Fundamentals of Droplet Flow in Microfluidics

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Outline of Presentation

- Review of droplet actuation mechanisms
 - Thermocapillarity
 - SAW
 - Electrostatic
 - Pressure on the meniscus
 - Dielectrophoresis
 - Electrostatic pressure
 - Electrowetting
 - Other
- Electrowetting fundamentals
 - Architectural choices
 - Digital microfluidics
- The digital microfluidic options and examples
- Summary and conclusions



Background & Motivation



Promise of Biochips

Applications : Biotechnology (eg: high throughput screening , Diagnostics...)



Can a lab-on-a-chip be as versatile as the macro lab it replaces?







Why droplets?

- Concept of fluid boluses (droplets)
 - Bolus of fluid placed in a reaction tube
 - Add reagents
 - Separate and remove reaction products
- Bolus format typically requires automating human lab activity and lab protocols
- Bolus format was replaced with synchronous, continuous flow systems (Petersen, et al, 1998)
- Limited functionality in continuous flow systems
- Bolus (droplet) format has reemerged



Droplet-based Flow Review



- Thermocapillarity (Marangoni)
- Surface acoustic wave (SAW)
- Electrostatic
 - Pressure on the meniscus
 - <u>Electro- wetting</u>



Electrostatic pressure (conductive liquid)



Thermocapillarity

 Liquid droplet movement under asymmetric heating (A. Anton, S. M. Troian, JMEMS, vol.12, no.6, 2003)





Basics

- Local heating reduces surface tension, pulling droplet towards cooler surface
- Surface temperature manipulated by local heater strips
- Issues:
 - Slow transport 600µm/sec
 - Low voltage (2-3V), but high power
 - Surface contamination
 - No droplet steering, except by physical channels



SAW Actuation

 20MHz surface acoustic waves are generated from interdigitated transducer on piezoelectric substrate







SAW Droplet Transport

- Piezoelectric surface is hydrophilic
 - Droplet transport difficult
- Pattern hydrophobic tracks on piezoelectric substrate to predefine droplet transport areas
- Requires 0.7Watts of power!



See movies: http://www.iemn.univ-lille1.fr/sites_perso/microflu/saw.html



Electrostatic Droplet Flow

- Dielectrophoresis
 - Motion of polarizable particles (or cells) suspended in an electrolyte and subject to a non-uniform electric field.
 - DEP force balanced by viscous drag
- DEP advantages
 - No electrical contact with liquid –no electrolysis
 - ac or dc fields
 - Only requires polarizable liquids
 - Single-sided planar electrode array



Electrostatic Pressure on Droplet

(Washizu)







Fig. 3. Maxwell stress distribution around a droplet when one of the electrode arrays is excited (calculated by two-dimensional model).



Electrostatic Pressure



Fig. 3. Maxwell stress distribution around a droplet when one of the electrode arrays is excited (calculated by two-dimensional model).

- Largest actuation near contact line
- Best results with large contact angle
- Electrode pitch << drop diameter
- Spatial period of electrode voltage larger than drop diameter





Performance

- 400V rms
- Slow: 400µm/s
- Not developed further







Other Droplet Transport Methods

Engineering drops in microsystems



Two phase flows in microsystems may be used to produce well controlled drops, emulsions, with all sort of chemicals encapsulated in them



Surface Modification

SEM pictures of structured surfaces. All hydrophobic coated.





Variable Surface Roughness Actuator (He, et al)



Released: 114.6°

Actuated: 144.7°



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18

Electrowetting

- Electrowetting: the general idea
- What basic concepts aid in understanding electrowetting?
 - Surface tension
 - Capillarity
 - Contact angle
 - Contact angle hysteresis
- Electrocapillarity: changing contact angles at will
- The jump from electrocapillarity to electrowetting
- Understanding droplet transport



Electrowetting on Dielectric

- Droplet on a hydrophobic insulator spreads (or wets) with an electrical potential
- Effect mediated through charge storage at the interface
 - Electrical modulation of the solid-liquid interfacial tension
 - Rapid and reversible effect
 - Voltage dependence in Lippmann's eq.: $\gamma_{SL}(V) = \gamma_{SL}(0) \epsilon V^2/2d$





