

STABILITY OF THIN EVAPORATING/CONDENSING FILMS IN THE PRESENCE OF SURFACTANTS

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Abstract—A new equation is presented for the evolution of film thickness which, in addition to van der Waals dispersive forces and surface tension, includes flow effects arising from surface tension gradients. The effect of surfactant is quantified in terms of its adsorption at the liquid-gas interface. A linear stability analysis shows that the dynamics of evaporating/condensing thin films in the presence of surfactant are entirely different from isothermal films with surfactant and non-isothermal films without surfactant. Thus, flows driven by surface tension gradients originating from surfactant concentration variations, i.e. Marangoni flows, are in a direction opposite to that of similar flows originating from surface temperature variations, i.e. thermocapillary flows. The former usually dominate; they are destabilizing for condensing films and stabilizing for evaporating films..

Key Words: thin film, evaporation, condensation, surfactant, stability

1. INTRODUCTION

In flow through porous media, the dominantly-wetting phase fills small-size pores and flows along the walls of larger pores as a continuous thin film. The bulk of the large pores is occupied by less-wetting and non-wetting phases. The wall films are subject to hydrodynamic, surface instabilities. Under certain flow conditions (Gauglitz & Radke 1988), and for specific pore throat-to-body ratios (Ransohoff *et al.* 1987), they “snap-off” to form free films, called lamellae, which block the pore-throat entrance to the incoming non-wetting phase.

In enhanced oil recovery (EOR) operations which utilize injected gas to displace the oil, the problem of an efficient sweep of the reservoir arises since the gas flows preferentially through the top of the formation or through high-permeability zones. One of the ways of slowing down the advance of the gas and redistributing it over a larger cross section of the reservoir is to render part or all of the gas phase discontinuous. To achieve this goal, the lamellae are stabilized by surfactant which is injected in the form of dilute aqueous solutions. The non-uniform gas-in-water dispersion, which is stabilized by surfactant in porous media, is called a foam, although its texture and features are quite different from those of common bulk foams outside porous media.

The wall films (figure 1a) are bounded in the transverse direction by the inside pore wall and a gas-liquid interface. Their stability is of primary importance to foam formation. The stability of the free films (figure 1a), which span the pore and have two gas-liquid interfaces, determines the rate of foam collapse. Film stability is a result of the interplay of viscous, capillary and intermolecular (disjoint pressure) forces. Variations of surfactant concentration and temperature at the gas-liquid interface add surface-tension gradients to the factors influencing film stability. Flows induced by surface-tension gradients due to surfactant excess concentration variations are known as Marangoni flows (Sternling & Scriven 1959); those arising from interfacial temperature variations are known as thermocapillary flows (Pearson 1958).

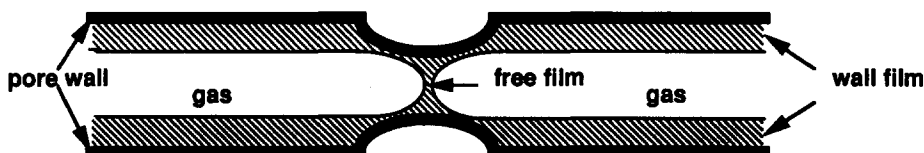


Figure 1a. Thin liquid films in a pore, relevant to foam.

For surfactants used in EOR operations, the rate-determining process is adsorption at the gas-liquid interface (Hirasaki & Lawson 1985). Interfacial temperature variations for foams in porous media are usually associated with a lack of thermal equilibrium between the gas and liquid phases. Depending on the sign of the temperature difference between the liquid and gas, condensation or evaporation occurs. This temperature difference between the liquid and gas ranges from the value associated with the pressure difference between these phases [capillary pressure (Falls *et al.* 1988)] and that associated with the temperatures of the injected fluid and the cold reservoir. Condensation is expected to increase the stability of thin liquid films; evaporation is expected to have the opposite effect.

A linear stability analysis of thin evaporating and condensing films with surfactant present is used as a way of comparing steam-foams to "cold"-gas-foams. Stability analyses are available only for evaporating/condensing films with no surfactant (Burelbach *et al.* 1988) and for isothermal films with surfactant (Sharma & Ruckenstein 1988; Prevost & Gallez 1986).

Free films (films bounded in the direction of their shortest dimension by two gas-liquid interfaces) are more difficult to analyze than wall films (films bounded in the direction of their shortest dimension by a solid wall and a gas-liquid interface). For a free film, a previous analysis (Prevost & Gallez 1986) has shown that there are two modes of film thickness variation: a bending mode, in which the two gas-liquid interfaces move parallel to each other in the direction of the shortest dimension; and a squeezing mode, in which the same interfaces move antiparallel in the direction of the shortest dimension. Only the squeezing mode is considered in their analysis, because it is the one that results in rupture. For the purposes of the work presented here, the dynamics of a free film are approximated by those of a wall film with thickness equal to half the thickness of the free film.

2. MODEL

Consider a thin film of a Newtonian liquid, uncharged and laterally unbounded, sandwiched between a rigid wall and an interface with a passive vapor (figure 1b). The dimensions of the film are very small, yet large enough compared to molecular length scales to allow a continuum description of the flow. Thinning of the film can occur through drainage by capillary suction and/or gravity. The film is always subject to surface perturbations originating from external or internal disturbances, and the growth of the surface perturbations is controlled by the interaction of surface tension and intermolecular forces (disjoining pressure). The assumption is made that the times characterizing the growth of surface disturbances are larger than those characterizing film draining. For the systems considered in this work, vapor density, viscosity and thermal conductivity are substantially smaller than the respective liquid properties. It is assumed that condensation or evaporation occurs at the interface due to a constant amount of superheat or subcooling, i.e. a temperature difference between the liquid and the vapor. The assumption is made that mass transfer due to phase change is negligible. However, momentum and energy transfer due to phase change cannot be ignored.

