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Thermocapillary effects in driven dewetting and self-assembly of pulsed laser-irradiated metallic films

Mikhail Khenner, *Western Kentucky University*

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Mikhail Khenner

Department of Mathematics, Western Kentucky University

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Outline

- Motivation for modeling
- Model description
- Temperature distribution in the film irradiated uniformly or non-uniformly in the plane of the film
- 3D Evolution equation for the film height
- The 2D approximation
  - Case of uniform irradiation: Stability analysis of the initial planar state of the film
  - Uniform or non-uniform irradiation: Computations of the nonlinear evolution of the film towards rupture
- Summary and future work

Snapshots from the experiments (Y. Kaganovskii *et al.*, JAP 100, 044317 (2006)

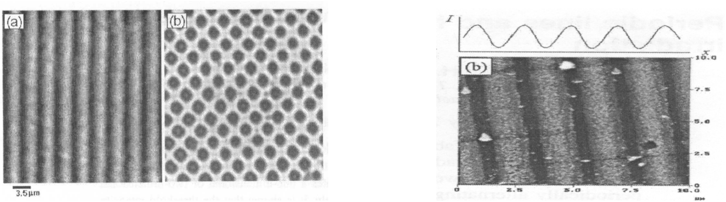
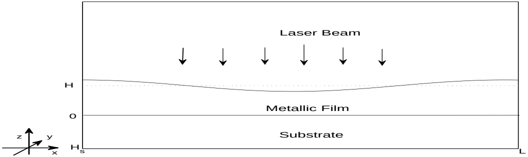


Figure:
Left: Micrographs of 1D and 2D optical interference gratings created on a Au film of 18 nm thickness. (a) "two-beam" and (b) "four-beam" gratings.
Right: AFM image of 8 nm Au film after two-beam interference irradiation. Note that film material accumulates in cold regions.

Problem geometry



Major physical factors contributing to pattern formation through film dewetting:

- Pulsed laser irradiation with or without spatial interference
- Capillary fluid flow (minimization of the surface area at given fluid volume)
- Thermocapillary fluid flow arising due to temperature dependence of the surface tension
- Long-range intermolecular (van der Waals) forces driving film rupture

Physical assumptions

- Film is in the molten (liquid) state at all times (between pulses the film cools down to $T > T_{solidification}$).
- Metallic melt is an incompressible Newtonian liquid.
- Surface tension is a linear function of the temperature

$$\tilde{\sigma} = \tilde{\sigma}_m - \tilde{\gamma}\left(\tilde{T} - \tilde{T}_m\right), \quad \tilde{T} > \tilde{T}_m, \quad \tilde{\gamma} > 0$$

- $H/L = \epsilon \ll 1 \rightarrow$ longwave (lubrication) approximation possible.
- Substrate is thin, $H_s \sim H$.

Governing PDEs

- The momentum equation

$$\rho(\tilde{\mathbf{v}}_{\tilde{t}} + (\tilde{\mathbf{v}} \cdot \tilde{\nabla})\tilde{\mathbf{v}}) = \tilde{\nabla} \cdot \tilde{\boldsymbol{\Omega}} + \rho\tilde{\mathbf{g}}, \tag{1}$$

- The continuity equation

$$\tilde{\nabla} \cdot \tilde{\mathbf{v}} = 0, \tag{2}$$

- The energy equation

$$\rho c_p \left(\tilde{T}_{\tilde{t}} + \tilde{\mathbf{v}} \cdot \tilde{\nabla}\tilde{T} \right) = \kappa \tilde{\nabla}^2 \tilde{T} + \tilde{\tau}_{ij} \frac{\partial \tilde{u}_i}{\partial \tilde{x}_j} + \tilde{Q}, \tag{3}$$

where

$$\tilde{Q} = \frac{\delta I (1 - R(\tilde{h}))}{2} f(\tilde{x}, \tilde{y}, \tilde{t}) \exp\left(\delta(\tilde{z} - \tilde{h})\right) \quad \text{(Bouguer's law)}$$

$$(0 \leq R(\tilde{h}) < 1 : \text{nonlinear reflectivity})$$

Boundary conditions (I)

