Stability analysis of pulsed laser-melted bilayer thin films

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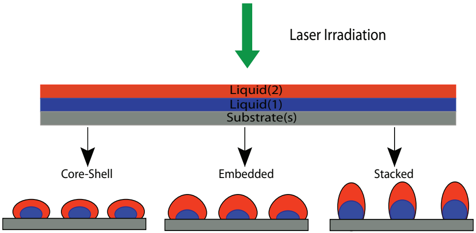
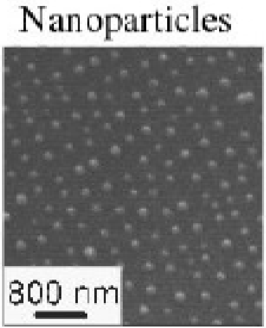
Project Goal

To provide an increased understanding of the physical mechanisms involved in pattern formation of nanoparticles from liquid film dewetting via the derivation, analysis and computation of a nonlinear PDE-based models

Dewetting $\equiv$ "uncovering" (exposure) of some areas the substrate

Collaboration with: Prof. Ramki Kalyanaraman, UTK Department of Chemical and Biomolecular Engineering, Department of Materials Science and Engineering, Sustainable Energy Education Research Center





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. Figure courtesy of R. Kalyanaraman, UTK

Let check out this Wikipedia page:
http://en.wikipedia.org/wiki/Benjamin_Franklin
Q: Is Dr. Khenner crazy ? Why is he getting the US President who's been dead for 250 years into his presentation on MATHEMATICAL MODELING OF LIQUID BILAYERS ?
A: NO, Dr. Khenner is perfectly sane. Let check out another online resource:
http://www2.avs.org/benjaminfranklin/richmond.pdf
Mr. Franklin is always here:
http://en.wikipedia.org/wiki/File:New100front.jpg
to remind you of MATHEMATICAL MODELING OF LIQUID BILAYERS ! :))

Challenges:

- Develop a model of the heat transfer within the film and incorporate this model into the evolution PDEs for the thicknesses of the layers ← ACCOMPLISHED; *this talk*
- Develop efficient computational methods for 1D and 2D simulations of evolution PDEs ← 1D ACCOMPLISHED, 2D IN WORK
- Using analysis, predict inter-particle spacing ← ACCOMPLISHED; *this talk*
- Using computation, predict particles morphology ← ACCOMPLISHED in 1D; *some results in this talk*
- Develop a model of interference control of a pattern formation ← ACCOMPLISHED
- Develop models that account for interdiffusion of metals and quantify impacts on spacing and morphology ← WORK HAS NOT STARTED

Our interest is to model the complete dewetting cycle - from a continuous film to a nanoparticles state