Following Williams & Davis (1982), the governing equations and boundary conditions are non-dimensionalized using the characteristic scales: h_0 for length; h_0^2/ν for time; ν/h_0 for velocity; and $\rho\nu^2/h_0^2$ for pressure (h_0 is the average or initial film thickness and ν and ρ are the liquid kinematic

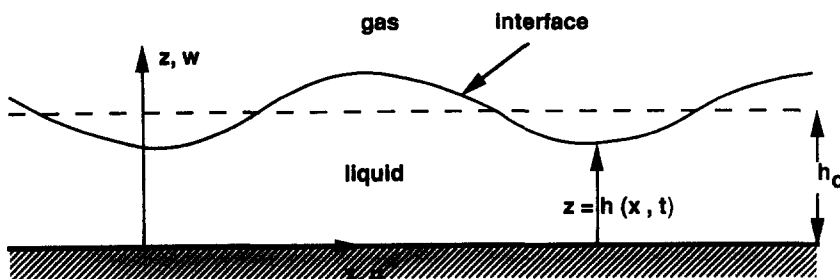


Figure 1b. Thin wall film with a cartesian coordinate system.

viscosity and density, respectively). The dimensionless temperature is defined as $(T - T_s)/\Delta T$, where T_s is the saturation temperature and ΔT is the difference in the wall or bulk liquid temperature and the saturation temperature. In a Cartesian coordinate system (x, z) , as in figure 1b, the flow and heat transfer in the film are described by the following equations (in dimensionless form):

$$u_t + uu_x + wu_z = \nabla^2 u - (p + \phi)_x, \quad [1]$$

$$w_t + uw_x + ww_z = \nabla^2 w - (p + \phi)_z, \quad [2]$$

$$u_x + w_z = 0 \quad [3]$$

and

$$T_t + uT_x + wT_z = \text{Pr}^{-1} \nabla^2 T, \quad [4]$$

where Pr is the Prandtl number of the liquid, the subscripts denote partial derivatives and ϕ is the potential for intermolecular dispersive forces (disjoining pressure) given (Ruckenstein & Jain 1974) as

$$\phi = \frac{A_0}{h^3}. \quad [5a]$$

Here A_0 is defined as

$$A_0 = \frac{A_H}{6\pi h_0 \rho v^2}, \quad [5b]$$

where A_H is the Hamaker constant.

Surface tension has a stabilizing influence on the film and the disjoining pressure has a stabilizing or destabilizing influence, depending on the sign of A_H , i.e. whether the dispersive forces are attractive or repulsive. Here, only the case of positive A_H is considered.

The boundary conditions at $z = 0$ for a wall film are

$$z = 0, \quad u = w = 0; \quad T = 1. \quad [6]$$

The boundary conditions at the liquid–vapor interface are given by (appendix A)

$$z = h, \quad (u_z + w_x)(1 - h_x^2) + 2(w_z - u_x)h_x = 3(S_x + h_x S_z)(1 + h_x^2)^{1/2}, \quad [7]$$

$$z = h, \quad \frac{3}{2}J^2 D_0 - p + 2[w_z(1 - h_x^2) - (u_z + w_x)h_x](1 + h_x^2)^{-1} = 3Sh_{xx}(1 + h_x^2)^{-3/2}, \quad [8]$$

$$z = h, \quad J\Lambda + T_z - h_x T_x = 0 \quad [9]$$

and

$$z = h, \quad h_t + J + uh_x - w = 0; \quad [10]$$

where $S = (h_0 \sigma)/(3\rho v^2)$ is the dimensionless surface tension and $\Lambda = \lambda \rho v/k \Delta T$, with λ being the latent heat of vaporization. The term $J = \beta(T|_h - T_s)h_0/(\rho v)$, with $T|_h$ being the temperature at the gas–liquid interface, is the dimensionless rate of vaporization (condensation). The term $\beta = (a\rho_v \lambda/T_s^{3/2})(M_w/2\pi R_G)$, where a is an accommodation coefficient of order 1, M_w is the molecular weight and R_G is the universal gas constant. The term $D_0 = 2/3(\rho/\rho_v)$ is the density ratio, where ρ_v is the vapor density. Equations [7], [8] and [9] are the balances of tangential stress, normal stress and energy, respectively. Equation [10], known as the kinematic condition, is the mass balance at the liquid–vapor interface.

Following Williams & Davis (1982), the long-wavelength approximation is made, in which the small parameter is defined as the wavenumber q of the disturbances in the film. The above equations are rescaled by defining new variables:

$$\xi = qx; \quad \zeta = z; \quad \tau = qt, \quad [11]$$

so that

$$\frac{\partial}{\partial \xi}, \frac{\partial}{\partial \zeta}, \frac{\partial}{\partial \tau} = O(1) \quad \text{as } q \rightarrow 0. \quad [12]$$

Based on an order of magnitude analysis, the dependent variables are expanded as

$$u = u_0 + qu_1 + O(q^2), \quad [13a]$$

$$w = q[w_0 + qw_1 + O(q^2)], \quad [13b]$$

$$T = T_0 + qT_1 + O(q^2) \quad [13c]$$

and

$$p = \frac{1}{q} [p_0 + qp_1 + O(q^2)]. \quad [13d]$$

When these expansions are substituted in the above equations, the leading order terms are given by:

$$u_{0\zeta\zeta} - (p_0 + \phi_0)_\xi = 0, \quad [14a]$$

$$(p_0 + \phi_0)_\zeta = 0, \quad [14b]$$

$$u_{0\xi} + w_{0\xi} = 0, \quad [14c]$$

$$T_{0\zeta\zeta} = 0, \quad [14d]$$

with

$$\zeta = 0, \quad u_0 = w_0 = 0; \quad T_0 = 1. \quad [14e]$$

It is assumed that the surface tension varies along the liquid–vapor interface due to both temperature and surfactant concentration variations. An approximation, in dimensional form, is introduced:

$$\sigma(\Gamma, T) = \sigma(\Gamma_0, T_0) + \sigma_T(T - T_0) + \sigma_\Gamma(\Gamma - \Gamma_0), \quad [15]$$

where Γ is the surface excess concentration in mol per unit area of the interface and Γ_0 is the surface excess concentration in equilibrium with the bulk surfactant concentration c_0 (known). In dimensionless form, [15] becomes

$$S(\Gamma, T) = S(T_0) - \Sigma_T(T - T_0) - \Sigma_\Gamma(\Gamma - 1), \quad [16]$$

where $\Sigma_T = (-\sigma_T \Delta Th_0)/(3\rho v^2)$, $\Sigma_\Gamma = (-\sigma_\Gamma \Gamma_0 h_0)/(3\rho v^2)$, $\sigma_T = \partial\sigma/\partial T$ and $\sigma_\Gamma = \partial\sigma/\partial\Gamma$. With the long-wavelength approximation, the excess surface concentration is given as

$$\Gamma = 1 + q\Gamma_1 + O(q^2), \quad [17]$$

where “1” is the dimensionless average or initial surface excess concentration.

In a similar way, the order q problem is given by

$$u_{0\zeta} + u_0 u_{0\xi} + w_0 u_{0\xi} = u_{1\zeta\zeta} - p_{1\xi}, \quad [18a]$$

$$p_{1\zeta} = 0, \quad [18b]$$

$$u_{1\xi} + w_{1\xi} = 0 \quad [18c]$$

and

$$T_{1\zeta\zeta} = 0, \quad [18d]$$

with

$$\zeta = 0, \quad u_1 = w_1 = 0; \quad T_1 = 0. \quad [18e]$$

The boundary conditions at the liquid–vapor interface are given as follows for [14] and [18]:

$$\zeta = h, \quad T_0 + KT_{0\xi} = 0 \quad [19]$$

and

$$\zeta = h, \quad T_1 + KT_{1\xi} = 0, \quad [20]$$

where $K = k/(\beta h_0 \lambda)$ and k is the thermal conductivity of the liquid.

The parameter K is a measure of the deviation from (thermodynamic) equilibrium. Thus, $K \rightarrow 0$ describes a situation, called "quasi-equilibrium" by Burelbach *et al.* (1988), in which the interfacial temperature is constant and equal to the saturation temperature. On the other hand, $K \rightarrow \infty$ describes a situation in which no phase change takes place. Any case with $K \neq 0$ corresponds to non-equilibrium, i.e. the temperatures of the liquid and gas at the interface are different from each other.

Because of its uncoupling from the equations of motion, the energy equation can be solved first to provide the temperature as

$$T_0 = -(h + K)^{-1}\zeta + 1 \quad [21]$$

and

$$T_1 = 0. \quad [22]$$

In view of these results, [7] and [8] yield:

$$\zeta = h, \quad u_{0\zeta} = 3\bar{\Sigma}_T(T_{0\zeta} + h_\zeta T_{0\zeta}) \quad [23a]$$

and

$$\zeta = h, \quad J^2 \bar{D}_0 - p_0 = 3\bar{S}h_{\zeta\zeta}; \quad [23b]$$

and

$$\zeta = h, \quad u_{1\zeta} = 3\bar{\Sigma}_T \Gamma_{1\zeta} \quad [24a]$$

and

$$\zeta = h, \quad p_1 = 0; \quad [24b]$$

where \bar{D}_0 is qD_0 , $\bar{\Sigma}_T$ and $\bar{\Sigma}_T$ and $q\Sigma_T$ and $q\Sigma_T$ and \bar{S} is q^3S .

The flow field, to a leading order approximation, is given by

$$u_0 = (p_0 + \phi_0)_\zeta (\frac{1}{2}\zeta^2 - \zeta h) + 3\Sigma_T [h(h + K)^{-1}]_\zeta \zeta \quad [25a]$$

and

$$w_0 = -(p_0 + \phi_0)_{\zeta\zeta} (\frac{1}{6}\zeta^3 - \frac{1}{2}\zeta^2 h) + \frac{1}{2}(p_0 + \phi_0)_\zeta \zeta^2 h_\zeta - \frac{3}{2}\Sigma_T [h(h + K)^{-1}]_{\zeta\zeta} \zeta^2. \quad [25b]$$

To get a similar solution to the q -order-approximation problem, it is assumed that the l.h.s. of [18a] is negligible. With this approximation, the flow field, to the q -order approximation, is given (appendix B) by

$$u_1 = -3\Sigma_T \epsilon^{-1} (u_{0\zeta}|_h)_\zeta \zeta \quad [26a]$$

and

$$w_1 = \frac{3}{2}\Sigma_T \epsilon^{-1} (u_{0\zeta}|_h)_{\zeta\zeta} \zeta^2, \quad [26b]$$

where $u_{0\zeta}|_h$ is the value of $u_{0\zeta}$ evaluated at $\zeta = h$ and $\epsilon = \alpha h_0^2/\nu$. In solving for u_1 and w_1 use of the expression

$$\Gamma_1 = \epsilon^{-1} u_{0\zeta}|_h \quad [27]$$

was made. The last equation is for a situation in which surfactant adsorption/desorption at the liquid-vapor interface is the rate-controlling process. Hirasaki & Lawson (1985) have shown this to be the case for surfactants used in generating foam in porous media. Surfactant transport for such systems (Levich 1962) is modeled in appendix B.

