation $2a$ is small, the doublet equation
simplifies to

\[ \psi_D = -\frac{ma \cdot r \sin \theta}{\pi \left( r^2 - a^2 \right)} = \frac{ma}{\pi} \frac{y}{x^2 + y^2 - a^2} \quad (3.4) \]

Here, the product \( ma \), also called the dipole moment, reflects the strength of the doublet. As the distance between the source and sink becomes small, \( m \) must increase proportionally in order to maintain the strength of the doublet. The doublet stream function is related to its velocity vector \((u, v)\) as:

\[ u = \frac{d\psi}{dy} = \frac{ma}{\pi} \left( \frac{x^2 - y^2}{\left(x^2 + y^2 - a^2\right)^2} \right) \quad (3.5) \]

\[ v = -\frac{d\psi}{dx} = \frac{ma}{\pi} \left( \frac{2xy}{\left(x^2 + y^2 - a^2\right)^2} \right) \quad (3.6) \]

Fig. 3.2 shows the theoretical model geometry of the source and sink as well as the streamlines (Eq. 3.4) and velocity contours (Eq. 3.5) for a doublet with a dipole moment \(25 \times 10^{-6}\), similar to that of experiments.

One way doublet flow could occur on the surface of a liquid layer is if both the sink and source singularities are realized. A source could be realized by simply heating a point on the fluid surface, as was shown in the previous chapter. The sink, on the other hand, could occur from two possible means. The first is by mass loss via evaporation. A local evaporative mass flux acts as a drain, removing fluid from the surface and thus pulling in fluid from the surrounding regions. The second possibility is evaporative cooling. As the evaporating water undergoes phase transition, a relatively large amount of heat is absorbed due to the high latent heat of evaporation of water, resulting in a negative heat flux on the water surface [Car92],
\[ Q_{\text{EVAP}} = -J_{\text{EVAP}}L_V \quad (3.7) \]
given in W/m\(^2\). \(J_{\text{EVAP}}\) is the evaporative mass flux (J/m\(^2\)-s), and \(L_V\) is the latent heat of vaporization (J/kg). This localized cooling, through the Marangoni effect, also causes fluid to flow radially inward.

In thin layers of water, which has a high latent heat (\(L_V = 2.44 \times 10^6\) J/kg), the evaporative cooling effect is often dominant over the mass flux in forming sink flow [Hu03]. This is demonstrated in two numeric simulations of localized evaporation in a 20 µm thick layer of water, conducted in FLUENT (results not shown). In the first simulation, the latent heat is assumed to be zero, so that only the mass flux determines the

**Figure 3.3:** Theoretical doublet model. (a) Schematic of doublet geometry illustrating a sink to the left of the origin and a source to the right of the origin. Velocity is calculated at an observation point P. (b) Streamlines of a doublet with dipole moment \(25 \times 10^{-6}\), plotted using Eq. 3.4. (c) Contours of x velocity for the same doublet, plotted using Eq. 3.5.
flow. Assuming a 20 µm square area with a 7 g/m²/s evaporation rate, velocities are generally < 10 µm/s. In the second simulation, where latent heat and Marangoni effects are included, the velocities are 3 orders of magnitude larger. The simulation, therefore, suggests that the fluidic sink is more likely to be a result of the Marangoni effect rather than simply mass loss.

We now develop a model for localized evaporation. The evaporation at a liquid-gas interface is given by [Car92, Hu05]:

\[ J_{EVAP} = -D \nabla C_v \]  

(3.8)

where \( J_{EVAP} \) is the evaporative mass flux, \( D \) is the diffusion coefficient of water vapor in air, and \( \nabla C_v \) is the water vapor gradient perpendicular to the liquid surface. It should be noted that at the liquid surface, the water vapor concentration is always equal to the saturation vapor concentration, which depends on fluid temperature. The gradient in concentration at the fluid surface is what determines the evaporation rate.

A thermal probe suspended above the liquid surface can cause high evaporation rates in one of two possible mechanisms. It is well known that, at ambient temperatures, many materials are covered with a thin water film [Car92] often < 100 nm thick. Thermal and AFM probes are no different; however, studies have shown that when a thermal probe tip is heated, it rejects the formation of water meniscus [Lef05]. In a simplified model, it is assumed that the water concentration on the heated probe tip is zero; therefore, the vapor concentration is also zero at the probe tip. As mentioned earlier, at the surface of a liquid layer, the vapor concentration is equal to the saturation vapor concentration [Hu03]. Thus, placing the tip in proximity to the liquid surface forces a sharp concentration gradient
\[ \nabla C_v = (C_{v_{\text{probe}}} - C_{v_{\text{surface}}}) / g = -C_{v_{\text{SAT}}} / g \quad (3.11) \]

where \( g \) is the space between the probe tip and the substrate. Assuming a gap of 15 \( \mu \text{m} \) and a saturation vapor concentration 22.8 g/m\(^3\) (room temperature), the evaporation rate is 40 g/m\(^2\)/s, roughly 20 times higher than the first model. In this case, the corresponding heat flux is \( \sim 10^5 \) W/m\(^2\), which is approximately the heat flux required to demonstrate doublet flow in simulations.

A second mechanism is also proposed; however the theoretical evaporation rates are lower. The basis for this mechanism is the sharp temperature gradient that exists between the probe and the liquid surface, as was shown in chapter 2 (see Fig. 2.4). The steep thermal gradient in the air is due to the relatively low thermal conductivity of air compared to the liquid. The ideal gas law states that the concentration of the vapor \( C_v \) is inversely proportional to its temperature \( T \). The density gradient with respect to temperature can be found as follows:

\[ C_v = \frac{P_v \cdot MW_v}{RT} \Rightarrow \frac{\partial C_v}{\partial T} = -\frac{P_v \cdot MW_v}{RT^2} \quad (3.9) \]

For water, the vapor pressure \( P_v \) is the saturation vapor pressure at room temperature, 3168 Pa. The molecular weight \( MW_v \) of water is 18 g/mol, and \( R \) is the gas constant. \( T \) is assumed to be the ambient temperature 300K, since simulations show that the liquid temperature rises only slightly.

In the presence of a vertical thermal gradient in the \( z \) direction, the corresponding density gradient can be found using the chain rule:

\[ \nabla C_v = \frac{\partial C_v}{\partial z} = \frac{\partial C_v}{\partial T} \frac{\partial T}{\partial z} \quad (3.10) \]
Typical values for the vertical thermal gradient ranges from 0.1-1 degrees/μm. Thus, taking the values given above and a vapor diffusion coefficient of $D = 2.1 \times 10^{-6} \text{ m}^2/\text{s}$, the range of evaporation rates is 2 g/m$^2$/s. The corresponding negative surface heat flux due to evaporative cooling is -4858 W/m$^2$. According to simulations, this value is 1 order of magnitude lower than what was is required to produce millimeter per second flow rates as observed in experiments.

Computational fluid dynamics (CFD) simulations of the source sink model show that a thermal dipole on a fluid surface can drive doublet flow through the Marangoni effect. Simulations were conducted in Fluent 6.0 (Fluent Corp.) using a 3 dimensional model of a water layer with dimensions 1 mm X 1 mm X 50 μm. No probe was included in this simulation. To form a doublet resulting from a thermal source/sink, a 2 dimensional heat flux profile was applied to the free surface of the water layer. This profile consisted of a positive and negative Gaussian heat fluxes separated by a distance of 20 μm. The magnitude of the negative heat flux was $-10^5 \text{ W/m}^2$, and the amplitude of the source was required to be set 20% less than the sink in order to obtain a symmetric velocity profile. Marangoni stresses are enabled on the free surface, and all remaining model boundaries are given an isothermal, no slip condition.

The results are shown in Fig. 3.4. The applied heat flux profile is shown in Fig. 3.4a. Fig. 3.4b shows the velocity vectors, illustrating doublet flow occurring at the free surface of the fluid layer. As predicted, flow is directed away from the hot point and towards the cold point. The contours of $x$ velocity (Fig. 3.4c) are given for comparison to the theoretical model. Velocities approach 5 mm/s to the left of the sink, and reach a very high speed of 60 mm/s flow occurs between the source and sink. This phenomenon
Figure 3.4: Simulation results of a doublet caused by a thermal dipole on the liquid surface. (a) Contours of the heat flux supplied to the surface of a 50 µm thick layer of water. The cold spot is on the left, hot spot on the right. Separation is 20 µm. (b) Velocity vectors, showing 5 mm/s flow to the left of the sink. (c) Contours of velocity in the +x direction.

was not observed in experiments.

The 3 dimensional thermal simulation shown earlier in Chapter 2 (Fig. 2.5) postulates how the interaction of the probe could result in doublet flow. Placing the cantilever close to the water surface results in an asymmetric heat flux supplied by the probe to the liquid. The cantilever temperature is highest at the tip, and decays linearly along its length; this pattern is reflected in the heat flux contours on the fluid surface. It is thought that localized evaporation occurs near the cantilever tip, and the remainder of the cantilever heats the adjacent liquid surface. In this way, a sink may be formed at the left end of the cantilever, while a source may be formed immediately to its right.
It is interesting to note that at room temperature (in ambient laboratory conditions) doublet flows occur in water, but not in oils. This fact supports some of the evaporation theories outlined above. In oil or other non-volatile media, the localized heating from the probe can create the hot point necessary for toroidal flows; however, the lack of evaporation precludes the fluidic sink required for doublet flow. By contrast, in water, both hot and cold points can be realized, and therefore doublet flow can occur.

4. EXPERIMENTAL CHARACTERIZATION

Fig. 3.5 shows the doublet flow resulting from a thermal probe suspended above the surface of a thin water layer. Deionized water was spread on a glass slide to the desired depths, typically 50-100 µm. Polystyrene beads (diameter 3 µm-10 µm, Polysciences) were immersed in the water to serve as tracer particles. The time–sequence

![Figure 3.5: High-speed doublet flow is illustrated in 4 sequential micrographs taken at 1/30 second intervals. Polystyrene beads are used to visualize the flow.](image)
micrographs, taken at 1/30 second intervals with a high speed CCD camera, show the movement of the tracers in a high speed, symmetric doublet flow. The maximum horizontal velocity, measured just to the left of the probe tip, was found to be ~5 mm/s. The streamlines and velocities are similar to the analytical model shown in Fig. 3.3, which assumed the source and sink have a separation $2a = 10 \mu m$ and have a strength $m = 5 \times 10^{-6}$. Based on this, the approximate dipole moment of the experimentally measured doublet is about the same as the simulation, or $25 \times 10^{-6}$. Streamlines are also similar to simulations shown in Fig. 3.4.

