Linear Analysis

To find the analytical solutions conveniently, the governing equations were linearized:

The film height and concentration were assumed to have the forms,

$$h = 1 + \eta(t)\frac{\cos\pi x}{2}$$

$$\mathrm{c} = \frac{1}{2} + \xi(t)\frac{\cos\pi x}{2}$$

$$\Rightarrow$$

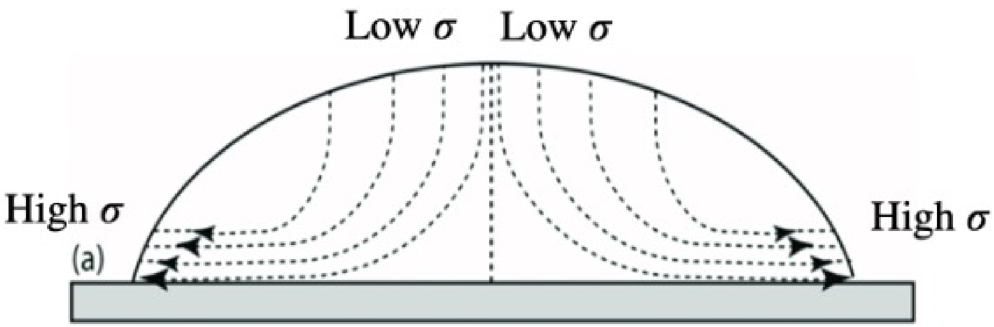
$$\frac{\partial\eta}{\partial t} + \frac{1}{3A}\left[\left(1+\frac{S_2}{2}\right)\pi^4\right]\eta - \left[\left(\frac{Ma}{2}\right)\pi^2\right]\xi = 0$$

---(1)

$$\frac{\partial\xi}{\partial t} + \left[\left(\frac{1}{Pe}\right)\pi^2\right]\xi = 0 \quad \text{---(2)}$$

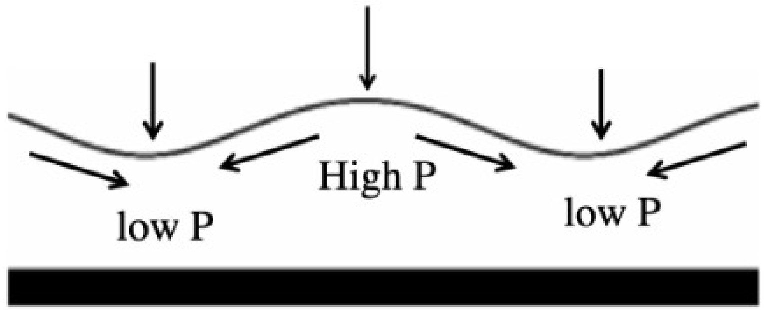
$$\boxed{\eta_{max}\left(=\frac{h_{max}}{h0}\right) = \frac{\frac{Ma\pi^2}{2}}{\psi_1-\psi_2}\left\{exp\left(\frac{\psi_1}{\psi_1-\psi_2}\ln\left(\frac{\psi_2}{\psi_1}\right)\right) - exp\left(\frac{\psi_2}{\psi_1-\psi_2}\ln\left(\frac{\psi_2}{\psi_1}\right)\right)\right\}}$$

Physical Mechanisms Involved



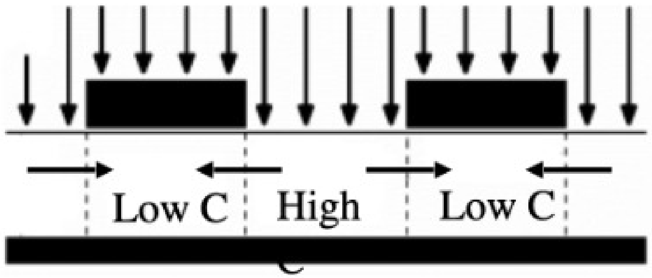
Marangoni Effect

S. Vafaei, *Nanomaterials*, 2020, **10**, 397.



Capillary Leveling Effect

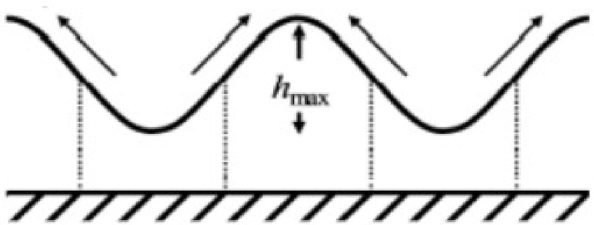
S. K. Stanley et al., *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2020, **603**, 125217.



