Gravity-Driven Reactive Coating Flow Down an Inclined Plane

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The coating flow of a reactive fluid on an inclined plane is studied. The fluid viscosity steadily increases due to a sustained cross-linking reaction. Using well-known long wave approximations and a simple kinetic relation, we find that the linear stability of a uniform coating is affected not only by the inclination angle but also by the reaction order. In the weakly nonlinear limit, a generalized Kuramoto-Sivashinsky (K-S) equation is derived. Two interesting cases are identified in the limit of creeping flow. One is when surface tension is moderate and a generalized Burger's equation results, and the other is when the surface tension is large and the traditional K-S equation is recovered when the inclination angle is greater than 90°. The solution in this case represents a shock-like traveling wave down the incline and it appears to be unique for reacting coating flows.

Introduction

A coating flow is a fluid flow used to cover a large surface area with uniform liquid layers. One problem commonly encountered in coating flow is the free-surface wave formation on the coating, which often results in streaks in the finished product. Coating flows relevant to industrial application have been discussed by Ruschak (1985). Reactive coating is a process in which a thermally initiated or chemically initiated polymeric fluid is used to coat a solid surface (substrate). In the former case, a polymeric reaction is initiated by raising the surrounding temperature; in the latter case, polymeric reaction takes place right after the mixing of two or more monomers.

Since the early work by Yih (1963) and Benney (1966), wave formation on a thin layer of viscous fluid has been studied extensively (see Nakaya, 1975; Pumir et al., 1983; Chang, 1989). The main findings from those analyses are:

(a) Linear waves become unstable at a critical Reynold's number which is only a function of the inclination angle, $R > \overline{R}_c$, where $R = (\rho u_0 h_0)/\eta_0$ and $\overline{R}_c = (5/4)\cot\alpha$. Here, ρ, η_0, u_0, h_0 and α are the liquid density, ambient viscosity, average coating velocity and coating thickness, and the inclined angle, respectively.

(b) Weakly nonlinear waves can form on the free surface when the surface tension is important, and a model equation of Kuramoto-Sivashinsky type is found to govern the weakly nonlinear permanent wave formation. Periodic solutions are found to be possible (reminiscent of the cnoidal waves in shallow water wave theory).

(c) Strongly nonlinear waves may also have periodic structures. These may be obtained by joining the possible solitary wave solutions.

Coating flows of variable viscosity have also been investigated by Goussis and Kelly (1985, 1987) and by Hwang and Weng (1987). They focused on the effect of variable viscosity due to an imposed temperature gradient across the thickness of the coating. The results they obtained show that cooling (heating) at the wall stabilizes (destabilizes) the coating flows. For the case of cooling, a cut-off Prandtl number exists, beyond which the flow is stable with respect to long waves.

The key to the study of reacting coating flows is the presence of the free surface and the transient nature of the reaction. Viscosity increases with time and the flow stops once the polymeric concentration reaches the gelling point. In this article, we present analytic results for gravity-driven reacting coating flows down an inclined plane.

First, by using a simple kinetic relation for the polymer reaction, a simplified governing equation is derived. Then, linear stability of surface waves is studied with this governing equation and it is shown that reacting coating flows are stable or neutrally stable for a wider range of inclination angles because of increasing viscosity due to reaction. Weakly nonlinear wave formation is subsequently studied in two limiting cases depending on the magnitude of surface tension. For cases of weak surface tension, a generalized Burger-type equation results and an interesting case of instability-to-stability transition, due to the effect of time-dependent viscosity, is identified. Finally, when surface tension is important, we pointed out a possible realization of a closed form solution of Kuramoto-Sivashinsky equation unique for reacting coating flows.

Formulation

Consider Figure 1 depicting a gravity-driven reacting coating flow down an inclined plane (substrate). We shall assume that the coating is thin, and the long wave approximation first developed by Benney (1966) can be applied.

Governing equations for reacting coating flows are coupled because of the variable viscosity, which depends on both the temperature and concentration distribution. To isolate the effect of polymeric reaction on the flow field, the following assumptions are made:

- Constant temperature field
- Uniform concentration field, $c=c(t)$
- Newtonian liquid
- Negligible curing stage.

The first assumption is valid when the external heating is applied uniformly (for example, placing the coating and the substrate in an oven), heat conduction dominates heat convection, and heat generation due to cross-linking reaction is negligible. The second holds when the mass diffusion is negligible and the temperature is uniform. The third assumption is supported by the fact that reacting liquids are found, within a wide region, to behave like Newtonian fluids. The last one assumes that reaction is complete once the gelling point is reached. For thin coatings and well-premixed liquids, these assumptions are reasonable.

The governing equations are now given by:

$$\frac{\partial u_i}{\partial x_i}=0, \tag{1}$$

$$\frac{\partial u_i}{\partial t}+u_j\frac{\partial u_i}{\partial x_j}=-\frac{1}{\rho}\frac{\partial p}{\partial x_i}+f_i+\frac{1}{\rho}\frac{\partial}{\partial x_j}\left[\eta\left(\frac{\partial u_i}{\partial x_j}+\frac{\partial u_j}{\partial x_i}\right)\right],\quad i,j=1,2 \tag{2}$$

$$\frac{d}{dt}c(t)=-A[c(t)]^n, \tag{3}$$

$$x_1=x,\ x_2=y,\ f_1=g\sin\alpha,\ f_2=-g\cos\alpha. \tag{4}$$

Equation 1 is mass conservation, Eq. 2 momentum conservation, and Eq. 3 concentration conservation. In Eqs. 1-4, u_1, u_2, p, g, ρ, η, c, and α are velocity components in x, y directions, pressure, gravitational constant, fluid density, viscosity, concentration, and inclination angle, respectively. The rate constant A and the reaction order n are known for given materials and in general $n\geq 1$. The long wave parameter to be introduced later is $\delta=h_o/l<<O(1)$, where h_o is the characteristic thickness and l is the characteristic wavelength. Note that we have not considered the energy equation here because the temperature field is assumed uniform.