The kinematic condition [10] can be written as

$$h_\tau + q^{-1}J_0 + (u_0 + qu_1)h_\zeta - (w_0 + qw_1) = 0. \quad [28]$$

With the flow field given by [25] and [26], [28] can be written as follows in the original x and t variables:

$$\begin{aligned} h_t + J_0 + S(h^3 h_{xxx})_x + A(h^{-1} h_x)_x + E_0^2 D_0 [h^3 (h + K)^{-3} h_x]_x + KM_0 \text{Pr}^{-1} [h^2 (h + K)^{-2} h_x]_x \\ + \frac{3}{2} G_0 \{ Sh^3 (hh^{(6)} + 6h_{xx} h_{xxxx}) + A(h_{xxxx} - 6h^{-1} h_{xx}^2) \\ + E_0^2 D_0 h^3 (h + K)^{-4} [(h + K) h h_{xxxx} + 3(-h + 2K) h_{xx}^2] \\ + \frac{4}{3} KM_0 \text{Pr}^{-1} h^2 (h + K)^{-3} h_x [h(h + K) h_{xxxx} + (-5h + K) h_{xx}^2] + \text{Terms containing } h^{(2m+1)} \} = 0, \quad [29] \end{aligned}$$

where $h^{(m)}$ is the m -order derivative of h with respect to x , $J_0 = \beta \Delta T h_0 T_0 |_{h=0} / (\rho v) = \beta \Delta T h_0 K (h + K)^{-1} / (\rho v) = E_0 (h + K)^{-1}$, $E_0 = (k \Delta T) / (\rho v \lambda)$, $M_0 = (-\sigma_T \Delta T) / (2 \rho v h_0 \kappa)$, $G_0 = (-\sigma_T \Gamma_0) / (2 \rho v h_0 \alpha)$ and α is the rate of net adsorption of the surfactant at the liquid-vapor interface. The algebra involved in deriving [29] was checked with *Mathematica* (Wolfram 1988), a software package for symbolic and numerical calculations.

The different terms in [29] can be identified as follows: the second term represents the mass gain/loss due to condensation/evaporation; the third term, the stabilizing effect of surface tension; the fourth term, the destabilizing effect of the van der Waals forces; the fifth term, the effect of vapor recoil; and the sixth term, the effect of thermocapillary flow; the rest of the terms which involve a product of G reflect the interaction of the convective flows due to temperature gradients (Pearson 1958) with the short-range forces and the convective flows due to surfactant concentration gradients (Sterling & Scriven 1959). Depending on the sign of ΔT , the equation applies equally well to evaporating ($\Delta T > 0$) as well as condensing ($\Delta T < 0$) films. Thus, the effects of temperature and surfactant concentration variations on the stability of the film can be separated from those for an isothermal, thin liquid film devoid of surfactant. Furthermore, in this approach temperature effects constitute a leading order correction to the isothermal pure liquid film evolution equation, while those of the surfactant comprise a $O(q)$ correction to the same equation.

For thin films associated with foams in porous media, following Falls *et al.* (1988), a low-bound estimate of the difference in (dimensional) temperature between the liquid and vapor phases is calculated according to

$$\Delta T = \left(\frac{\partial T}{\partial p} \right)_s (p_L - p_V) = - \left(\frac{\partial T}{\partial p} \right)_s \frac{2\sigma}{r_p}, \quad [30]$$

where r_p is the average pore radius.

After rescaling of [29] with

$$X = \left(\frac{A_0}{S} \right)^{1/2} x; \quad \Theta = \left(\frac{A_0^2}{S} \right) t, \quad [31]$$

and assuming that the mass gain/loss due to condensation/evaporation is negligible, the following equation is obtained:

$$\begin{aligned} h_\Theta + (h^3 h_{xxx})_X + (h^{-1} h_X)_X + D [h^3 (h + K)^{-3} h_X]_X + KM [h^2 (h + K)^{-2} h_X]_X \\ + G \{ h^3 (hh^{(6)} + 6h_{XX} h_{XXXX}) + (h_{XXXX} - 6h^{-1} h_{XX}^2) \\ + Dh^3 (h + K)^{-4} [(h + K) h h_{XXXX} + 3(-h + 2K) h_{XX}^2] \\ + \frac{4}{3} KM h^2 (h + K)^{-3} h_X [h(h + K) h_{XXXX} + (-5h + K) h_{XX}^2] + \text{Terms containing } h^{(2m+1)} \} = 0, \quad [32] \end{aligned}$$

where $D = (E_0^2 D_0) / A_0$, $M = M_0 \text{Pr}^{-1} / A_0$, $G = 3/2 (G_0 A_0) / S_0$ and $h^{(m)}$ derivatives now are with respect to X . With this rescaling the effects of surface tension and van der Waals forces become indistinguishable.

Solutions to the free film problem have been presented in the literature for isothermal films only for cases of tangentially immobile interfaces ($u|_h = 0$) and surface inactive solutes ($\nabla_s \sigma = 0$) (Sharma & Ruckenstein 1988).

3. LINEAR STABILITY ANALYSIS

Equation [32] governs long-wavelength interfacial disturbances on a static film for which $h = 1$. Because the disturbance amplitude is unrestricted, non-linear interactions can be included. In this analysis, terms quadratic in the disturbances are neglected. The linear theory provides the wavelength and growth rate of the most unstable disturbance, as well as a rough estimate of the rupture time at which the film attains zero thickness. It is a rough estimate, since linear theory does not apply when the disturbance amplitude becomes large. The linearized problem is obtained from [32] by substituting $h = 1 + H(X, \Theta)$. The resulting equation is

$$H_{\Theta} + GH_{XXXXXX} + \{1 + G[1 + D(K + 1)^{-3} + \frac{4}{3}KM(K + 1)^{-2}]\}H_{XXXX} + [1 + D(K + 1)^{-3} + KM(K + 1)^{-2}]H_{XX} = 0. \quad [33]$$

For similar problems, a weakly non-linear stability analysis was pursued by Sharma & Ruckenstein (1988) and a non-linear theory based on numerical solution of the complete film thickness equation was advanced by Burelbach *et al.* (1988). The same techniques can be applied to [32] to obtain a more accurate estimate of the rupture time.

