Lubrication approximation-based model and computations of pulsed laser induced dewetting in thin metallic films

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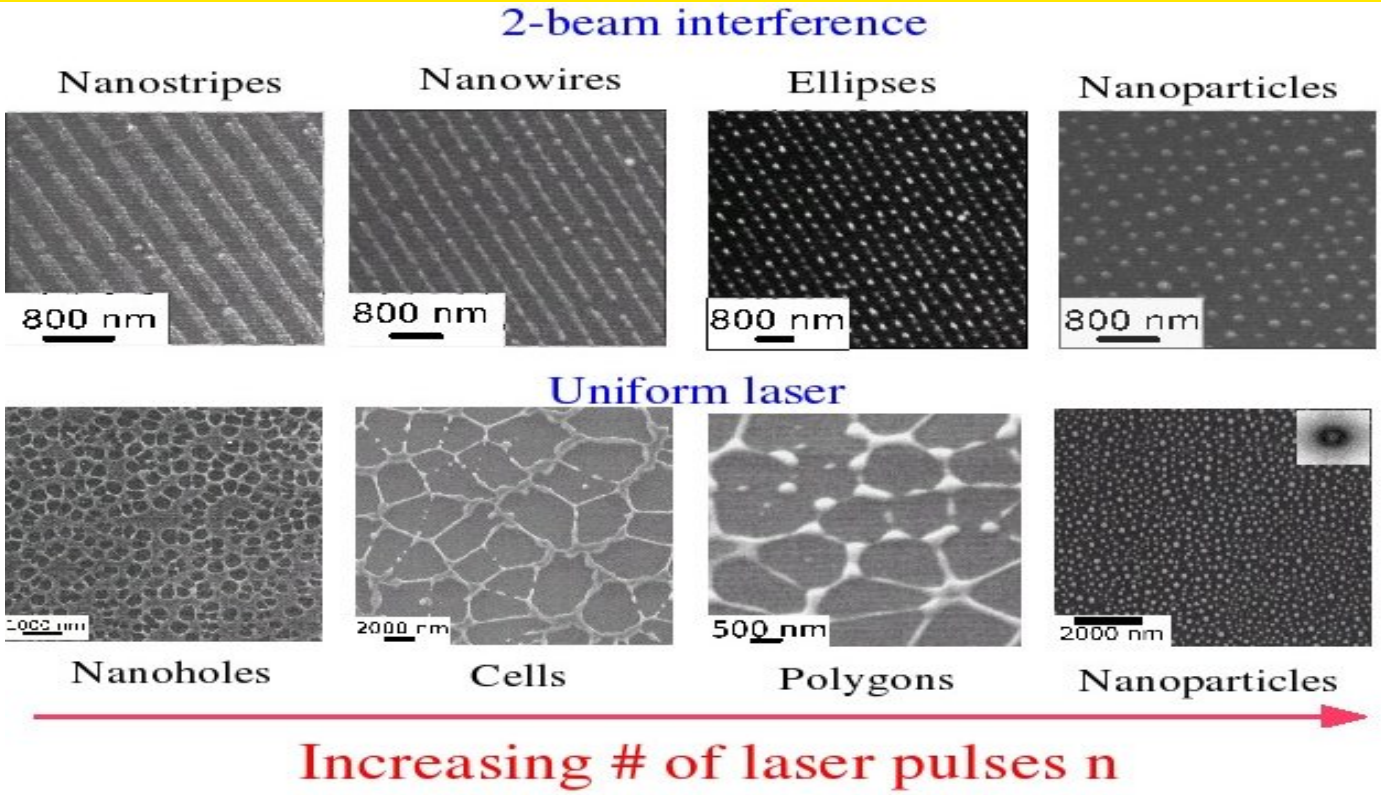
Single-layer films: Nanoscale arrays



Selected publications by Kalyanaraman group (experiment & theory):

C. Favazza et al., J. Appl. Phys. 102, 104308 (2007)

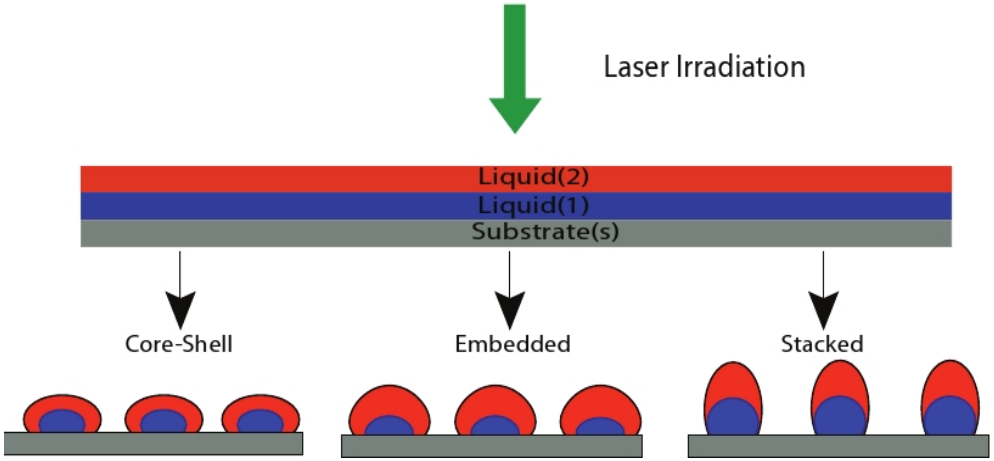
J. Trice et al., Phys. Rev. Lett. 101, 017802 (2008)

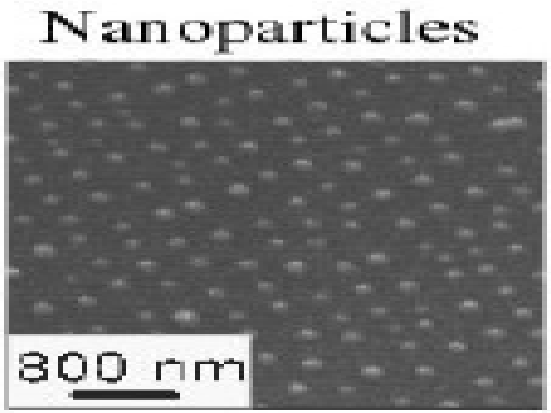
L. Longstreth-Spoor et al., J. Phys. D: Appl. Phys. 39, 5149 (2006)

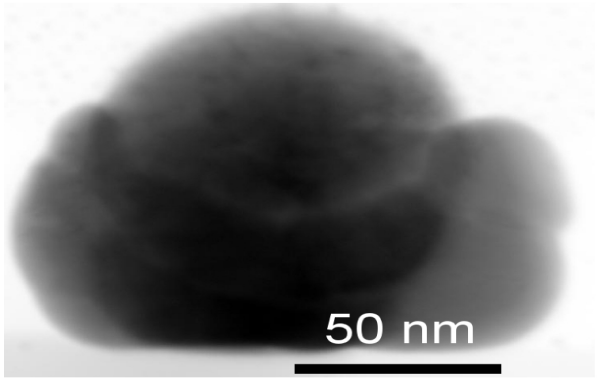
C. Favazza et al., Appl. Phys. Lett. 91, 043105 (2007)