In order to confirm that the doublet flow is in fact thermally driven, the flow and rotational velocities were characterized as a function of input power (Fig. 3.6). The

![Figure 3.6: Control of flow velocities. (a,b) Peak linear flow velocity as a function of (a) input power, and (b) air gap. (c) Rotation rate in the eddies, as a function of air gap. (d) Flow velocity vs air gap repeated for three different ambient liquid temperatures. Experimental conditions are shown. The lines in (a) are a linear fit, and the lines in (b,c) are a fit to $1/x^2$.](image)

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cantilever was held at a fixed angle and air gap above the liquid surface, and the input power was ramped from 0-32 mW. Particle velocities scale approximately linearly, increasing 90 µm/sec for every 1 mW applied. Since it is known that tip temperature increases linearly with input power [Li03], these results indicate that the flow is proportional to tip temperature. It is thought that increasing the probe temperature proportionally increases the evaporation rate which drives the sink, as well as the local heating driving the source. Marangoni flows scale linearly with temperature gradient. In theory, doublet flow velocities scale linearly with the dipole moment, thus experiments show that the dipole moment can be proportionally controlled through the input power.

Also shown is the dependence of flow velocities on the probe-liquid separation (Fig. 3.5b,c). Reduction of the air gap permits more efficient heat transfer, also resulting in increased velocities. A probe was biased at a fixed input power and lowered at 10 µm intervals until it came into contact with the liquid. Fig. 3.6 shows that with a 15 mW input power, particle velocities of nearly 5000 µm/sec are achieved at air gaps of < 10 µm, along with rotational velocities of 1200 rpm in the adjacent vortices. Particle velocities decrease as 1/x^2 with increasing air gap, indicating that heat transmission through the gap is inversely proportional to the gap thickness. Both temperature control and air gap provide a means to control doublet velocities.

The dependence of flow velocities on liquid temperature (Fig 3.6d) provides further evidence supporting thermally driven flow. In this experiment, the glass slide below the water sample was biased at 13, 27, and 41 °C using a circulating heating/cooling plate. At each temperature, particle velocities were measured as a function of air gap while holding the probe at constant power and angle. Trends of faster
velocities with smaller air gaps hold true as before, but it can also be seen that higher liquid temperatures shift the entire trend upward. For example, at a \(~10\ \mu m\) air gap, the particle velocity at 13 °C is only 165 \(\mu m/sec\), compared to nearly 900 \(\mu m/sec\) at 41 °C. Increased liquid temperature, therefore, enhances the speed of doublet flow. Overall, particle velocities in this experiment were slower than the results shown in Fig 3.5b due to lower input powers and the fact that a thinner probe (R01) was used, both of which reduce the surface heat flux.

An unusual feature of the doublet flow is that its orientation can be reversed. For example, a probe (R02) suspended at a 15° angle with respect to the liquid plane results in doublet flow from left to right; however, when the probe angle is doubled to 30° (while keeping all other parameters constant), the direction of flow is reversed, and the location of the adjacent vortices shifts to the left as shown in Fig. 3.7. According this geometrical shift, it is believed that the fluidic sink does not move, but the location of the source shifts from below the cantilever to a region beyond the edge of the probe. This would

![Probe: R02, Power: 15 mW, Gap: \sim 15 \mu m](image)

**Figure 3.7**: Flow reversal. The direction of the flow can be reversed by changing the angle of the heater. For example, using probe R02 at a 15° tilt, 15 mW input power, and a \sim 15 \mu m air gap, the doublet flows left to right, and the rotation in the vortices is counter-clockwise (left). Increasing the angle to 30° while keeping all other parameters constant reverses the direction of the flow and rotation and shifts the location of the vortices to the left of the cantilever (right).
effectively switch the orientation and cause the shift to the left. This theory is still somewhat uncertain, but we can conclude, however, that the geometry of the heat source plays a significant role in the orientation of the doublet pattern.

Complex flow patterns can be formed by forming arrays of doublets using multiple thermal sources. In order to predict the theoretical flow pattern which would arise from multiple doublets, the stream equations for each doublet may be added up by

![Figure 3.8](image)

**Figure 3.8:** Uniform flow generated with a linear array of doublets. (a) Theoretical streamlines of flow generated by an array of 8 doublets with 85 µm spacing obtained by summing the respective stream functions. (b) Linear flow generation using an 8-probe array, numbered 1-8 from the top down. The array was placed ~15-20 µm above the liquid surface, held at a 15° tilt, and biased with a total power of 92 mW. Probes 1 and 4 were nonfunctional. Trajectories for 3 particles are marked with a square, triangle, and circle on micrographs taken at 3 second intervals.
applying the principle of superposition. For example, the flow pattern generated by a linear array of 8 doublets with 85 µm spacing is shown in Fig. 3.8a. This particular geometry was chosen to model the structure of the multiprobe array. The flow pattern, which resembles a uniform flow channel, was confirmed in experiments. An array of 8 thermal probes [Bas05A] was biased at 2.3V, dissipating 92 mW total power in six probes (probes 1 and 4 were nonfunctional). The resulting flow pattern has a linear flow region with adjacent rotational regions as predicted by simulations (Fig. 3.8b).

Deviations from uniform flow observed in several regions, such as the trajectory marked with a triangle, can be attributed to the difference in air gap between the various probes in the array in addition to the fact that two probes were not operational. The noticeably smaller velocities (190 µm/sec) compared to single probes may be attributed to the reduced temperatures of the heaters in the multiprobe array. These results illustrate that flow is highly dependent on the geometry of the heat transmitted to the liquid surface. Therefore, it is possible to obtain custom flow patterns by arranging the heat sources in various configurations.

Subsurface particle flow, visualized by focusing the microscope at the bottom of an 80 µm thick layer of water, differs significantly from the doublet flow patterns observed at the surface. Particles flow radially inward over time, converging on a point directly below the tip of the cantilever. Once at this point, the particles are accelerated upwards towards the surface of the liquid layer (Fig. 3.9). The column of vertically-directed current is likely due to the fluidic source, which pulls in water below the surface, and outward and accelerates it outward on the surface as shown in Chapter 2. A similar behavior was observed in the CFD simulations (data not shown); however, further
modeling and experimentation is needed to clarify the mechanism driving the surface and subsurface flow patterns observed.

5. SUMMARY

This chapter has demonstrated surface doublets, a unique flow pattern which occurs only in films of water when driven by a thermal probe. The supporting theory suggests that a doublet can be generated by a fluidic source and sink in close proximity. The latter can be caused by localized evaporation, due to the sharp concentration gradient between the probe tip and the liquid surface. The orientation of the source and sink is
determined by the geometry and attack angle of the probe, suggesting that the
temperature gradient along the probe plays a significant role in generating doublet flow.
CHAPTER 4:  
A PROGRAMMABLE ARRAY FOR CONTACT-FREE MANIPULATION OF FLOATING DROPLETS BY MODULATION OF SURFACE TENSION

One of the fundamental limitations of present programmable microdroplet actuation systems is that they rely on the droplet’s interactions with a solid surface. Such an approach leads to surface adsorption resulting in device contamination and sample loss. This chapter presents a contactless droplet manipulation system which relies on thermally generated Marangoni flows. Programmable, two dimensional control of microdroplets suspended in an oil film is achieved using a 128-pixel heater array suspended 100-500 µm above the oil layer. The heaters create surface temperature perturbations, resulting in local Marangoni flows which can move droplets in either a push or pull mode. Programmed movement is achieved by the sequential activation of the heaters, with digital control circuitry and a graphical interface providing addressable control of each heater. Droplets with diameters 300-1000 µm can be manipulated and merged at speeds up to 140 µm/s. Several system level issues are discussed: surface temperature elevation can be reduced from 25°C to <2.5°C by using fluids with low thermal conductivity; thermal crosstalk and thermal time constants can be improved by 20% and 80%, respectively, by using a heat sink; evaporation rates can be reduced by almost two orders of magnitude by using a two layer oil medium; and the choice of an
appropriate carrier fluid can achieve fluid velocities over 17,000 µm/s and reduces power consumption to 30 mW/heater at moderate flow velocities. Microfabrication provides added opportunities for power reduction and efficiency due to the favorable scaling of Marangoni flows. The system provides a contactless platform for parallel droplet-based assays.

1. INTRODUCTION

   Digital microfluidic systems use microdroplets in an immiscible phase to encapsulate reagents and to serve as reaction containers. Precise, user-defined chemical reactions may be achieved by transporting and merging droplets containing the appropriate samples and reagents [Son03A]. Compared to the traditional microfluidic systems where samples are flowed through microchannels, digital microfluidics provides an elegant approach to high throughput assays, offering inherent encapsulation, low reagent consumption, and fast reaction times.

   Programmable fluidic processors (PFPs) refer to systems which can dynamically control the movement of droplets [Gas04, Sri04]. Droplets are manipulated in real time on a 2-dimensional space using methods such as electrowetting-on-dielectric (EWOD) [Cho03], optoelectrowetting [Chi03], dielectrophoresis (DEP) [Gas04], and magnetic fields [Rid03]. As described in Chapter 2, all of these approaches, require a substrate patterned with electrodes or coils, and the increased cost may not be suitable for a disposable device.

   A more important concern is that these approaches allow contact between the droplet and the substrate. Any degree of contact or wetting between a liquid sample and the substrate can result in surface adsorption. Proteins and other biomolecules readily
adsorb to hydrophobic surfaces like Teflon and PDMS as a result of hydrophobic interactions [Yoo03, Sia03, Son03A]. In the traditional continuous flow devices, the adsorption of proteins and cellular debris leads not only to contamination, but also causes channel blockages [McC03]. In general, surface adsorption raises concerns for device contamination, sample loss, and in most cases, makes device reuse impossible.

The problem of surface adsorption remains a concern with existing droplet manipulation technologies because many of the current techniques rely on surface interaction with the droplet. For example, EWOD applies voltages to a two-dimensional grid of Teflon-coated electrodes to dynamically control surface energies. Due to its high hydrophobicity, Teflon is particularly susceptible to adsorption. It has been suggested that if silicone oil is used as the encapsulating medium, the droplet may be separated from the Teflon surface by a thin film of oil [Sri04]; however, the effectiveness of the technique depends significantly on the interfacial tension between the oil and the protein concentration in the droplet. Protein adsorption can also render hydrophobic surfaces hydrophilic, which interferes with EWOD and other surface based actuation techniques [Sri04, Yoo03].