Appropriate boundary conditions are given as follows:

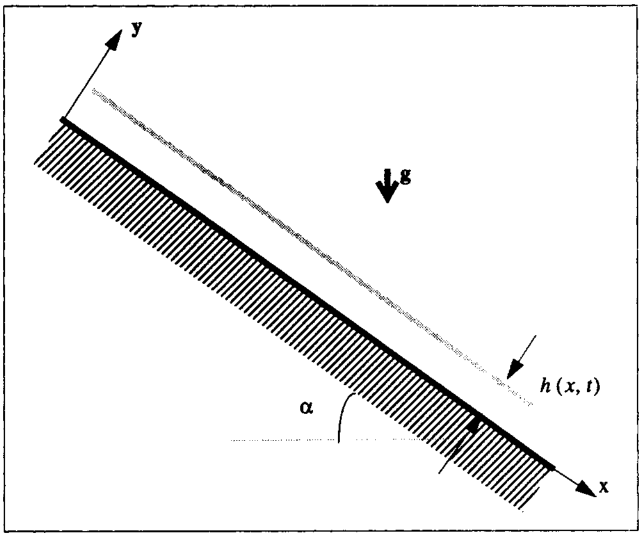

Figure 1. Reactive coating flow geometry.

α is the inclination angle, g is the gravity constant and $h(x,t)$ is the free surface profile.

$$u_i=0,\ i=1,2 \text{ at } y=0, \tag{5}$$

which is the nonslip condition at the substrate surface. At the free surface $y=h(x,t)$,

$$(n\cdot S\cdot t)=0,\ (n\cdot S\cdot n)=2H\sigma, \tag{6}$$

$$\frac{\partial h}{\partial t}+u\frac{\partial h}{\partial x}=v, \tag{7}$$

where S is the stress tensor, n is the unit normal, t is the unit tangent, σ is the surface tension coefficient, and H is the mean curvature. Equation 6 is the surface traction condition, and Eq. 7 is the kinematic boundary condition at the free surface.

Raising the temperature beyond the gelation temperature for the given reacting liquid, one can thermally initiate a polymeric reaction. The initial concentration is given by:

$$c=c_o \text{ at } t=0. \tag{8}$$

The following dimensionless variables may be introduced to make the governing equations dimensionless:

$$\hat{x}=\frac{x}{l},\ \hat{y}=\frac{y}{h_o},\ \hat{u}=\frac{u_1}{u_o},\ \hat{v}=\frac{u_2}{\delta u_o},\ \hat{p}=\frac{p-p_o}{(\rho u_o\eta_o)/h_o},\ \delta=\frac{h_o}{l}, \tag{9}$$

$$\hat{Z}=1-\frac{c}{c_0},\ \hat{t}=t\frac{l}{u_o}\text{ and }\hat{\mu}=\frac{\eta}{\eta_o}, \tag{10}$$

where $\hat{}$ is used to represent dimensionless quantities, $\hat{Z}$ is the degree of cure, l is the characteristic wave length, h_o is the average coating thickness, p_0 is the ambient pressure, u_o is the characteristic velocity to be defined, $\delta=h_o/l$ is the long wave parameter assumed to be small, and η_o is an ambient viscosity at the initial concentration. Keeping terms up to $O(\delta)$, the governing equations can be written in the following dimensionless form:

$$\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}=0, \tag{11}$$

$$R\delta\left(\frac{\partial u}{\partial t}+u\,\frac{\partial u}{\partial x}+v\,\frac{\partial u}{\partial y}\right) = -\delta\,\frac{\partial p}{\partial x} +\Gamma+\frac{\partial}{\partial y}\left(\mu\,\frac{\partial u}{\partial y}\right)+O(\delta^2), \tag{12}$$

$$O(\delta^2)=-\frac{\partial p}{\partial y}-\Gamma B+\delta\,\frac{\partial}{\partial y}\left(\mu\,\frac{\partial}{\partial y}\,(v)\right) +\delta\left(\frac{\partial \mu}{\partial x}\frac{\partial u}{\partial y}+\frac{\partial \mu}{\partial y}\frac{\partial v}{\partial y}\right) \tag{13}$$

and

$$\frac{dZ}{dt}=\kappa(1-Z)^n, \tag{14}$$

where ˆ is dropped hereafter for convenience. The parameter $\kappa=(lc_o^{n-1}A)/u_o$ is the dimensionless reaction constant. In the analyses to follow, further assumptions will be made concerning the magnitude of κ. Other parameters are defined by:

$$R=\frac{\rho u_o h_o}{\eta_o},\ \Gamma=\frac{\rho g h_o^2}{\eta_o u_o}\sin\alpha, \tag{15}$$

where R is the Reynolds number and Γ is a ratio of Reynolds number to Froude number. At the leading order, gravity and viscous shear stress balance each other, and consequently, $\Gamma\sim O(1)$. Consistent with traditional analysis, we take $\Gamma=2$ and the choice defines the characteristic velocity,

$$u_o=(\rho g h_o^2\sin\alpha)/2\eta_o. \tag{16}$$

The corresponding kinematic boundary condition (Eq. 7) can be combined with mass conservation (Eq. 11) to give:

$$\frac{\partial h}{\partial t}+\frac{\partial}{\partial x}\int_0^h u\,dy=0. \tag{17}$$

The initial condition for the degree of cure now becomes:

$$Z=0 \text{ at } t=0. \tag{18}$$

The leading order boundary conditions are:

$$u=v=0 \text{ on } y=0, \tag{19}$$

$$\frac{\partial u}{\partial y}=0,\ p=-\delta^2 w^{-1}\,\frac{\partial^2}{\partial x^2}\,h(x,t) \text{ on } y=h(x,t), \tag{20}$$

where $w=(\rho\sin\alpha g h_o^2)/(2\sigma)$ is the Weber number. Note that $\delta^2 w^{-1}$ term is retained, because in some cases surface tension is large enough to make this term significant.

Without loss of generality, we follow Osinski (1983) and take:

$$\eta=\eta_o\left(\frac{1}{1-Z}\right), \tag{21}$$

where it is clear that η_o is the ambient viscosity at $Z=0$. Correspondingly, the dimensionless viscosity becomes:

$$\mu(Z)=\frac{1}{1-Z}. \tag{22}$$

Z can be found from the conservation of degree of cure (Eq. 14) and the initial condition (Eq. 18) to be:

$$Z(t)=1-[1+(n-1)\kappa t]^{1/(1-n)}. \tag{23}$$

Note that when $n=1$, $Z(t)=1-\exp(-\kappa t)$. Correspondingly, the variable viscosity depends on time alone and is given by:

$$\mu(t)=\exp(\kappa t) \text{ for } n=1, \tag{24}$$

$$\mu(t)=[(n-1)\kappa t+1]^{1/(n-1)} \text{ for } n\neq 1. \tag{25}$$

Note that for a fixed reaction constant κ, large n corresponds to a relatively slow reaction and small n corresponds to a relatively fast reaction.