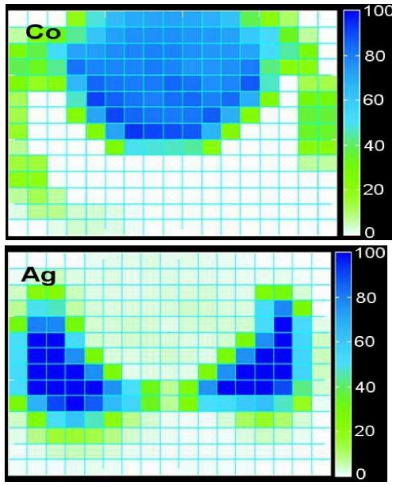
J. Trice et al., Phys. Rev. B 75, 235439 (2007)

Nanoparticle morphologies from bilayer dewetting

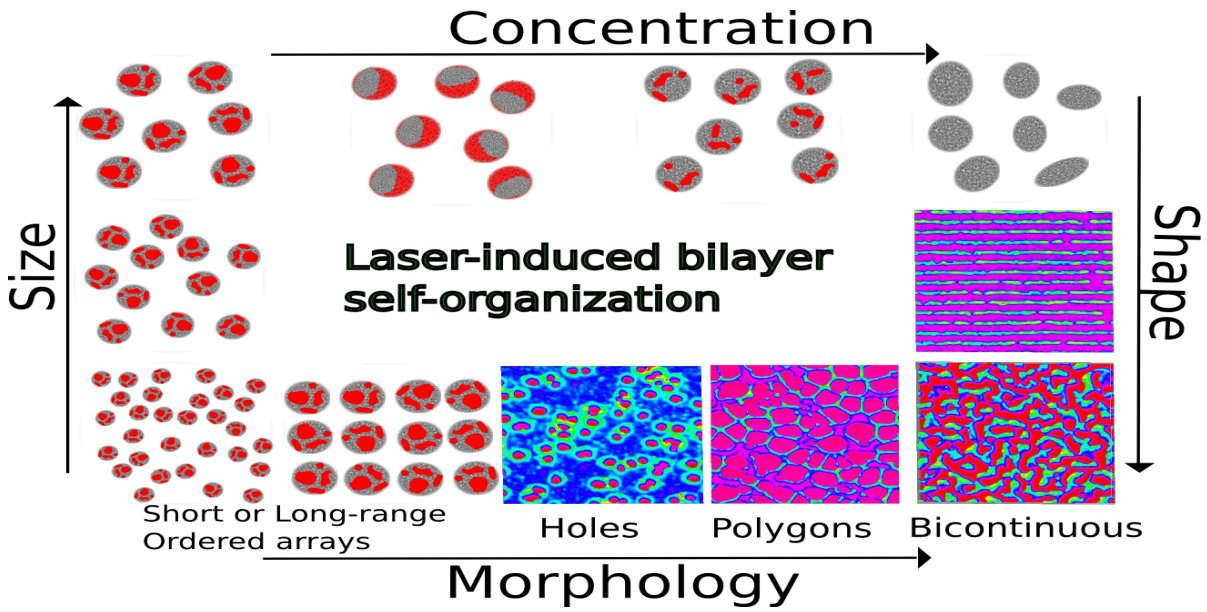








Vision of a multifunctional nanostructured surface platform based on multi-layer films



Pulsed laser self-organization of multilayer films made from immiscible metals, 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.*

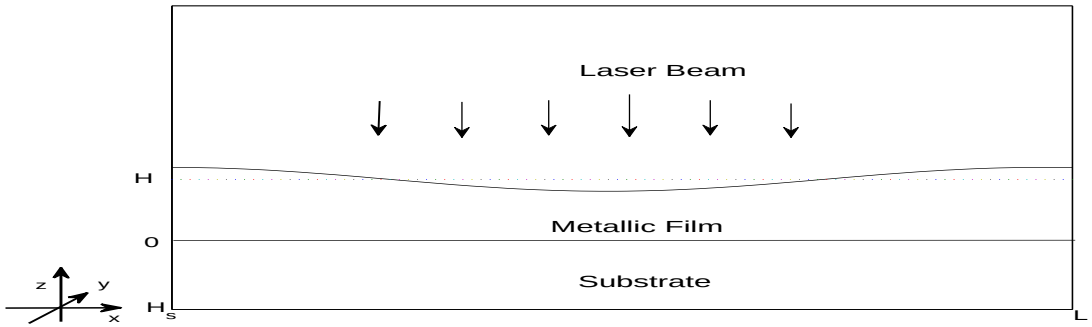
Modeling the complete dewetting cycle from a continuous film to a nanoparticles state

Treat thin film ($h \sim 10nm$) as liquid at all times, and model dewetting as continuous in time

Justification:

- Film is melted "instantaneously" when a pulse hits - energy flux $\sim 10^{11}$ J/sm^2;
- Film dewets while the pulse lasts (10 ns);
- Film solidifies "instantaneously" after the pulse is gone - due to large heat loss to a substrate, freezing the morphology;
- Next pulse quenches in the morphology and the cycle repeats (50 cycles/second).

A model for single layer films



Major physical factors contributing to particles self-organization through film dewetting:

- 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
- Capillary fluid flow (minimization of the surface area at given fluid volume by the surface tension)

Lubrication approximation: leading-order expansion in $\epsilon = H/L\,(<<1)$

- Momentum (Stokes) and continuity equations

$$\nabla \cdot \mathbf{\Omega} = 0, \quad \nabla \cdot \mathbf{u} = 0$$

- Energy equation

$$\frac{\kappa}{\rho c_p}\nabla^2 T + Q = 0,$$

where

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

$$Q = \frac{\delta J(1 - R(h))}{2} f(x, y, t) \exp\left(\delta(z - h)\right) \quad \text{(Beer-Lambert law)}$$

$$(0 \leq R(h) = r_0\left(1 - \exp\left(-a_r h\right) < 1 : \text{nonlinear reflectivity}\right)$$

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

Boundary conditions (I)

At the free surface:

(i) The normal and shear stress balances;

$$\mathbf{n}\cdot\mathbf{\Omega}\cdot\mathbf{n} = -\sigma\nabla\cdot\mathbf{n} + \frac{A}{6\pi}h^{-3}, \quad \mathbf{t}\cdot\mathbf{\Omega}\cdot\mathbf{n} = \mathbf{t}\cdot\nabla\sigma$$

