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Interfacial instabilities driven by chemical reactions

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Abstract. We investigate the interaction of thin films with chemical reactions by using as a model system a horizontal film with a reactive mixture of insoluble surfactants on its free surface. The reaction is modeled by a bistable/excitable FitzHugh-Nagumo (FHN) prototype. The chemical reaction can destabilize the film leading to the propagation of solitary pulses on its free surface.

1 Introduction

Thin liquid films on solid substrates are frequently encountered in numerous problems in the engineering, chemistry or biology fields. Not surprisingly therefore they have been the subject of intensive research for several decades both theoretically and experimentally. Thin films are known to give rise to interesting patterns like solitary waves on the surface of a film falling down an inclined planar substrate as highlighted first experimentally by the Kapitzas [1]. Another class of problems that also exhibits a rich pattern formation dynamics is that of reaction-diffusion systems which have applications in a wide variety of fields, including chemistry and biology, and have also received considerable attention. For example the FHN prototype, which has been used to model biological systems e.g. nerve signal transmission, can give rise to pulses, fronts and Turing patterns [2].

However, thin films and reaction-diffusion processes have mainly been examined separately although they often interact strongly in applications. Examples include emulsification, coating processes and cell membrane deformation during phagokytosis (e.g. [3] while future applications might include microfluidics e.g. utilizing reaction-diffusion processes to structure thin films by appropriately tuning the chemical parameters. In this paper we offer a model that couples the dynamics of a horizontal thin film with a chemical reaction involving surface active species. The latter takes place on the film surface only (insoluble surfactants) and is governed by the FHN prototype. The coupling occurs through the solutocapillary Marangoni effect induced by the reactive surfactants. We show that reaction-diffusion fronts can trigger solitary pulses on the free surface.

2 Problem definition

We consider a horizontal liquid film of viscosity μ, density ρ and surface tension σ on a horizontal planar substrate as shown in Fig. 1. A cartesian coordinate system (x, y) is chosen so that x is in the direction parallel to the substrate and y is the outward pointing coordinate normal to the

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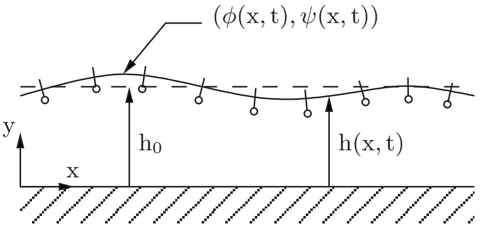

Fig. 1. Sketch of a thin film of thickness $h(x,t)$ on a horizontal substrate. h_0 denotes the flat film thickness. The surface of the film is covered by two reactive chemical species with effective concentrations $\phi(x,t)$, $\psi(x,t)$.

substrate. Governing equations for the flow are the conservation of mass and the Navier-Stokes equations:

$$\boldsymbol{\nabla}\cdot\mathbf{u}=0, \qquad \rho(\mathbf{u}_t+\mathbf{u}\cdot\boldsymbol{\nabla}\mathbf{u})=-\boldsymbol{\nabla}p+\mu\boldsymbol{\nabla}^2\mathbf{u}+\rho\mathbf{g}, \tag{1}$$

where $\boldsymbol{\nabla}=(\partial/\partial x,\partial/\partial y)$ is the gradient operator on the (x,y) plane, $\mathbf{u}=(u,v)$ is the fluid velocity vector, $\mathbf{g}=(0,-g)$ with g is the gravitational acceleration and p is the fluid pressure. The above equations are subject to the no-slip and no-penetration condition on the wall,

$$\mathbf{u}=0 \qquad \text{on} \qquad y=0 \tag{2}$$

and the kinematic boundary condition and normal and tangential stress balances on $y=h(x,t)$,

$$h_t+uh_x=v, \quad p_\infty-p+(\boldsymbol{\tau}\cdot\mathbf{n})\cdot\mathbf{n}=-\sigma\boldsymbol{\nabla}_s\cdot\mathbf{n}, \quad (\boldsymbol{\tau}\cdot\mathbf{n})\cdot\mathbf{t}=\boldsymbol{\nabla}_s\sigma\cdot\mathbf{t}, \tag{3}$$

where p_∞ is the pressure of the ambient gas phase, $\boldsymbol{\tau}=\mu[(\boldsymbol{\nabla}\mathbf{u})+(\boldsymbol{\nabla}\mathbf{u})^t]$ is the deviatoric stress tensor, $\mathbf{n}$ and $\mathbf{t}$ are unit vectors, normal and tangential to the interface, respectively, defined from $\mathbf{n}=n^{-1}(-h_x,1)$, $\mathbf{t}=n^{-1}(1,h_x)$ where $n=(1+h_x^2)^{1/2}$ and $\boldsymbol{\nabla}_s=(\mathbf{I}-\mathbf{n}\otimes\mathbf{n})\cdot\boldsymbol{\nabla}$ is the surface gradient operator with $\mathbf{I}$ the 2×2 unitary matrix.

