Fundamentals of Thermocapillary Sculpting of Liquid Nanofilms and Applications to Thin Film Micro-Optics

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For Sam

"It’s the song of a promising heart, of the souls that the ocean unite."

-Roy Khan

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ABSTRACT

This doctoral thesis describes experimental work conducted as part of ongoing efforts to identify and understand the source of linear instability in ultrathin liquid films subject to large variations in surface temperature along the air/liquid interface. Previous theoretical efforts by various groups have identified three possible physical mechanisms for instability, including an induced surface charge model, an acoustic phonon model, and a thermocapillary model. The observed instability manifests as the spontaneous formation of arrays of nano/microscale liquid protrusions arising from an initially flat nanofilm, whose organization is characterized by a distinct in-plane wavelength and associated out-of-plane growth rate. Although long range order is somewhat difficult to achieve due to thin film defects incurred during preparation, the instability tends toward hexagonal symmetry within periodic domains achieved for a geometry in which the nanofilm is held in close proximity to a cooled, proximate, parallel, and featureless substrate.

In this work, data obtained from a previous experimental setup is analyzed and it is shown how key improvements in image processing and analysis, coupled with more accurate finite element simulations of thermal profiles, lead to more accurate identification of the fastest growing unstable mode at early times. This fastest growing mode is governed by linear instability and exponential growth. This work was followed by re-examination of real time interference fringes using differential colorimetry to quantify the actual rate of growth of the fastest growing peaks within the protrusion arrays. These initial studies and lingering questions led to the introduction of a new and improved experimental setup, which was redesigned to yield larger and more reproducible data sets. Corresponding improvements to the image analysis process allowed for the measurement of both the wavelength and growth rate of the fastest growing mode simultaneously. These combined efforts establish that the dominant source of instability is attributable to large thermocapillary stresses. For the geometry in which the nanofilm surface is held in close proximity to a cooled and parallel substrate, the instability leads to a runaway process, characterized by exponential growth, in which the film is attracted to the cooled target until contact is achieved.

The second part of this thesis describes fabrication and characterization of microlens arrays and linear waveguide structures using a similar experimental setup. However, instead of relying on the native instability observed, formation and growth of liquid shapes and protrusions is triggered by pre-patterning the cooled substrate with a desired mask for replication. These preformed cooled patterns, held in close proximity to an initially flat liquid nanofilm, induce a strong non-linear response via consequent patterned thermocapillary stresses imposed along the air/liquid interface. Once the desired film shapes are achieved, the transverse thermal gradient is removed and the micro-optical components are affixed in place naturally by the resultant rapid solidification. The use of polymer nanofilms with low glass transition temperatures, such as polystyrene, facilitated rapid solidification, while providing good optical response. Surface characterization of the resulting micro-optical components was accomplished by scanning white light interferometry, which evidences formation of ultrasmooth surfaces ideal for optical applications. Finally, linear waveguides were created by this thermocapillary sculpting technique and their optical performance characterized. In conclusion, these measurements highlight the true source of instability in this geometry, and the fabrication demonstrations pave the way for harnessing this knowledge for the design and creation of novel micro-optical devices.

PUBLISHED CONTENT AND CONTRIBUTIONS

[1] K. R. Fiedler, and S. M. Troian, "Early time instability in nanofilms exposed to a large transverse thermal gradient: improved image and thermal analysis", J. Appl. Phys. **120**, 205303 (2016),

KRF assisted with the design of the project, remeasured characteristic instability wavelengths, improved the numerical simulations, prepared draft plots and figures, and participated in the writing of the manuscript.

[2] K. R. Fiedler, E. McLeod, and S. M. Troian, "Differential colorimetry measurements of instability growth in nanonfilms exposed to a large transverse thermal gradient", To be submitted to J. Appl. Phys. (May 2017),

KRF recomputed the interference fringe spectra of nanofilms to establish local film thickness, measured the peak heights as a function of time and associated growth rates, compared results to theoretical predictions of the thermocapillary model, prepared draft plots and figures, and participated in the writing of the manuscript.

[3] K. R. Fiedler, and S. M. Troian, "Optical observations of a long-wavelength thin film instability driven by thermocapillary forces", To be submitted to Phys. Rev. E. (2017),

KRF assisted with the design of the project, built the experimental setup, measured the wavelength of the fastest growing mode, performed the numerical simulations, prepared draft plots and figures, and participated in the writing of the manuscript.

[4] S. W. D. Lim, K. R. Fiedler, C. Zhou, and S. M. Troian, "Converging and diverging microlens arrays by spatiotemporal control of thermocapillary forces", To be submitted to Appl. Phys. Lett. (2017),

KRF assisted with the design of the project, measurements obtained, discussions of the results, and preparation of the manuscript.

[5] K. R. Fiedler, S. W. D. Lim, Y. Zhu, and S. M. Troian, "Fabrication of microdevices through thermocapillary sculpting of molten polymer nanofilms", In preparation (2017),

KRF assisted with the design of the project, built the fabrication setup, assisted with device characterization, prepared draft plots and figures, and participated in the writing of the manuscript.