The best way to avoid surface adsorption is to keep the droplets away from any walls or the solid substrate; however, there are presently no droplet manipulation techniques which can avoid all surface contact. This chapter discusses a contactless, programmable system for actuating droplets in which suspended droplets are manipulated using Marangoni flows. Chapter 2 described the use of Marangoni flows of various geometries for droplet mixing and control [Bas05B, Bas05C, Bas07A, Bas07B, Bas08A]; however, these flows were generated using fixed heat source geometries and were not
Figure 4.1: A complete system for programmable, non-contact droplet actuation based on Marangoni flows, including a 128-pixel array of resistive heaters suspended above the oil layer, control circuitry, and a graphical user interface.

programmable. If a programmable system is desired, dynamic control of the heat flux is needed. This chapter discusses a way to trap and manipulate droplets using a two dimensional grid of heaters suspended above a fluid layer (Fig. 4.1). Programmed two dimensional control of Marangoni flows and droplet movement is achieved through the sequential activation of individual heaters.

The chapter begins with a theoretical and simulation model of the push and pull mode of actuation in section 2. Section 3 gives a brief discussion of system level design and issues. Experimental results are presented in section 4, and a critical assessment of the approach is given in section 5. Section 6 gives conclusions.
2. THEORETICAL

As noted earlier, local Marangoni flows can be initiated on the free surface of a liquid layer by placing a millimeter-scale heat source above the surface and in close proximity to it (i.e. typically < 1 mm away). Heat transfer through the air gap increases the surface temperature of liquid directly beneath the heat source, and creates a radial temperature gradient. In most liquids, the surface tension is inversely related to temperature, thus the temperature gradient creates an inverse gradient in surface tension. The resulting shear stress boundary condition is the same as described in Chapter 2. It is repeated here for convenience [Bas07B, Hig00]:

\[
\tau_s = \mu \frac{d\tilde{u}_s}{dN} = -\sigma_T \nabla T_s \quad (4.1)
\]

where \( \mu \) is the liquid viscosity, \( \sigma_T \) is the surface tension temperature coefficient, \( \nabla T_s \) is the surface temperature gradient, \( \tilde{u}_s \) is the tangential surface velocity, and is \( \vec{N} \) is the surface normal vector. The resulting surface Marangoni flow \( \tilde{u}_s \) is directed away from the heat source, and it is accompanied by subsurface flows oriented in the opposite direction.

With ‘static’ heat sources it is difficult to achieve linear movement of droplets unless either 1) the heat source is scanned laterally (which requires an XY scanning stage), or 2) a tapered heat source geometry is used. More importantly, with static heat sources it is not practical to actuate multiple droplets simultaneously.

This chapter discusses a versatile approach which utilizes a 2 dimensional array of heaters to achieve dynamically-controlled movement. Each heater, when activated, creates a local temperature gradient on the liquid surface which generates surface and
subsurface Marangoni flows (see simulation, Fig. 4.2). The heater can either push a droplet away with its surface flow (push mode actuation), or pull a droplet toward it via its subsurface flows (pull mode actuation) depending on the size of the droplet and the depth of the flow region. Droplet movement can therefore be programmably controlled through the sequential activation of individual heaters.

**Push and Pull Mode Actuation.** Droplets can be actuated in either a push or pull mode. The mechanisms of both are shown using a computational fluid dynamics simulation (FLUENT 6.0, Fluent Corp). The software uses an iterative procedure to compute the coupled thermal-fluid problem. In each iteration, it solves the energy equation, equates the surface temperature gradient to a shear stress using Eq 4.1, and then calculates the flow in the liquid layer using the continuity and Navier Stokes equations. The process repeats until all sets of equations converge.

Fig. 4.2 shows the temperature contours and flow vectors generated by a resistive heater held 100 µm above a layer of mineral oil. The heater consists of a 800 µm-wide surface mount resistor mounted on a printed circuit board (PCB). The problem is modeled in a two dimensional axisymmetric geometry. A heat generation boundary condition is applied to the surface of the chip in order to tune the temperature of the heat source to the desired temperature. The thermal conductivity of the alumina chip and PCB are 27.6 and 0.3 W/m-K, respectively, and the liquid is assumed to be DC-550 silicone oil (Dow Corning, Midland MI) with the properties listed in Table 4.1. In the example shown in Fig. 4.2a, the chip temperature increase is 100 °C, the liquid temperature increase is 24 °C. The outward temperature gradient results in a flow velocity of 1.6 mm/s.
Simulations over a range of heat input conditions (Fig. 4.2b) demonstrate that the flow velocity is proportional to the temperature gradient imposed on the liquid surface (which, in turn, is proportional to the heater temperature). Also, to maximize the thermal coupling requires that the heater be placed as close to the surface as possible. Due to the low thermal conductivity of air, the thermal coupling between the heater and the liquid is
strongly dependent on the separation gap. For example, at a 100 µm separation, the temperature increase at the liquid surface (i.e. the coupling ratio) is 23% of the increase.

**Figure 4.3:** 3-D CFD simulation of push and pull mode actuation on a Φ=200µm and Φ=800µm droplet, respectively. The droplet volumes were meshed as an immiscible spherical volume within the fluid layer. (a) Flow vectors showing pressure and viscous forces on a 200 µm droplet offset 1 mm from the center of the heat source. (b) Moment force on an 800 µm droplet offset 500 µm from the center of the heat source. (c) A trapped 800 µm droplet after it has been pulled into the center of the heat source.
in the heat source. At a 500 μm gap, the coupling ratio falls to 10%. A small gap is also important in maintaining a sharp lateral temperature gradient, which translates directly into flow velocity. In this regard, the approach of having suspended heaters benefits from the low thermal conductivity of air. Were the heaters embedded in the liquid, the relatively high thermal conductivity would preclude the formation of sharp gradients, limiting the velocity of Marangoni flow. Furthermore, it would cause undesirable heating in the bulk fluid.

The interaction of droplets with the flow is shown in Fig. 4.3. This set of simulations includes a 3-dimensional fluid layer with an embedded spherical volume to represent the immiscible droplet. A surface heat flux of 50 mW/mm² is added to a 1 mm square region in the fluid layer to model the local heating. Assuming the properties of DC-550 fluid, this results in a recirculating flow (maximum surface flow velocity of 6 mm/s) which applies pressure and viscous forces to a droplet. The lateral pressure and viscous forces on the droplet were calculated by integrating the respective forces along the surface area of the droplet, and moment forces were integrated in a similar manner using the droplet centroid as the moment axis.

Qualitative results (Fig. 4.3a) demonstrate the operation of the push and pull modes. A droplet < 200 μm in diameter gets pushed away from the active heater by surface flows (push mode). In this case, the center of mass is near the fluid surface, which is dominated by outward-directed surface Marangoni flows. A combination of pressure and viscous forces (Fig. 4.3a) push the droplet outward. In contrast, a larger droplet (for example, Φ=800 μm) tends to get pulled into the active heater. In this case,
the droplet’s center of mass is deeper below the surface, where the inward-directed subsurface flows are more significant.

It is also interesting to note that the opposing surface flows and subsurface flow create a *moment* force on the droplet, which causes the droplet to rotate as observed in experiments (Fig. 4.3b). It is believed that the spinning motion along with the buoyant force helps to ‘roll’ the droplet towards the center. Once at the center, the droplet is stabilized by the balanced forces on either end of the droplet (Fig. 4.3b). A quantitative comparison of the moment and lateral forces on a large ($\Phi=800 \, \mu m$) and small ($\Phi=200 \, \mu m$) droplet is shown in Fig. 4.4.

![Figure 4.4](image)

**Figure 4.4:** Simulated results. Forces acting on a $\Phi=800 \, \mu m$ and $\Phi=200 \, \mu m$ droplet, taken from the simulation in Fig. 4.3. (a) Moment force on the two sizes of droplets at various lateral offset distances from the center of the heat source. (b) Lateral pressure force (directed away from the heat source) for the two droplets, also at various distances from the heat source.
µm) droplet is shown in Fig. 4.4. The large droplet clearly experiences a large moment force at a distance of 500 µm from the center, while the small droplet experiences virtually no moment force. With regards to pressure forces, the small droplet experiences a small force directed away from the heat source. The large droplet, by contrast, experiences a larger force (up to 0.6 µN) in the reverse direction.

**Choice of fluid.** Several aspects must be considered when choosing an appropriate carrier fluid in which to create the Marangoni flows. First, the fluid must be hydrophobic so that the water droplets within it are immiscible, and biocompatible to allow for biomolecular reagents. Second, the fluid should have a higher density than water, which ensures that the droplets float on top of the oil layer and make no contact with the glass substrate below. Third, the liquid should be of low volatility to prevent undesired evaporation.

Most importantly, the oil should be chosen to maximize coupling between flow speed and applied heat. To represent this criteria, a figure of merit may be used. Equation 1 implies that, under a given temperature gradient, the Marangoni flow velocity is proportional to $\sigma_T/\mu$. The gradient itself is inversely proportional to the thermal conductivity $\kappa$. Therefore, the figure of merit for a given fluid is

$$FOM = -\frac{\sigma_T}{\mu \kappa}$$

(4.2)

This figure of merit gives an indication of the Marangoni flow velocity in various liquids under identical heating conditions. Temperature coefficients of surface tension are seldom provided for most chemicals, but they can be estimated using the Eötvös law

$$\sigma_T = k_T/V_m^{2/3}$$

where $V_m$ is the molar volume of the liquid and $k_T = 2.1 \times 10^{-7}$ J/K for
virtually all liquids [Pil51, Eöt86]. They can also be experimentally measured using the DeNouy ring method [Nou19] or drop shape analysis [Son96]. Over the range of carrier fluids examined in this work, the surface tension coefficients do not vary by more than 2-5X.

Thermal conductivity data for fluids is typically available. Aqueous films, for example, have relatively high thermal conductance (0.6 W/m-K) which limits the formation of sharp surface temperature gradients. In contrast, typical mineral and silicone oils have conductivity only 20% that of water, and also have fairly low vapor pressures to reduce evaporative effects. Fluorinated organic liquids function as suitable carrier fluids for Marangoni flows, due primarily to their low thermal conductivity on the order of 0.06 W/m-K; however, their evaporation rates are somewhat higher than mineral oils.