The reaction-diffusion process is described by two effective concentration variables, ϕ' and ψ', which obey the FHN prototype written in the following form in the absence of flow:

$$\phi'_t=D_{s\phi}\boldsymbol{\nabla}_s^2\phi'+k_\phi[(\phi'-\phi_\mathrm{m})-b'_2(\phi'-\phi_\mathrm{m})^3-b'_1(\psi'-\psi_\mathrm{m})], \tag{4a}$$

$$\psi'_t=D_{s\psi}\boldsymbol{\nabla}_s^2\psi'+k_\psi[(\phi'-\phi_\mathrm{m})-a'_1(\psi'-\psi_\mathrm{m})-a'_0], \tag{4b}$$

where $D_{s\phi}$ and $D_{s\psi}$ are surface diffusion coefficients, k_ϕ and k_ψ are reaction rate constants, a'_0, a'_1, b'_1 and b'_2 are kinetic parameters and ϕ_m, ψ_m are mean (reference) values. ϕ is frequently referred to as the"activator" and ψ as the "inhibitor". Instead of ϕ' and ψ', we shall subsequently use deviation concentrations defined by $\phi=\phi'-\phi_\mathrm{m}$ and $\psi=\psi'-\psi_\mathrm{m}$, so that the actual concentrations are equal to the mean values ϕ_m and ψ_m and a fluctuating component. Note that the original FHN prototype represents a reduction of an initial complex set of equations so that ϕ, ψ represent combinations of concentrations and as such they can be negative. Nevertheless, by introducing ϕ_m and ψ_m we can assume that we have two actual chemical species so that the overall concentrations $\phi+\phi_\mathrm{m}$, $\psi+\psi_\mathrm{m}$ are positive (if $\phi_\mathrm{m}=\psi_\mathrm{m}=0$ and ϕ,ψ are negative then these variables do not represent actual concentrations but combinations of concentrations).

In the presence of flow, ϕ and ψ satisfy the following transport equations at $y=h(x,t)$:

$$\phi_t+u\phi_x+(\phi+\phi_\mathrm{m})\boldsymbol{\nabla}_s\cdot\mathbf{u}=D_{s\phi}\boldsymbol{\nabla}_s^2\phi+k_\phi(\phi-b'_2\phi^3-b'_1\psi), \tag{5a}$$

$$\psi_t+u\psi_x+(\psi+\psi_\mathrm{m})\boldsymbol{\nabla}_s\cdot\mathbf{u}=D_{s\psi}\boldsymbol{\nabla}_s^2\psi+k_\psi(\phi-a'_1\psi-a'_0). \tag{5b}$$

These equations are coupled to the hydrodynamics through the solutal Marangoni effect in the tangential stress balance in Eq. (3). For simplicity we shall assume that the surface tension depends only on one of the species, the inhibitor ψ, and that it obeys the linear constitutive equation, $\sigma(\phi)=\sigma_\mathrm{m}-\gamma\phi$. The coupling of the hydrodynamics and the chemical system has consequently two components: the species concentration is influenced by the convection while the chemical system affects the flow through the surface tension. Note that the parameters $\phi_{\rm m}$, $\psi_{\rm m}$ do not have any influence on the chemical system in the absence of flow (they are constants and all their derivatives vanish) but they do appear in the left-hand-side of Eqs (5a) and (5b) and so they are an important element of the influence of the chemical system by the flow.