[6] K. R. Fiedler, Y. Zhu, T. Le, N. Yu, and S. M. Troian, “Characterization of linear optical waveguides formed by thermocapillary sculpting of nanoscale polymer melt films”, In preparation (2017),

KRF assisted with the design of the project, fabricated and characterized the waveguides, performed the numerical simulations of waveguide properties, prepared draft plots and figures, and participated in the writing of the manuscript.

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NOMENCLATURE

This is a compilation of the abbreviations and symbols which are used in this work. Generally, dimensional variables are lower case letters while dimensionless variables are the corresponding upper case letters. In the case of operators, the nomdimensional analogs typically have a tilde over them. Within the body of this document, certain variables will be subscripted by i. This subscript will typically represent different layers in the system, primarily either "film" or "air".

$[\cdot]$	Denotes a difference across the air/nanofilm interface
α	RGB channel index
α_4	First aspheric coefficient
β	Nondimensional growth rate
$\Delta\mathrm{T}^{\mathrm{curr}}$	Temperature drops computed using the expanded domain in Ch. 3
$\Delta\mathrm{T}^{\mathrm{orig}}$	Temperature drops computed in Ref. [1]
$\delta\phi$	Perturbed electric potential
$\Delta\mathrm{T}_{\mathrm{out}}$	Difference between the heater and chiller setpoints
$\Delta\mathrm{T}_{\mathrm{sin}}$	Temperature drop across the sinusoidally perturbed bilayer
$\delta\vec{D}$	Perturbed electric displacement field
$\delta\vec{E}$	Perturbed electric field
$\delta h_{k'}$	Fourier coefficients describing the current interface height
Δl	Fabry-Pérot etalon change in length
Δt	Time step between peak observation images
δ	Normalized mask pin height
$\Delta\mathrm{T}$	Temperature difference between the bounding plates
$\delta_j(\lambda_{\mathrm{opt}})$	Optical phase
$\dot{\mathrm{Q}}_{\mathrm{ITO}}$	Volumetric heat flux density within the ITO heater
ϵ	Long wavelength expansion parameter
Γ	Dimensionless surface tension
γ	Surface tension of the fluid/air interface
Γ_c	Characteristic scale of the surface tension
γ_T	Thermocapillary coefficient
$\hat{n}$	Unit normal vector at the nanofilm/air interface
$\hat{t}$	Tangential unit vector
$\hbar$	Reduced Planck's constant
κ	Thermal conductivity ratio

λ_{opt}	Wavelength of optical illumination
λ_o	Lateral spacing of instability protrusions
$\mathbf{E}$	Rate of strain tensor
$\mathbf{M}_{j,j+1}$	Optical transmission matrix from layer j to layer $j+1$
$\mathbf{M}_j$	Optical transmission matrix through layer j
$\mathbf{T}$	Stress tensor
$\mathbf{T}^{\text{em}}$	Maxwell stress tensor
$\mathcal{F}(k,t)$	Peak fitting function
$\mathcal{G}(k)$	Gaussian fitting function
$\mathcal{L}(k)$	Lorentzian fitting function
T	Temperature
T_+	Temperature measured by the thermocouple on the chiller
T_-	Temperature measured by the thermocouple underneath the heater
T_{C}	Temperature of the cooled top plate
T_{H}	Temperature of the heated bottom plate
$\mathrm{T}_{\mathrm{Int}}$	Temperature at the interface of the molten nanofilm
T_g	Glass transition temperature
μ	Dynamic viscosity of the fluid
∇_s	Surface gradient
$\nabla_{\parallel}$	Horizontal components of the gradient
ν	Mode order
ω	Frequency of an oscillator
$\overline{Ca}$	Modified capillary number
$\overline{Ma}$	Modified Marangoni number
$\overline{Q}$	Acoustic quality factor
ϕ	Electric potential
ϕ^o	Base state electric potential
Φ_c	Characteristic scale of the electric potential
Φ'_c	Alternative electric potential scale in the EHD model
Φ_o	Applied potential difference
Π	MicroAngelo mask pitch
ρ	Density of the fluid
σ	Surface charge density at the fluid/air interface
σ_{free}	Free charge density at an interface
τ	Dimensionless time
$\mathrm{v}_{\text{exp}}(x,y,t,\alpha)$	Experimental fringe color values