Electrowetting Actuation



ITO Electrodes







Contact Angle

Since $W_{SL} = \gamma_{LV} + \gamma_{SV} - \gamma_{SL}$

The *hydrophilicity* of a surface can be gauged by measuring the *contact angle* of a droplet of water on the surface. The balance of interfacial forces is described by *Young's Equation*:



$$\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL}$$

θ	Wettability
0	Complete
<90	Partial
>90	Non wetting



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 \implies W_{SL} = γ_{LV} (1+cos θ)

Basics

In measuring contact angles, you are creating and altering the free total surface of a drop:





Basics

In measuring contact angles, you are creating and altering the free total surface of a drop:





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24

Contact Angle

 In most cases a liquid placed on a solid will not wet it but remains as a drop having a definite angle of contact between the liquid and solid phases.



Fig. X-9. Zisman plots of the contact angles of various homologous series on Teflon; \bigcirc , RX; \ominus , alkylbenzenes; ϕ , *n*-alkanes; \bullet , dialkyl ethers; \Box , siloxanes; \triangle , miscellaneous polar liquids. (Data from Ref. 78.)



Electrocapillarity

Gabriel Lippman (1875)



- Hermann von Helmholtz (1821-1894)
 - Electric double layer formed when potential is applied across the interface between metal and conducting electrolyte



- C/A= $\epsilon_r \epsilon_o / \xi$







Liquid/Solid Capacitance

- Energy stored in capacitor:
 - $E = 1/2CV^2$
 - $= \frac{1}{2} \operatorname{A} \varepsilon_{\rm r} \varepsilon_{\rm o} V^2 / \xi$
 - Assume all energy is stored in the interface rather than in the interphase, then total energy/unit area required to create the new surface is
 - $\gamma_{SL} = \gamma_{SL}(max) \epsilon_r \epsilon_o (V-V^{zc})^2/2\xi$
 - Where $\gamma_{SL}(max)$ is surface tension corresponding to V=V^{ZC}
 - Lippman's equation shows how an applied voltage will alter the apparent surface tension at the liquid/solid interface.



Electrocapillarity vs. Electrowetting

- Major problem with electrocapillarity was electrolytic decomposition for V>300mV
- Berge (1993) introduced dielectric to separate liquid from metal
 - Became known as electrowetting on dielectric (EWOD)
 - Main difference is interface capacitance





<u>Electrocapillarity</u>

Electrowetting on Dielectric

Capacitance	10µF/cm ²	nF-pF/cm ²
Dielectric thickness	ξ ~1nm	d=1-10µm
Contact angle hysteresis	Moderate	Depends on dielectric
Applied voltage	$\Delta \theta = 40^{\circ}$ change at 0.8V	$\Delta \theta = 60^{\circ}$ change at 40V



Electrowetting Saturation

- $cos\theta(V) = cos\theta(0) + \epsilon_r \epsilon_o(V)^2/2d\gamma_{LG}$ predicts complete wetting (*i.e.*, $cos\theta=1$)
 - This condition has never been observed experimentally!
 - Contact angle saturation occurs at 30° for AC and 60-100° for DC experiments depending on system
 - Verheijen and Prins
 - Different physical mechanisms proposed: (see Mugele pp.722-725



Figure 4. (a) The capacitance between a 10 μ L liquid droplet and counter electrode as a function of applied dc potential. The insulator thickness is 10 μ m. We used a 700 Hz ac signal with 5 V amplitude and a sweep rate ~10 V/s. (b) The contact angle derived from the capacitance measurement. The contact-angle hysteresis is less than 2° in the range -240 < V < 240 V. For higher voltages, the contact angle saturates around 60°. The continuous line is according to eq 8, using $\theta_0 = 119^\circ$, $d = 10 \,\mu$ m, $\epsilon_r = 2.65$, and $\gamma_{\rm LV} = 72$ mN/m.



Contact Angle Hysteresis

• The contact angle measured for a liquid advancing across a surface is less than that of one receding from the surface

 This difference can be quite large, as much as 500 for water on mineral surfaces. This can be quite important in coating processes.

 Although not fully understood, contact line hysteresis is generally attributed to surface roughness, surface heterogeneity, solution imputities adsorbing on the surface, or swelling, rearrangement or alteration of the surface by the solvent.