(ii) The kinematic condition:
$u_3 = h_t + u_1 h_x + u_2 h_y$ $\leftarrow$ **this condition is used to derive the evolution PDE for h after u_1 an u_2 have been averaged in the z-direction**

(iii) Newton's law of cooling:
$\kappa T_z = -\alpha_h (T - T_a)$

Boundary conditions (II)

At the film-substrate interface $z = 0$:

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

$$T = \theta, \quad \kappa T_z = \kappa_s \theta_z$$

θ is the temperature field in the transparent substrate ($R = 0$ for $-H_s \leq z \leq 0$):

$$\frac{\kappa_s}{\rho_s c_{ps}} \nabla^2 \theta + Q = 0$$

$$z = -H_s : \quad \theta = T_s \quad \text{(value from experiment)}$$

Dimensionless 1D evolution equation for the film height $h(x,t)$

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

Lines 3 and 4: unconventional terms due to laser heating
C: capillary numer, G: gravity number, β: 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 $\Gamma = \kappa/\kappa_s$

$$
\begin{aligned}
R(h) &= r_0\left(1 - \exp\left(-a_r h\right)\right), \\
F(h,D,\Psi) &= \left(-\Psi + \exp\left(-Dh\right)(\Psi - 1/D) - h + 1/D\right)/2
\end{aligned}
$$

Linear stability analysis for uniform irradiation ($f = 1$)

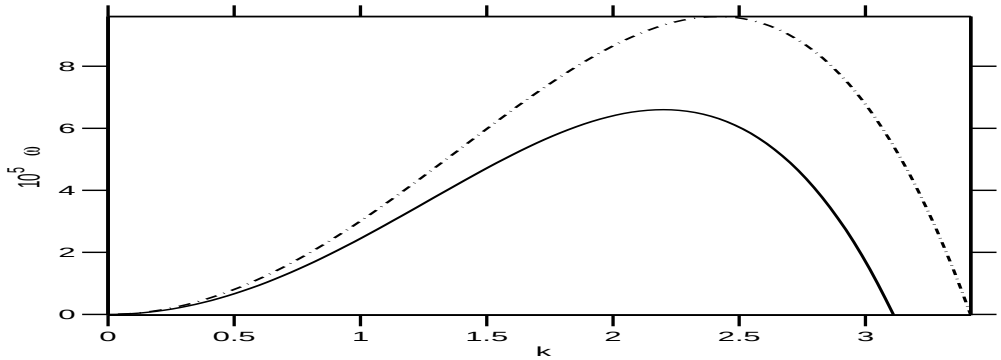


Figure: Variation of ω with k: Dash-dot curve: heat source is zero; solid curve: heat source is non-zero.

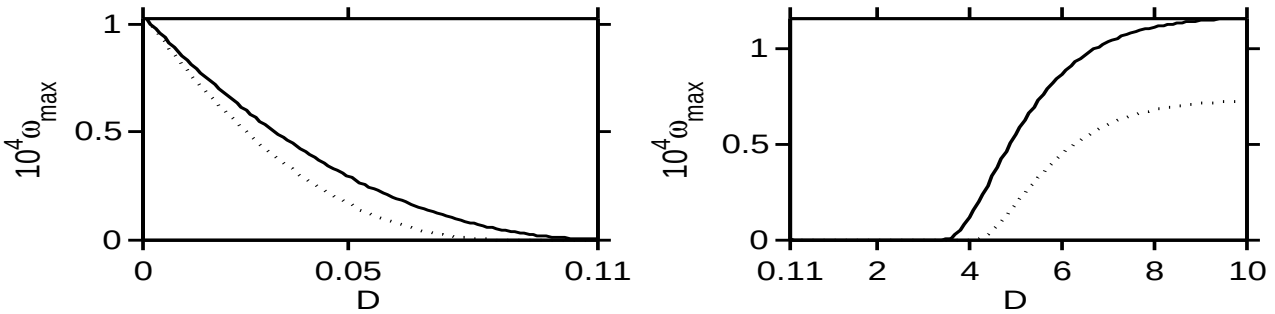


Figure: Variation of ω_{max} with D. Dot curve: $R(h) = 0$; solid curve: $R(h) \neq 0$.

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

Computation of a nonlinear evolution of the film (I)

Single laser beam ($f = 1$)

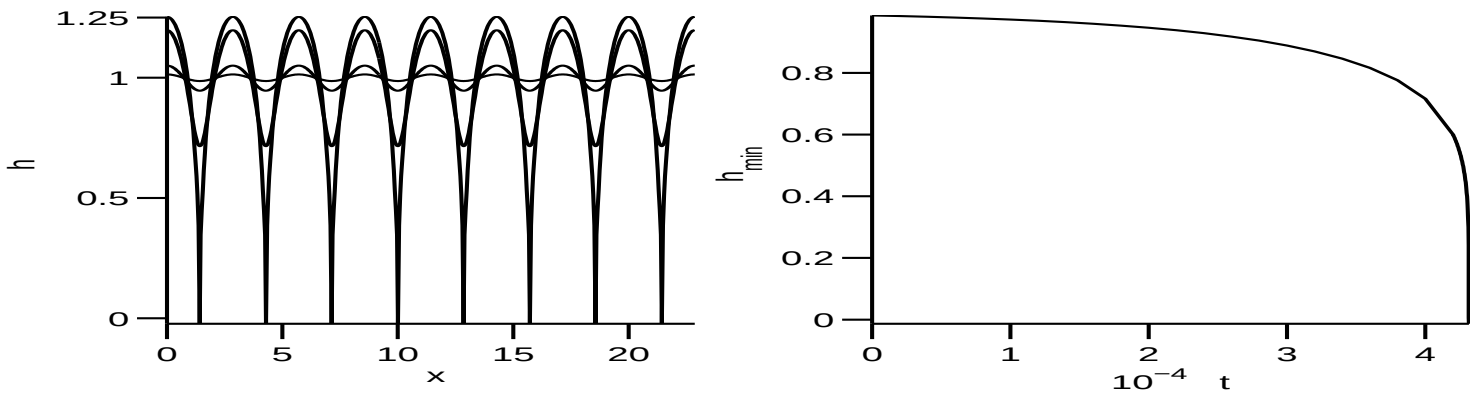


Figure: Profile of the film height (left), and the evolution of the minimum point on the film surface (right). Note the formation of a nanowire array. Spacing equals $2\pi/k_{max} \equiv$ wavelength of the fastest growing perturbation ($\omega = \omega_{max}$).

Rupture time $T_r \approx 0.9$ ms (depends on the amplitude of the initial film height).