At the free surface:

(i) The normal and shear stress balances;

$$\mathbf{n}\cdot\tilde{\boldsymbol{\Omega}}\cdot\mathbf{n} = -\tilde{\sigma}\nabla\cdot\mathbf{n} + \tilde{\Pi},$$

$$\mathbf{t}\cdot\tilde{\boldsymbol{\Omega}}\cdot\mathbf{n} = \mathbf{t}\cdot\nabla\tilde{\sigma}, \quad \mathbf{n} = \frac{\left(-\tilde{h}_{\tilde{x}}, -\tilde{h}_{\tilde{y}}, 1\right)}{\sqrt{1+\tilde{h}_{\tilde{x}}^2+\tilde{h}_{\tilde{y}}^2}},$$

where $\tilde{\Pi} = (\tilde{A}/6\pi)\tilde{h}^{-3} + \tilde{B}\tilde{h}^{-2}$ is the disjoining pressure,

(ii) The kinematic condition:
$\tilde{w} = \tilde{h}_{\tilde{t}} + \tilde{u}\tilde{h}_{\tilde{x}} + \tilde{v}\tilde{h}_{\tilde{y}}$

(iii) Newton's law of cooling:
$\kappa\tilde{T}_{\tilde{z}} = -\alpha_h\left(\tilde{T} - \tilde{T}_a\right)$

Boundary conditions (II)

At the film-substrate interface:

- No-slip: $\tilde{u} = 0, \;\; \tilde{v} = 0$
- No-penetration: $\tilde{w} = 0$
- Continuity of temperature and thermal flux:

$$\tilde{T} = \tilde{\theta}, \quad \kappa \tilde{T}_{\tilde{z}} = \kappa_s \tilde{\theta}_{\tilde{z}}, \tag{4}$$

where $\tilde{\theta}$ is the temperature field in the substrate, which is obtained by solving the heat conduction equation

$$\rho_s c_{ps} \tilde{\theta}_{\tilde{t}} = \kappa_s \tilde{\nabla}^2 \tilde{\theta} + \tilde{Q} \tag{5}$$

given $R(\tilde{h}) = 0$ in the substrate and the boundary condition
$\tilde{z} = -H_s : \quad \tilde{\theta} = \tilde{T}_s$

Dimensionless parameters

Dimensionless group	Definition	Typical values
Scaling parameter (ϵ)	H/L	0.01
Reynolds number (Re)	$\rho UH/\mu$	1
Brinkman number (Br)	$\mu U^2/HI$	0.11
Peclet number (Pe)	$\rho c_p UH/\kappa$	0.019
Capillary number (C)	$\mu U/\sigma$	0.1184
Gravity parameter (G)	$\epsilon \rho g H^2/\mu U$	$3.93 * 10^{-13}$
Biot number (β)	$\alpha_h H/\kappa$	10^{-6}
Surface tension (σ_m)	$\epsilon \tilde{\sigma}_m/\mu U$	0.084
Marangoni number (M)	$\epsilon IH\tilde{\gamma}/2\mu U\kappa$	$1.125 * 10^{-5}$
Hamaker constant (A)	$\epsilon \tilde{A}/6\pi\mu UH^2$	$3.37 * 10^{-5}$
Hamaker constant (B)	$\epsilon \tilde{B}/\mu UH$	$1.17 * 10^{-6}$
Melting temperature (T_m)	$\kappa \tilde{T}_m/IH$	1768
Ambient temperature (T_a)	$\kappa \tilde{T}_a/IH$	300
Substrate temperature (T_s)	$\kappa \tilde{T}_s/IH$	1900
Optical thickness (D)	δH	1
Substrate thickness (h_s)	H_s/H	1
Ratio of thermal conductivities (Γ)	κ_s/κ	$1.3 * 10^{-2}$
Pre-factor, reflectivity function	r_0	0.44