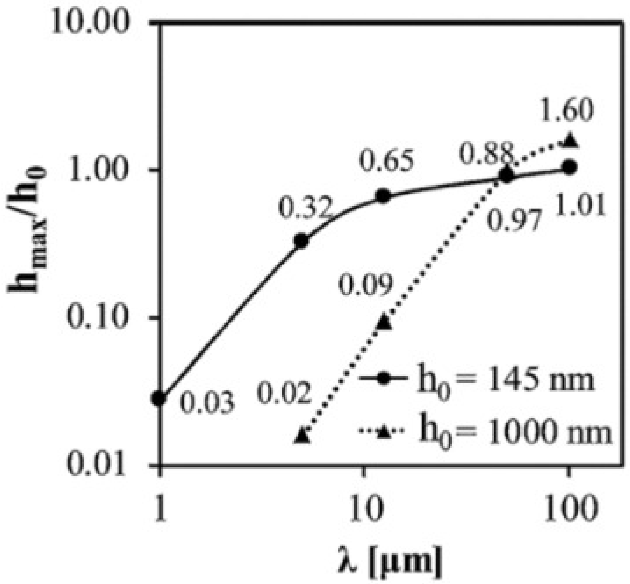
Photoproduct Diffusion

Objective

Study the behavior of h_{max}/h_0 with increasing λ (photomask-half-periodicity) and h_0 (initial height of polymer film);
(h_{max} is a key parameter of interest in patterned films and governs feature resolution and aspect ratio)