Computation of a nonlinear evolution of the film (II)

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**

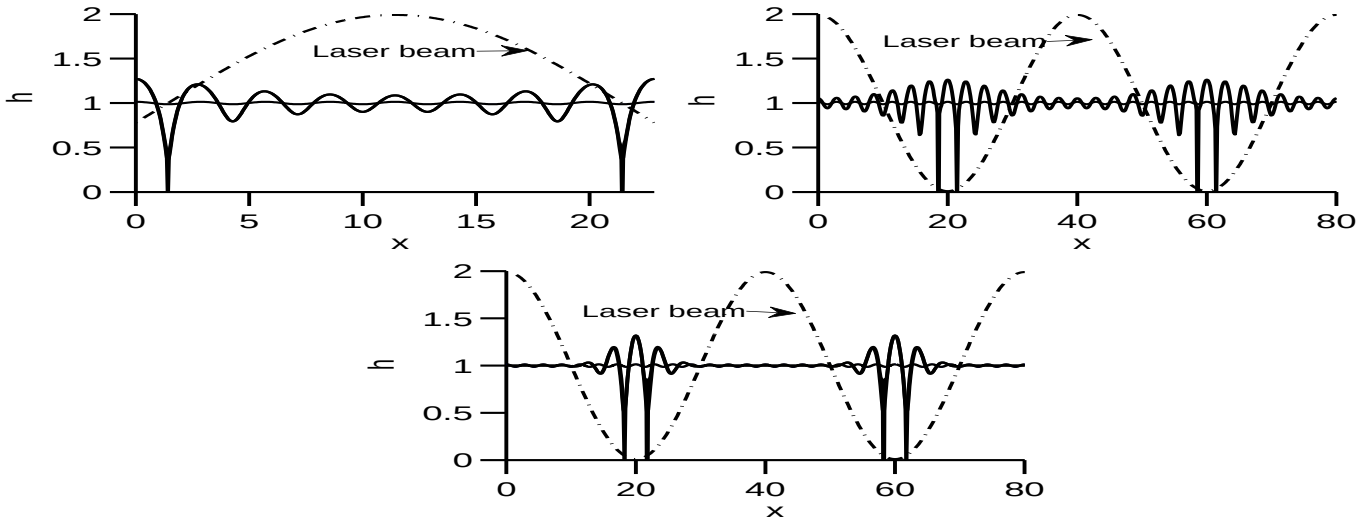


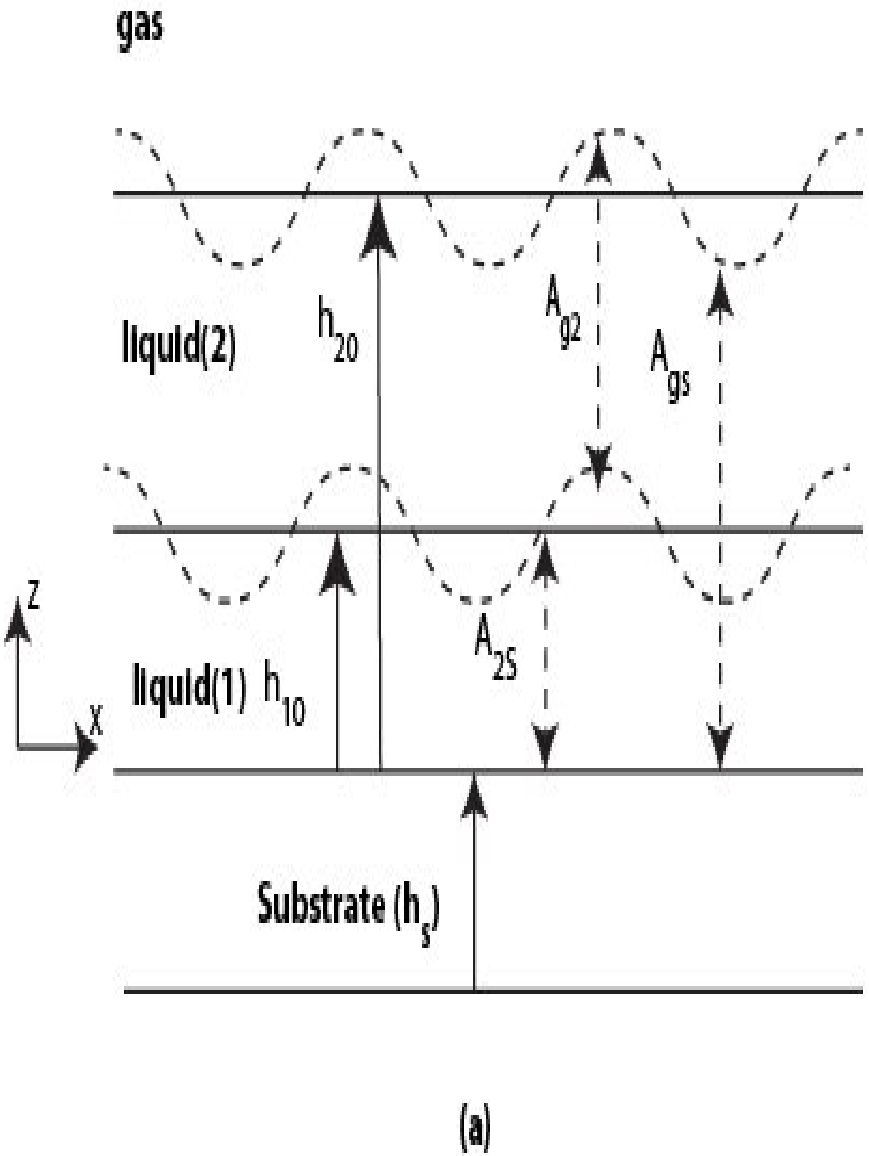
Figure: Top row, left: $H = 10$ nm, 8 wavelengths; Top row, right: $H = 10$ nm, 28 wavelengths; Bottom row: $H = 15$ nm, 28 wavelengths.

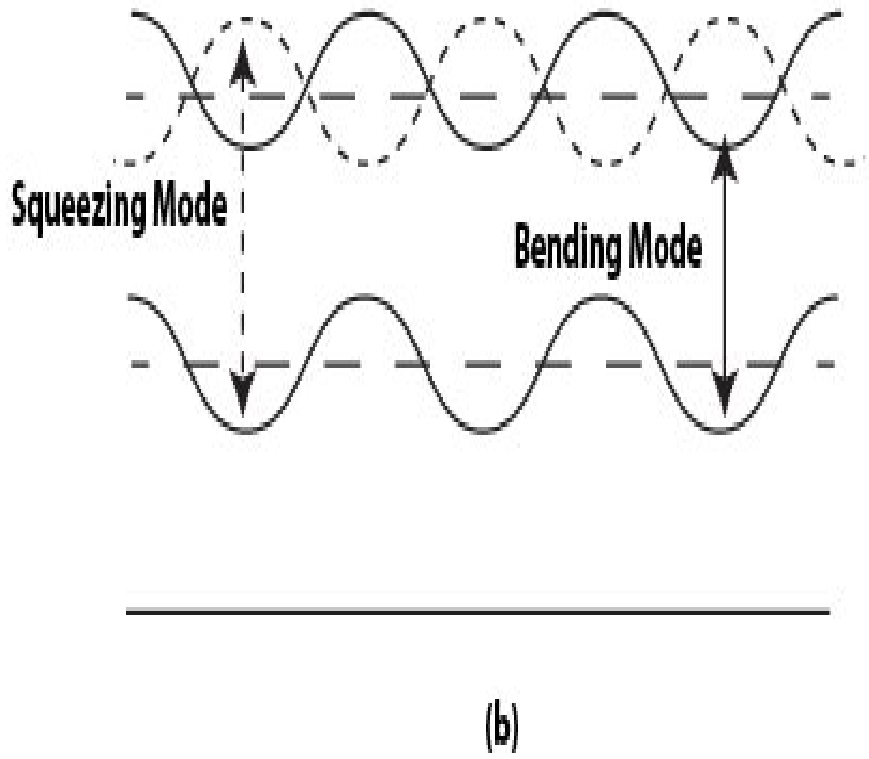
The spatial periodicity of nanowires follows the interference imprint.