Temperature distribution (I)

Dimensionless energy
equation: (note that $\epsilon(= H/L)$, Pe, $Br \ll 1$) !

$$
\begin{aligned}
\epsilon Pe \left(T_t + uT_x + vT_y + wT_z \right) = \\
& T_{zz} + \epsilon^2 \left(T_{xx} + T_{yy} \right) + (D/2)(1 - R(h)) \exp\left(D(z-h) \right) f(x,y,t) \\
& + \epsilon^2 Br \left(u_x^2 + u_y^2 + v_x^2 + v_y^2 + w_z^2 \right) \\
& + Br \left(u_z^2 + v_z^2 \right) + \epsilon^4 Br \left(w_x^2 + w_y^2 \right) . \qquad (6)
\end{aligned}
$$

Temperature distribution (I)

Dimensionless energy
equation: (note that $\epsilon(= H/L)$, Pe, $Br \ll 1$) !

$$\begin{aligned}
&\epsilon Pe\left(T_t + uT_x + vT_y + wT_z\right) = \\
&\qquad T_{zz} + \epsilon^2\left(T_{xx} + T_{yy}\right) + (D/2)(1 - R(h))\exp\left(D(z-h)\right)f(x,y,t) \\
&\qquad + \epsilon^2 Br\left(u_x^2 + u_y^2 + v_x^2 + v_y^2 + w_z^2\right) \\
&\qquad + Br\left(u_z^2 + v_z^2\right) + \epsilon^4 Br\left(w_x^2 + w_y^2\right). \qquad (6)
\end{aligned}$$

Keeping dominant terms only:

$$T_{zz} + (D/2)(1 - R(h))\exp\left(D(z-h)\right)f(x,y,t) = 0, \qquad (7)$$

$$\theta_{zz} + (D/2)\exp\left(D(z-h)\right)f(x,y,t) = 0 \qquad (8)$$

$$z = h: \quad T_z = -\beta(T - T_a), \qquad (9)$$

$$z = 0: \quad T = \theta, \quad T_z = \Gamma\theta_z, \qquad (10)$$

$$z = -h_s: \quad \theta = T_s. \qquad (11)$$

Temperature distribution (II)

Approximate solution at the film surface:

$$
\begin{aligned}
T^{(h)} \equiv \; & T(x,y,h,t) = T_s - F(h,D,\Upsilon)(1-R(h))f(x,y,t) + \\
& (\Upsilon + h)\left(F(h,D,\Upsilon)(1-R(h))f(x,y,t) + T_a - T_s\right)\beta.
\end{aligned} \tag{12}
$$

This has been linearized in β ($\beta \sim 10^{-6}$ - surface Biot number).

Remark 1: Nonuniformity in the plane of the film enters through $f(x,y,t)$.

Remark 2: In the (complicated) expression for $F(h,D,\Upsilon)$:
$D = \delta H, \; \Upsilon = h_s/\Gamma$.
$D << 1$: radiation passes through the film - film is transparent
$D >> 1$: radiation is concentrated near the film surface - film is opaque

Remark 3: We use $R(h) = r_0\left(1 - \exp\left(-a_r h\right)\right)$ as suggested by R. Kalyanaraman *et al.*, PRB 75, 235439 (2007)

Temperature distribution (III)

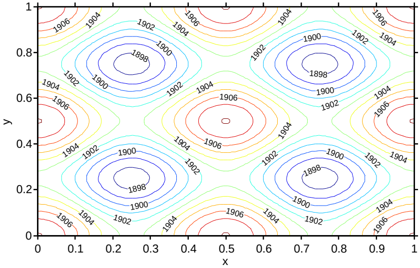


Figure: Surface temperature when beam is uniform in t but nonuniform in x, y (periodic): $f \equiv f(x, y) = 1 + 0.1\cos(4\pi(x - 1/2))\cos(4\pi(y - 1/2))$

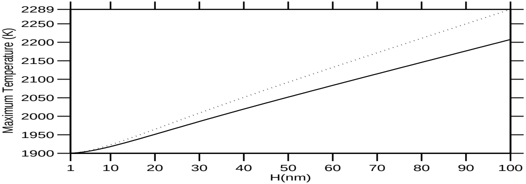


Figure: Plot of the maximum dimensional film temperature vs. film height. Dot curve: $R(h) = 0$; solid curve: $R(h) \neq 0$.

The 2D evolution equation for the film height $h(x, t)$

$$
\begin{aligned}
h_t \quad = \quad & \frac{\partial}{\partial x}\left[-(\epsilon^3 C^{-1}/3)h^3 h_{xxx} + (G/3)h^3 h_x - \left(Ah^{-1} - 2B/3\right) h_x\right. \\
& + M\beta(T_a - T_s)h^2 h_x \\
& + \{MF_1(h, D, \Upsilon)(1 - R(h)) \\
& + MR'(h)F(h, D, \Upsilon) \\
& - M\beta(h + \Upsilon)R'(h)F(h, D, \Upsilon) \\
& + M\beta(1 - R(h))\left(F(h, D, \Upsilon) - (h + \Upsilon)F_1(h, D, \Upsilon)\right)\} \\
& \left. * f(x, y, t)h^2 h_x\right].
\end{aligned}
\tag{13}
$$

Linear stability analysis of the initial planar state of the film (I)

Assume $f = 1$, $h = 1 + \xi(x,t) = 1 + e^{\omega t}\cos kx$ and linearize Eq. (13) in ξ:

$$\begin{aligned}\omega(k) &= -\frac{G}{3}k^2 - \frac{\hat{C}}{3}k^4 + (A - \frac{2B}{3})k^2 - M\beta(T_a - T_s)k^2 \\ &\quad + MR'F(-1 + \beta(1+\Upsilon))k^2 \\ &\quad + M(1-R)\left(-F_1 - \beta\left(F - (1+\Upsilon)F_1\right)\right)k^2.\end{aligned} \tag{14}$$

$h = 1$: Dimensionless film height at $t = 0$
$\xi(x,t)$: Small perturbation
ω : Growth rate of the perturbation
k : Wavenumber of the perturbation (wavelength $= 2\pi/k$)
R, R', F, F_1 are evaluated at $h = 1$

Linear stability analysis (II)

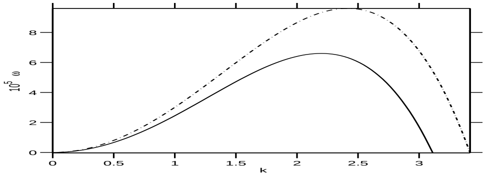


Figure: Variation of ω with k: The dash-dot curve shows ω calculated without the term containing the effect of the heat source in Eq. (14), the solid curve shows ω calculated with all terms included.

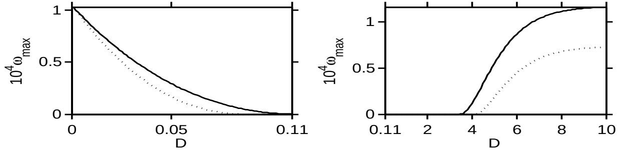


Figure: Variation of ω_{max} with D. Dot curve: $R(h) = 0$; solid curve: $R(h) \neq 0$. Remark: The inclusion of reflectivity reduces the heat generation in the film, thus reducing the stabilization.