Given the diverse set of requirements, three oils are chosen. The first is mineral oil (USP, Rite Aid Pharmacy), a biocompatible, transparent oil often used in biochemical assays for reagent encapsulation (for example, to encapsulate embryos, and high throughput assays). This oil is less dense than water, so it is used primarily for characterization and for particle experiments. The second group of fluids includes high density silicone oils which allow the droplets to float on the surface. These include DC-550 and DC-704 fluids (Dow Corning). The last fluid is Fluorinert™ (FC-3283, 3M Corp.), a fully fluorinated dielectric fluid which has low very thermal conductivity, low miscibility to water, and high density. FC-3283 has often been used as a carrier fluid in microdroplet systems [Son03A]. Material properties for each of these fluids are given in the Table 4.1.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Units</th>
<th>Mineral Oil USP</th>
<th>DC550 Silicone oil</th>
<th>DC704 Silicone oil</th>
<th>FC-3283 dielectric liquid</th>
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</thead>
<tbody>
<tr>
<td>Density</td>
<td>ρ</td>
<td>kg/m³</td>
<td>886</td>
<td>1070</td>
<td>1070</td>
<td>1820</td>
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<td>Surface tension coefficient</td>
<td>σₜ</td>
<td>mN/m·K</td>
<td>-0.220</td>
<td>-0.069**</td>
<td>-0.036 *</td>
<td>-0.410 *</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>κ</td>
<td>W/m·K</td>
<td>0.12</td>
<td>0.1463</td>
<td>0.16 **</td>
<td>0.066</td>
</tr>
<tr>
<td>Viscosity</td>
<td>μ</td>
<td>kg/m·s</td>
<td>0.026</td>
<td>0.134</td>
<td>0.042</td>
<td>0.0014</td>
</tr>
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<td>Figure of Merit</td>
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<td></td>
<td>7.1x10⁻²</td>
<td>3.5x10⁻³</td>
<td>5.3x10⁻⁵</td>
<td>4.44</td>
</tr>
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<td>[Sam99A, Ber03]</td>
<td>[DC98A, Van97]</td>
<td>[DC98B, Ber03]</td>
<td>[3M01]</td>
</tr>
</tbody>
</table>

**Table 4.1:** Material properties for 3 liquids used in generating Marangoni flows. Values marked with a * are calculated using the Eötvös law, and those marked with ** are estimated from similar fluids.
3. SYSTEM DESIGN AND EXPERIMENTAL SETUP

The 16x8 heater array used to initiate Marangoni flow consists of #0603 surface-mount resistors (1x0.8x0.3 mm) placed at 1.9 mm pitch on a two sided printed circuit board (PCB) (Fig. 4.5). The 100 Ω resistors are electrically connected via thru-holes to the opposite side of the PCB which provides routing, cable connectors, and a heat sink (Fig. 4.6). This two sided design allows the resistors to be placed near the liquid without obstruction. Commercial foundries are used to manufacture PCBs (Sunstone Circuits, Mulino OR) and to assemble the resistors in a solder reflow process (Screaming Circuits, Canby OR).

Figure 4.5: Micrograph of heater array
A separate PCB houses the addressing logic and driver circuitry, with electrical interconnect provided by two 64 pin ribbon cables. A bank of power DMOS transistors, one for each resistor, can provide a maximum of 250 mA current, or 6.25 W power, to each heater. The range of power actually used is much smaller, typically <1.3 W. The heater power is set globally for all the resistors by adjusting the voltage $V_R$, with typical voltages ranging from 8-12V.

Heaters are individually set and reset via a graphical interface and control circuitry (Fig. 4.7). D-latches are used to maintain the on/off state of each heater. A PCMCIA digital I/O card (NI-6062E, National Instruments) connected to a laptop computer can toggle the state of each heater using a 4 line serial protocol. The *shift register clock* signal synchronizes the loading of a command sent via *serial input* line into the shift register. During the first 8 clock cycles, the shift register is loaded with 7 bits indicating the address of the resistor, and 1 bit signifying an on or off state. Once the command register is loaded, the *latching signal* is pulsed low to commit the state of the heater. Therefore, each set/reset command takes < 10 cycles. With a 1 MHz clock signal, the refresh rate is $10^5$ heaters/second; therefore, a 128 pixel array can be set in <5

**Figure 4.6:** Experimental setup, showing the heater array above a glass slide on which the liquid samples are placed.
ms. The *asynchronous reset* line, when pulsed low, resets all the heaters in the array to an off state.

A user interface, written using Labview software (National Instruments, Austin TX), allows the user to graphically toggle individual heaters in the array, and also provides a batch-mode interface in which commands can be read from a text file.

Fig. 4.6 shows the experimental setup. The carrier oil is loaded in a reservoir with

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**Figure 4.7:** (a) Schematic of logic and driver electronics. There are 128 joule heaters, and one D-latch and driver for each (these elements are represented by the <128>). The remaining components are shared. The forward slash indicates a multi-line bus, and the number beneath indicates the number of lines on the bus. (b) Timing diagram, showing the serial input scheme for toggling heaters on and off.
a transparent bottom so that droplet motion can be imaged from below with a CCD camera. The reservoir is placed on a glass platform which is actively cooled with a circulating refrigerated water bath (Neslab Endocal). The purpose of the water bath is to prevent heating of the bulk fluid which can reduce the surface temperature gradients needed for Marangoni flow and also can cause loss of function or other damage to thermally-sensitive samples such as enzymes and other biomolecules. Droplet samples are deposited directly into the oil using a micropipette. The heater array, with the chip resistors facing the oil sample, is then lowered to within 100 µm above the liquid surface using a micromanipulator. Parallel alignment and leveling of the glass platform and the heater array board must be done prior to the experiment to help ensure that heater-liquid separation is uniform through the entire array. (A bubble alignment tool is useful for this purpose.)

4. EXPERIMENTAL RESULTS

Test Setup and Characterization. Individual heaters were first characterized for thermal efficiency by using a fine gauge thermocouple (CHAL-0005, Omega Engineering) to measure the temperature as a function of input power. The typical thermal isolation of each heater is ≈120 K/W, and a maximum temperature of 175°C (Fig. 4.8a) can be achieved without burnout. The parasitic temperature on an adjacent
**Figure 4.8:** Experimental results. (a) Temperature of an active heater ($T_H$) vs. input power. Also shown is the temperature increase one pixel away ($T_1$), two pixels away ($T_2$), and on the substrate 2 cm away ($T_S$). (b) Flow velocity (25 µm pollen) and droplet velocity ($\Phi=300$ µm droplet) vs. input power and heater temperature. This experiment used Dow Corning 550 silicone oil and a heater-liquid gap of ~100 µm. (c) Comparison of maximum flow velocities obtained with 4 fluids including mineral oil, Dow Corning 550 and 704 silicone oils, and Fluorinert FC-3283 dielectric liquid. Calculated figures of merit for each fluid are given in the figure.
heater 1.9 mm away is 80°C, roughly 38% of the increase on the first heater. On a heater two pixels away, the parasitic increase is 30%. The bulk substrate remains close to room temperature. The thermal crosstalk can be improved by 10-20% by adding attaching a passive fin-type heat sink to the opposite side of the PCB. The presence of the heat sink reduces lateral heat conduction by maintaining an isothermal base opposite the heaters. The consequence is that it reduces the temperature of the active heater by 15-30%.

The thermal time constant of the heater was measured by switching the heater on or off and monitoring its real-time temperature with the microthermocouple connected to a data acquisition card (NI-6062E, National Instruments). The thermal mass and time constant of the microthermocouple (0.05 s) is much smaller than the heaters and therefore does not impact the measurement. Without a heat sink, the probe temperature can be switched between room temperature and 175°C with 1.13 W applied to the heater. The 10-90% heating time constant is 41 s, and the cooling time constant is 83 s. The 2x difference between the heating and cooling times is due primarily to the lack of an efficient cooling mechanism. Adding the passive fin-type heat sink provides remarkable improvement in both thermal time constants – the heating time constant is reduced 80% to 6.8 s, and the cooling time constant is reduced 95% to 5.6 s. In most cases, the speed improvement is well worth the reduction in temperature.

Bulk fluid temperatures are kept in check by the circulating water bath. For example, if a 1.3 W heater is placed 200 µm above the liquid surface, it eventually brings the liquid temperature to > 200°C if the liquid is not actively cooled. By contrast, with the cold water bath set to 10°C, the liquid temperature can be maintained under 37°C. In
practice, the bath temperatures were set to 15-20°C because the increased liquid viscosity at low temperatures results in slower Marangoni flow velocities.

Surface flow velocities were measured by tracking the movement of particles in video clips with frame rates of 30 f/s. Surface flow velocities up to 1700 µm/s can be achieved in DC-550 silicone oil and in mineral oil using 1.3W power and using 25 µm pollen particles as flow tracers (Fig. 4.8b). As predicted from simulations, the flow velocity is proportional to the power supplied by the heater. Simulations also predict that the surface temperature change for achieving 1700 µm/s flow velocity is 24 °C (assuming a 100 µm gap), while the experimentally measured temperature change is between 20-30 °C. Thus, the simulations and experiments show good agreement. The flow velocity of droplets is small compared to pollen due to their larger mass and drag (Fig. 4.8b). A Φ=300 µm droplet, for example, moves at speeds up to 73 µm/s in the push-mode.

**Selecting the Fluid Medium.** In order to obtain faster flow velocities and lower temperature perturbation, alternative fluids can be used (Fig. 4.8c). One alternative is Dow Corning 704 fluid, a high density silicone oil with lower viscosity than DC-550, which helps it attain 2X greater flow velocity than the DC-550 fluid. As mentioned earlier, fluorinated liquids such as Fluorinert™ have properties well suited for Marangoni flow generation. Within this family of liquids, FC-3283 is chosen for its low thermal conductivity and low viscosity. The maximum flow velocity measured with FC-3283 is 17 mm/s, approximately 10x greater than mineral oil and DC-550 fluid at the same power level. Moreover, moderate flow velocities (2.4 mm/s) can be achieved with only 29 mW of input power to the heater, only 1/40th of the power required to achieve the same velocity in DC-550. Thus, FC-3283 is an appropriate carrier fluid for obtaining flows
with low power and low temperature elevation to the fluid. The consequence is its higher evaporation rate compared to the silicone oils.