Molecular Kinetic Theory of Wetting

- Dynamics of the wetting line depend on individual molecular displacements that occur along its length
- Speed of the wetting line, v, depends on frequency, f, and length, λ, of molecular displacements
- Molecular displacements occur to and from adsorption sites on the solid insulator surface with frequency f⁺ and f⁻ respectively





Molecular Kinetic Theory of Wetting

- If $f_{net}=f^+-f^-$, where f_{net} is the net frequency (forward-backward), then $v = f_{net} \lambda = (f^+ f^-)\lambda$
 - At equilibrium, v = 0; $f_{net} = 0$; $f^+=f^-=f^o$
- For wetting line movement, work must overcome energy barriers to the molecular displacements in the preferred direction
- This work is provided by out-of-balance surface tension force:

 $\gamma_{LG}(\cos\theta(0) - \cos\theta(V))$

- $v = 2f^{\circ}\lambda \sinh[\gamma_{LG}(\cos\theta(0) \cos\theta(V))/2nkT]$ (Blake, 1969)
 - n=number of adsorption sites/unit area; k=Boltzmann's constant; T=absolute temperature
- Equation ignores electrostatic contribution



Electrowetting Actuation

Electrowetting



- Electric-field-induced charge gradient
- Creates surface tension gradient
- Imbalance in surface tension acts on contact line
- Effective external force $F_m = \epsilon_r \epsilon_o V^2/2d = \gamma_{LG}(\cos\theta(0) \cos\theta(V))$







Transport Model

Forces in electrowetting system

- F_{dd} = viscous flow force within droplet
- F_{do} = viscous flow force in the oil medium
- F_f = contact-line friction force
- v(z) = velocity profile in droplet
- F_m = external force/unit length acting on droplet
- U = average droplet transport velocity




Viscous Dissipation

Hydrodynamic dissipation in droplet and oil characterized by two friction coefficients that depend on corresponding viscosity and aspect ratio



$$F_{do} = \frac{3\pi\eta_{o} LU}{4} (\frac{L}{h_{2}}) \qquad F_{dd} = \frac{3\pi\eta_{d} LU}{4} (\frac{L}{h_{1}})$$

- F_d viscous resisting force scale proportional to diameter if aspect ratio (length/height) kept constant
- F_d viscous force scale linearly to velocity
- Existing of oil film could possibly cause more viscous dissipation than droplet viscous flow (h1>> h2)



Contact Line Friction



$$F_f = \frac{\pi \zeta_0 UL}{4}$$

- F_f contact line friction force scale proportional to diameter
- F_f scale linearly to velocity
- F_f scales linearly to friction coefficient ζ_0



Two Dimensional Forces



$$F_{m} = LF_{0} \sin(\arccos(1 - \frac{2x}{L}))$$

$$F_{m} = \frac{1}{L} \int_{0}^{L} F_{m} dx$$

$$F_{m_{-}av} = \frac{\pi}{4} LF_{0}$$

- F_m driving force as a function of position
- Average driving force scale proportional to the droplet diameter



Transport Model



- At low and intermediate speed, as long as droplet aspect ratio is kept constant, the speed vs actuation voltage profile is independent of pitch size, which is consistent with experimental data
- At low and intermediate speeds, velocity is ~ to square of actuation voltage
- At high speed, velocity varies with actuation voltage linearly due to the oil damping force
- Friction and hydrodynamic terms dominate dissipation
- Force derived from kinetic energy term is insignificant in the total dissipation





Model Results

 Ren used model to predict effect of pitch size on linear droplet velocity



• Combined model fitting C_d , ζ_0 , X



Electrowetting Issues

- The "C" in electrowetting: dynamic v static capacitance
- How much power does it take to move a droplet?
- How is the power partitioned?
- MIST v. MOSFET?





Dynamic Droplet Capacitance (Woo and Pollack)





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43

Oil Viscosity Effect (Woo and Pollack)



- Rise is slower
- Spike is more pronounced (percentage wise)



Static Droplet Capacitance (Drop Larger Than Electrode)



- Measurements taken where the electrode is smaller than the droplet. Therefore, capacitance cannot increase due to additional spreading of the droplet.
- ^{ol} The capacitance change in oil must be due to interaction between the oil and the droplet.
- The fact that the capacitance in oil never reaches the level seen in air indicates that oil is being trapped between the electrode and the droplet.
- There is clearly a trend in oil of increasing capacitance with increasing voltage. This is logical, as a higher electric field would put more force on the droplet to displace the oil. However, the static measurements in oil were very unstable.