$\mathrm{v}_{\mathrm{theor}}(h, \alpha)$	Fringe color values
Θ	Nondimensional temperature
θ	Angle between principal axes and the raw data axes
$\tilde{\mathrm{v}}_{\mathrm{theor}}(h, \alpha)$	Normalized fringe color values
ε	Relative permittivity
ε_o	Permittivity of free space
$\vec{D}$	Electric displacement field
$\vec{E}$	Electric field
$\vec{E}^o$	Base state electric field
$\vec{f}_{\mathrm{body}}$	Body forces acting on the bulk of the fluid
$\vec{K}$	Nondimensional wavevector of the instability
$\vec{k}$	Wavevector of the instability
$\vec{q}$	Heat flux density
$\vec{u} = (u, v, w)$	Velocity field within the nanofilm
$\vec{u}_{\|} = (u, v)$	Horizontal components of the velocity
$\widetilde{\delta h}$	Nondimensional perturbation used in linear stability analysis
$\widetilde{\nabla}_s$	Dimensionless surface gradient
$\widetilde{\nabla}_{\|}$	Dimensionless lateral gradient
$\widetilde{\phi}_i$	Nondimensional electric potential
$\widetilde{\vec{E}}_i$	Nondimensional electric field
A	Amplitude of peak fitting function
a	Width of an infinite square well
A_{lens}	Individual MLA lens area
A_{wg}	Waveguide amplitude
b_o	Growth rate of peak fitting function
C^{AP}	Fitting constant for the material constants in the AP model
C^{TC}	Fitting constant for the material constants in the TC model
c_p	Specific heat capacity
D	Dimensionless gap separation
d_1	MicroAngelo mask pin or block height
d_2	MicroAngelo mask depression height
D_{lens}	Characteristic MLA lens diameter
d_o	Separation between bounding plates
D_p	MicroAngelo mask pin or depression diameter
D_{wg}	Gaussian decay of waveguide envelope
E_ν	Energy of mode ν

f_1	Larger microlens focal length
f_2	Smaller microlens focal length
F_{array}	Fresnel number of the microlens array
F_{lens}	Fresnel number of an individual microlens
f_p	Mask pin protrusion function
G	Functional form of the mask topography
$g(x, y, t, h)$	Peak height cost function
H	Dimensionless film thickness
$h(x, y, t)$	Interface position between molten nanofilm and air
$h_{\text{meas}}(x, y, t)$	Measured peak height as a function of time
h_{paste}	Thermal paste thickness
$h_{\text{pk}}(t)$	Peak height during film growth
h_o	Initial film thickness
I	Measured intensity signal
$I(\lambda_{\text{opt}})$	Intensity spectrum of the halogen light source
I_R	Reflected intensity from a Fabry-Pérot etalon
k	Thermal conductivity
k_+	Right half maximum point of peak fitting function
k_-	Left half maximum point of peak fitting function
k_{max}	Upper bound for the peak fitting function
k_{min}	Lower bound for the peak fitting function
k_o	Maximum point of peak fitting function
l	Fabry-Pérot etalon length
m	Mass of a particle in an infinite square well
n	Index of refraction
P	Dimensionless pressure
p	Pressure within the fluid
P_{ac}	Nondimensional acoustic pressure used in the AP model
p_{ac}	Acoustic pressure used in the AP model
P_{el}	Nondimensional electric pressure used in the SC model
p_{el}	Electric pressure used in the SC model
P_c	Characteristic scale of the pressure in the fluid
Pr	Prandtl number
$R(\lambda_{\text{opt}}, h)$	Reflectance from a multilayer stack
R_1	Microlens radii of curvature along the larger principal axis
R_2	Microlens radii of curvature along the smaller principal axis

r_{paste}	Thermal paste radius
$r_{j,j+1}$	Fresnel amplitude reflection coefficient
Re	Reynolds number
$rn(x, y)$	Random number generator in COMSOL
$S\left(\vec{k}, t\right)$	Power spectral density
$S_\alpha(\lambda_{\text{opt}})$	Spectral responsivity of the camera
t_{final}	Last time which was analyzed in the wavelength analysis
t_{meas}	Time of initial wavelength measurement
t_f	Final time of the peak observation
t_{ref}	Time stamp of the image which was used as the reference image
$t_{j,j+1}$	Fresnel amplitude transmission coefficient
U, V, W	Dimensionless fluid velocities
u_c	Characteristic lateral scale of the flow velocity
u_p	Speed of sound in the molten nanofilm
$W(k)$	Background plus peak fitting function
w_c	Characteristic vertical scale of the flow velocity
w_{wg}	Waveguide width
x', y'	Microlens principal axes
X, Y, Z	Dimensionless position variables
$x_{\text{pk}}, y_{\text{pk}}$	Peak location as a function of time
x_f, y_f	Location of peak at final time
x_o, y_o	Coordinates of the microlens vertex in raw data coordinates
z_j	Thickness of layer j
z_{max}	Height of individual microlens
AP	Abbreviation for the acoustic phonon model
AR	Asphericity ratio
EHD	Abbreviation for the electrohydrodynamic model
HeNe	Helium neon
IPA	Isopropyl alcohol
ITO	Indium tin oxide
JPL	Jet Propulsion Laboratory
LIS^{2}T	Laboratory of Interstitial and Small Scale Transport
NSTRF	NASA Space Technology Research Fellowship
PBS	Polarizing beam splitter
PDMS	Polydimethylsiloxane
PID	Proportional integral derivative

PMMA	Poly(methyl methacrylate)
PS	Polystyrene
RGB	Red green blue
RMS	Root mean square
RTD	Resistance temperature detector
SC	Abbreviation for the surface charge model
SHWS	Shack-Hartmann wavefront sensor
SSR	Sum of squared residuals
TC	Abbreviation for the thermocapillary model
TE	Transverse electric electromagnetic wave polarization
TM	Transverse magnetic electromagnetic wave polarization