In linear stability analysis, a disturbance is decomposed into Fourier modes and the growth of the modes is investigated. To this end, the disturbance is given by

$$H = \text{Re}[H_0 \exp(\omega\Theta + iqX)], \quad [34]$$

where ω is the growth rate and q is the wavenumber of the disturbance. If H and its derivatives are substituted from [34] into [33], we obtain the dispersion relation

$$\omega = q^2 \left[Gq^4 - \{1 + G[1 + D(K + 1)^{-3} + \frac{4}{3}KM(K + 1)^{-2}]\}q^2 + [1 + D(K + 1)^{-3} + KM(K + 1)^{-2}] \right]. \quad [35]$$

A critical wavenumber, q_c , can be defined for which $\omega = 0$. Small disturbances grow for $\omega > 0$ and decay for $\omega < 0$. In addition, the most unstable disturbance, (q_M, ω_M) , can be found by requiring that $(d\omega/dq)|_{q_M} = 0$.

When no surfactant is present ($G = 0$), i.e. for an evaporating or condensing film of a pure liquid, [35] reduces to (Sharma & Ruckenstein 1988)

$$\omega = q^2[1 + D(K + 1)^{-3} + KM(K + 1)^{-2} - q^2]. \quad [36]$$

Finally, for an isothermal liquid film with no surfactant present ($G = 0, K \rightarrow \infty$), [35] reduces to (Williams & Davis 1982):

$$\omega = q^2(1 - q^2), \quad [37]$$

from which

$$q_c = 1; \quad q_M = 2^{-1/2}; \quad \omega_M = \frac{1}{4}. \quad [38]$$

For the isothermal film with surfactant present the dispersion relation becomes

$$\omega = q^2[Gq^4 - (G + 1)q^2 + 1]. \quad [39]$$

Although linear theory is valid only for infinitesimal disturbances from the planar interface, its predictions are taken as rough estimates of growth rates up to film rupture. Similarly, the predictions are assumed to be valid for the snap-off case, i.e. the case in which the thin liquid film wetting the inside wall of a capillary grows to a thickness equal to the capillary radius, thus forming a lamella extending across the capillary.

For films associated with foam in porous media, the rupture time, Θ_R , is defined as the time at which the most unstable disturbance (q_M, ω_M) , for at least one X value, yields

$$1 + H(X, \Theta_R) = 0 \quad [40a]$$

or, in view of [34],

$$1 - \text{Re}[H_0 \exp(\omega_M \Theta_R)] = 0. \quad [40b]$$

Similarly, the snap-off time, Θ_s is given by

$$1 + H(X, \Theta_s) = R \quad [41a]$$

or

$$1 + \text{Re}[H_0 \exp(\omega_M \Theta_s)] = R, \quad [41b]$$

where R is the pore (capillary) radius made dimensionless with the average or initial film thickness h_0 .

The times of rupture and snap-off are then given by

$$\Theta_R = -\frac{1}{\omega_M} \ln H_0 \quad [42a]$$

and

$$\Theta_S = \frac{1}{\omega_M} \ln \frac{R-1}{H_0}, \quad [42b]$$

respectively, where H_0 is the initial disturbance (< 1).

4. RESULTS

The theory presented above was used to calculate the stability of steam-foam in a reservoir. The average reservoir temperature and pressure were taken to be 100°F and 200 psia, respectively. This pressure corresponds to an average saturation temperature of 380°F.

The initial film thickness, h_0 , was calculated from Bretherton's (1961) theory to be approx. 50 Å. Based on the above saturation temperature and the steam properties (Keenan & Keyes 1940), a transport coefficient for evaporation/condensation $\beta = 192,326 \text{ lb}/(\text{ft}^2 \text{ }^\circ\text{R day})$ was calculated. The degree of superheating or subcooling, ΔT , was calculated from [30] to be approx. 0.14°F. Finally, the dimensionless number G_0 , which provides a measure of the convective flow driven by the surface-tension gradient due to surfactant concentration variations, was taken to be equal to that measured by Hirasaki & Lawson (1985). Table 1 summarizes the numerical values of the various system parameters.

In the calculations presented below, both the superheating or subcooling, ΔT , and the surfactant number, G , were varied. ΔT values spanned the range -100°F (high subcooling) to 0°F (isothermal case) to 100°F (high superheating); G varied from 0 (no surfactant or inactive surfactant) to 1000 (tangentially immobile interface). The dimensionless superheating or subcooling is represented by E_0 .

The easiest case to analyze is the isothermal liquid film with no surfactant present (Williams & Davis 1982). The film is unstable for disturbances whose wavenumber is $0 < q < 1$.

For the isothermal film with surfactant present, the dispersion relation [39] shows that the film is unstable for disturbances whose wavenumber is given by

$$q^2 > \max\{1, 1/G\} \quad \text{or} \quad q^2 < \min\{1, 1/G\}.$$

Table 1. Steam-foam parameters

$\Delta T = \text{from [30]}$	0.14°F
$K = k/(h_0 \lambda \beta)$	0.252
$\text{Pr} = \nu/\kappa$, Prandtl number	15.5
$A_0 = A_H/(6\pi h_0 \rho v^2)$, dimensionless disjoining pressure	5.2×10^{-5}
$S = \sigma_0 h_0/3\rho v^2$, dimensionless surface tension	0.392
$D_0 = 2\rho/3\rho_v$	121.2
$E_0 = k\Delta T/(\rho v \lambda)$	1.1×10^{-5}
$M_0 = (-\partial\sigma/\partial T)\Delta T h_0/(2\rho v \kappa)$	1.16×10^{-2}
$G_0 = (-\partial\sigma/\partial\Gamma)\Gamma_0/(2\rho v \alpha h_0)$	5×10^6
$D = E_0 S/A_0$, differential vapor recoil number	2.82×10^{-4}
$M = M_0/(\text{Pr} A_0)$, thermocapillary number	14.4
$G = \frac{3}{2}(G_0 A_0/S)$, surfactant number	995