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Capacitance (pF)

Electrowetting Issues

- The "C" in electrowetting: dynamic v static capacitance
- How much power does it take to move a droplet?
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Power

- It can be reasonably assumed that all of the displacement current going into the droplet is used to charge the droplet capacitor.

- Furthermore, since the capacitance is at most 40 pF, and the sampling is done in increments of ~2ms, the droplet capacitor is clearly fully charged in the time between samples.

- Using q=Cv, i= Δ q/ Δ t, and P=iv, we can derive the expression P=v²dC/ dt.

- This expression ignores the time-varying component of v, which is reasonable given that the DC component is large compared to the AC component, and because the capacitance is very small.

$$dq/dt = (v_{AC} + V_{DC})dC/dt + Cdv_{AC}/dt$$



Power Required to Move a 950nL Drop (50V in Oil)

Note that these results are only preliminary and should be verified using another method of power measurement.





Power Dissipation Analysis

- Consider charging of time-varying capacitance of droplet/insulator/electrode system
 - Droplet area dependence
 - Oil film thickness dependence
- $P(t) = v^2 dC(t)/dt$
- Summary of dynamic power delivered:
 - Stored power
 - 1/2 stored electrically in droplet capacitor
 - 1/2C_fv²f; C_f is final capacitance
 - Dissipated power
 - 1/2 dissipated through combination of viscous, friction, kinetic effects
 - Loss due to transport initiation (V_T) is considerable



Power Dissipation Analysis

Pitch Size	Contact Line	Hydrodynamic	Medium	Kinetic	Total power
	Friction(%)	Dissipation(%)	Dissipation(%)	Dissipation(%)	Dissipation(nW)
0.15mm	86.90	10.38	2.3	0.4	64.5
$0.3 \mathrm{mm}$	75.35	22.83	1.62	0.2	200.0
$0.6 \mathrm{mm}$	53.62	40.28	5.26	0.83	174.5
0.9mm	48.62	39.13	10.77	0.4	232.6
1.2mm	47.83	36.84	13.69	1.64	367.1
$1.5 \mathrm{mm}$	42.94	35.91	18.88	2.27	399.2

Table 6: Distribution of Power Dissipation for effect of the pitch size at 4cm/s velocity

- Total power delivered to droplet transport (not including the initiation power characterized by V_T) scale down with pitch size
- Friction and hydrodynamic dissipation dominate with friction dissipation increasing in percentage with decrease in pitch size
- Oil dumping effect decrease in percentage with decrease in pitch size



Effect of Droplet Velocity





Electrowetting Issues

- The "C" in electrowetting: dynamic v static capacitance
- How much power does it take to move a droplet?
- How is the power partitioned?
- MIST v. MOSFET?



MIST vs. MOSFET

 Metal-Insulator-Solution-Transport (MIST)



 $MOSFET = Id \sim C(V - V_{T})^{2}$



Common traits:

- Bilateral transport
- Electrically isolated
- Gate for charge-controlled transport
- Threshold voltage
- Square-law device:

U = ε/2d (V-V_T)² Id = $με/t_{ox}$ (W/L) (V-V_T)² MIST MOSFET

EWD Actuator Scaling

- Scaling parameters:
 - Threshold voltage
 - Splitting voltage
 - Dispensing voltage
 - Optimum droplet velocity
 - Mixing time
 - Maximum safe operating voltage
- Approach:
 - Develop hydrodynamic-based scaling model
 - Compare scaling model with data
 - Fabrication of scaled picoliter devices



Scaling Effects on Threshold Voltage

• Threshold voltage from model:

$$U = \frac{\sin \phi \{\cos \alpha \frac{\varepsilon_{r} \varepsilon_{o} V^{2}}{2t} - \gamma_{lg} \sin \alpha [\sin \theta(V) + \sin \theta(0)]\}}{12 \mu_{o} \frac{d}{L} + 2C_{v} \frac{\mu_{d}}{d}L}$$

• When U=0, V=V_T: $V_T \sim \{2t\gamma_{Ig}/\epsilon_r\epsilon_o [sin\alpha (sin\theta(V_T) + sin\theta(0)]\}^{1/2}$

– where α is amount of contact angle hysteresis

 $-\alpha = 1.5-2^{\circ}$ (water in silicone oil); 7-9° (water in air)