Another challenge with using FC-3283 is the instability of droplets within the hydrophobic fluid. Aqueous droplets deposited at the center of the fluid reservoir tend to move to the edges of the reservoir where they eventually attach to the reservoir wall. The stabilization problem is solved by adding the fluorous surfactant 1H,1H,2H,2H-perfluoro-1-octanol (PFO, Sigma-Aldrich) to the FC-3283 carrier fluid in a 1:10 v/v ratio. The surfactant molecules, which are soluble only in the fluorous phase, assemble at aqueous-fluorous interface and stabilize the droplet [Roa05]. No droplet instability is observed after adding the surfactant.

**Push and Pull Mode of Actuation of Droplets.** Droplets immersed in the carrier fluid can be actuated in either the push or pull mode. The push-mode of actuation occurs in single layers of DC-550 fluid when the center of gravity of the droplet is near the surface. This can be ensured in one of two ways: 1) by pipetting the droplets above the surface of the liquid so that the droplet floats on top of the surface, or 2) by using small droplets (Φ<200 µm). In this mode, surface Marangoni flows drive the droplet away from the active heaters (Fig. 4.9). Multi-heater configurations may be used to direct a droplet in the desired direction. For example, two adjacent heaters activated next to a droplet push the droplet in a straight line, while a right-angle turn can be accomplished using three heaters in an L-shape. Arbitrary movements at speeds up to 200 µm/s can be generated with sequential activation of such configurations.
In the pull mode of actuation, droplets are pulled toward the active heater by the subsurface flows. To obtain the pull-mode, it is important that the center of gravity of the droplet is several hundred microns below the surface. To do this, 1) the droplet must be dispensed while the pipette tip is submerged beneath the carrier fluid to ensure the droplet is not floating above the carrier, and 2) the droplet diameter must be larger than 500 \( \mu m \). Experimental results demonstrate that droplets can be transported at speeds up to 140 \( \mu m/s \) in the pull mode. Compared to the push mode, this mode offers a more scalable control because only activated pixel is necessary to trap a droplet. The sequential

Figure 4.9: Push-mode actuation. (a) Surface Marangoni flows create a droplet force \( (F_D) \) oriented away from the active heater. (b-e) A \( \Phi=900 \mu m \) floating droplet is moved along a square path by activating multi-heater configurations sequentially. Active heaters are shaded. \( P_H=1 \) W/heater, \( \text{gap} \approx 400 \mu m \), and the fluid is DC-550 silicone oil.
activation of adjacent pixels can translate the droplet along a virtual 2-dimensional grid. As a consequence, the pull mode enables the simultaneous actuation and merging of multiple droplets (Fig. 4.10). Droplet merging, as indicated earlier, is one of the essential functions for droplet-based assays. In this platform, typical droplet volumes are on the order of 100’s of nL.

Due to elevated temperatures, droplet evaporation can present a challenge. For example, 1 mm droplets floating on top of the oil layer tend to evaporate in <2 min. To address this issue, two miscible oils were combined, one with density less than water (mineral oil), and the other with density greater than water (DC-550 Fluid). In the two
layer system, aqueous droplets remain suspended between the two layers, unexposed to the both air and the glass surface below. The suspended droplets are manipulated using subsurface flows (pull mode actuation). In the multilayer oil system, evaporation times are on the order of hours, 100x higher than the single layer system where the droplet is exposed (Fig. 4.11), allowing for assays which require longer incubation times. An added benefit is that it also reduces the overall temperature elevation in the droplet, since the majority of the temperature perturbation occurs at the liquid surface. The depth of each of the fluid layer plays an important role in the two layer system. In order to achieve pull mode actuation in a two layer system, two conditions must be satisfied: 1) the diameter of the droplet should be between 500 and 1000 µm, and 2) the thickness of the mineral oil layer should be > ½ the thickness of the DC-550 layer. If either of these two conditions is not satisfied, the droplet will be moved in the ‘push’ mode or no actuation will occur at all.

**Figure 4.11**: Preventing droplet evaporation. Measurements showing variation of droplet size over time (log scale) for a Φ=650 µm droplet in single and double layer oil system. The single layer oil system consists of DC-550 silicone oil, and two layer system consists of DC-550 and mineral oil.
5. DISCUSSION

The design issues with Marangoni flow-based droplet manipulation include 1) coupling efficiency (maintaining fast droplet flow velocities while minimizing the temperature perturbation and power consumption), and 2) scaling to small length scales.

**Efficiency.** The efficiency of the Marangoni technique depends on the system providing a sharp temperature gradient at the fluid interface, and then translating that gradient into a high speed flow. To do this, one must first choose a liquid with a high figure of merit, as demonstrated in Fig. 4.8c. Fluorinated carrier fluids, with their relatively high surface tension coefficient and low thermal conductivity, make them a good carrier fluid for Marangoni flows, giving 10X higher velocities at the same power, and 1/40th the power consumption at the same velocity; however, one must be careful to use appropriate surfactants to stabilize the droplets. Furthermore, they are immiscible to many oils, which makes it difficult to create multilayer oil systems for evaporation reduction.

Efficiency can also be improved by placing the heat sources as close to the surface as possible. This not only increases the coupling ratio ($\Delta T_{\text{Surface}}/\Delta T_{\text{Heater}}$), but it also increases the lateral temperature gradient necessary for producing flow. With an array of heaters, the challenge is to keep the heater-liquid separation small and equal for all of the heaters in the array. The present approach can obtain gaps as low as 100-200 $\mu$m; but this can be improved by using an optical feedback system or a more precise leveling system.

Finally, one can increase the efficiency of the heater itself. Microfabricated devices with thermally insulative materials and small cross sections provide high
efficiency and fast time constants. For example, a polyimide cantilever with an integrated heater can achieve 100 °C temperature while dissipating only 10 mW of applied power [Li03]. Such heaters would reduce power consumption by up to 2 orders of magnitude, which is important especially if the number and density of the heaters in the array is scaled up.

In order to allow localized control, thermal crosstalk between heaters is a concern. Present experiments show a crosstalk ratio of 35% between adjacent pixels (Fig. 4.8) due to parasitic heat flow through the PCB board. As shown earlier, a 10-20% improvement can be obtained by placing a heat sink on the backside of the array. Additional improvements can be made by a number of means, such as using a thinner PCB board, removing portions of the board to decrease conduction, or by placing a thermally insulative barrier between the heaters and the PCB (while maintaining electrical conductivity).

An alternative is to use a lithographic process to batch fabricate high density arrays. Thin film devices with small cross sections would improve the thermal isolation between heaters and reduce power consumption. Integrated addressing electronics, such as those found in commercial active pixel bolometers [Co98], could also be leveraged to provide electronic control of large arrays. However, one of the challenges of a microfabricated array is placing the heaters on relief structures in order to facilitate local heat transfer to the liquid surface. An alignment process to ensure an equal gap between the heaters and the liquid surface is especially important for all the elements in the array.

Scaling Study. In general, as a surface dependent phenomena, the Marangoni effect scales favorably to small length scales when compared to body-force driven
mechanisms. Therefore, the possibility of downscaling this technique merits a theoretical study. To do this, simulation models spanning a large range of length scales were created and analyzed for trends. Both the size of the heater and the gap between the heater and liquid are varied over two orders of magnitude: the heater radius is scaled from 1 mm to 10 µm, and gap is correspondingly scaled from 500 µm down to 5 µm, while keeping a constant ratio between the radius and gap. The liquid depth remains constant in order to avoid the increased viscous effects in thin layers. In all of the simulations, the heater power is tuned in order to get a liquid temperature change of 10 K. This is done to compare the effects of downscaling. Fig. 4.12a shows an important result: the temperature gradient increases at smaller length scales. Eq. 4.1 suggests that this should result in faster flow velocities however, it is also necessary to consider the increasing viscous forces when scaling down. Fig. 4.12b shows that the flow reversal depth becomes smaller at the smaller length scales. In other words, the cross-sectional thickness of the flow region decreases with the size of the heat source. This increases the viscous forces between the flow layers, resulting in smaller surface velocities. As a result, the Marangoni flow velocities begin to fall at length scales below 100 µm. As such, it is concluded that 100 µm heaters are a suitable size scale for maximum efficiency. It should also be noted that the range of droplets which can be trapped depends on the flow reversal depth. At the present length scale (2 mm), droplets with diameter 400-1000 µm (30-500 nL) can be efficiently actuated in the pull mode. At a 100 µm length scale, with a flow reversal depth is 80 µm, it is estimated that 80-100 µm-diameter (~200-500 pL) can be efficiently actuated in the pull mode. Overall, scaling to
smaller dimensions results in 1) decreased power consumption, 2) increased velocity (as long as the length scale is > 100 µm), and 3) the ability to manipulate smaller droplets.

Miniaturization and scaling to large arrays is not without challenges. For example, miniaturization may offer lower power consumption per heater, but the larger number of heaters in a high density device would increase the overall system power consumption. Thermal crosstalk between heaters must also be considered when placing heaters at a smaller pitch. Issues such as these will require the careful design of a high

**Figure 4.12:** Scaling study (simulation). (a) The surface temperature gradient and corresponding shear stress is plotted at various length scales. In all cases, the absolute temperature change on the liquid surface (ΔTₜ) is 10°C. (b) Flow velocity (blue diamond) and flow reversal depth (red square) plotted for each length scale, under the same condition of ΔTₜ = 10°C.
density array and appropriate heat sinking in order to deliver efficient, isolated temperature perturbations on the liquid surface.

6. SUMMARY

This chapter explores how Marangoni flows can be deliberately controlled by creating dynamic temperature profiles on the liquid surface. A contactless, programmable droplet manipulation system which utilizes the Marangoni effect is described. The distinguishing feature of the approach is that the droplets are suspended can be controlled without contact with solid surfaces, thus preventing contamination. Furthermore, there is no complexity in the substrate. Programmable manipulation and merging of multiple droplets was demonstrated using a system with 128 heaters and a software controlled interface. One of the challenges of the technique, particularly for biomedical assays, is the temperature change required in the liquid. Initial experiments using common silicone oils have shown a 20-30K elevation. However, it was shown that the temperature change and power consumption can be reduced by a factor of 40 by using a fluid such as Fluorinert which has a high figure of merit. Scaling to smaller sizes does not increase flow speeds; however, it does reduce power consumption, and allows digital control of smaller droplets. The future direction of this work is to develop a microfabricated heater array which will achieve these performance improvements, and also allow high throughput manipulation of a larger number of droplets.
CHAPTER 5:  
CONCLUSIONS

This thesis has explored the use of the Marangoni effect for fluidic actuation at small length scales. By placing small heat sources < 1 mm above a thin liquid layer, sharp temperature gradients can be generated at the fluid surface. Due to the inverse relation between surface tension and temperature, shear stresses are generated at the surface, inducing local flow which travels away from the heat source on the surface, and in the opposite direction below the surface. At submillimeter length scales, it is possible to efficiently generate flow due to the sharp temperature gradients and the strong viscous coupling at low Reynold’s numbers. With regards to microfluidic systems, the advantage of this approach is that flow can be generated without contact to the liquid sample (avoiding contamination), and without any components in the fluidic substrate (reducing cost).