When linear theory is applied to the case of the non-isothermal liquid film with no surfactant present (Burelbach *et al.* 1988; Sharma & Ruckenstein 1988), additional effects appear. The perturbed liquid vapor interface is assumed to have a wavy shape with crests and troughs. When evaporation takes place, the rate of evaporation is greater at a trough than at a crest. This results in a force on the film interface (in a direction opposite to the evaporating flux) greater at troughs than at crests, i.e. vapor recoil is destabilizing for the film interface. For condensing films, the condensation rate is higher at a crest than at a trough. Thus, for condensing films, the force on the film interface (in a direction opposite to the condensing flux) is greater at crests than at troughs, i.e. the vapor recoil is again destabilizing. For evaporating films, the interfacial temperature is higher at troughs than at crests, resulting in surface-tension values lower at the former than at the latter. The resulting thermocapillary flow, for evaporating films, is from troughs to crests, i.e. destabilizing for the film interface. In an analogous way, in condensing films, temperatures at crests are higher than those at troughs and the resulting capillary flow is from crests to troughs, i.e. stabilizing. Thus, thermocapillarity, depending on the sign of the temperature difference, ΔT , can be stabilizing or destabilizing.

Application of the dispersion relation [36] shows that, in the case of a condensing film with no surfactant present, linear stability analysis predicts stability for all infinitesimal disturbances; similarly, in the case of an evaporating film with no surfactant present, the film is unstable to disturbances with wavenumbers satisfying the inequality

$$q < [1 + D(K + 1)^{-3} + KM(K + 1)^{-2}]^{1/2}.$$

The numerical value of the r.h.s. of the above expression, for $\Delta T = 0.14^\circ\text{F}$, is 1.821.

For the non-isothermal film with surfactant present, condensing and evaporating films are examined separately because of their distinct behaviors. In thermal recovery of oil with steam, both types of films are possible; condensation occurs throughout injection stages or at injection sites and evaporation throughout production stages or at production sites.

Figure 2a shows the marginal or neutral stability ($\omega = 0$) curves for evaporating liquid films with or without surface active material. As earlier discussed, in the absence of surface active material, evaporating films are unstable to disturbances with wavenumbers less than a certain critical wavenumber. It can be shown that, for $G > 0$, [35] has two positive roots, and this results in a

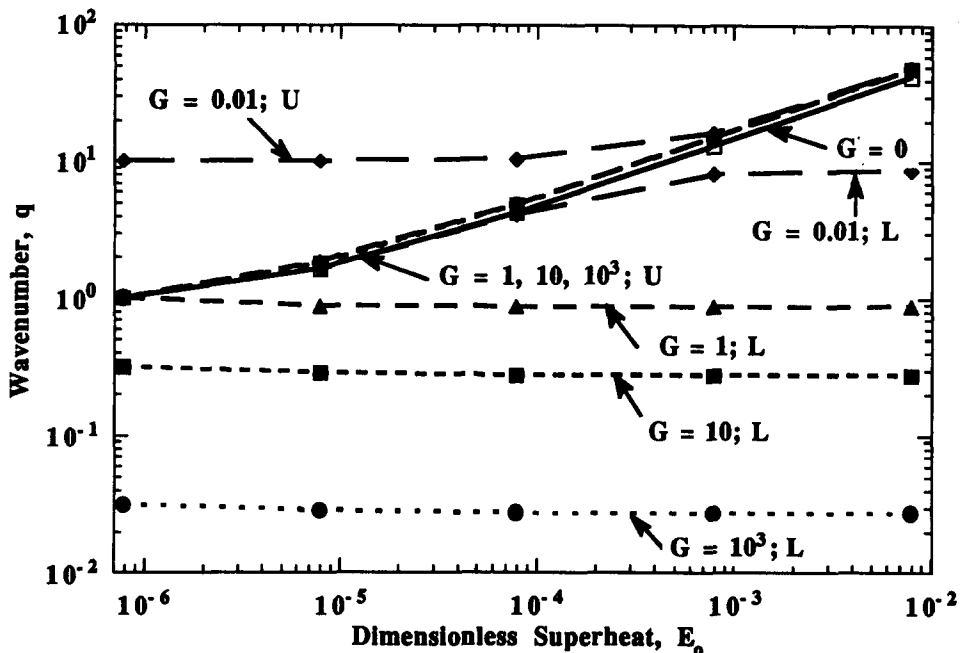


Figure 2a. Evaporating films. Wavenumber (q) vs dimensionless superheat (E_0) for varying surfactant effect (G).

neutral stability curve with two branches, an upper (U) and a lower (L). Evaporating films with surface active material present are unstable for

$$q > q_{c,U} \text{ or } q < q_{c,L}.$$

For small G and small ΔT , $q_{c,U}$ is insensitive to ΔT variations; similarly, $q_{c,L}$ does not vary with ΔT for large ΔT . For small G and large ΔT , the upper branch of the neutral stability curve converges to the neutral stability curve in the absence of surface active material. For large G , the upper branch of the neutral stability curve, for the entire range of ΔT variations, overlaps with the neutral stability curve for the surfactant-devoid case. For large G , the lower branch of the neutral stability curve is insensitive to ΔT variations. It is clear that thermocapillary flow (its magnitude measured by the value of KM) has less of an effect on film stability than Marangoni flow (its magnitude measured by the value of G). It can be observed that as G increases, the region of stability ($q_{c,L}$, $q_{c,U}$) increases. As discussed before, for evaporating films, thermocapillary flow is from troughs to crests, i.e. has a destabilizing effect on the film. For these films, as a result of lower rates of evaporation at crests and thermocapillary flows from troughs to crests, the excess concentration of surfactant is higher at crests than troughs, thus resulting in surface-tension values lower at crests than troughs. The resulting Marangoni flow is in a direction opposite to that of thermocapillary flow, i.e. it has a stabilizing effect on the film.