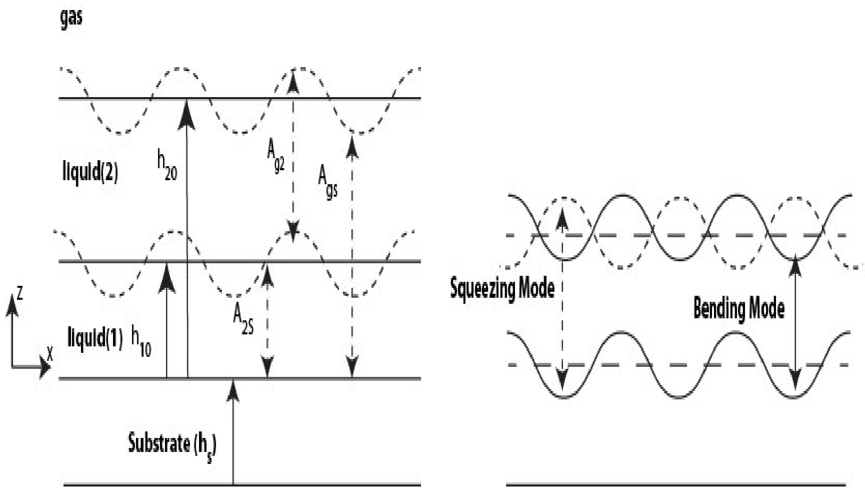
Modeling assumption

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

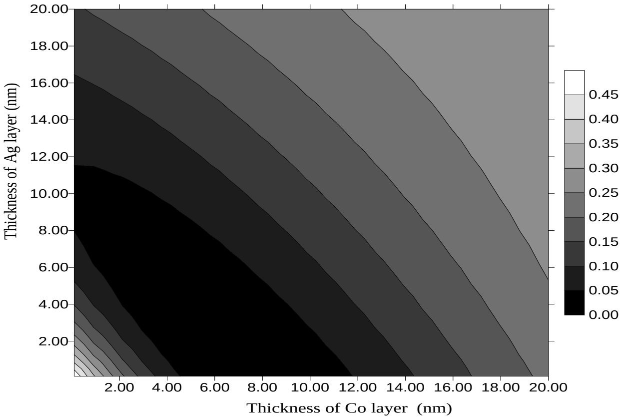
In reality, pulse width = 10 ns, pulse frequency = 50 Hz. Nanometer-scale film is:

- 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.

1D Problem Geometry: bilayer + transparent SiO_2 substrate + reflective support layer



Reflectivity (shown: AgCo bilayer, model)



$R = R(h_1, h_2 - h_1)$ 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).

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

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

Pressures:

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

Disjoining pressures:

$$\begin{aligned}
\Pi_1(h_1, h_2 - h_1) &= \frac{A_{s2}}{h_1^3} - \frac{A_{g2}}{(h_2 - h_1)^3} + \frac{S_1 \exp\left(-\frac{h_1}{\ell_1}\right)}{l_1} - \frac{S_2 \exp\left(-\frac{(h_2 - h_1)}{\ell_2}\right)}{l_2}, \\
\Pi_2(h_1, h_2 - h_1) &= \frac{A_{g2}}{(h_2 - h_1)^3} + \frac{A_{sg}}{h_2^3} + \frac{S_2 \exp\left(-\frac{(h_2 - h_1)}{\ell_2}\right)}{l_2}
\end{aligned}$$

Surface tensions:

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

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

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

Add physical boundary conditions on the three interfaces: liquid/gas, liquid/liquid and liquid/substrate and solve using Mathematica
$\rightarrow \mathrm{T}_{1,2} = T_{1,2}(z, h_{1,2}(x))$

Surface tensions gradients: (Note the Chain Rule !)

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

The tool is the Linear Stability Analysis (LSA) - a "simple" procedure based on Taylor's expansion

This is how LSA may look like in the context of a single ODE (which is **not** our present context - ours is a SYSTEM of TWO PDEs, if you noticed)

$$\frac{dx}{dt} \equiv x' = f(x), \text{ where } f(x) \text{ is } \textbf{nonlinear}$$

Let x^* is the fixed (equilibrium) point, i.e. $f(x^*) = 0$. Let $\delta(t) = x(t) - x^*$ be a small perturbation from x^*. Then:

$$\begin{aligned} \delta' &= \frac{d}{dt}(x(t) - x^*) = x'(t), \ \delta' = x' = f(x) = f(x^* + \delta) \\ &= f(x^*) + \delta f'(x^*) + O(\delta^2) \approx \delta f'(x^*), \text{ if } f'(x^*) \neq 0 \end{aligned}$$

This is *linearization* about x^*.

- $\delta(t)$ grows exponentially if $f'(x^*) > 0$, and the equilibrium x^* is *unstable*; $f'(x^*)$ is the growth rate
- $\delta(t)$ decays exponentially if $f'(x^*) < 0$, and the equilibrium x^* is *stable*; $|f'(x^*)|$ is the decay rate

The tool is the Linear Stability Analysis (LSA)

- Gives information on stability or instability of equilibrium, constant heights $h_{10,20}$ with respect to **small sinusoidal perturbations ($\sim \cos kx$), called standing waves** of the period $2\pi/k$, defined on $x : (-\infty, \infty)$; $0 \leq k < \infty$ is the wavenumber
  1. Using linearization of the PDE about these constant heights and the separation of variables in the linearized PDE, predicts the interval of k values such that the amplitudes of the corresponding standing waves increase with time. Interfaces are unstable with respect to such standing waves;
  2. Predicts the wavenumber (k_{max}) from the set of unstable wavenumbers, such that the corresponding standing wave has the fastest (exponentially) growing amplitude, and provides the numerical value of this growth rate. The wave having the wavenumber k_{max} will dominate over other growing waves after a short while, and $2\pi/k_{max}$ is hopefully a sought after inter-particle spacing