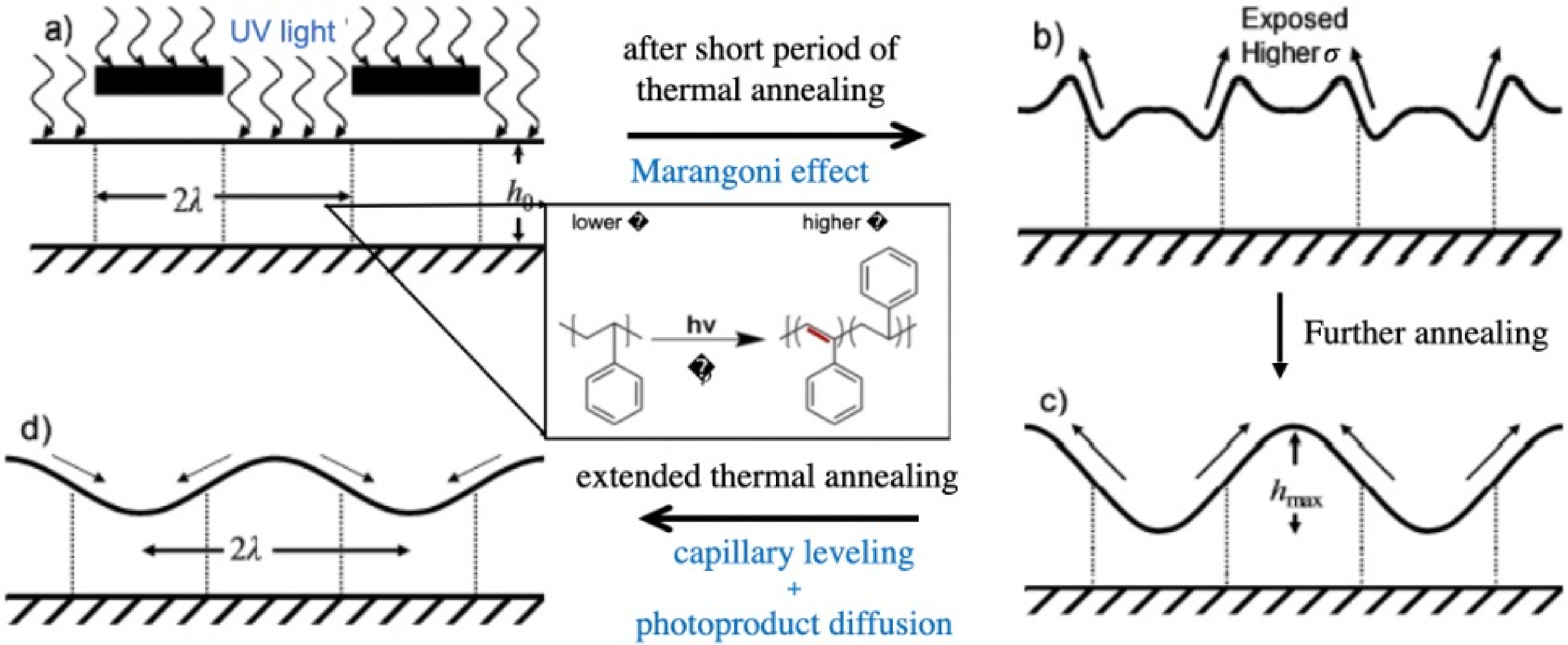


Physical mechanism unclear



T. A. Arshad et al., Soft Matter, 2014, 10, 8043–8050.

Photochemically Induced Marangoni Patterning



T. A. Arshad et al., Soft Matter, 2014, 10, 8043–8050.

Key findings

- The variation of h_{max}/h_0 with λ and h_0 is well understood physically
- Different physical mechanisms dominate in extreme regimes of parameter space
- Our findings can be helpful for achieving desired height of patterned films

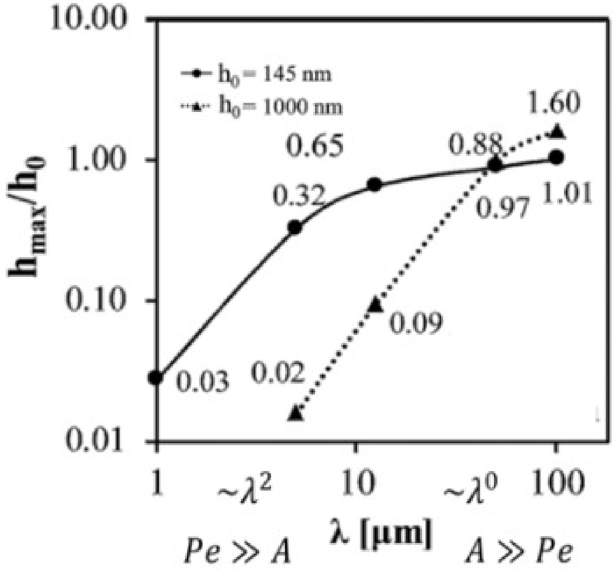
Variation of h_{max}/h_0 with λ

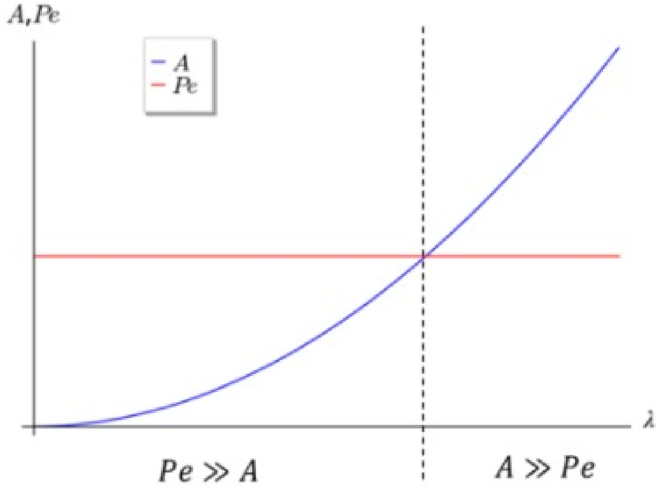
For low λ: $\boldsymbol{Pe \gg A}$ (capillary leveling dominates)

$$\lim_{y\to 0} \eta_{max} = \frac{3MaA}{2\pi^2\left(1+\frac{S_2}{2}\right)} \sim A \sim \lambda^2 \sim \frac{1}{Surface\ Tension}$$

For high λ: $\boldsymbol{A \gg Pe}$ (diffusion dominates)

$$\lim_{y\to 0} \eta_{max} = \frac{MaPe}{2} \sim Pe \sim \lambda^0 \sim \frac{1}{Diffusive\ forces}$$





Analytical expression for $\frac{h_{max}}{h0}$ (or η_{max})