By engineering the shape of the heat source, it is possible to generate unique Marangoni flow patterns which can manipulate microdroplets suspended in an oil layer. As discussed in Chapter 2, the point, linear, annular, and tapered geometries generate flows emulating (respectively) droplet collectors, channels, traps, and pumps. The advantage of these virtual components is that they have no physical structures, and can accomplish their function entirely by virtue of the interaction of the flows with the droplets. Many of these flows have a size selectivity as well, allowing for the possibility
of droplet sorting. The simulation model described in this thesis illustrates each of these flows and gives an understanding of the mechanism of operation.

The doublet pattern (described in chapter 3) is another type of surface flow which is achieved by placing a thermal probe near a layer of water. This type of flow achieves 5 mm/s linear velocity and 1300 rpm rotational velocity, making it useful as an in-plane mixer. It is notable that doublet flow occurs in water, a liquid of high thermal conductivity, but this flow pattern cannot be achieved in oil. The toroidal flows, on the other hand, occur in oil but not in water. Doublet flow is consistent with a thermal dipole on the fluid surface, and the directionality of the temperature gradient across the probe appears to play a major role in this type of flow pattern.

Programmable actuation of droplets using Marangoni flows can be achieved with dynamic heat fluxes rather than static heat fluxes. Chapter 4 discusses a two-dimensional actuation system which consists of an array of heaters suspended above the surface. The system can push and pull droplets (depending on their size) from place to place through the sequential activation of heaters, rather than by scanning the heaters themselves. The pull mode proves to be more useful than the push mode because only one active heater is needed per droplet. Using the pull mode, the simultaneous control and merging of two 400 nL droplets is demonstrated at speeds up to 200 µm/s. Power consumption required for flow generation can be as little as 30 mW/heater if a low thermal conductivity fluid such as Fluorinert is used, and up to 1 W/heater for other fluids such as mineral oil. Thermal crosstalk is 35% in the present implementation, which uses surface mount resistors on a printed circuit board at a 2 mm pitch. Both power consumption and
crosstalk can be greatly improved by using microfabrication to make thermally isolated heat sources which consume less power.

In general, the efficiency of this technique relies on having a thermally efficient heat source and maximizing the coupling between temperature gradient and flow. Microfabricated heat sources, with thermal efficiency of 10,000 K/W, offer nearly two orders of magnitude lower power compared to surface mount resistors. For example, Marangoni flows of 1,700 µm/s can be achieved in mineral oil with <20 mW power if a microfabricated thermal probe is used. By combining the probe heat source with an optimized carrier fluid, power consumption could potentially be reduced to < 1 mW.

Maximizing the surface temperature gradient requires that 1) the heat sources are suspended in air above the sample (rather than embedded within the fluid), and 2) a low thermal conductivity liquid is used. In order to maximize the coupling between temperature gradient and flow, the liquid should have a high temperature coefficient of surface tension and low viscosity. As mentioned above, flow velocities can be improved nearly 10 fold, and required powers can be reduced by >10 fold if a low thermal conductivity, low viscosity carrier fluid such as Fluorinert is used. In addition to these material properties, the liquid must be of high density (to allow droplets to float) and should have low volatility.

Other issues to consider include liquid heating and evaporation. Long-term heating of the fluid can be prevented by actively cooling the liquid with a water bath underneath the liquid sample. However, it is important to note that the viscosity of the fluid will increase at lower temperatures, and this will decrease flow speeds. Evaporation of droplets can be reduced by two orders of magnitude by using a multilayer oil system.
An immediate possibility for future work is reducing the size of the heater array by one order of magnitude using microfabrication. As shown in Chapter 4, this will give benefits in terms of power consumption, because thin film heaters have better power efficiency and thermal isolation as mentioned above. A smaller flow cell also allows manipulation of smaller droplets, which reduces reagent consumption and allows for higher density processing. Downscaling, does, however, have some implications. While it is possible to generate sharper temperature gradients and large shear stress at smaller length scales, absolute flow velocities do not improve at length scales below 100 µm due to the increased viscous resistance in small convection cells. Therefore, downscaling beyond one order of magnitude may not be beneficial.

A second area of future work is the general design and application of Marangoni flows. Chapter 2 demonstrated the fundamental flow patterns resulting from point, line, annular, and tapered heat sources, but it is clear that more complex flow patterns can generated by using other geometries, or combinations of them. Future research could design complex flow patterns and investigate their application to droplet manipulation and other areas. This thesis provides a simulation model which can be used to design these flow patterns from a hypothesized heat flux. Such flow patterns could prove to be useful in the trapping, filtering, separating, or manipulation of particles for various assay protocols. Physical heat sources of various shapes can be used to supply the heat flux; or, alternatively, optical approaches may offer a more scalable approach. Infrared lasers have been shown to generate Marangoni flows [Sur04], and these methods could be extended to design Marangoni flows for droplet manipulation and other applications.
A third area of work is investigating the interaction of Marangoni flows with textured or patterned substrates. This is interesting from a physical perspective, as well as practical applications. For example, it is possible that a complementary set of droplet manipulation techniques may be achieved through the combination of Marangoni flows and patterned substrates.

One excellent example of the practical use of Marangoni flows was shown by Hu and Larson [Hu06]. It is well known that in an evaporating droplet, particles eventually deposit themselves along the outer circumference. The phenomenon is responsible for the familiar ring shaped stains from dried coffee or paint. Marangoni flows can be used to direct the particles towards the center of the droplet, so that particles concentrate and deposit themselves in the center of the droplet footprint. Hu and Larson demonstrated this in organic liquids; but for aqueous liquids, a controlled method using probes could be equally useful. Direct deposition of particles by droplet is important for the manufacturing of high-density DNA microarrays, gene spotting, and several other biomedical techniques [Hu06].

Overall, the Marangoni effect could have other potential applications in microfluidics. As mentioned by Feynman, and as demonstrated by this thesis, it is an example of a physical phenomenon that becomes significant at the small scale. Due to the prevalence of surface tension driven phenomena in nature, particularly at small length scales, the ability to control Marangoni flows, whether by temperature gradients or other means, could allow opportunities to interact with Feynman’s “marvelous biological systems”.

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APPENDIX 1: STRUCTURE, FABRICATION, AND OPERATION OF THERMAL PROBES

Scanning thermal probes microfabricated devices are similar to AFM probes, composed of a thin film cantilever with a sharp tip (< 100 nm diameter) at the far end. What distinguishes the thermal probe from the AFM probe are the integrated heating and temperature sensing elements, which control and simultaneously monitor the tip temperature. Thermal probes were originally designed for scanning thermal microscopy [Wil86, Maj99], but later have been adapted for thermomechanical data storage [Mam92, Chu97, Bin99, Vet00, Lee02, Kin02], thermal dip pen lithography [She04], microcalorimetry [Li00], thermomechanical analysis and spectroscopy [Ham00, Pol01],

Fig. A1.1: The microfabricated thermal probe which is used to generate flow. (a) Schematic showing a polyimide cantilever overhanging the edge of a silicon substrate. The integrated heater is located on the cantilever just beneath the tip. The shading along the length of the cantilever indicates the thermal gradient that is present when the heater is powered. (b) Scanning electron micrograph of the fabricated thermal probe, with inset showing the pyramidal tip (from [Li03]).
and nanosampling [Rea02].

The microfabricated thermal probes are chosen as heat sources because they have a number of desirable features including fast heating times, low power consumption, and most relevant to this dissertation, highly localized heating capabilities [Bas04B, Li03]. When placed near a liquid surface, they provide a local heat flux profile critical to both toroidal and doublet flows. This chapter describes the probe structure, characteristics, and simulations describing its interaction with the nearby fluid surface.

1. STRUCTURE

The microfabricated thermal probe is shown in Fig. A1.1. Its structure consists of a thin film cantilever similar to an atomic force microscopy probe, except that it contains an integrated joule heater near the tip [Li03]. The cantilever, composed of thermally insulative polyimide, extends from the edge of a silicon chip. A pyramidal tip points downward at the distal end. An embedded thin film of gold forms the tip and as well as

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**Fig. A1.2**: Scanning electron micrograph of a microfabricated thermal probe array [McN04B] used to generate flow. The inset shows the scanning tip with approximately 100 nm tip diameter.
the adjacent heater. The heater, which contributes the majority of the probe’s resistance, also functions as a thermistor to monitor tip temperature. Electrical interconnect is provided by thicker metal lines extending the length of the cantilever. The length and width of the cantilever as well as probe resistance vary depending on the type of probe. In this work, two probe geometries are used: R01 (length 360 µm, width 42 µm, resistance 25-40 Ω), and R02 (length 360 µm, width 120 µm, resistance 20-35 Ω). In addition to the single probes, an 8-probe array reported in [McN04B] is also used to drive multipole flow patterns. These probes are spaced 85 µm apart along a common shank and can be heated individually.

2. FABRICATION

Both single probes and multiprobe arrays are fabricated in the same low-cost, 7-
mask process (Fig. A1.3) [McN04B]. A pyramidal mold for the tip structure is first created by anisotropic etching of a (100) silicon wafer, masked by a thin layer of silicon nitride (Fig. A1.3a). To obtain a sharper tip, the silicon is optionally thermally oxidized at 950 °C. A layer of sacrificial titanium is deposited below the cantilever structures and inside the mold to facilitate the release of the cantilevers (Fig. A1.3b). The cantilever itself is formed of two polyimide layers (HD Microsystems P2610) with two metal layers embedded within. The first layer of polyimide is etched from the mold region (Fig. A1.3c). A thin metal layer consisting of Cr/Au (100 Å / 1200 Å) is then deposited in the mold to form both the metal tip and the resistor. A second, thicker metal layer consisting of Cr/Au/Cr (100 Å / 2500 Å / 100 Å) forms low-resistance electrical interconnects from the bonding pads to the probe tip (Fig. A1.3d). The top layer of polyimide is used to insulate the metal and provide strength to the probe tip (Fig. A1.3e). Thick gold patterns are deposited on top of the second polyimide layer for thermo-compression bonding (Fig. A1.3f). The cantilevers are released by etching the sacrificial titanium layer in dilute hydrofluoric acid. Finally, the probe shank is manually flipped over (for which the mechanical flexibility of the probe shank is essential), and a thermo-compression bond is formed at a temperature of 200 °C (Fig. A1.3g), resulting in a probe shank overhanging the edge of the wafer die with the probe tip pointed away from the substrate.