The nonlinear evolution PDEs for $h_1(x,t)$ and $h_2(x,t)$ have been presented

(i) Plug $h_1(x,t) = h_{10} + f_1(x,t)$, $h_2(x,t) = h_{20} + f_2(x,t)$ into the PDEs; $f_1(x,t)$ and $f_2(x,t)$ are *small* perturbations

(ii) Linearize PDEs, i.e., say, $h_1(x,t)h_2(x,t) = h_{10}h_{20} + h_{10}f_2(x,t) + h_{20}f_1(x,t)$, etc. Due to differential operators ∂_t in the *lhs* and $\partial_x[..]$ in the *rhs* the constant contributions, i.e. h_{10}, h_{20}, $h_{10}h_{20}$, etc. vanish. What emerges is two linear, fourth-order PDEs for the perturbations:

$$
\begin{aligned}
\partial_t f_1 &= G_1(\partial_{xx} f_1, \partial_{xx} f_2, \partial_{xxxx} f_1, \partial_{xxxx} f_2),\\
\partial_t f_2 &= G_2(\partial_{xx} f_1, \partial_{xx} f_2, \partial_{xxxx} f_1, \partial_{xxxx} f_2)
\end{aligned}
$$

(iii) Assume $f_1 = U(t)\cos kx$, $f_2 = V(t)\cos kx$ (a standing waves) and substitute in the above PDEs. Through separation of variables this gives the linear ODE system for the wave's amplitudes:

$$\begin{aligned} \dot{U}(t) &= a_{11}U(t) + a_{12}V(t), \\ \dot{V}(t) &= a_{21}U(t) + a_{22}V(t), \end{aligned}$$

where a_{ij}'s are the complicated functions of k, $h_{10,20}$, and the physical parameters

(iv) Next, substitute $U(t) = u\exp(\omega t)$, $V(t) = v\exp(\omega t)$ in the ODE system:

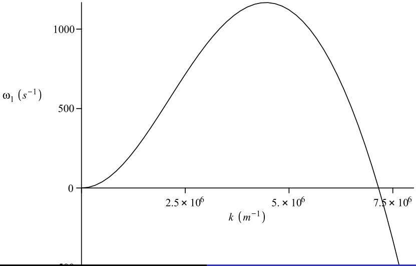
$$\begin{aligned} (a_{11} - \omega)\,u + a_{12}v &= 0, \\ a_{21}u + (a_{22} - \omega)\,v &= 0 \end{aligned}$$

This is linear, homogeneous algebraic system for u and v. ω is the growth rate of a perturbation (wave).

(v) A non-trivial solution to this linear system exists iff the determinant of the system's matrix equals zero. Which translates into:

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

For the realistic physical parameters, both roots of this quadratic are real and distinct. Moreover, $|\omega_2(k)| \ll |\omega_1(k)|$ and, at least for AgCo bilayer, $\omega_2(k) < 0\ \forall k$. Thus only such perturbations destabilize the interfaces that have $\omega_1 > 0$ on some interval of the wavenumber k.



(vi) The wavenumber k_{max} of fastest growing perturbation corresponds to the maximum of the $\omega_1(k)$ curve, and thus it is determined from the condition:

$$\frac{d\omega_1(k)}{dk} = 0,$$

and the growth rate of this perturbation is $\omega_1(k_{max})$.

Thus we had determined the inter-particle spacing $2\pi/k_{max}$.

For more details on LSA see, for instance, http://www.dur.ac.uk/suzanne.fielding/teaching/HST/sec6.pdf

Critisism: Really ? Real perturbations are not sinusoidal, thus LSA makes little sense.