Figure 2b also shows that the neutral stability curves for isothermal and evaporating films in the presence of surfactant have two branches. For the isothermal case, the two branches meet at $G = 1$, which is a double root for [40a, b]. For $G > 1$, the lower branches for isothermal and evaporating films collapse into one curve, i.e. there is no ΔT effect on $q_{c,L}$; this is not the case for $G < 1$, where $q_{c,L}$ increases as ΔT increases. On the other hand, $q_{c,U}$, irrespective of the G value, increases as ΔT increases; for a given ΔT , however, $q_{c,U}$ is independent of G . In general, as in figure 2a, as G increases, the stability region for evaporating films with surfactant present increases.

Figures 3a and 3b show the marginal stability curves for condensing films in the presence of surfactant. In contrast to the evaporating film case, here neutral stability follows single-branch curves. For a given $G > 1$, irrespective of the amount of subcooling ΔT , there is an instability region defined for $q > q_c$. As G increases, the instability region increases. For condensing films, thermocapillary flows are from crests to troughs, i.e. they have a stabilizing effect. As a result of

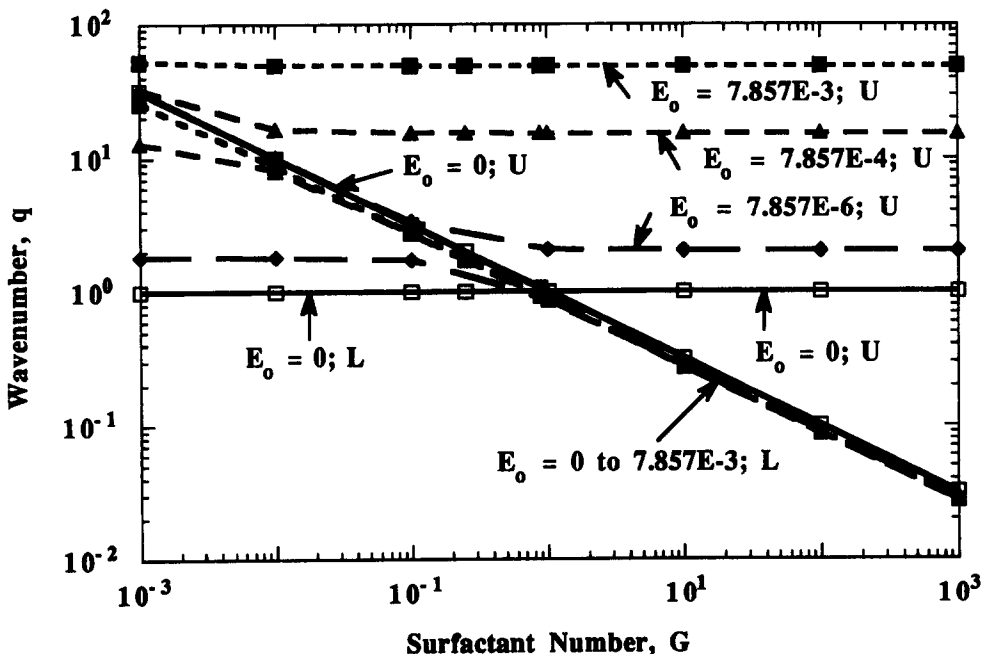


Figure 2b. Evaporating films. Wavenumber (q) vs surfactant effect (G) for varying superheat (E_0).

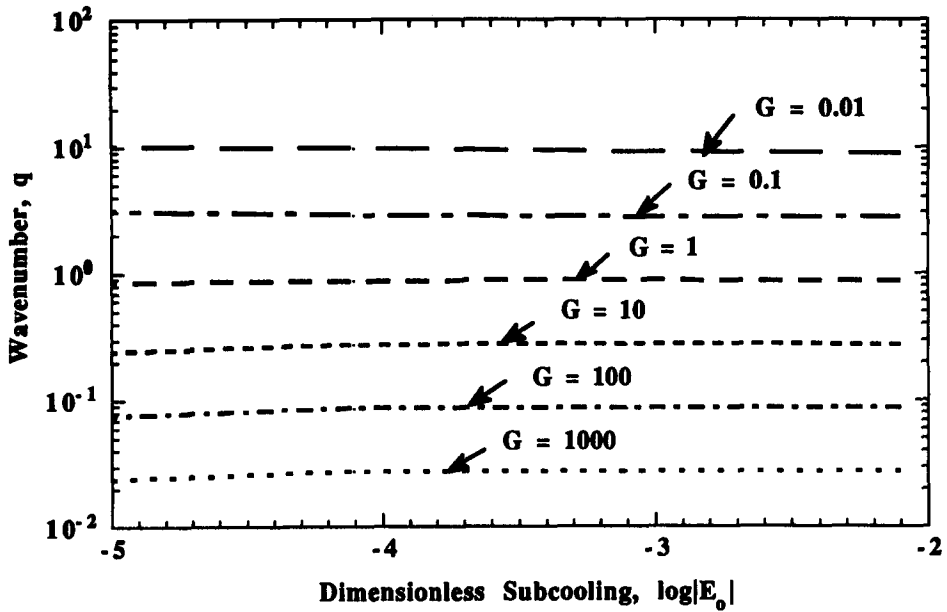


Figure 3a. Condensing films. Wavenumber (q) vs dimensionless subcooling (E_0) for varying surfactant effect (G).

lower condensation rates at troughs and thermocapillary flows from crests to troughs, the excess surfactant concentration is higher at troughs than crests, thus resulting in surface-tension values lower at troughs than crests. The resulting Marangoni flow is now from troughs to crests with a destabilizing effect on the film.