Publication: A. Atena and M. Khenner, Phys. Rev. B 80, 075402 (2009)

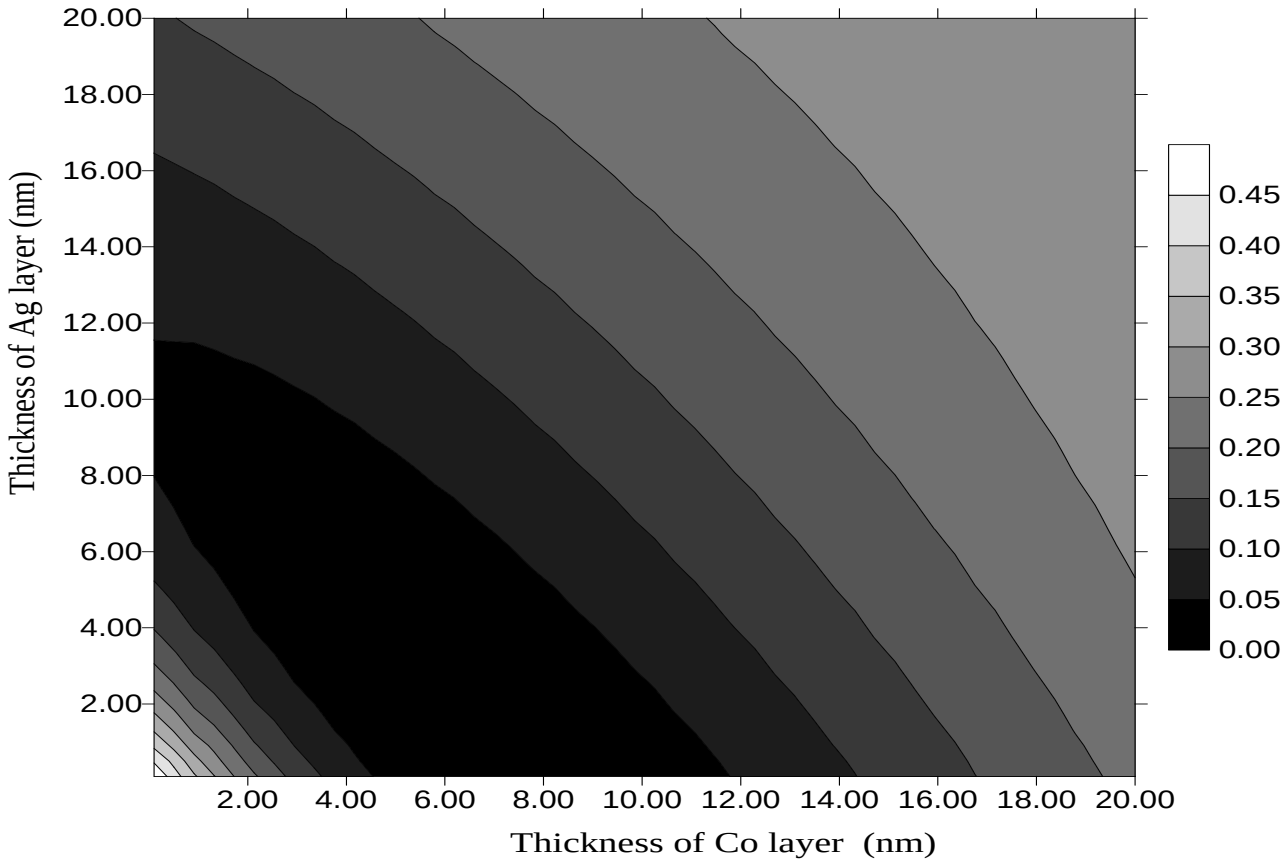
A model for 1D bilayer films

Problem Geometry: bilayer + transparent SiO_2 substrate + reflective support layer





Reflectivity (shown: AgCo bilayer, model)



$R = R\left(h_1, h_2 - h_1\right)$ 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).

Evolution equations for layers thicknesses (Pototsky et al. (2005))

$$\begin{aligned}\partial_t h_1 &= -\partial_x \left[F_{11}\partial_x P_1 + F_{12}\partial_x P_2 + \Phi_{11}\partial_x \sigma_1 + \Phi_{12}\partial_x \sigma_2\right], \\ \partial_t h_2 &= -\partial_x \left[F_{21}\partial_x P_1 + F_{22}\partial_x P_2 + \Phi_{21}\partial_x \sigma_1 + \Phi_{22}\partial_x \sigma_2\right]\end{aligned}$$

Here $F_{\ell m}\left(h_1, h_2 - h_1\right)$ and $\Phi_{\ell m}\left(h_1, h_2 - h_1\right)$ are certain polynomials of a degree at most three

Pressures:

$$\begin{aligned}P_1 &= -\sigma_1 \partial_{xx} h_1 - \sigma_2 \partial_{xx} h_2 + \Pi_1 + \Pi_2 + \rho_1 g h_1 + \rho_2 g \left(h_2 - h_1\right), \\ P_2 &= -\sigma_2 \partial_{xx} h_2 + \Pi_2 + \rho_2 g h_2\end{aligned}$$

Disjoining pressures:

$$\Pi_1\left(h_1, h_2 - h_1\right) = \frac{A_{s2}}{h_1^3} - \frac{A_{g2}}{\left(h_2 - h_1\right)^3} + \frac{S_1 \exp\left(-\frac{h_1}{\ell_1}\right)}{l_1} - \frac{S_2 \exp\left(-\frac{\left(h_2 - h_1\right)}{\ell_2}\right)}{l_2},$$

$$\Pi_2\left(h_1, h_2 - h_1\right) = \frac{A_{g2}}{\left(h_2 - h_1\right)^3} + \frac{A_{sg}}{h_2^3} + \frac{S_2 \exp\left(-\frac{\left(h_2 - h_1\right)}{\ell_2}\right)}{l_2}$$