A: Indeed, real perturbations are not sinusoidal, and moreover, they certainly have a compact support (since the horizontal size of the system is finite). But, the procedure is perfectly general: an absolutely integrable, non-periodic perturbation $f(x)$ on $[a,b]$ can be represented as a sum of standing waves on $x:(-\infty,\infty)$ with different wavenumbers (a convergent trigonometric Fourier series)

$$f(x)=\sum_{n=0}^{\infty}\left(a_n\cos\frac{2n\pi x}{b-a}+b_n\sin\frac{2n\pi x}{b-a}\right),\ \text{if}\ \int_a^b|f(x)|dx<\infty$$

$$a_n=\frac{2}{b-a}\int_a^b f(x)\cos\frac{2n\pi x}{b-a}dx,\quad b_n=\frac{2}{b-a}\int_a^b f(x)\sin\frac{2n\pi x}{b-a}dx$$

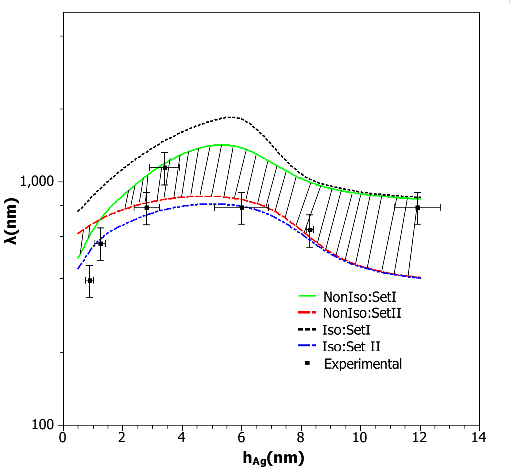
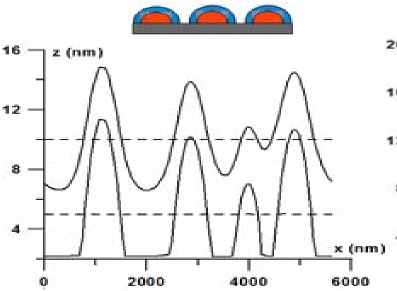
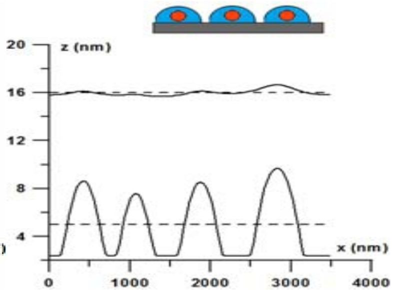


Figure: Particle spacing vs. the thickness of the top layer, for $Ag/Co/SiO_2/Si$ system with the Co layer thickness fixed at 5 nm.

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



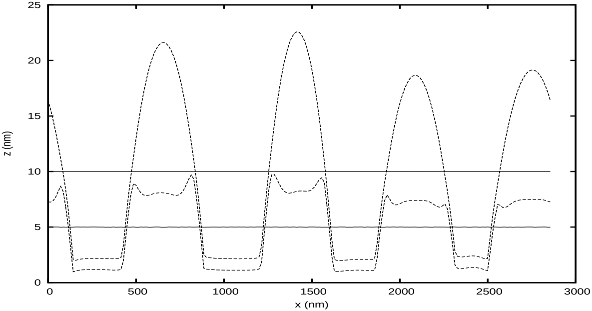
Core-shell particles



Embedded particles

Outcomes as for AgCo (*core-shell or embedded* particles), and also *stacked* particles

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



Stacked particles

Bilayer films:

1. M. Khenner, S. Yadavali, and R. Kalyanaraman, "Formation of organized nanostructures from unstable bilayers of thin metallic liquids" (submitted)
2. M. Khenner and R. Kalyanaraman, "Controlling Nanoparticles Formation in Molten Metallic Bilayers by Pulsed-Laser Interference Heating" (submitted)

Single-layer films:

1. H. Krishna, R. Sachan, J. Strader, C. Favazza, M. Khenner, and R. Kalyanaraman, "Thickness-dependent spontaneous dewetting morphology of ultrathin Ag films", Nanotechnology 21, (2010) 155601
2. A. Atena and M. Khenner, "Thermocapillary effects in driven dewetting and self-assembly of pulsed laser-irradiated metallic films", Phys. Rev. B 80, 075402 (2009)

See http://people.wku.edu/mikhail.khenner for slides of this presentation and for more information