3. OPERATIONAL CHARACTERISTICS

A temperature characterization of the probe under 3 different conditions is shown in Fig A1.4. In order to estimate the tip temperature, the probe is connected in a Wheatstone bridge configuration which supplies electrical power and simultaneously
measures the probe resistance. The tip temperature is calculated by multiplying the fractional change in resistance by the probe temperature coefficient or resistance (TCR), which is calibrated in a separate procedure not detailed here.

Fig. A1.4 shows that the tip temperature increases linearly with respect to the applied electrical power, and due to the low thermal conductivity of the polyimide shank, can reach nearly 250 °C with less than 20 mW input power. The silicon chip, which has a much larger mass and high thermal conductivity, acts as a heat sink and remains at room temperature. As a result, a sharp temperature gradient is formed along the length of the cantilever. It is also notable that the probe temperatures depend greatly on the environment. For example, at the same input power, the temperature of a probe near a solid surface is 20 % less than when it suspended in air, and 90% less when submerged in water. This is because the probe easily transfers heat to its surroundings, which is a key

![Fig. A1.4: Temperature characterization of the R01 type thermal probe. The three lines show the fractional resistance change of probe R01 as the input power was ramped under various conditions. The probe is connected to a wheatstone bridge circuit which supplies measures the probe resistance. tip temperature is calculated by the resistance change](image)

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capability for fluidic actuation.

The probe can be also heated and cooled very quickly, due to its small thermal mass. Fig. A1.5 shows a plot of the cooling time constant. To obtain this curve, the probe was again connected to a wheatstone bridge to monitor its resistance. The bridge supply voltage, set initially to 1 V, was stepped down from 0.1 V, and the bridge output voltage was monitored. The temporal decay in voltage reflects the decrease in probe resistance as it cools. The cooling time constant for most of the probes is around 5 ms, and the heating time constant (not shown) is about 30% smaller. Fast thermal cycling is beneficial to nearly all applications of the thermal probe, but specifically in terms of fluid actuation, it implies that the probe can quickly initiate fluid flow, and may be able to drive pulsatile or oscillating flows.

Fig. A1.5: Thermal time constant of a typical probe. The x axis shows time in 1 ms divisions, and the y axis shows the voltage, with 50 mV/division. The time constant is approximately 5 ms.
APPENDIX 2:
INTERACTION OF PROBES WITH THE LIQUID SURFACE

When placed near the surface of a thin liquid layer, the probes locally heat the surface, providing the basis for both toroidal and doublet flow patterns. Due to their bolometer-like design, the probes are not perfectly symmetric point heat sources; however, this asymmetry proves to be particularly important in the orientation of doublet flows. To study the interaction of the probes with the liquid surface, a 3 dimensional model of the probe was constructed in Fluent 6.0 (Fluent Corp.), a finite element software for computational fluid dynamics and heat transfer. In this model (Fig. A2.1), a 360 µm

![Fig. A2.1](image)

**Fig. A2.1:** Schematic of simulation model, showing the thermal probe is held in air above a liquid film. Symmetry is used to simplify the simulation so that only ½ of the model is solved. All perpendicular field gradients are set to null at the mirror symmetry plane.
x 120 µm x 3 µm probe is suspended in air 15 µm above the liquid surface, and is angled 15° with respect to surface plane. A 7 µm-tall pyramidal tip protrudes from the far end of the cantilever, and the other end is attached to a silicon substrate. The fluid layer, either water or oil, has dimensions 1 mm x 1 mm x 100 µm. Volumetric heat generation rates, ranging 10^{10}-10^{12} W/m³, are applied in a region just above the tip to model the heater. The substrate, meanwhile, is fixed at the ambient temperature of 300 K. Symmetry is used to simplify the simulation so that only half the model is solved, and all perpendicular field gradients are set to zero at the symmetry plane. The lateral, upper, and lower boundaries of the fluid and the local air are set to ambient temperature, and no slip boundary conditions are applied to each. Air convection is included in the model; however, it plays a negligible effect on simulation results because heat conduction appears to be the dominant heat transfer mechanism.

Fig. A2.2: Typical heat flux and temperature profiles on the liquid surface driven by the probe. (left) A composite image showing qualitative heat flux and temperature contours on the fluid surface. (right) This graph shows the parallel cross section of a heat flux profile supplied by the thermal probe to the liquid surface under typical conditions. An approximate Gaussian fit is shown.
Typical simulation results are shown in Fig. A2.2. The graded heat flux which appears on the fluid surface reflects the temperature gradient along the probe shank. The temperature contours appear circular far away from the probe, resembling a point heat source, but directly beneath the probe they also reflect the cantilever profile. The resemblance to a point heat source is relevant to toroidal flows (Chapter 2), while the asymmetry appears to be important to the orientation of doublet flows (Chapter 3). Typical heat fluxes supplied by the probe are in the range of $10^3$-$10^4$ W/m$^2$, depending on the input power to the probe, and the separation between the probe and liquid surface.

A side view of the temperature contours (Fig. A2.3) gives insight to the efficiency of heat transfer. A sharp temperature gradient forms between the probe and the liquid surface. Due to the low thermal conductivity of air, however, the heat transfer between the probe and surface is not efficient. The temperature increase at the liquid surface is typically $< 3\%$ of the temperature elevation of the probe tip. Furthermore, of the several milliwatts of heat generated in the thermal probe, less than 1\% travels by conduction to

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**Fig. A2.3**: Side view of simulation results, showing qualitative temperature contours in the probe and the liquid surface. The magnitude of temperature depends on the input power applied; however the contour shapes remain the same.
the fluid surface. The remaining heat is likely lost to the probe shank or ambient surroundings. The transferred heat energy also decays quickly (\(\sim 1/d^2\)) as the probe moves away from the surface. For highest efficiency, therefore, it is important that the probe be placed as close to the liquid surface as possible. To accomplish this, the probe is usually mounted on a digitized micromanipulator in order to place it close to the liquid.

The shape of the heat flux profile also depends on the attack angle of the cantilever. Fig. A2.4 shows the changing heat flux profile for angles of 15, 30, and 45 degrees. Increasing the attack angle results in more symmetry, as expected. When generating doublet flows, the probe angle proves to play a key role in determining which way the doublet is oriented.

**Fig. A2.4:** Heat flux supplied to the liquid surface from the probe at various attack angles. (simulation). The probe is suspended 15 \(\mu\)m above the liquid surface and is angled at 15, 30, and 45 degrees with respect the liquid plane. These contours are qualitative; their magnitudes scale with the amount of input power. The line across the middle of the heat flux plots represents the probe axis.
This appendix introduces a scanning probe lithography (SPL) technique in which ultracompliant thermal probes are used in the selective thermo-chemical patterning of the commercially available photoresist. The micromachined single probe and multiprobe arrays include a thin film metal resistive heater and sensor sandwiched between two layers of polyimide. The low spring constant (<0.1 N/m) and high thermal isolation provided by the polyimide shank is suitable for contact mode scanning across soft resists without force feedback control. The probes provide what is effectively a spatially localized post exposure bake which crosslinks the photoresist in the desired pattern, rendering it insoluble in developer. For 450 nm-1400 nm thick AZ5214E (Clariant Corp.), line and dot features with sizes of 450 nm-1800 nm can be printed using probe powers of 13.5-18 mW, and durations of 1-60 s per pixel. Variation of feature sizes with process parameters is described.

1. INTRODUCTION

With the increasing costs of photomasks – often in excess of 1 million dollars for state of the art CMOS processes – alternatives to optical lithography have been sought,
particularly for low-volume manufacturing and prototyping in conventional processes. As a maskless lithography approach, scanning probe lithography (SPL) offers the promise of high spatial resolution (which is not limited by the diffraction of light) and for low volume applications, substantial savings in mask and equipment costs.

It is interesting to note that as methods in scanning probe microscopy developed over the last few decades, most have been applied to lithography [Nyf97]. Years after the invention of the scanning tunneling microscope (STM) in the 1960’s, scanning probe lithography was born when an STM was later used to selectively oxidize hydrogen terminated Si surfaces with nanometer resolution [Dag90]. Likewise, the atomic force microscope (AFM), originally used for mapping topography, was later modified to ‘scratch’ thin metals [Sil93] and soft polymers [Soh95], again with resolution in the 10’s of nanometers. The near field scanning optical microscope (NSOM), which employs scanning probe tips to focus light, was used directly to optically pattern photoresist with resolutions beyond the far-field diffraction limit [Smo95]. Several other lithographic techniques have grown out of AFM and STM technology, two of which are electrostatic [Lyu03] and dip-pen lithography [Pin99].

Scanning thermal microscopy (SThM), introduced in 1986, has also found complementary efforts in lithography, but nearly all are based on thermomechanical indentation, that is, the use of heat and pressure in submicron tips to etch pits into polymers with glass transition points. In early research efforts, heat was provided by an external laser pointed at a conventional AFM tip [Mam92], and later by thin film heaters embedded in the cantilever [Chu96]. Thermomechanical indentation has been pursued with interest in ultra high density data storage, the most notable device being the IBM
“millipede” [Vet00]. In this work, we demonstrate that scanning thermal probes can be applied towards lithography by thermally catalyzing a chemical reaction in a submicron region (Fig. A3.1) rather than by thermomechanical indentation. We have demonstrated this principle on the positive tone photoresist AZ5214E (Clariant Corp.) in a process similar to image reversal. The use of localized heat to pattern this resist has been previously explored by focusing semiconductor lasers [Kuw02]. Some potential advantages of the proposed method are that it is less prone to tip wear and produces less debris when compared to purely mechanical SPL techniques; however, it does require scanning over soft photoresist. An enabling device for this technique has been the ultracompliant probe technology reported previously by our group [Li03, McN04A], which minimizes damage to both the sample and the probe tip. Both single probes and 8 probe arrays are shown to provide thermo-chemical patterning of photoresist.