The procedure to derive the simplified long wave $[\delta=h_0/l\ll O(1)]$ governing equation is precisely the one first adopted by Benney (1966) and can be summarized as follows.

Expanding all the dependent variables in the following generic form:

$$g\sim g^{(0)}+\delta g^{(1)}+\delta^2 g^{(2)}+\ldots \tag{26}$$

and substituting these expansions in the dimensionless governing equations, as well as boundary conditions, we obtain a hierarchy of governing equations and boundary conditions in the order of δ and its powers. At each order, the governing equation can be solved with the corresponding boundary conditions. This procedure is well known and straightforward, and has been used by many researchers (Benney, 1966; Nakaya, 1975). For brevity, we present only the outcome of this derivation:

$$h_t+\frac{2}{\mu(t)}\,h^2h_x+\delta\left\{\frac{1}{\mu^3(t)}\left[\frac{8}{15}Rh^6-\mu^2(t)\,\frac{2\cot\alpha}{3}\,h^3\right]h_x +\frac{2w^{-1}\delta^2}{3\mu(t)}\csc\alpha(h^3h_{xxx})+\left(\frac{R\mu_t}{2\mu^3(t)}\right)h^5\right\}_x=0, \tag{27}$$

where we have neglected terms of $o(\delta)$. The first term is the temporal variation of the surface profile and the second term denotes the spatial variation. The first two terms give leading order kinematic (strongly) nonlinear waves. For example, if we were to neglect all the terms of $O(\delta)$, the following simple kinematic wave equation would result:

$$h_t+\frac{2}{\mu(t)}\,h^2h_x=0,$$

from which an analytical solution can be found:

$$h = h_0(\zeta) \text{ and } \zeta = x - 2h_0^2 \int_0^t \frac{d\tau}{\mu(\tau)},$$

where ζ is the characteristic variable and $h_0(\zeta)$ is the initial surface profile of the coating. The first square bracket in Eq. 27 involves second-order spatial derivative. When it is positive, inertia dominates over gravity, and the coating flow is destabilized. The reverse is true when gravity dominates over inertia. The term associated with $\delta^2 w^{-1}$ represents the effect of surface tension which always tends to stabilize the flow. The last term in Eq. 27 is a result of variable viscosity alone. As we shall see, this term will not affect the stability of the coating flows.

The comparison of Eq. 27 with its counterpart in nonreacting coating flows shows that the noticeable difference is the presence of the variable viscosity function $\mu(t)$. This feature makes reactive coating flows different from nonreactive coating flows. When $\mu(t) = 1$ the result given by Benney (1966) is recovered. Following the conventional procedure, we may discuss solutions in different limits, namely, the weakly nonlinear limit and the linear limit.

Solutions

Linear waves

Assuming $h = 1 + \epsilon g(x,t)$ where $\epsilon \ll O(\delta, \delta^2 w^{-1})$ allows us to consider the linear limit. From Eq. 27 we obtain:

$$g_t + \frac{2}{\mu} g_x + \delta \left\{ \frac{1}{\mu^3} \left(\frac{8}{15} R - \frac{2\mu^2}{3} \cot \alpha \right) g_{xx} + \frac{2w^{-1}\delta^2 \csc \alpha}{3\mu} g_{xxxx} + \frac{5R\mu_t}{2\mu^3} g_x \right\} = 0. \quad (28)$$

Substituting $g(x,t) = q(t)\exp(ikx)$ into Eq. 28, where k is the dimensionless wave number in the streamwise direction, we find:

$$\frac{dq}{dt} + \frac{2}{\mu(t)} (ik)q + \delta \left\{ [1/\mu^3] \left(\frac{8}{15} R - \frac{2\mu^2}{3} \cot \alpha \right)(-k^2) + \frac{2w^{-1}\delta^2 \csc \alpha}{3\mu} k^4 + \left(\frac{5R\mu_t}{2\mu^3} \right)(ik) \right\} q = 0. \quad (29)$$

The solution $q(t)$ can be assumed to have the following form:

$$q(t) = q_0 \exp\,[\Phi(t)]. \quad (30)$$

Since only the real part $Re\Phi$ leads to temporal growth or decay, we shall only concern ourselves with the solution of:

$$\frac{d}{dt} Re\Phi = \delta \left[\frac{8}{15} \frac{R}{\mu^3} - \frac{2}{3} \frac{\cot \alpha}{\mu} \right] k^2 - \frac{2w^{-1} \csc \alpha \delta^2}{3\mu} k^4. \quad (31)$$

Clearly when there is no reaction, the viscosity is constant $[\mu(t) = 1]$, and the first term on the righthand side of Eq. 31 gives the well-known result that when $R > 5 \cot \alpha/4$, long waves ($k \ll 1$) first become unstable. In our case, viscosity varies and we can substitute the expression for $\mu(t)$ given in Eqs. 24 and 25 to obtain the following: for $n = 1$,

$$Re\Phi = \frac{2}{3} \delta k^2 \left[\frac{4}{5} \frac{R}{3\kappa} (1 - e^{-3\kappa t}) - (\cot \alpha + w^{-1} \csc \alpha \delta^2 k^2) \frac{1}{\kappa} (1 - e^{-\kappa t}) \right]; \quad (32)$$

for $n = 2$,

$$Re\Phi = \frac{2}{3} \delta k^2 \left\{ \frac{4}{5} \frac{R}{2\kappa} [1 - (\kappa t + 1)^{-2}] - (\cot \alpha + w^{-1} \csc \alpha \delta^2 k^2) \frac{1}{\kappa} \log(\kappa t + 1) \right\}; \quad (33)$$

for $n = 4$,

$$Re\Phi = \frac{2}{3} \delta k^2 \left\{ \frac{4}{5} \frac{R}{3\kappa} \log(1 + 3\kappa t) - (\cot \alpha + w^{-1} \csc \alpha \delta^2 k^2) \frac{1}{2\kappa} [(1 + 3\kappa t)^{2/3} - 1] \right\}; \quad (34)$$

finally, for $\infty > n \neq 1, 2, 4$, we have:

$$Re\Phi = \frac{2}{3} \delta k^2 \left(\left[\frac{4}{5} \frac{R}{(n-4)\kappa} \right] \{ [(n-1)\kappa t + 1]^{n-4/n-1} - 1 \} - [\cot \alpha + w^{-1} \csc \alpha \delta^2 k^2] \frac{1}{(n-2)\kappa} \times \{ [(n-1)\kappa t + 1]^{n-2/n-1} - 1 \} \right), \quad (35)$$

where note the initial condition $Re\Phi = 0$ at $t = 0$ has been enforced. Since stability requires that $Re\Phi < \infty$ as $t \to \infty$, the results for linear stability are summarized in Figure 2.

Cases where $0 < \alpha < \pi/2$ or $\cot\alpha > 0$:

- When $n = 1$,

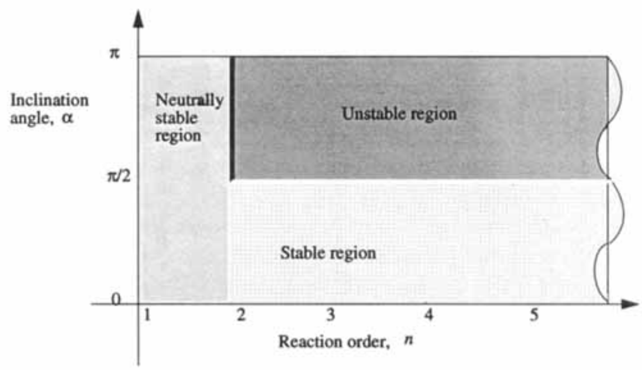

Figure 2. Stability for linear waves on a reacting coating flows under gravity.

The inclination angle is α and n is the reaction rate. Note smaller values of n correspond to faster reactions and *vice versa*. When $\alpha = \pi/2$, $R_c = (5/4) \cot \alpha = 0$ and long linear waves are neutrally stable for $2 > n \geq 1$ and stable for $n < \infty$ when surface tension is present. When $n = 2$, linear waves are unstable for $\alpha > \pi/2$ and stable for $\alpha \leq \pi/2$.

$$Re\Phi \rightarrow \frac{2k^2\delta}{3\kappa}\left[\frac{4}{15}R-(\cot\alpha+\delta^2 w^{-1}k^2\csc\alpha)\right] \text{ as } t\rightarrow\infty. \quad (36)$$

If the righthand side of the above equation is positive (negative), the final amplitude to the disturbance will be larger (smaller) than the initial amplitude. In either case, the initial disturbance will reach a finite amplitude as $t\rightarrow\infty$. This situation does not fall into any category of traditional linear stability. We shall refer to this case as neutral stability because of no unsustained growth with time.

- When $n=2$, $Re\Phi\rightarrow-\infty$ as $t\rightarrow\infty$, therefore, linear waves are stable for all wave numbers.
- When $n\neq 1, 2$, $Re\Phi\rightarrow-\infty$ for $\infty>n>2$ and for $2>n>1$,

$$Re\Phi - \delta k^2\left\{\left[\frac{8}{15}\frac{R}{(4-n)\kappa}\right] - \left[\frac{2\cot\alpha}{3}+\frac{2w^{-1}\csc\alpha\delta^2}{3}k^2\right]\frac{1}{(2-n)\kappa}\right\}. \quad (37)$$

As before, for $2>n>1$ the final finite amplitude of the disturbance will be larger (smaller) than the initial amplitude if the righthand side of Eq. 37 is positive (negative). Consequently, the flow is stable for $n\geq 2$ and neutrally stable for $1\leq n<2$, for all wave numbers.

Cases where $\alpha=\pi/2$ or $\cot\alpha=0$ (vertical wall):

- When $1\leq n<2$, $Re\Phi$ asymptotes to the constant value given in Eq. 37 (with $\cot\alpha=0$ and $\csc\alpha=1$) as $t\rightarrow\infty$, that is, neutrally stable.
- When $2\leq n<4$, $Re\Phi\rightarrow-\infty$ as $t\rightarrow\infty$, that is, stable.
- When $4\leq n$, $Re\Phi\rightarrow-\infty$ as $t\rightarrow\infty$ and the flow is stable provided surface tension is present. In the absence of surface tension $w^{-1}=0$, then $Re\Phi\rightarrow\infty$ as $t\rightarrow\infty$, that is, unstable.

Therefore, when the plane is vertical, linear waves are either stable or neutrally stable for $n<4$. For $4\leq n$, linear waves are either stable or unstable depending on the presence of surface tension.

Cases where $\pi>\alpha>\pi/2$ or $\cot\alpha<0$ (underside of the incline):

- When $1\leq n<2$, the limiting behavior discussed above in Eq. 37 is still valid and $Re\Phi$ approaches a finite value that is larger than its initial value as $t\rightarrow\infty$, and the linear waves are neutrally stable.
- When $n=2$, $Re\Phi\rightarrow\infty$ as $t\rightarrow\infty$, and the linear waves are unstable.
- When $n\neq 1, 2$, $Re\Phi\rightarrow\infty$ as $t\rightarrow\infty$ for $n>2$, and the linear waves are unstable.

Although for $n\geq 2$ and $\pi/2\leq\alpha<\pi$, linear stability can be achieved eventually, the initial disturbance actually grows for some time prior to its final decay when the following inequalities hold:

$$\frac{4R}{10}>\cot\alpha+w^{-1}\csc\alpha\delta^2k^2 \quad \text{for } n=2,$$

$$\frac{4R}{15}>\frac{\cot\alpha+w^{-1}\csc\alpha\delta^2k^2}{2} \quad \text{for } n=4,$$

$$\frac{4R}{5(n-4)}>\frac{\cot\alpha+w^{-1}\csc\alpha\delta^2k^2}{n-2} \quad \text{for } n\neq 4.$$

In fact, the time of growth of the initial disturbance can be found implicitly from Eqs. 33-35 by setting $Re\Phi=0$. For example, on a vertical plane ($\alpha=\pi/2$) when the waves are long or the surface tension is weak, that is, $w/\delta^2k^2\gg 1$, the growth of the initial disturbance occurs until

$$t\cong\left[\frac{4R(n-2)}{5(n-4)}\frac{w}{\delta^2k^2}\right]^{(n-1)/2}\Big/[\kappa(n-1)].$$

Note that large Reynolds number ($R>1$), weak surface tension ($w>1$), long waves ($k\ll 1$), and small reaction constant ($\kappa<1$) all prolong the time of growth of the initial disturbance. Even though the basic flow is ultimately stable, the existence of an initial growth phase can be undesirable in applications.

Clearly, these possibilities arise because the rates of growth or decay are not constant due to variable viscosity: inertia and gravity do not affect the growth rate on the same time scales. These results may be compared with the nonreactive coating flows. Linear long waves in that case become unstable whenever $R>(5/4)\cot\alpha\equiv\overline{R}_c$, where $\overline{R}_c$ is the critical Reynolds number for nonreacting coating flows. When the inclined plane is vertical ($\alpha=\pi/2$) or the coating fluid is on the underside of the plane ($\alpha>\pi/2$), coating flows of constant viscosity are unstable with respect to long wave disturbances. Here, it is possible for reactive coating flows to be neutrally stable on the underside of the inclined plane. For relatively fast reactions ($2>n\geq 1$), flows are neutrally stable for all inclination angles $0<\alpha<\pi$. For relatively slow reactions ($n\geq 2$), flows may be stable or unstable depending on the inclination angle. Specifically, when the coating is on the upperside of the inclined plate ($0<\alpha<\pi/2$) reacting coating flows are stable; when the coating is on the underside of the inclined plane ($\pi/2<\alpha<\pi$), reacting coating flows become unstable (Figure 2).

The cases where $1\leq n<2$ are interesting and deserve a comment here. In the limit $t\rightarrow\infty$, the amplitude of the disturbance acquires a value larger or smaller than its initial value depending on whether:

$$\left[\frac{4}{5}\frac{(2-n)R}{(4-n)}\right]>[\cot\alpha+w^{-1}\csc\alpha\delta^2k^2] \quad \text{or} \quad \left[\frac{4}{5}\frac{(2-n)R}{(4-n)}\right]<[\cot\alpha+w^{-1}\csc\alpha\delta^2k^2].$$

Suppose the effect of surface tension is unimportant, then we have according to the above inequalities:

$$R>\frac{5}{4}\frac{(4-n)}{(2-n)}\cot\alpha \quad \text{or} \quad R<\frac{5}{4}\frac{(4-n)}{(2-n)}\cot\alpha.$$

The critical Reynolds number $(5/4)\cot\alpha\equiv\overline{R}_c$ for constant viscosity coating flows appears in the above inequalities. Unlike the unsustained growth or decay for nonreacting flows, these inequalities correspond to an increase or a decrease in the amplitude of disturbance, that is, amplification or deamplification of the initial disturbance.

In the next section, we examine nonlinear effects. Nonlinear waves may be important for two reasons: one is when $n>2$ and $\alpha>\pi/2$, linear waves may become unstable and nonlinear waves may form; the other is that at the time the temperature field is raised from T_0 to T_1, the initial coating flows may already be in the nonlinear regime.

Weakly nonlinear waves

Assuming $h=1+\epsilon g(x,t)$ where $\epsilon \ll O(1)$, we find from Eq. 27:

$$g_t+\frac{2}{\mu}g_x+\epsilon\frac{2}{\mu}(g^2)_x+O(\epsilon^2)+\delta\left\{\frac{1}{\mu^3}\left[\frac{8}{15}R-\frac{2}{3}\cot\alpha\mu^2\right]g_{xx}+\frac{2w^{-1}\delta^2\csc\alpha}{3\mu}g_{xxxx}+\frac{5R\mu_t}{2\mu^3}g_x+O(\epsilon)\right\}=0.$$

Taking the distinguished limit $\epsilon=\delta$ and neglecting terms of $o(\epsilon)$ give us the following weakly nonlinear equation:

$$g_t+\frac{2}{\mu}g_x+\delta\left\{\frac{2}{\mu}(g^2)_x+\frac{1}{\mu^3}\left(\frac{8}{15}R-\frac{2\mu^2}{3}\cot\alpha\right)g_{xx}+\frac{2w^{-1}\delta^2\csc\alpha}{3\mu}g_{xxxx}+\frac{5R\mu_t}{2\mu^3}g_x\right\}=0. \quad (38)$$

If a regular perturbation is applied to Eq. 38, it can be shown that the asymptotic expansion is not uniformly valid when $n\geq 2$. This occurs because of the accumulative effect of nonlinearity and the fact that more than one time scale exists in the problem. In what follows, the well-known multiple-scale method is applied to take into account the accumulative weakly nonlinear effect. We introduce the fast time scale

$$t'=\int_0^t (d\bar{t})/[\mu(\bar{t})],$$

the slow time scale $\tau=\delta t'$, and a new coordinate $\xi=x-2t'$. The new coordinate is a coordinate moving with the wave packet (that is, a characteristic) and the new time scale τ may be interpreted to be the time scale for observing the evolution of the wave while moving with the wave packet. Considering $g\equiv g(\xi,\tau)$, we obtain from Eq. 38:

$$\frac{\partial g}{\partial \tau}+2g\frac{\partial g}{\partial \xi}+\left(\frac{8}{15}\frac{R}{\tilde{\mu}^2}-\frac{2}{3}\cot\alpha\right)\frac{\partial^2 g}{\partial \xi^2}+\frac{2w^{-1}\csc\alpha\delta^2}{3}\frac{\partial^4 g}{\partial \xi^4}+\frac{5}{2}R\delta\frac{\tilde{\mu}_\tau}{\tilde{\mu}^3}\frac{\partial g}{\partial \xi}=0, \quad (39)$$

where $\tilde{\mu}(\tau)$ is now given by:

$$\tilde{\mu}(\tau)=\frac{1}{1-\bar{\kappa}\tau}\ \text{for}\ n=1, \quad (40)$$

$$\tilde{\mu}(\tau)=[1+(n-2)\bar{\kappa}\tau]^{1/(n-2)}\ \text{for}\ n\neq 1, \quad (41)$$

Note that consistent with the "slow" time scale, we require that κ be:

$$\kappa=\bar{\kappa}\delta\ \text{and}\ \bar{\kappa}\sim O(1). \quad (42)$$

Equation 39 represents the balance of the accumulative effect of nonlinearity, inertia, gravity and surface tension. Since the sustained polymeric reaction is assumed to be a slow process $\tilde{\mu}_\tau\sim O(1)$, it is consistent in this case to neglect the last term in Eq. 39 to give:

$$\frac{\partial g}{\partial \tau}+4g\frac{\partial g}{\partial \xi}+\left(\frac{8}{15}\frac{R}{\tilde{\mu}^2}-\frac{2}{3}\cot\alpha\right)\frac{\partial^2 g}{\partial \xi^2}+\frac{2w^{-1}\csc\alpha\delta^2}{3}\frac{\partial^4 g}{\partial \xi^4}=0. \quad (43)$$

Equation 43 is a generalized Kuramoto-Sivashinsky (K-S) equation. Solution to the standard K-S equation has been discussed extensively elsewhere (Hooper and Grimshaw, 1988). However, general solutions to Eq. 43 are more difficult to obtain because of the added complexity of the variable coefficient. Consequently, two special cases are explored.

Moderate Surface Tension. In this case, the Weber number w is of order one and the last term in Eq. 43 may be neglected. The resulting equation is a generalized Burgers equation:

$$\frac{\partial g}{\partial \tau}+4g\frac{\partial g}{\partial \xi}+\left(\frac{8}{15}\frac{R}{\tilde{\mu}^2}-\frac{2}{3}\cot\alpha\right)\frac{\partial^2 g}{\partial \xi^2}=0 \quad (44)$$

It can be shown that for given $\tilde{\mu}(\tau)$, no analytical solution is available. However, when the inertia effect is negligible ($R\ll 1$), the well-known Burgers equation can then be obtained:

$$\frac{\partial g}{\partial \tau}+4g\frac{\partial g}{\partial \xi}=\frac{2}{3}\cot\alpha\frac{\partial^2 g}{\partial \xi^2}. \quad (45)$$

In this case, analytical solution can be found with the Hopf-Cole transformation. Substituting $g=(-\cot\alpha\phi_\xi)/(3\phi)$ in Eq. 45 gives:

$$\phi_\tau=\frac{\cot\alpha}{3}\phi_{\xi\xi}. \quad (46)$$

Since the discussion of this procedure can be found elsewhere (Whitham, 1974), we will not repeat them here. However, we do wish to point out that the second-order derivative corresponds to diffusion, and the coefficient of this term is an effective diffusion coefficient. For vertical planes $\alpha=\pi/2$, $\cot\alpha=0$ and this implies neutral stability. When $\alpha<\pi/2$, $\cot\alpha$ is positive and stable wave formation can be obtained. When $\alpha>\pi/2$, $\cot\alpha$ is negative and no stable wave formation is possible because there is negative diffusion.

For cases where $R\sim O(1)$, no exact solution of Eq. 44 is known to exist. However, numerical solutions can be readily obtained. Here, a finite difference scheme based on the MacCormack predictor and corrector scheme is employed. At each time step, $\tilde{\mu}(\tau)$ is updated and the construction of the solution proceeds spatially.

One case investigated is especially interesting. By assigning appropriate initial conditions, we may have at $\tau=0$, $R>(5\cot\alpha/4)\,\tilde{\mu}^2(0)=5\cot\alpha/4$. Therefore, linear surface waves are initially unstable. However, we noted that the viscosity function $\tilde{\mu}(\tau)$ increases with time and so does $R_c(\tau)\equiv(5\cot\alpha/4)\tilde{\mu}(\tau)$ (R_c is the time-dependent critical Reyn-

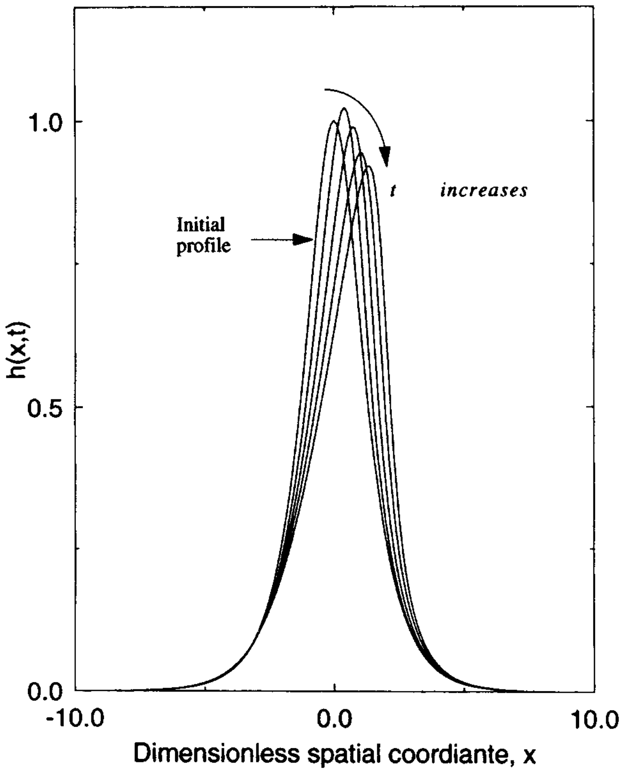

Figure 3a. Evolution with time of an initial hyperbolic secant (solitary wave) free-surface profile described by the generalized Burgers equation.

The following data are used for obtaining (a), (b) and (c): $\alpha = 45°$, $R = 2.0$, $\kappa = 2.0$, $dx = 0.1$, $dt = 0.005$. Clearly, since $R > 5/4 \cot \alpha$ we have the initial growth of the profile. Note that $n = 1$ and wave propagations stop once τ reaches τ_{max} given in Eq. 50. The calculation terminates at τ_{max}.

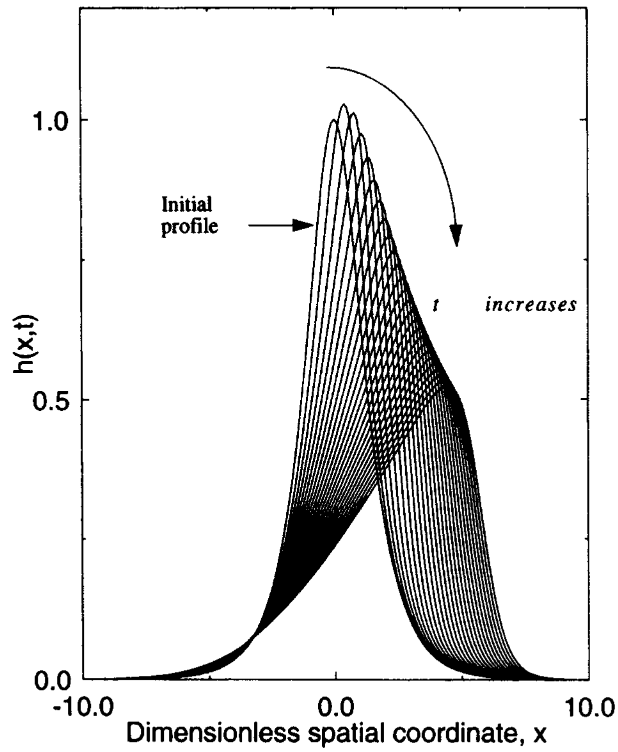

Figure 3b. Evolution with time of an initial hyperbolic secant free-surface profile described by the generalized Burgers equation.

In this case, reaction order $n = 2$.

olds number for reacting coating flows). It is then possible for the time-dependent diffusion coefficient to change sign with increasing time and stabilize the surface waves. Indeed, this is seen from the numerical solution. A hyperbolic secant initial profile (solitary wave) is used for this case study, and the results are presented in Figures 3a, 3b and 3c for three different values of reaction rate, $n = 1, 2, 3$, respectively. Initially, the wave profile grows due to instability caused by the inertia effect dominating over gravity, but gradually gravity wins the "competition," with the help of increasing viscosity. The final result is a continuously decreasing profile due to the time-dependent damping mechanism of gravity. For the example considered, we see that the growth of the initial profile takes place for the first time step: $\tau = 0.005$ for $n = 1$ and $n = 2$. For $n = 3$, it appears that growth continues after the first time increment and the maximum appears to be between the interval (0.005, 0.01). On the other hand, gelation halts the flow at $\tau = 0.025$ for $n = 1$. It is conceivable that for the right combination of parameters, flows may terminate at a time when the initial profiles achieve their maximum. To obtain good quality coatings, this situation should be avoided.

One unique feature about weakly reacting coating flows is the finiteness of τ for relatively fast reactions. In fact, we have:

$$\tau = \delta \int_0^t \frac{dt'}{\mu} = \left[\frac{1}{\bar{\kappa}} \left(1 - \exp(-\bar{\kappa}\delta t)\right) \right] \quad \text{for } n = 1, \qquad (47)$$

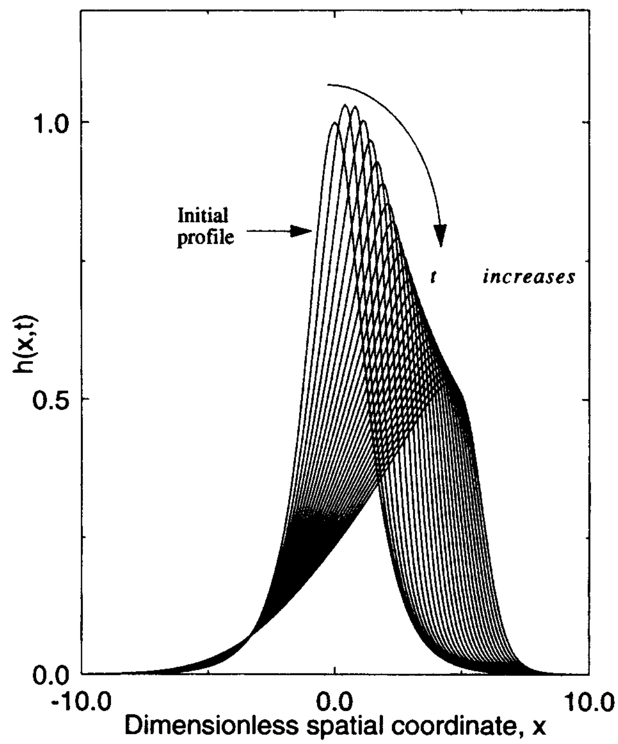

Figure 3c. Evolution with time of an initial hyperbolic secant free-surface profile described by the generalized Burgers equation.

In this case, reaction order $n = 3$.

$$\tau = \delta \int_0^t \frac{dt'}{\mu} = \left[\frac{1}{\bar{\kappa}} \log(\bar{\kappa}\delta t + 1) \right] \quad \text{for } n = 2, \tag{48}$$

and

$$\tau = \delta \int_0^t \frac{dt'}{F} = \frac{1}{(n-2)\bar{\kappa}} \{ [(n-1)\bar{\kappa}\delta t + 1]^{(n-2)/(n-1)} - 1 \} \quad \text{for } n \neq 1,2. \tag{49}$$

It follows from Eqs. 47 and 49 that for $n<2$, τ has an upper limit given by:

$$\tau_{\max} = \frac{1}{(2-n)\bar{\kappa}}. \tag{50}$$

This means that for fast reaction ($n<2$) wave propagation is only possible for some finite distance before polymeric reaction brings the flow to a halt. It is based on this result that the calculation in Figure 3a stops at time $\tau_{\max}$. Since $\tau_{\max}$ is obtained by taking the limit $t \to \infty$, only the large time behavior of the linear disturbance can be related to this limiting value. Recall the discussion on the rate of decay or growth. We see that for $n<2$ the linear disturbance is always neutrally stable while nonlinear wave formation has a limited life span.

Large Surface Tension. In this case, we may define a modified Weber number $w_o \equiv w\delta^{-2} \sim O(1)$ and the surface tension effect must be included. In general, no closed form solution is possible for arbitrarily given $\tilde{\mu}(\tau)$. Again, we consider the limit $R \ll 1$ and the generalized K-S equation (Eq. 43) then becomes:

$$\frac{\partial g}{\partial \tau} + 4g\frac{\partial g}{\partial \xi} + \left(-\frac{2}{3}B \right) \frac{\partial^2 g}{\partial \xi^2} + \frac{2 \csc \alpha w_o^{-1}}{3} \frac{\partial^4 g}{\partial \xi^4} = 0. \tag{51}$$

When $\alpha < \pi/2$ or $B = \cot \alpha > 0$, both the second- and the fourth-order derivatives represent dissipative effects. The case is of little interest because the solutions are strongly damped: when $\alpha > \pi/2$ or $B = \cot \alpha < 0$, Eq. 51 becomes the conventional K-S equation. It has been shown by Michelson (1986), Hooper and Grimshaw (1988), and Chang (1989) that the following three categories of travelling waves exist: 1) regular shocks, 2) solitary waves, and 3) periodic and quasi-periodic solutions.

For $n \geq 2$, we have shown from the linear analysis that surface waves are unstable for $\alpha > \pi/2$, in which case only the periodic or quasi-periodic solutions are physically realizable. For $n<2$, however, the reaction stabilizes the flow, and localized solutions like shocks or solitary waves are possible. To find the traveling wave solutions, yet another new coordinate $\varsigma \equiv \xi - U\tau$ can be substituted in Eq. 51 to give:

$$\frac{w_o^{-1} \csc \alpha}{3} g_{\varsigma\varsigma\varsigma\varsigma} + \left(-\frac{B}{3} \right) g_{\varsigma\varsigma} + (g^2)_\varsigma + (-U) g_\varsigma = 0, \tag{52}$$

where U is the traveling speed of the waves and it is to be determined from upstream and downstream conditions. Since similar numerical studies have been carried out by many researchers, we shall discuss a closed-form analytic solution

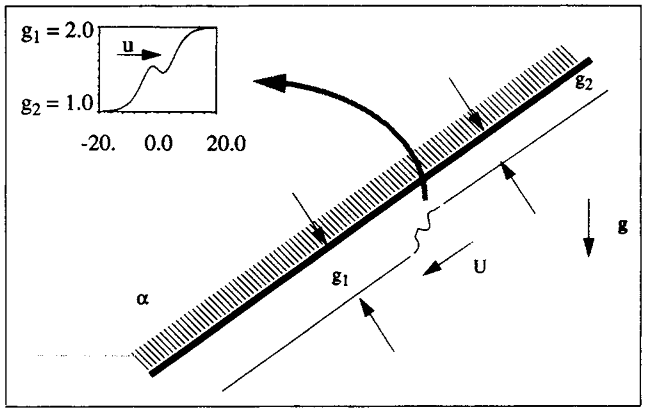

Figure 4. Special solution of K-S equation in reacting coating flows.

Solution of K-S equation provides the transition between two uniform coating flows. The actual profile of the solution is given in the insert.

(Hooper and Grimshaw, 1988), which is realizable in the reacting coating flows. This solution is given by:

$$g(\varsigma) = \frac{U}{2} + \left(g_1 - \frac{U}{2} \right) \tanh \left[\frac{19(2g_1 - U)\varsigma}{20|B|} \right] \times \left\{ 1 - \frac{11}{2} \left(\operatorname{sech} \left[\frac{19(2g_1 - U)\varsigma}{20|B|} \right] \right)^2 \right\}, \tag{53}$$

where $U = g_1 + g_2$ and g_1, g_2 are the values of g as the spatial variable $\varsigma \to \pm\infty$, respectively. The solution given by Eq. 53 is a single shock-like solution representing a reacting fluid film draining down the underside of the inclined plane under gravity, that is, a "draining-wave." An example is shown in Figure 4. Note that nonreacting coating flows cannot have solutions similar to this one because uniform up/down stream flows are not stable. In contrast, when $n<2$ reacting coating flows are neutrally stable. In this sense, the solution given in Eq. 53 is unique for reacting coating flows. It should be noted that the life span of the "draining-wave" obeys the limit given in Eq. 50.

Case where $R \sim O(1)$ can be studied numerically. However, because of the presence of the surface tension term in the governing equation, no unsustained growth will emerge. The generalized K-S equation will not show the similar interesting transition from instability to stability due to variable viscosity, as in the case of the generalized Burgers equation.

Conclusions

We have shown that reacting coating flows behave differently from their nonreacting counterpart. The stability of linear waves on a uniform depth is studied. We find that the linear stability of a reacting coating is determined not only by the inclination angle but also by the reaction order. Figure 2 summarizes the linear stability results. Generally, the effect of polymer reaction increases the viscosity and therefore alters the behavior of the linear disturbance and nonlinear wave formation.

For coating flows on the upper side ($\alpha < \pi/2$) of the inclined plane, uniform flows are either stable or neutrally stable. Furthermore, some neutrally stable uniform flows can also be achieved on the underside ($\pi/2<\alpha<\pi$) of the inclined plane. In contrast, constant-viscosity uniform coatings are always unstable when $\pi/2<\alpha<\pi$ and can be stable or unstable depending on the inclination angle when $\alpha<\pi/2$.

Using the method of multiple scales, we derive a generalized Kuramoto-Sivashinsky equation for the weakly nonlinear waves. Similarity solutions can be obtained in two limiting cases with the neglect of the inertia effect. In the case of negligible surface tension, a variable coefficient Burgers equation results, and the study of the wave formation based on this equation shows that a possible transition from unstable to stable wave formation may take place due to the effect of variable viscosity. In the other case, a generalized Kuramoto-Sivashinsky equation emerges. A special analytical solution to this equation appears to be unique for reacting coating flows on the underside of the inclined plane.

Note that the isothermal assumption of the reacting coating flows does not allow the comparison with the work performed by Gousis and Kelly (1985, 1987) and Hwang and Weng (1987). The key difference is that here viscosity is time-dependent and therefore there exist no steady-state solutions as in the case considered by these researchers.

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Notation

A, κ = dimensional and dimensionless reaction constant
c = concentration
f_i = body force
g, $g(x,t)$ = gravity constant and the perturbation of the free surface profile
h, h_0 = free surface profile and average thickness of the coating
H = mean curvature of the free surface
k = wave number
l = characteristic wavelength
n = reaction order
p = pressure
R, R_c, $\bar{R}_c$ = Reynolds number and critical Reynolds numbers
t, τ = dimensional and dimensionless time
x_i = spatial coordinate
u_i = velocity components
w, w_0 = Weber's number and modified Weber's number
Z = degree of cure

Greek letters

α = inclination angle
η, μ = dimensional and dimensionless viscosity
η_0 = ambient viscosity
Γ = ratio of Reynolds number to Froude number
σ = surface tension
δ = long-wave perturbation parameter
ρ = density of the fluid
ξ, ζ = transformed coordinates

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