3 Non-dimensionalization and long-wave equations

The horizontal length and time scales are given by the inhibitor, which is the driving force, as it alters the surface tension. The vertical lengthscale is given by the flat film thickness h_0 of the base state. We thus define

$$l^* = \sqrt{\frac{D_{s\psi}}{k_\psi}\frac{\psi^*}{\phi^*}}, \quad U = \sqrt{D_{s\psi}k_\psi\frac{\phi^*}{\psi^*}}, \quad \phi^* = \frac{1}{\sqrt{b_2'}}, \quad \psi^* = \frac{\phi^*}{b_1'} \tag{6}$$

and perform the following change of variables: $x \to l^*x$, $(y, h) \to h_0(y, h)$, $t \to l^*t/U$, $u \to Uu$, $v \to Uh_0v/l^*$, $p \to \mu U l^* p/h_0^2$, $\phi \to \phi^*\phi$ and $\psi \to \psi^*\psi$. We also define the following dimensionless groups and parameters:

$$R = \frac{\rho U h_0}{\mu}, \quad B = \varepsilon\frac{\rho g h_0^2}{\mu U}, \quad W = \varepsilon^3\frac{\sigma_{\rm m}}{\mu U}, \quad M = \varepsilon\frac{\gamma\psi^*}{\mu U}, \quad \varepsilon = \frac{h_0}{l^*}, \tag{7a}$$

$$\delta = \frac{D_{s\psi}}{D_{s\phi}}, \quad K = \frac{\psi^*}{\phi^*}\frac{k_\phi}{k_\psi}, \quad \phi_{\rm m} = \frac{\phi_{\rm m}'}{\phi^*}, \quad \psi_{\rm m} = \frac{\psi_{\rm m}'}{\psi^*}, \quad a_0 = \frac{a_0'}{\phi^*}, \quad a_1 = a_1'\frac{\psi^*}{\phi^*}. \tag{7b}$$

R, B, W, M are the Reynolds, Bond, Weber and Marangoni numbers, respectively, and ε is the "film parameter". The last six groups refer to the chemical system only.

The free-boundary problem in Eqs. (1–3) and (5a) and (5b) can be simplified with the long-wave approximation, $\varepsilon \ll 1$. We also assume $R = O(1)$, so that inertial effects are delayed at a higher order and $B, W, M = O(1)$ so that the corresponding physical effects appear in the long-wave expansion at the smallest possible order. At $O(1)$ the result is:

$$h_t = \left(\frac{1}{3}Bh^3h_x - \frac{1}{3}Wh^3h_{xxx} + \frac{1}{2}Mh^2\psi_x\right)_x, \tag{8a}$$

$$\phi_t = \left(\frac{1}{2}Bh^2(\phi_{\rm m}+\phi)h_x - \frac{1}{2}Wh^2(\phi_{\rm m}+\phi)h_{xxx} + Mh(\phi_{\rm m}+\phi)\psi_x\right)_x + \frac{1}{\delta}\phi_{xx} + K(\phi - \phi^3 - \psi), \tag{8b}$$

$$\psi_t = \left(\frac{1}{2}Bh^2(\psi_{\rm m}+\psi)h_x - \frac{1}{2}Wh^2(\psi_{\rm m}+\psi)h_{xxx} + Mh(\psi_{\rm m}+\psi)\psi_x\right)_x + \psi_{xx} + \phi - a_1\psi - a_0. \tag{8c}$$

4 Solitary waves

We now seek solitary wave solutions of (8) in the form $h(x,t) = \hat{h}(z)$, $\phi(x,t) = \hat{\phi}(z)$ and $\psi(x,t) = \hat{\psi}(z)$ where $z = x - ct$ is a coordinate moving with the speed of the waves c. Particular emphasis is given on the influence of the parameters involved in the coupling between hydrodynamics and reaction-diffusion, i.e. M, $\phi_{\rm m}$ and $\psi_{\rm m}$.

The solutions are constructed numerically by using the continuation software AUTO97 [4]. In all cases, the values of the dimensionless groups are: $B = 1$, $W = 1$, $K = 10$, $\delta = 1$, $a_0 = 0.1$ and $a_1 = 2$. The values of the last two parameters correspond to the bistable regime where the reaction-diffusion system develops fronts connecting two spatially uniform concentration states for each of ϕ, ψ, the most stable of the two invading the least stable one. Here, the most stable state corresponds to a low surface tension region.