Fig. A3.1: Process flow for scanning thermal lithography of AZ5214E resist. (a) Flood exposure generates photoacids. (b) Spatially localized thermal cross-linking occurs under the heated probe tip (inset) as a result of the photoacids and elevated temperatures. (c) The insoluble cross-linked region remains after development in TMAH developer.
2. PROCESS AND DEVICE CONCEPTS

Several structural features of the ultracompliant probes (Fig. A3.2) make them well suited towards the lithography process, the most important of which is use of a thin film polyimide as the structural material for the cantilevers. The excellent thermal resistance of the polymer allows the probe tips to be heated to temperatures of nearly 300°C by embedded thin film heaters operating at <20 mW, while the low spring constant (~0.08 N/m for the single probe) allows for scanning over photoresists and other soft polymers in the absence of mechanical feedback without scratching the resist and with minimal wear to the tip. The elimination of force feedback is especially important when

![Image: Schematic of the micromachined single probe, and SEM of the 8-probe array surface micromachined from polyimide on a Si substrate. Thin film resistors integrated on the tip of the cantilevers allow the individual probes in the array to be heated independently of one another.](image-url)

**Fig A3.2:** (a) Schematic of the micromachined single probe, and (b) SEM of the 8-probe array surface micromachined from polyimide on a Si substrate. Thin film resistors integrated on the tip of the cantilevers allow the individual probes in the array to be heated independently of one another.
scaling to arrays of probes. If rigid cantilevers are used, tip height non-uniformity across
the array can result in significant variation in contact force when it is lowered to the
substrate, necessitating feedback control at the probe level to prevent excessive force in
any one tip. The low spring constant in the ultracompliant array passively accomplishes
the same function, thus eliminating the need for force feedback. An additional feature of
the array is that each probe has individual heater control which can allow for independent
patterning if desired.

Both single probes and multiprobe arrays are fabricated in the same low-cost
micromachining process in which a thin film metal bolometer is sandwiched between two
insulating layers of polyimide. The thin metal film, consisting of 300-1200Å Au between
two adhesion layers of 100Å Cr, is molded into an anisotropically wet-etched notch in the
Si substrate to form the scanning tip. Two lines extending outwards from the tip region
form the heating element. Electrical connection to the bolometer is provided by thicker
metal lines extending the length of the cantilever. The total resistance ranges from 20-
200 ohms depending on design and process parameters. The probe is then released from
the substrate, flipped out over the die edge, and held in place by a thermo-compression
bond between two thin films of Au.

With regard to the patterning of the sample by the probes, the photoresist
AZ5214E is one of the very few positive tone photoresists that can function as a negative
tone resist by a process called image reversal. Conventional image reversal begins with a
patterned UV exposure which generates photoacids in unmasked regions. A subsequent
post exposure bake (PEB) thermally activates a crosslinking reaction catalyzed by the
photoacids in the previously exposed regions [Gij86]. The crosslinked regions become
insoluble in alkali developer, and insensitive to any further UV processing. The substrate is then flood exposed to solubilize all non-crosslinked regions. Development in tetra-methyl ammonium hydroxide (TMAH) leaves a negative photoresist image.

3. EXPERIMENTAL RESULTS

Temperature calibration of the single probe is relatively straightforward because the fractional change in the probe resistance (\(\Delta R/R\)) is directly proportional to the increase in tip temperature (\(\Delta T\)) by a constant \(K\). The thin film heater accounts for the majority of the probe’s resistance and results in a linear relationship between the measured resistance and tip temperature. To determine the constant \(K\), the single probe cantilever was immersed in water and the current was ramped until bubble formation and rapid evaporation was observed. Water was found to boil at a 2.16% increase in probe resistance, and by correlating this to a 75ºC increase in tip temperature, \(K\) was found to be 288 ppm/ºC. Repeating the same experiment with isopropyl alcohol (boiling point 85ºC) resulted in a virtually identical figure. Using the above calibration, the tip temperature can be correlated to the measured resistance during probe operation. The probes can be heated to approximately 300ºC before high temperatures begin to damage the cantilever structures. It should be noted that the temperature vs. power relationship differs depending on the degree of thermal isolation from the surrounding environment. A probe operating in proximity or in contact with the substrate requires about 30% more power than when suspended in air due to the heat loss to the substrate. Nevertheless, the typical input powers needed to reach temperatures in excess of 250ºC while in contact was <20mW.
The scanning thermal lithography (Fig. A3.1) proposed for this effort is similar to
the conventional process, except that it involves patterning the post exposure bake instead
of the initial exposure. AZ5214E photoresist at full concentration was spun on Si wafers
to obtain a thickness of 1.4 µm, and diluted 50% with PGMEA solvent (Nano EBR,
Clariant Corp.) to obtain 450 nm thickness. Further dilution resulted in poor uniformity;
however, in general it is expected that thinner resists will permit smaller feature sizes to
be patterned (discussed later in this report). After softbaking, the resist was flood
exposed to generate photoacids globally. The heated thermal probes were then scanned
across the surface point-by-point, each point being heated anywhere between 1 and 60 s.
Regions under the probe tip crosslink and become alkali insoluble. The resist was
developed in diluted TMAH (0.21N) in order to maintain the highest contrast between
crosslinked and noncrosslinked regions [Spa85].

To fully crosslink AZ5214E requires temperatures of about 90°C, but it was found
that simply biasing the probe tip at this temperature was inadequate due to the thermal
contact resistance between the tip and the photoresist. Except where indicated, the single
probe was biased at 18 mW, corresponding to a tip temperature of 275°C. In addition, the
substrate was biased at 45°C using a hot plate in order to further reduce the amount of
heat that the probe needed to provide. Tests showed that when the contact force was
made excessively high by flexing the cantilever towards the substrate, the increased
pressure in combination with the high tip temperature resulted in thermomechanical
indentations penetrating all the way through the resist, and no thermal patterns were
observed after development. Conversely, weak contact forces resulted in poor thermal
contact, also resulting in no pattern formation. An intermediate contact force of about
480 nN was found to be successful. The advantage of using flexible probes is again noted here in that once the probe is biased at some contact force, that force does not change significantly over the sample topography, thereby increasing the uniformity of the patterned structures.

Using the process described above, submicron dots and lines were obtained, in some cases when the photoresist was partially developed, and in other cases when it was fully developed. It was found that dot sizes could be well controlled by the changing the

![Fig. A3.3](image)

**Fig. A3.3**: Dot sizes can be controlled by the heating times as well as heating power. (a) Reduction in size with shorter heating times using a probe biased at 18 mW on 450 nm resist. (b) Dot sizes vs. heating time for 18 mW and 13.5 mW power.
probe temperature as well as the heating times (Fig. A3.3). Using an 18 mW bias on 450 nm resist resulted in features that ranged from 400 nm-1800 nm as heating times were increased from 1-60 s. Reducing the power to 13.5 mW power resulted in the same feature sizes, but required longer heating times. The above results were found after partially developing the 450 nm photoresist. Features patterned at 18 mW for longer than 30 s remained after full development of both 1.4 µm and 450 nm resist (Fig. A3.4). Biassing at high powers and heating for longer times results in a higher degree of crosslinking because the crosslinking reaction is, in effect, both temperature and time dependent.

Feature sizes shrink with photoresist thickness due to the decreased lateral flow of heat. Two dimensional ANSYS heat flow models (Fig. A3.4a) qualitatively show that as the thickness of the resist is reduced below the diameter of the scanning tip, the cylindrical flow of heat results in features of approximately the same size as the tip. A thick resist permits the heat to spread laterally, increasing feature sizes. For example, using identical heating powers and times (18 mW, 30 s) on both 1.4 µm and 450 nm resist produced dot sizes of 590 nm and 450 nm after full development of the photoresist (Fig. A3.4b). The use of a thick resist also runs the risk of creating reentrant cross sectional profiles which can be undercut during development.

The 450 nm dot size was the minimum feature size obtained in fully developed dot patterns in our process using photoresist of approximately the same thickness. Further scaling down of features sizes for the purposes of lithography can be accomplished by using sharper tips and thinner resists, particularly those which are chemically amplified (chemical amplification can also help to reduce heating times and
The diameter of the scanning tips in the present design can be made as small as 50 nm using oxide sharpening [Lee00], and others have reported custom fabrication of thermal probes with tip sizes as small as 20 nm [Shi01].

Line patterns formed by heating successive pixels are shown in Fig. A3.5a. Line-widths of 500 nm were observed in partially developed resist at effective speeds of 200 nm/sec, while slower speeds of 10-20nm/sec were needed to retain the lines after full development. This is likely because a stronger degree of crosslinking was required to prevent undercutting of the resist. The torsional flexing of the compliant cantilever resulted in some line distortion (Fig. A3.5b), but this can be minimized by lifting the
probe between each pixel. The structure of the probe itself could also be modified to provide a stiff torsional spring constant while maintaining a low vertical spring constant.

The final experiment demonstrated the use of the multiprobe array to perform parallel lithography. The 8 probe array was used to write pixels at 5 µm pitch, and the patterns produced by two adjacent probes are shown in Fig. A3.5(c-d). Probe tips were lifted up between pixels, thereby reducing the line distortion; however, during the course of this experiment, external vibrations shifted some of the probes, resulting in double patterning in some areas. With the exception of this, the feature sizes are fairly uniform between probe tips. Although not shown in this experiment, the probes can also be operated at different powers, allowing the formation of independent patterns.

During the course of the experiments, reliability of the probes was found to be excellent in that all of the probes appeared to run many samples with no noticeable tip damage or deterioration in thermal performance. Longevity of scanning probe tips is an
important aspect to consider if they are to be used in a manufacturing process.

In conclusion, this effort has demonstrated that scanning thermal probes can be used, both singly and in parallel, in the thermo-chemical patterning of AZ5214E. While the resolution of this technique can be scaled down in a relatively straightforward manner, the lessons are: first, the throughput can be addressed to some degree by the use of multiprobe arrays; second, pixel sizes can be controlled by heating times and powers, and finally, the procedure is less costly in the sense that it does not require photomasks or optics, nor does it require a vacuum or UV filtered environment. Ultimately, the resolution and throughput of this technique are determined by the size of the tips, the number of probes that can be scanned in parallel, and the thickness and thermal sensitivity of the resist. In a broader sense, this work has shown that scanning thermal lithography can be used for patterning any thin film for semiconductor and biological applications or for triggering a chemical reaction at the surface of a material.
BIBLIOGRAPHY