Surface tensions, heat equations and surface tensions gradients

Surface tensions:

$$\begin{aligned}\sigma_1 &= \sigma_1^{(m)} - \gamma_1 \left(T_1 \left(z = h_1 \right) - T_1^{(m)} \right), \quad \gamma_1 > 0, \; T_1 \left(z = h_1 \right) > T_1^{(m)}, \\ \sigma_2 &= \sigma_2^{(m)} - \gamma_2 \left(T_2 \left(z = h_2 \right) - T_2^{(m)} \right), \quad \gamma_2 > 0, \; T_2 \left(z = h_2 \right) > T_2^{(m)}\end{aligned}$$

Heat equations are ODEs in z for $T_{1,2} = T_{1,2}(z, h_{1,2}(x))$:

$$\begin{aligned}\frac{\kappa_{1,2}}{\rho_{1,2} C_{eff}} \partial_{zz} T_{1,2} + \frac{\delta_2 J}{\rho_{1,2} C_{eff}} \left(1 - R\right) \exp\left(\delta_{1,2} \left(z - h_2\right)\right) &= 0, \\ \frac{\kappa_s}{\rho_s C_{eff}} \partial_{zz} T_s &= 0\end{aligned}$$

Add physical boundary conditions on the three interfaces: liquid/gas, liquid/liquid and liquid/substrate and solve in CAS

$\rightarrow T_{1,2} = T_{1,2}(z, h_{1,2}(x))$

Surface tensions gradients:

$$\begin{aligned}\partial_x \sigma_1 &= -\gamma_1 \left(\left(\partial_{h_1} T_1 \right) |_{z=h_1} \partial_x h_1 + \left(\partial_{h_2} T_1 \right) |_{z=h_1} \partial_x h_2 \right), \\ \partial_x \sigma_2 &= -\gamma_2 \left(\left(\partial_{h_1} T_2 \right) |_{z=h_2} \partial_x h_1 + \left(\partial_{h_2} T_2 \right) |_{z=h_2} \partial_x h_2 \right)\end{aligned}$$

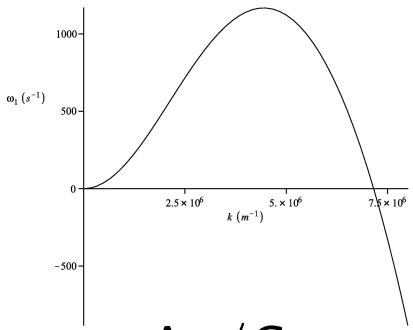
Linear stability analysis for Ag/Co and Co/Ag bilayers

Dispersion relation:

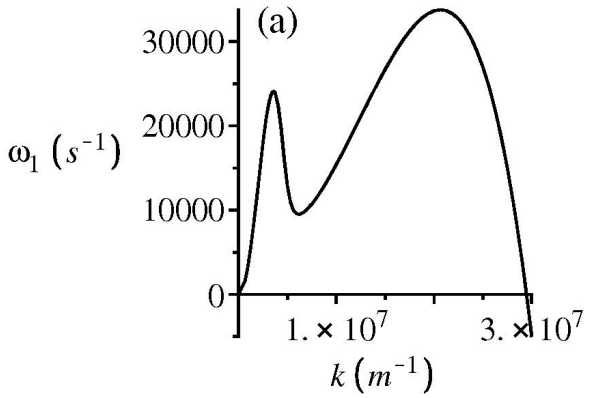
$$\omega(k)^2 - (a_{11} + a_{22})\,\omega(k) + a_{11}a_{22} - a_{12}a_{21} = 0$$

- Coefficients a_{ij} are functions of the wavenumber k, initial thicknesses h_{10}, h_{20}, Hamaker coefficients and other parameters
- Roots ω_1 and ω_2 are real and distinct
- $|\omega_2(k)| \ll |\omega_1(k)|$

$\rightarrow$ Only such perturbations destabilize the interfaces that have $\omega_1 > 0$ on some interval of the wavenumber k