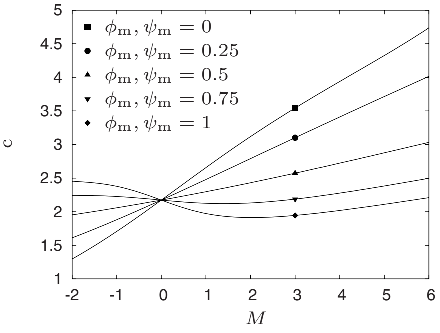

Fig. 2. Bifurcation diagram depicting the waves speed c as a function of the Marangoni number M for several values of ϕ_{m} and ψ_{m}.

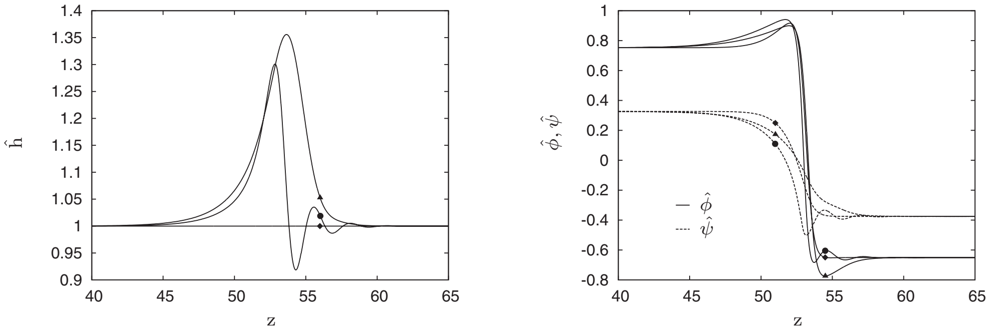

Fig. 3. Waves profiles for the free surface (left) and the chemical system (right) for several values of M and (ϕ_{m}, ψ_{m}). ◆: $M = 0$, $\phi_{\mathrm{m}} = 1$, $\psi_{\mathrm{m}} = 1$, ▲: $M = 6$, $\phi_{\mathrm{m}} = 1$, $\psi_{\mathrm{m}} = 1$, ●: $M = 6$, $\phi_{\mathrm{m}} = 0$, $\psi_{\mathrm{m}} = 0$.

Fig. 2 depicts the bifurcation diagram for c as a function of M and for different values of $\phi_{\mathrm{m}}, \psi_{\mathrm{m}}$. The value for c at $M = 0$ corresponds to the front velocity of the chemical system. Fig. 3 shows typical profiles for $\hat{h}$, $\hat{\phi}$ and $\hat{\psi}$. The waves travel from the left to the right. As the free surface at the back of the front has a surface tension smaller than the free surface ahead, a Marangoni flow appears in the film around the front area, where the surface tension gradients are large and results in the formation of a solitary wave on the free surface. The free-surface waves resemble the ones observed in falling films (e.g. [5]) which in turn are reminiscent of the "dissipative solitons" analyzed in [6].

As is also evident from the figure, the main effect of the coupling is to increase the amplitude of the free-surface waves, but some modifications in their shape are also observed, in particular the presence in some cases of small oscillations ahead of the main hump. As the Marangoni flow is directed from the small surface tension areas to the large surface tension ones, it has the same direction as the main flow and contributes to the convection of the species from the left to the right. As such it accelerates the propagation of the front as demonstrated by the dependence of c with M for large values of M in Fig. 2. Conversely, c decreases as ϕ_{m} and ψ_{m} increase for a given M. However, the effect of the coupling on the waves propagating in the system can be more complex as demonstrated by the c curve for $\phi_{\mathrm{m}} = 1$ and $\psi_{\mathrm{m}} = 1$: in that case, a decrease in the speed is observed for small M even though the Marangoni flow has the same direction as the flow.

Clearly this is a system with a rather rich and complex behavior only a small part of which has been analyzed here and indeed there are several open questions e.g. the stability of the solitary waves. We aim to address these questions in future studies.

References

1. P.L. Kapitza, S.P. Kapitza, Zh. Eksp. Teor. Fiz. **19**, 105 (1949)
2. E. Meron, Phys. Rep. **218**, 1 (1992)
3. A.M. Haywood, N. Y. Acad. Sci. **308**, 275 (1978)
4. E. Doedel, A. Champneys, T. Fairfrieve, Y. Kuznetsov, B. Sandstede, X. Wang, Department of Computer Science, Concordia University, Montreal, Canada (1997)
5. P.M.J. Trevelyan, S. Kalliadasis, J. Eng. Math. **50**, 177 (2004)
6. C.I. Christov, M.G. Velarde, Physica D **86**, 323 (1995)