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Modeling diverse physics of nanoparticle self-assembly in pulsed laser-irradiated metallic films

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Modeling diverse physics of nanoparticle self-assembly in pulsed laser-irradiated metallic films

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Motivation for modeling, challenges

Single layer films

- Model description
- Lubrication and 2D approximations
  - (i) Uniform irradiation: Stability analysis
  - (ii) Computations of the nonlinear dynamics of the film

Bilayer films

- (i) Model equations (2D)
- (ii) Stability analysis, simulations

Future work

IDewetting ≡ ”uncovering” (exposure) of some areas the substrate
Experimental setup

Figure courtesy of R. Kalyanaraman, UTK
Irradiation by 10 laser pulses. Ag film thickness from (a) to (f): 2, 4.5, 7.4, 9.5, 11.5, 20 nm. (Figure courtesy of R. Kalyanaraman, UTK)
Single-layer films, one laser beam: Progression of dewetting towards formation of nanoparticles

Top row: 4.5 nm thick Ag film. (a)-(c): 10, 100, 10500 laser pulses. Bottom row: 11.5 nm thick Ag film. (e)-(g): 10, 100, 10500 laser pulses. (Figure courtesy of R. Kalyanaraman, UTK)

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Modeling diverse physics of nanoparticle self-assembly...
Single-layer films: Nanoscale arrays

2-beam interference

Nanostripes
Nanowires
Ellipses
Nanoparticles

800 nm
800 nm
800 nm
800 nm

Uniform laser

Nanoholes
Cells
Polygons
Nanoparticles

1000 nm
2000 nm
500 nm
2000 nm

Increasing # of laser pulses n

Figure courtesy of R. Kalyanaraman, UTK
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. (From Y. Kaganovskii et al., JAP 100, 044317, 2006)
Vision of a multifunctional nanostructured surface platform based on multi-layer films

Pulsed laser self-organization of multilayer films made from immiscible materials, like Co and Ag, can be used to synthesize a matrix of discrete micro-regions with varying nanoscale morphology, size, shape, and composition. Thus a platform with unique multifunctional behavior for sensing and detection can be made. (Figure courtesy of R. Kalyanaraman, UTK)
Challenges:

- Understand film instabilities resulting in nanopatterning
- Develop a realistic model of heat transfer within the film
- Develop a model of interference control of a pattern formation
- For bilayers, develop models that account for interdiffusion and chemical reactions
- Develop efficient computational methods for 3D simulations (especially for a bilayer system)
Our interest is to model the complete dewetting cycle - from a continuous film to a nanoparticles state

**Modeling assumption**

**Film is liquid at all times, and dewetting is modeled as continuous in time.**

In reality, pulse width = 10 ns, pulse frequency = 50 Hz. Nanometer-scale film is:

- Melted “instantaneously” when a pulse hits (energy flux $\sim 10^{11}$ J/sm$^2$);
- Dewets while the pulse lasts;
- Solidifies “instantaneously” after the pulse is gone, freezing the instantaneous morphology;
- Next pulse quenches in the morphology and the cycle repeats.
Single layer films
Major physical factors contributing to pattern formation through film dewetting:

- Capillary fluid flow (minimization of the surface area at given fluid volume by the surface tension)
- Unusual, thickness-dependent heat transfer in the film - due to nonlinear optical absorption of light and nonlinear reflectivity
- Thermocapillary (Marangoni) fluid flow arising due to the surface tension dependence on temperature
- Long-range intermolecular (van der Waals) forces between the substrate and film surface molecules
Molten metal is an incompressible Newtonian liquid.

Surface tension decreases linearly with increasing temperature

\[ \sigma = \sigma_m - \gamma (T - T_m), \quad T > T_m, \quad \gamma > 0 \]

\[ H/L = \epsilon \ll 1, \text{ also } H_s \sim 10 \div 20H \rightarrow \text{will derive model equations in the lubrication (longwave) approximation.} \]

Lubrication approximation is, essentially, a procedure of systematic scalings of governing equations (Navier-Stokes) and expansion of all fields in powers of small parameter \( \epsilon \).

Lubrication equations are the equations that result in the leading zeroth-order (\( \epsilon^0 \)) of such expansion (Oron, Davis, and Bankoff, *Reviews of Modern Physics* (1997); Craster and Matar, *Reviews of Modern Physics* (2009)).
Lubrication approximation: leading-order expansion in $\epsilon (<< 1)$

- **Momentum equation (Stokes) and continuity equation**

\[ \nabla \cdot \Omega + \rho g = 0, \quad \nabla \cdot u = 0 \]  \hspace{1cm} (1)

- **Energy equation**

\[ \frac{\kappa}{\rho c_p} \nabla^2 T + Q = 0, \] \hspace{1cm} (2)

where

\[ \Omega = -P\delta_{ij} + \eta \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \] : stress tensor

\[ Q = \frac{\delta J(1 - R(h))}{2} f(x, y, t) \exp(\delta(z - h)) \] (Beer-Lambert law)

\[ (0 \leq R(h) < 1 : \text{nonlinear reflectivity}) \]

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

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Modeling diverse physics of nanoparticle self-assembly ...
At the free surface:

(i) The normal and shear stress balances;

\[ n \cdot \Omega \cdot n = -\sigma \nabla \cdot n + \Pi, \quad t \cdot \Omega \cdot n = t \cdot \nabla \sigma \]

where \( \Pi = (A/6\pi)h^{-3} \) is the **disjoining pressure** due to long-range intermolecular attraction.