Ag/Co



CoAg

Comparison of LSA and the experiment

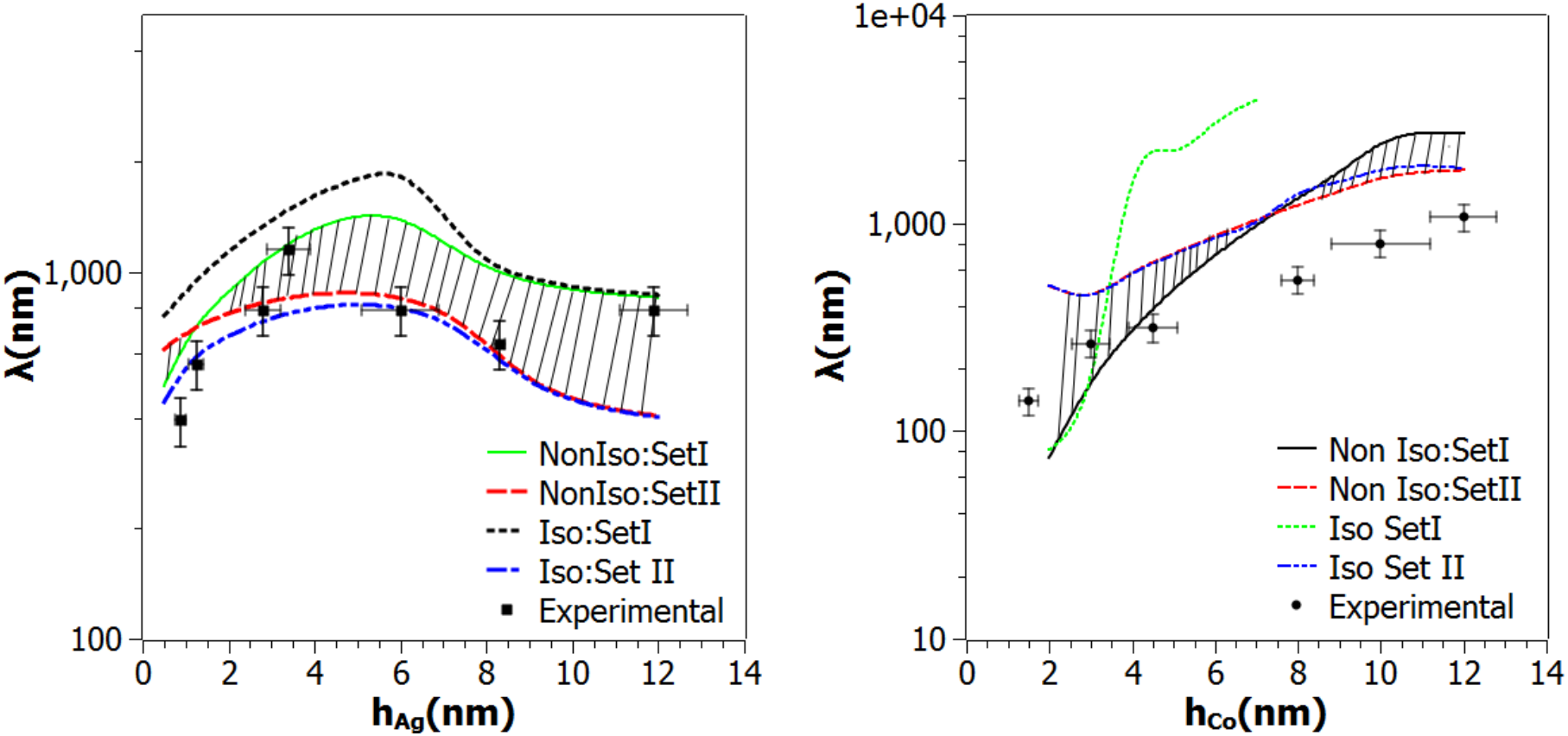
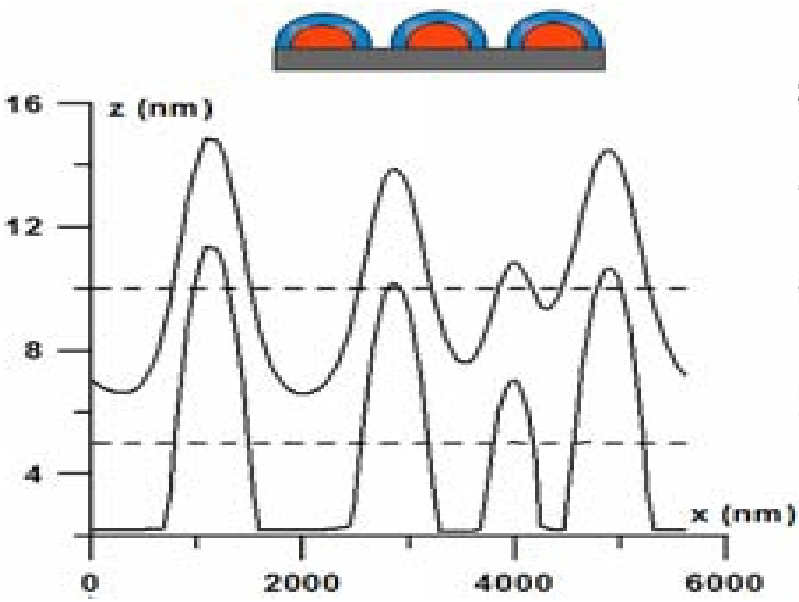


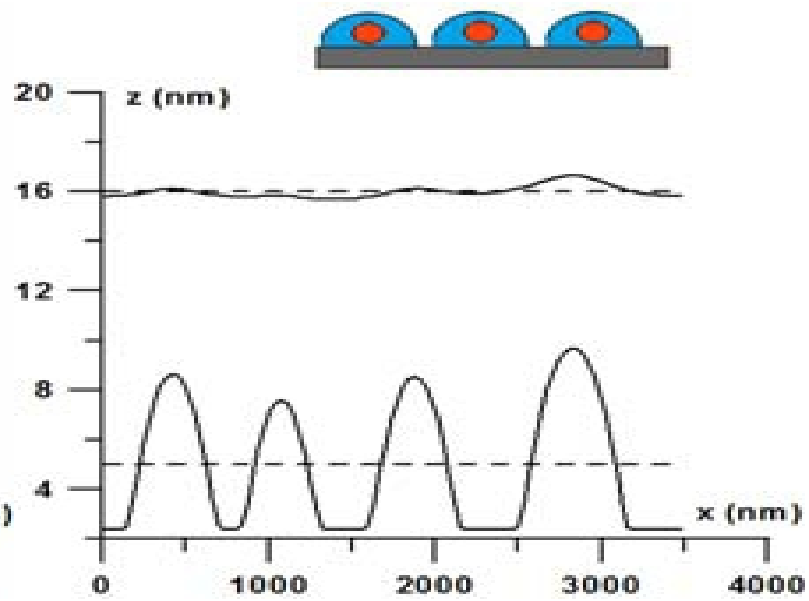
Figure: Particle spacing vs. the thickness of the top layer, for $Ag/Co/SiO_2/Si$ and $Co/Ag/SiO_2/Si$ systems with the bottom layer thickness fixed at 5 nm.

Simulation of the full nonlinear PDE system for Ag/Co bilayer

Co thickness = 5 nm fixed

Bilayer evolves in bending mode $\rightarrow$ Formation of core-shell or embedded particles





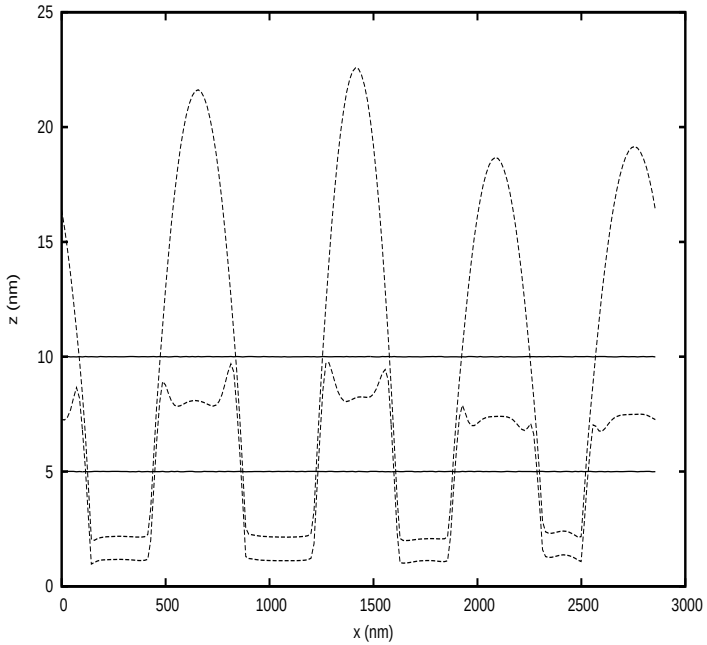
Core-shell particles
Ag thickness = 5 nm