After solving equations (1) and (2),

$$\eta = \frac{\frac{Ma\pi^2}{2}}{\psi_1 - \psi_2}\left\{e^{\psi_1 t} - e^{\psi_2 t}\right\}$$

$$\xi = \left(\frac{\frac{\pi^4}{3A}\left(1 + \frac{S_2}{2}\right) + \psi_1}{\psi_1 - \psi_2}\right)e^{\psi_1 t} - \left(\frac{\frac{\pi^4}{3A}\left(1 + \frac{S_2}{2}\right) + \psi_2}{\psi_1 - \psi_2}\right)e^{\psi_2 t}$$

$$\eta_{max}\left(= \frac{h_{max}}{h0}\right) = \frac{\frac{Ma\pi^2}{2}}{\psi_1 - \psi_2}\left\{exp\left(\frac{\psi_1}{\psi_1 - \psi_2}\ln\left(\frac{\psi_2}{\psi_1}\right)\right) - exp\left(\frac{\psi_2}{\psi_1 - \psi_2}\ln\left(\frac{\psi_2}{\psi_1}\right)\right)\right\}$$

Effect of Process Parameters on Attainable Feature Heights in Photoinduced Marangoni Patterning

Pankaj Chaudhary (NIT Agartala)

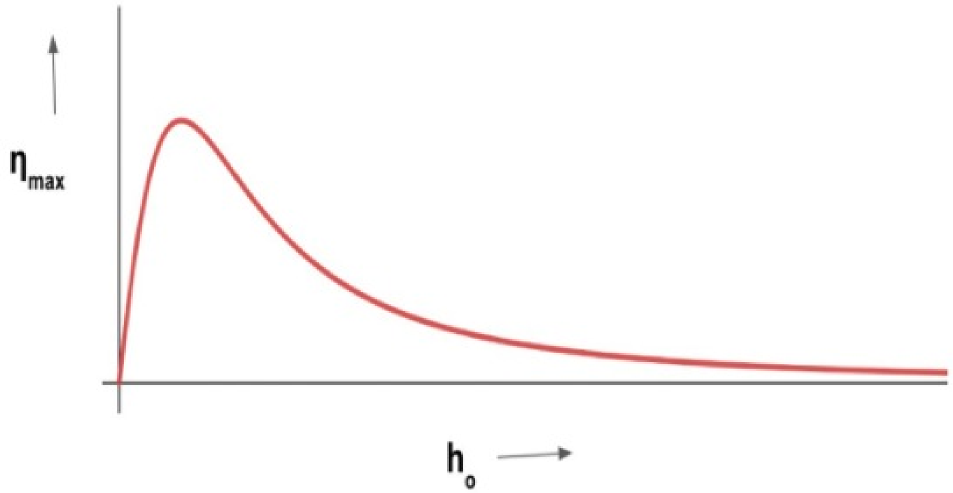
Variation of h_{max}/h_0 with h_0

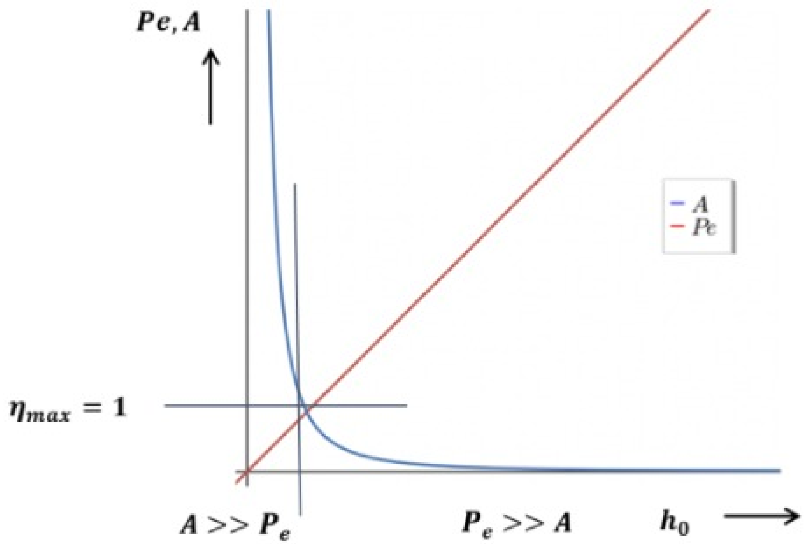
For low h_0: $A \gg Pe$ (diffusion dominates)

$$\lim_{y\to 0}\eta_{max} = \frac{MaPe}{2} \sim Pe \sim h_0 \sim \frac{1}{Diffusive\ forces}$$

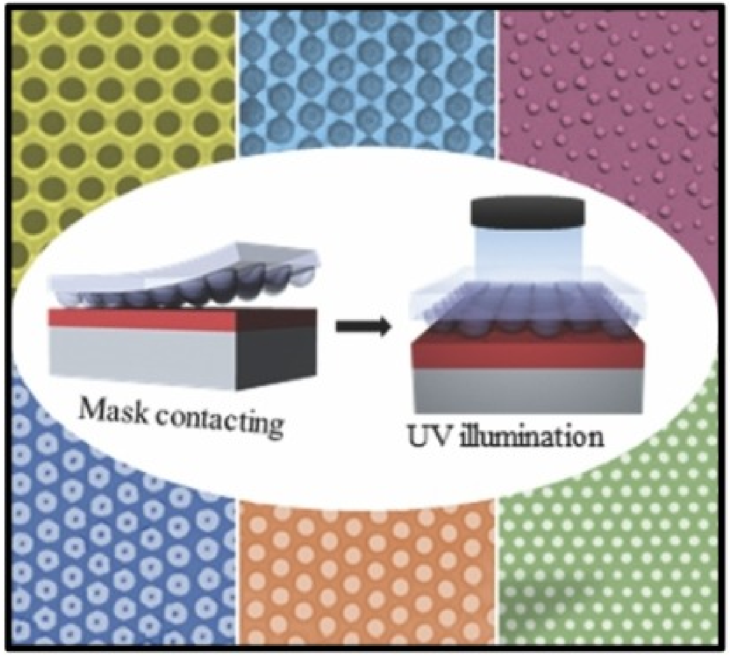
For high h_0: $Pe \gg A$ (capillary leveling dominates)

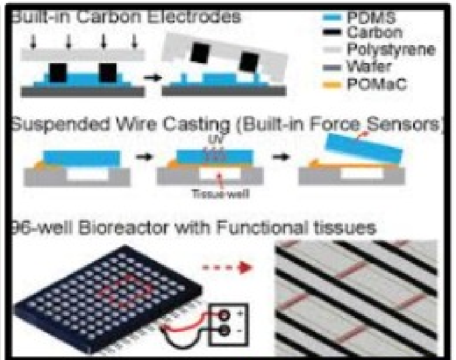
$$\lim_{y\to 0}\eta_{max} = \frac{3MaA}{2\pi^2\left(1+\frac{S_2}{2}\right)} \sim A \sim {h_0}^{-2} \sim \frac{1}{Surface\ Tension}$$

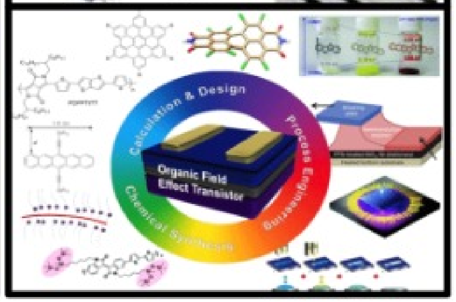




Applications of Patterned Polymer Films







Clockwise:
(1) M. Fang et al., *Advanced Optical Materials*, 2014, **2**, 855–860.
(2) Y. Zhao et al., *Advanced Healthcare Materials*, 2019, **8**, 1801187.
(3) J. Mei et al., *Journal of the American Chemical Society*, 2013, **135**, 6724–6746.

One technique to create patterned films – Marangoni patterning

Governing Equations: Mass and Momentum Conservation

$$\frac{\partial h}{\partial t} = -\frac{\partial}{\partial x}\left[\frac{h^3}{3A}\frac{\partial}{\partial x}\left(\underbrace{(1+S_2 c)\frac{\partial^2 h}{\partial x^2}}_{\text{capillary leveling}}\right) + \underbrace{Ma\frac{h^2}{2}}_{\text{Marangoni effect}}\frac{\partial c}{\partial x}\right]$$ .... film height evolution

$$\frac{\partial c}{\partial t} + \underbrace{u\frac{\partial c}{\partial x}}_{\text{convection}} = \underbrace{\frac{1}{Pe}\frac{1}{h}\frac{\partial}{\partial x}\left(h\frac{\partial c}{\partial x}\right)}_{\text{diffusion}}$$ .... photoproduct concentration evolution

$$A \equiv \frac{\lambda^2}{{h_0}^2} \sim \frac{1}{Surface\ Tension} \quad ; \quad Pe \equiv \frac{h_0\gamma_0}{\mu D} \sim \frac{1}{Diffusive\ forces}$$

Pe $\longrightarrow$ Peclet number
A $\longrightarrow$ Capillary number
Ma $\longrightarrow$ Marangoni number
$S_2 \rightarrow$ Strength of Marangoni Forces