(ii) The kinematic condition:

\[ u_3 = h_t + u_1 h_x + u_2 h_y \leftarrow \text{this condition is used to derive the evolution PDE for } h \text{ after } u_1 \text{ an } u_2 \text{ have been averaged in the } z\text{-direction} \]

(iii) Newton’s law of cooling:

\[ \kappa T_z = -\alpha h (T - T_a) \]
Boundary conditions (II)

At the film-substrate interface:

- No-slip: \( u_1 = u_2 = 0 \)
- No-penetration: \( u_3 = 0 \)
- Continuity of temperature and thermal flux:

\[
T = \theta, \quad \kappa T_z = \kappa_s \theta_z, \quad (3)
\]

where \( \theta \) is the temperature field in the substrate, which is obtained by solving the heat conduction equation

\[
\frac{\kappa_s}{\rho_s c_{ps}} \nabla^2 \theta + Q = 0 \quad (4)
\]

given \( R(h) = 0 \) in the optically transparent substrate (such as SiO\(_2\)) and the boundary condition \( z = -H_s : \quad \theta = T_s \)
Figure: Surface temperature when four-beam interference is active, modeled by \( f \equiv f(x, y) = 1 + 0.1 \cos(4\pi(x - 1/2)) \cos(4\pi(y - 1/2)) \)

Figure: Plot of the maximum film temperature vs. film height. Dot curve: \( R(h) = 0 \); solid curve: \( R(h) = r_0 (1 - \exp(-a_r h)) \).
2D evolution equation (dimensionless) for the film height $h(x, t)$

\[
    h_t = \frac{\partial}{\partial x} \left[ -(C/3)h^3 h_{xxx} + (G/3)h^3 h_x - Ah^{-1} h_x 
    + M\beta(T_a - T_s)h^2 h_x 
    + \{ -MF_h(1 - R(h)) + MR'(h)F - M\beta(h + \Psi)R'(h)F 
    + M\beta(1 - R(h)) (F + (h + \Psi)F_h) \} f(x, y, t)h^2 h_x \right]
\]

Lines 3 and 4: unconventional terms that emerge due to laser heating

- $C$: capillary number
- $G$: gravity number
- $\beta$: Biot number
- $M$: Marangoni number
- $T_a$: ambient temperature
- $T_s$: substrate temperature
- $A$: Hamaker constant
- $D = \delta H$: optical thickness
- $\Psi = H_s/H\Gamma$, where $\Gamma = \kappa/\kappa_s$

\[
    R(h) = r_0 (1 - \exp(-a_r h)), \\
    F(h, D, \Psi) = \left( -\Psi + \exp(-Dh)(\Psi - 1/D) - h + 1/D \right)/2
\]
Take $f = 1$, $h = 1 + \xi(x, t) = 1 + e^{\omega t} \cos kx$ and linearize in $\xi$:

$$
\omega(k) = -\frac{G}{3}k^2 - \frac{\epsilon^3}{3C}k^4 + Ak^2 - M\beta(T_a - T_s)k^2
+ MR'F(-1 + \beta(1 + \Psi))k^2
+ M(1 - R)(F_h - \beta(F + (1 + \Psi)F_h))k^2.
$$

(5)

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

**Figure:** Variation of $\omega$ with $k$: Dash-dot curve: heat source is zero; solid curve: heat source is non-zero.

**Figure:** Variation of $\omega_{\text{max}}$ with $D$. Dot curve: $R(h) = 0$; solid curve: $R(h) \neq 0$.

The uniformly heated film is completely stable against small perturbations in some interval of the optical thickness parameter.
Single laser beam (no interference, i.e. $f = 1$):

Figure: Profile of the film height (left), and the evolution of the minimum point on the film surface (right). Note the formation of a nanowire array. Spacing equals $2\pi / k_{\text{max}} \equiv$ wavelength of the fastest growing perturbation ($\omega = \omega_{\text{max}}$).

Rupture time $T_r \approx 0.9$ ms (depends on the amplitude of the initial film height).
Two-beam interference: \( f \equiv f(x) = 1 + 0.99 \cos(0.157(x - \frac{\pi}{2.2})) \)

Note: \( 2\pi/0.157 = 40 \): the distance between interference fringes

**Figure:** Top row, left: \( H = 10 \) nm, 8 wavelengths; Top row, right: \( H = 10 \) nm, 28 wavelengths; Bottom row: \( H = 15 \) nm, 28 wavelengths.