The uniformly heated film is completely stable against small perturbations in some interval of the optical thickness parameter

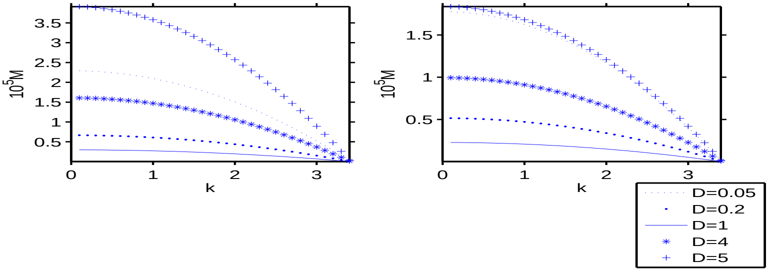


Figure: Neutral stability curves ($\omega = 0$) for various values of D. $R \neq 0$ (left), $R = 0$ (right). Below the curve the film is unstable, above - stable.

Stabilization is the maximum in films with $D \sim 1$, and minimum in films with $D \ll 1$ or $D \gg 1$.

Single laser beam with uniform spatio-temporal power intensity distribution ($f = 1$):

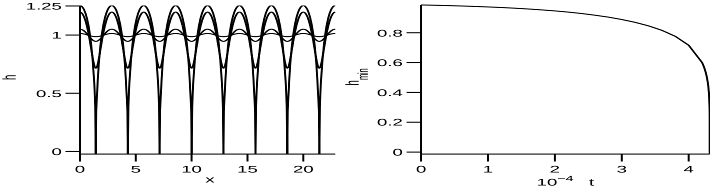


Figure: Profile of the film height (left), and the evolution of the minimum point on the film surface (right).

Rupture is spatially periodic with the wavelength of the fastest growing perturbation. Rupture time $\tilde{T}_r \approx 0.9$ ms (depends on the amplitude of the initial film height).

Numerical simulation of a nonlinear evolution of the film (II)

Static two-beam interference:
$f \equiv f(x) = 1 + 0.99\cos(0.157(x - \frac{\pi}{2.2}))$

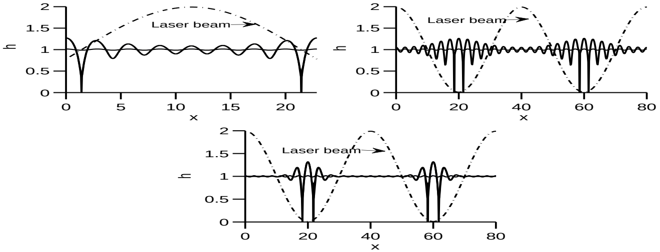


Figure: Top row, left: $H = 10$ nm, 8 wavelengths; Top row, right: $H = 10$ nm, 28 wavelengths; Bottom row: $H = 15$ nm, 28 wavelengths.

(Note: $2\pi/0.157 = 40 = \ell$: distance between two neighboring interference fringes)

The spatial distribution of particles follows the spatial periodicity of the interference imprint. Rupture time $\tilde{T}_r \approx 0.6$ ms.

Summary

- Developed a mathematical model describing the dynamics of a molten, laser-irradiated thin film, including the following major effects:
  - fluid flow
  - heat conduction in the film and in the substrate
  - volumetric heat absorption
  - nonlinear reflectivity
  - spatiotemporal nonuniformity of irradiation
  - temperature dependence of the surface tension (Marangoni)
  - long-range intermolecular attraction to the substrate (van der Waals)
- Derived the surface evolution PDE in the lubrication approximation.
- Studied the 2D surface evolution PDE by means of the linear stability analysis and numerical simulations:
  - Analytically investigated the stabilizing and destabilizing effects of various system parameters
  - Numerically investigated impacts of the different modes of irradiation

Future Work

- 3D stability analysis
- Simulations of the nonlinear dynamics in 3D
- Development of the adaptive grid methods in 2D and 3D to compute accurate statistics of structures ordering/distributions
- Modeling of film solidification with simultaneous dewetting during the cooling phase

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