Effect of α and γ_{Ig} on V_{T}





Threshold Voltage Scaling





Static Splitting Model



(Cho et al. 2002)



(c)

Section B-B'

(b)

Criteria for static splitting:

For N' electrodes, the minimum voltage for splitting is:

 $V^{2}-V_{T}^{2} \approx 4\gamma_{lg}[t(d/L)]/\epsilon_{r}\epsilon_{o}[1-1/(N'^{2}+1)]$





Uniform Splitting





Variables in Uniform Droplet Splitting

- Aspect ratio, d/L
- ζ_{lg}
- Electrode shape
- Time sequencing
- Initial droplet position
- Contact angle saturation
- Electrode voltages



Best Splitting Conditions

d/L=0.2, V_T=16V Insulator: Teflon/0.5 μ m parylene C V_{sat} >50V



Applied Voltage (V)



Dispensing





Liquid Front

$$\frac{\varepsilon_0 \varepsilon}{2\gamma_{LM} t d} (V - V_T)^2 > \frac{1}{R_2} - \frac{1}{R_1}$$

•If R1=2mm, R2=250 μ m, d=200 μ , then V_{min} =45V •If R2=250 μ m, d=100 μ m V_{max}=50V, then R1_{max}=2.3mm



$$P_{2} > P_{1} \Longrightarrow \frac{1}{r_{2}} - \frac{1}{r_{1}} = \frac{\varepsilon_{0}\varepsilon}{2\gamma_{LM}td}V^{2} > \frac{1}{R_{1}} - \frac{1}{R_{2}}$$
$$\Longrightarrow \frac{\varepsilon_{0}\varepsilon}{2\gamma_{LM}t}V^{2} > \frac{d}{R_{1}} + \frac{2d}{(N^{2} + 1)R_{3}} \qquad (\text{Ren, 2003})$$

- •if the aspect ratio is kept constant, scaling down leads to less linear displacement and fast pinch-off.
- large aspect ratio d/R_3 is favorable



Scaled Droplet Dispensing in Oil



 $[t/\epsilon_r(d/L)]^{1/2}(\mu m^{1/2})$





Combined Scaling





Scaling EWD Actuators

- Scaling variables: electrode size (L); aspect ratio (d/L), insulator thickness (t/ε_r), electrode gap (d)
 - Maximum droplet velocity \rightarrow d/L~1
 - Low dispensing voltage \rightarrow t/ ϵ_r (d/L) small
 - Optimum mixing rate \rightarrow d/L ~0.4
 - Low threshold voltage \rightarrow d/L>0.2, t/ ϵ_r small
 - Low splitting voltage \rightarrow t/ ϵ_r (d/L) small



EWD Actuator Voltage Limits

- Lippman-Young equation valid up to V_{sat}
- Insulator charge trapping/leakage observed at V_{sat} (Berry et al.; Papathanasiou et al.)
- Time-dependent V_T results:



Teflon/Parylene/Oil V ≥60V Pollack



Contact Angle Saturation

 $V_{sat} = \{2\gamma_{Ig}/\epsilon_{o}\epsilon_{1}[t_{1}+t_{2} (\epsilon_{1}/\epsilon_{2})][\cos\theta(V_{sat})-\cos\theta(0)]\}^{1/2}$



Safe Operating Ranges





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69

Picoliter Droplet Scaling

 Demonstrated dispensing, actuation, and merging/splitting of picoliter droplets



Dispensing and actuating 35pL droplet (40µm electrodes, 9.4um gasket height, 70V, 2µm parylene

Splitting ~100pL droplets (60µm electrode, 7.5µm gasket, 2um parylene, 80V)



Summary and Conclusions

- Scaling model developed
 - Useful for determining trends in V_T , V_{sat} , oil vs. air
 - Splitting, dispensing, protrusion all scale with on $[t/\epsilon_r(d/L)]^{1/2}$
 - With t/ ϵ_r (d/L) held constant while L is decreased, number of dispensing electrodes is constant for constant V and V_T
- Reliable EWD actuator operation if V≤ V_{sat}
- Oil vs. air filler media
 - Lower V_T allows larger reliable safe operating voltages in oil
 - Minimum splitting/dispensing voltages in air may place limits on d/L for reliable operation
 - Uniform splitting may test reliable voltage limits
- Scaling to 35pl demonstrated



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