The spatial periodicity of nanowires follows the interference imprint.
Bilayer films
(Interference not included yet; 2D analysis)
Problem geometry: bilayer + transparent SiO$_2$ substrate + reflective support layer
$R = R(h_1, h_2 - h_1)$ is a smooth convex function of its arguments; model adapted from J.S.C. Prentice, “Coherent, partially coherent and incoherent light absorption in thin-film multilayer structures,” J. Phys. D: Appl. Phys. 33, 3139 (2000).
\[
\begin{align*}
\partial_t h_1 + \partial_x \left[ F_{11} \partial_x P_1 + F_{12} \partial_x P_2 + \Phi_{11} \partial_x \sigma_1 + \Phi_{12} \partial_x \sigma_2 \right] &= 0, \\
\partial_t h_2 + \partial_x \left[ F_{21} \partial_x P_1 + F_{22} \partial_x P_2 + \Phi_{21} \partial_x \sigma_1 + \Phi_{22} \partial_x \sigma_2 \right] &= 0,
\end{align*}
\]

\(F_{\ell m}(h_1, h_2 - h_1)\) and \(\Phi_{\ell m}(h_1, h_2 - h_1)\) are polynomials of a degree at most three, and \(\sigma_i = \sigma_i(T_i(h_i(x, t)))\) (next slide)

**Pressures:**
\[
\begin{align*}
P_1 &= -\sigma_1 \partial_{xx} h_1 - \sigma_2 \partial_{xx} h_2 + \Pi_1 + \Pi_2 + \rho_1 gh_1 + \rho_2 g (h_2 - h_1), \\
P_2 &= -\sigma_2 \partial_{xx} h_2 + \Pi_2 + \rho_2 gh_2,
\end{align*}
\]

**Disjoining pressures:**
\[
\begin{align*}
\Pi_1(h_1, h_2 - h_1) &= \frac{A_{s2}}{h_1^3} - \frac{A_{g2}}{(h_2 - h_1)^3} + \frac{S_1 \exp\left(-\frac{h_1}{\ell_1}\right)}{l_1} - \frac{S_2 \exp\left(-\frac{(h_2 - h_1)}{\ell_2}\right)}{l_2}, \\
\Pi_2(h_1, h_2 - h_1) &= \frac{A_{g2}}{(h_2 - h_1)^3} + \frac{A_{sg}}{h_2^3} + \frac{S_2 \exp\left(-\frac{(h_2 - h_1)}{\ell_2}\right)}{l_2}.
\end{align*}
\]
Energy equations, reflectivity, surface tension etc.

Energy equations:

\[
\frac{\kappa_{1,2}}{\rho_{1,2} C_{\text{eff}}} \partial_{zz} T_{1,2} + \frac{\delta_2}{\rho_{1,2} C_{\text{eff}}} J (1 - R) \exp (\delta_{1,2} (z - h_2)) = 0,
\]

\[
\frac{\kappa_{s}}{\rho_{s} C_{\text{eff}}} \partial_{zz} T_s = 0.
\]

(Add physical boundary conditions on all three interfaces and solve using CAS)

Surface tensions decrease linearly with increasing temperature:

\[
\sigma_1 = \sigma_1^{(m)} - \gamma_1 \left( T_1 (z = h_1) - T_1^{(m)} \right), \quad \gamma_1 > 0, \quad T_1 (z = h_1) > T_1^{(m)},
\]

\[
\sigma_2 = \sigma_2^{(m)} - \gamma_2 \left( T_2 (z = h_2) - T_2^{(m)} \right), \quad \gamma_2 > 0, \quad T_2 (z = h_2) > T_2^{(m)},
\]
Interwire spacing $\lambda$ from the linear stability analysis of Ag/Co bilayer

Co thickness $= 5$ nm fixed, Ag thickness varies

Solid squares: experimental points; Solid line: nonisothermal model; dashed line: isothermal model ($T_i = \text{const.}$, $\sigma_i = \text{const.}$, thus no thermocapillary (Marangoni) effect)
Simulation of the full nonlinear PDE system for Ag/Co bilayer

Co thickness = 5 nm fixed, Ag thickness = 5 nm (left), = 11 nm (right)
Evolves in bending mode

Core-shell wires

Embedded wires
Outcomes as for AgCo (*core-shell, embedded*), and also *stacked*

Evolves in bending mode

*Stacked wires*
Squeezing mode: wires do not form

Tentatively, only the bending mode of evolution results in practically useful outcomes, such as core-shell, embedded, or stacked.

We derived criterium for mode type in the linear regime (small $t$).
Future Work

- Inclusion of interference (bilayer model)
- Inclusion of interdiffusion and chemical reactions (bilayer model)
- Development of the efficient FD code for 3D simulations

Publications:

