A multiple-scale approach to evaporation-induced Marangoni convection

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A bit of history

The story of Marangoni convection begins over a century ago:

- Around 1900 Henri Bérnard was experimenting with thin films of liquid that were heated from below.
- He found that sufficient heating could lead to the onset of convection.
- In 1916 Lord Rayleigh published his famed article that predicts convection based on thermally-induced density differences in the fluid.

![Rayleigh–Bénard convection](image)

**Figure:** Rayleigh–Bénard convection
A bit of history

However...

In 1956 Block showed experimentally that Bernard’s films were too thin for convection to be caused by density differences.

Instead, he conjectured that convection was caused by thermally-induced gradients in the surface tension \( \gamma = \gamma(T) \).

A mathematical analysis by Pearson in 1958 verified Block’s claims.

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Figure: Marangoni convection
Evaporation-induced Marangoni convection

In the 50 years since Pearson’s pioneering work, various forms of Marangoni instabilities have emerged

- We’re interested in compositional-Marangoni convection that is induced by evaporation
- That is, convection in a solvent-solute mixture that is evaporating

Figure: (i) Strong surface tension
Evaporation-induced Marangoni convection

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![Diagram showing weak surface tension with depleted and rich regions as well as solvent rich areas.]

**Figure:** (i) Weak surface tension.
Applications

This type of convection arises in many industrial situations

- Drying of paint (Howison et al. 1997)
- Fabrication of polymeric organic solar cells

![Diagram of polymeric solar cell production by spin coating](image)

**Figure:** (a) - (d): Polymeric solar cell production by spin coating. (e): Film morphology of a PS-PI (dark-bright) blend (from Ebbens et al. 2011)
Organic solar cell production

The efficiency of an organic solar cell depends crucially on the morphology of the interface between the two polymers.
Our problem

One of the things we are interested in is the stability of the bilayer and how compositional-Marangoni forces influence this

- The linear stability problem is not trivial
- Evaporation causes the base solution and the domain to change with time
- Hence the typical $\exp(\lambda t)$ ansatz no longer works (in general)

What if evaporation is slow compared to the time scale of the instability?

- Maybe we can systematically construct an asymptotic solution to the linear stability problem
- We’ll explore this possibility by studying a simpler Marangoni problem
Linear stability of a solvent-polymer layer

We simplify the problem to one layer of a single polymer blended in a volatile solvent

- Neglect rotation and the effects of the overlying gas layer
- Assume the evaporation of solvent is slow compared to its diffusion
Nondimensional model

Stokes equation for the mixture velocity and pressure

\[-\nabla p + \nabla^2 \mathbf{u} = 0,\]
\[\nabla \cdot \mathbf{u} = 0,\]

Advection-diffusion equation for volume fraction of solvent

\[c_t + \mathbf{u} \cdot \nabla c = \nabla^2 c.\]

Initial conditions: \[c(x, z, 0) = c_i(x, z), \ h(x, t) = h_i(x).\]
Boundary conditions

No slip and no flux on substrate $z = 0$:

$$
\mathbf{u} = 0,
$$
$$
c_z = 0.
$$

Free boundary at air/fluid interface $z = h(x, t)$:

$$
\mathbf{u} \cdot \mathbf{n} - v_n = \delta \beta [1 + \delta (1 - \beta) c],
$$
$$
\nabla c \cdot \mathbf{n} = -[1 + \delta (1 - \beta) c](1 - \delta \beta c),
$$
$$
-p + \mathbf{n} \cdot (\nabla \mathbf{u} + \nabla \mathbf{u}^T) \cdot \mathbf{n} = -Ga h - Ca^{-1} h_{xx} (1 + h_x^2)^{-3/2},
$$
$$
\mathbf{n} \cdot (\nabla \mathbf{u} + \nabla \mathbf{u}^T) \cdot \mathbf{t} = -Ma \nabla c \cdot \mathbf{t}.
$$
Nondimensional numbers

Five nondimensional numbers appear in the model:

\[ \beta = \frac{\langle C_i \rangle}{\rho}, \quad \delta = \frac{k_m h_m}{D} \ll 1, \]

\[ \text{Ga} = \frac{\rho g h_m^3}{\mu D} \gg 1, \quad \text{Ca}^{-1} = \frac{\gamma_0 h_m}{\mu D} \gg 1, \quad \text{Ma} = \frac{\delta \beta (1 - \beta) \rho \gamma_ch_m}{\mu D}. \]

The fact that \( \text{Ga} \gg 1 \) and \( \text{Ca}^{-1} \gg 1 \) means we can assume the interface is nondeformable (for now).
Analysis

We seek solutions of the form

\[ u(x, z, t) = \bar{u}(z, t) + \epsilon \tilde{u}(z, t)e^{ikx}, \]
\[ p(x, z, t) = \bar{p}(z, t) + \epsilon \tilde{p}(z, t)e^{ikx}, \]
\[ c(x, z, t) = \bar{c}(z, t) + \epsilon \tilde{c}(z, t)e^{ikx}, \]
\[ h(x, t) = \bar{h}(t), \]

where \( \epsilon \ll 1 \) corresponds to the size of the initial perturbation.

- The \( O(1) \) problem (nonlinear) tells us the evolution of the 1D, time-dependent base state
- The \( O(\epsilon) \) problem (linear) tells us the stability of the base state
Base state

In the $O(1)$ problem for the base state find two time regimes

- $t = O(1)$: growth of diffusive boundary layer at free surface
- $t = O(\delta^{-1})$: quasi-steady evolution, thinning of film

![Figure: Base state solvent concentration profiles](image)
Base state

In the $O(1)$ problem for the base state find two time regimes

- $t = O(1)$: growth of diffusive boundary layer at free surface
- $t = O(\delta^{-1})$: quasi-steady evolution, thinning of film

Figure: Left: film thickness. Right: average concentration gradient
Base state

We now consider only the quasi-steady evolution of the base state

- Neglect the fast initial transients
- Base state depends only on the slow time $\tau = \delta t$

![Graphs showing film thickness and concentration gradient](image)

**Figure:** Left: film thickness. Right: average concentration gradient
Linear stability

The $O(\epsilon)$ problem that determines the stability can be written as

$$\tilde{\zeta}_t = \mathcal{L}(\tau)\tilde{\zeta}, \quad \tau = \delta t,$$

where $\tilde{\zeta} = (\tilde{u}, \tilde{p}, \tilde{c})^T$ and $\tilde{\zeta}(z, 0) = \tilde{\zeta}_i$.

An asymptotic solution to this problem found in two steps:

1. Reducing the equation to an ODE system by projecting the solution onto the (slowly varying) eigenfunctions of $\mathcal{L}$
2. Using the method of multiple scales to approximate the solution of the ODE system
Step 1 - Reduction to an ODE

Write the solution as

$$\tilde{\zeta}(z, t) = \sum_{l=1}^{\infty} \alpha_l(t) v_l(z; \tau),$$

where $v_l$ are eigenfunctions of the problem

$$\mathcal{L}(\tau)v_l(z; \tau) = \lambda_l(\tau)v_l(z; \tau)$$

The system of ODEs for $\alpha$ is

$$\alpha_{l,t}(t) - [\lambda_l(\tau) + \delta \gamma_{ll}(\tau)] \alpha_l(t) = \delta \sum_{j \neq l} \gamma_{lj}(\tau) \alpha_j(t),$$

where $\alpha_l(0) = \alpha_{li} = \langle v_l^*, \tilde{\zeta}_i \rangle$ and $\gamma_{lj} \equiv -\langle v_l^*, v_{j,\tau} \rangle.$
Step 2 - The multiple-scale approximation

We introduce additional time scales $T_l$ that are defined via

$$T_l(t) \equiv \int_0^{\delta t} \left[ \delta^{-1} \lambda_l(s) + \gamma_l(s) \right] ds$$

and expand the $\alpha_l$ as

$$\alpha_l = \alpha_l^{(0)}(\tau, T_l) + \delta \alpha_l^{(1)}(\tau, T_1, T_2, \ldots) + \ldots$$

By eliminating secular terms at each order, the solution is found to be

$$\alpha_l(t) = \alpha_{l,i} e^{T_l(t)} + \delta \sum_{j \neq l} \frac{\alpha_{j,i} \gamma_{j,l}(\tau)}{\lambda_j(\tau) - \lambda_l(\tau)} e^{T_j(t)}$$

$$+ \delta \sum_{j \neq l} \left[ \alpha_{l,i} \int_0^{\tau} \frac{\gamma_{l,j}(s) \gamma_{j,l}(s)}{\lambda_l(s) - \lambda_j(s)} ds - \frac{\alpha_{j,i} \gamma_{j,l}(0)}{\lambda_j(0) - \lambda_l(0)} \right] e^{T_l(t)}$$
Key properties of the solution

- Eigenvalues need to remain well-separated, but can cross through zero
- The dominant contribution to the solution is

$$\tilde{\zeta}_1(z, t) = \alpha_1 i v_1(z; \delta t) \exp \left\{ \delta^{-1} \int_0^{\delta t} [\lambda_1(s) + \delta \gamma_{11}(s)] \, ds \right\}$$

where $\lambda_1$ is the eigenvalue with largest real part
- The amplitude of this main contribution, defined as

$$A(t) = \| \tilde{\zeta}_1(z, t) \|_\infty / \| \tilde{\zeta}_i(z) \|_\infty,$$

changes according to

$$A_t = \lambda_1(\tau) A + O(\delta)$$

- The top eigenvalue still tells us much about the system
Figure: Neutral stability curves for various $\tau$. These are curves for which $\lambda_1(\tau; k, \text{Ma}) = 0$ and can be used to deduce regions of stability.
Amplification and stabilization

Figure: Numerical and asymptotic perturbation amplitudes. The amplitude of the perturbations are defined by $\|\tilde{\zeta}(z, t)\|_\infty / \|\tilde{\zeta}_i(z)\|_\infty$. 
Comparison with experiment

Bassou and Rharbi (2009) observed convective instabilities in an evaporating polystyrene-toluene mix.

- Based on their data, concluded convection is a result of a solutal Marangoni instability (induced by evaporation)

**Figure:** Convection cells observed by Bassou and Rharbi. The scale bar represents 2.5 mm
Comparison with experiment

They find that convection occurs in films that are at least 100 $\mu$m thick

- Our results say that the films need to be at least 235 $\mu$m thick
- Generally, our films are more stable than the experimental ones
- Perhaps thermal effects, compositional buoyancy important

Long-wavelength deformations also appear in their films.

- Perhaps the stabilizing effects of gravity are reduced in the long term

Figure: 3D and 2D film morphologies taken from Bassou and Rharbi (2009)
Long-wavelength surface deformations

If we account for surface deformations, then we find that long-wavelength perturbations have eigenvalues

\[ \lambda_{1,2}(\tau) = \pm \frac{ik}{\bar{h}(\tau)} \sqrt{\frac{M(\tau)}{2}} + \left( \frac{5M(\tau)}{48} - \frac{1}{2} - \frac{G(\tau)}{6} \right) k^2 + O(k^3) \]

where \( M(\tau) \) and \( G(\tau) \) are given by

\[ M(\tau) = \left( \frac{\bar{h}(\tau) - 1 + \beta}{\beta} \right) \text{Ma}, \quad G(\tau) = \bar{h}^3(\tau) \text{Ga} \]

Some interesting features:

- Complex eigenvalues, oscillatory instability
- The effects of gravity decrease with the cube of the film thickness
- Marangoni effects decrease linearly with film thickness
Summary and conclusions

Investigated Marangoni convection in an evaporating fluid layer

- Evaporation leads to a slowly evolving base state, makes the linear stability analysis nontrivial
- Computed an asymptotic solution to the linear stability problem using the method of multiple scales
- Compared our theory to experiment

Current/future work:

- Multiphase modelling of solvent-polymer systems (with CB, CP, AM)
- Investigating the formation of the polymer bilayer and looking at phase separation in confined geometry (with AM, BW, VB, AG)
- Investigate the stability of the bilayer
Thank you!

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