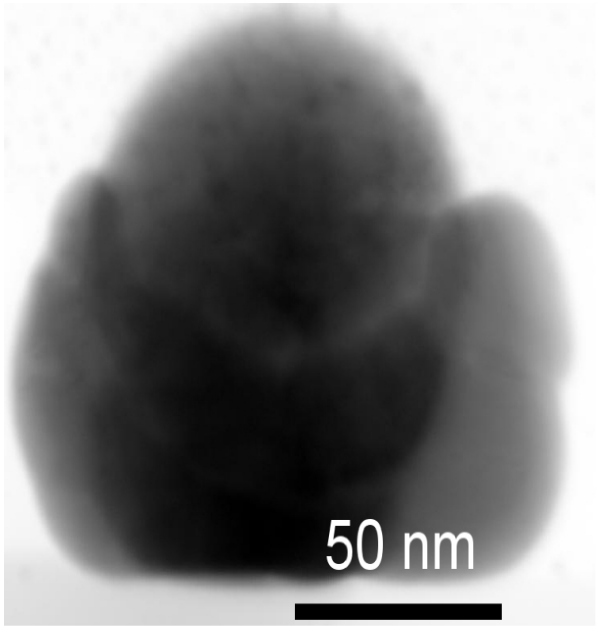
Embedded particles
Ag thickness = 11 nm

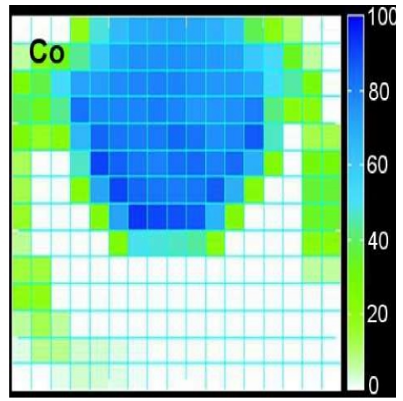
Simulation of the full nonlinear PDE system for Co/Ag bilayer

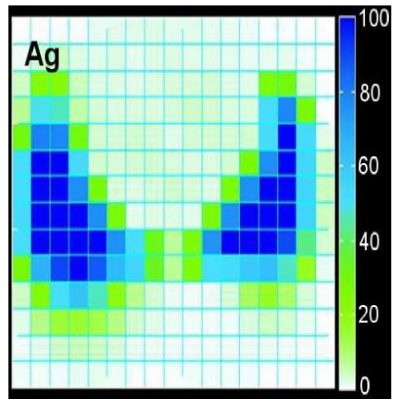
Bilayer evolves either in bending, or squeezing, or mixed bending/squeezing mode, depending on parameters (especially the Hamaker coefficients)

→ Formation of core-shell, embedded, or stacked particles



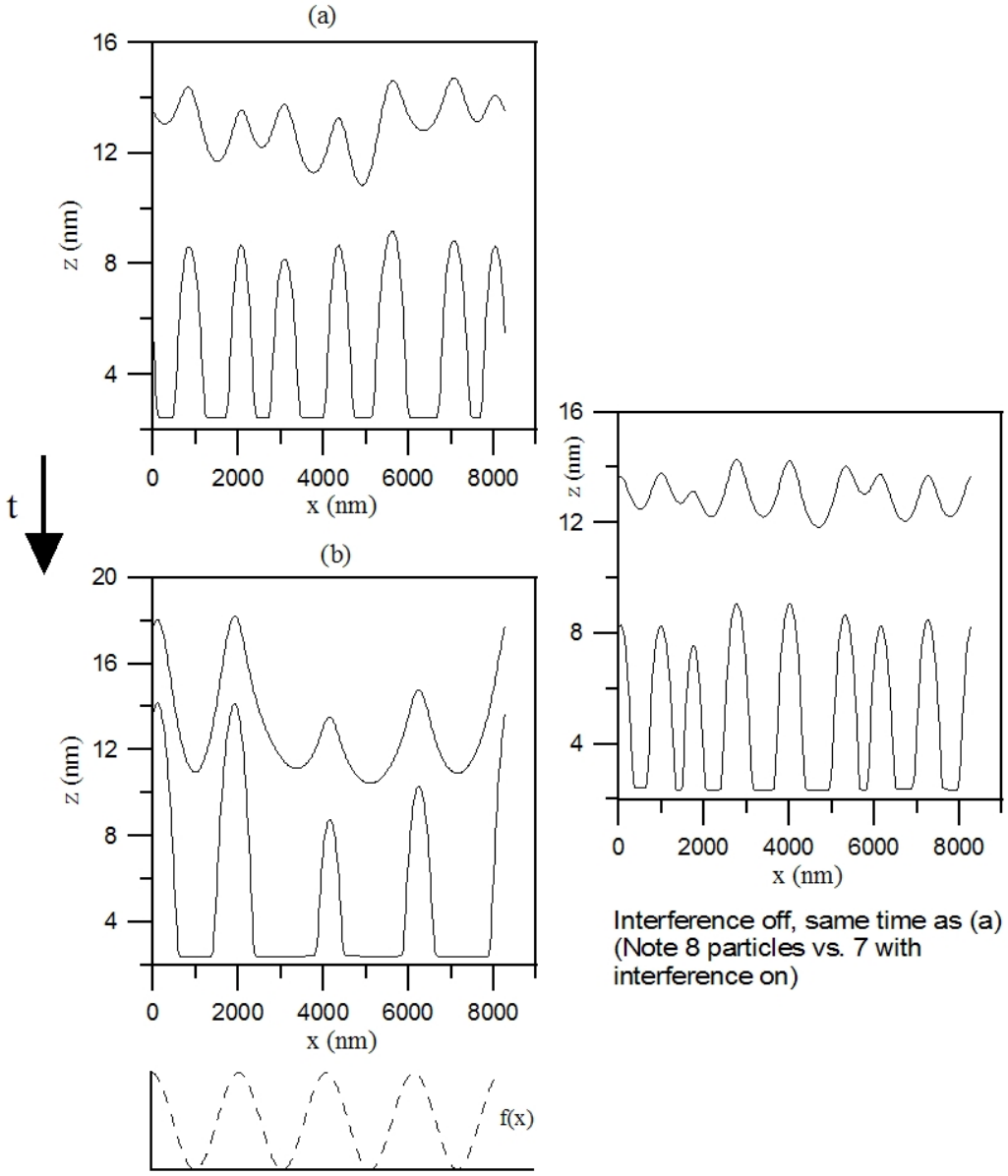






Stacked particles

Effect of interference heating on bilayer evolution



Publications (collaborative)

Single-layer films:

1. H. Krishna, R. Sachan, J. Strader, C. Favazza, M. Khenner, and R. Kalyanaraman, Nanotechnology 21, 155601 (2010) (experiment & theory)

Bilayer films:

1. H. Krishna, N. Shirato, S. Yadavali, R. Sachan, J. Strader, and R. Kalyanaraman, ACS Nano 5, 470-476 (2011) (experiment)
2. M. Khenner, S. Yadavali, and R. Kalyanaraman, "Formation of organized nanostructures from unstable bilayers of thin metallic liquids" (submitted, theory)
3. M. Khenner and R. Kalyanaraman, "Controlling Nanoparticles Formation in Molten Metallic Bilayers by Pulsed-Laser Interference Heating" (submitted, theory)