A few final remarks are due at this point. As discussed earlier, the results presented here were derived from a linear stability analysis for long-wavelength infinitesimal disturbances. Results for $q \gg 1$ should be viewed with caution. The value of linear stability analysis lies in its ability to produce the marginal stability curve and determine the initial growth of infinitesimal

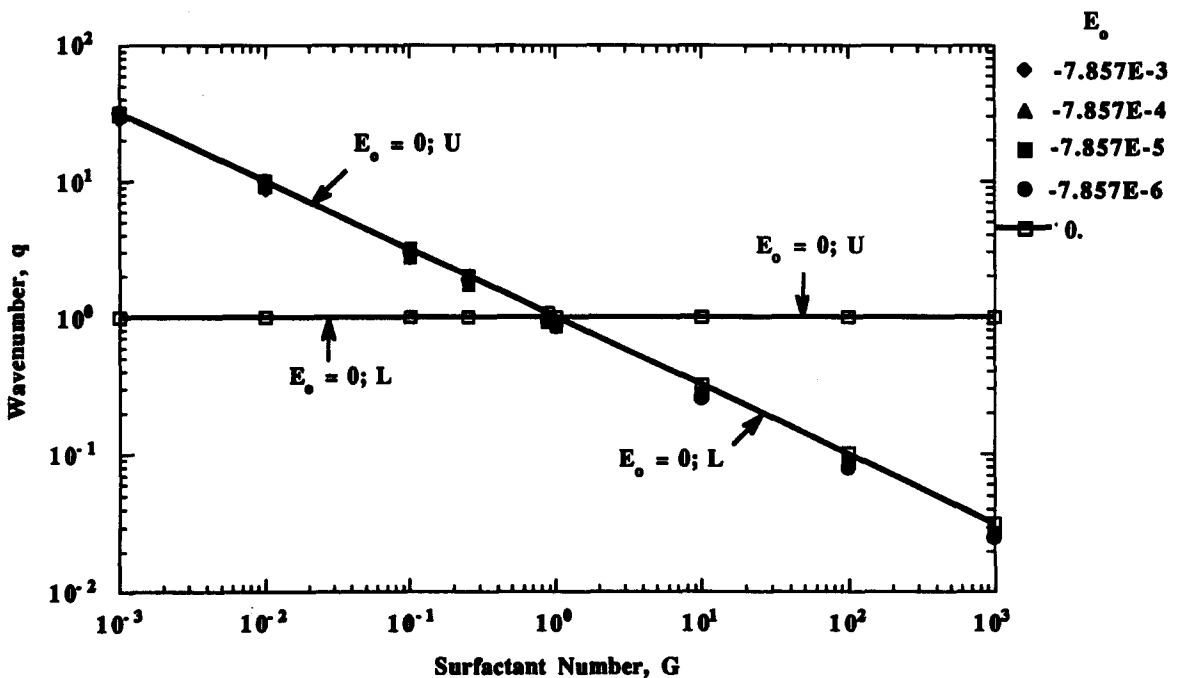


Figure 3b. Condensing films. Wavenumber (q) vs surfactant effect (G) for varying subcooling (E_0 : $-7.857E-3$ to 0).

disturbances. The basic state of the film in this analysis consists of a planar interface (stationary and homogeneous state). Weakly non-linear (Sharma & Ruckenstein 1988) and non-linear stability analyses (Burelbach *et al.* 1988) based on solution of the full equation of film thickness evolution for isothermal and evaporating films in the absence of surfactant have appeared in the literature. In these analyses, the basic state of the film is again stationary but non-homogeneous. The aforementioned analyses demonstrate that the times of film rupture predicted by them vary from those predicted by corresponding linear analyses by as much as one order of magnitude.

In the model adopted here, the rate-determining process for the surfactant is adsorption/desorption at the interface; diffusion of surfactant in the bulk and surface diffusion are considered relatively fast when compared to the former. This eliminates the need for resorting to a vaguely defined and difficult to measure interfacial viscosity. The rate constant of adsorption/desorption at the interface, α , depends on both the bulk and the surface excess concentration. The effect of temperature on surfactant adsorption/desorption at the interface is not known and, therefore, neglected in this analysis. Note that in the analogous case of surfactant adsorption on the rock, the adsorbed amount is drastically reduced at elevated temperatures. Finally, the coverage of the gas-liquid interface by surfactant might suppress the mass gain or loss due to phase change. This effect is also not included in the present analysis.

In conclusion, a new equation for the evolution of evaporating or condensing films with surface active solutes is presented. The new equation includes surface-tension gradients at the liquid-gas interface due to both temperature (thermocapillary) and surface excess concentration (Marangoni/surfactant effect) variations. The present model shows that, for systems of interest, Marangoni flows (Sternling & Scriven 1959) are stronger than thermocapillary flows (Pearson 1958) and act in the opposite direction. In view of these differences in stability characteristics between thin isothermal and non-isothermal liquid films, steam-foams need to be applied and modeled differently than "cold"-gas-foams in porous media.

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APPENDIX A

We consider the liquid–gas interface to be a singular surface which contains no material but which allows material to be transferred through it. For the thin two-dimensional liquid films considered here the equation of the interface is

$$h = h(x, t). \quad [\text{A.1}]$$

The unit normal and tangent to the interface vectors are given by

$$\boldsymbol{\xi} = \left(-\frac{h_x}{(1+h_x^2)^{1/2}}, \frac{1}{(1+h_x^2)^{1/2}} \right) \quad [\text{A.2a}]$$

and

$$\mathbf{t} = \left(\frac{1}{(1+h_x^2)^{1/2}}, \frac{h_x}{(1+h_x^2)^{1/2}} \right), \quad [\text{A.2b}]$$

respectively.

The principal curvatures of the interface are

$$\frac{1}{R_1} = 0; \quad \frac{1}{R_2} = \frac{h_{xx}}{(1+h_x^2)^{3/2}}. \quad [\text{A.3}]$$

The jump condition for mass at the interface (Slattery 1981),

$$[\rho(\mathbf{u} \cdot \boldsymbol{\xi} - w_{R(\xi)})] = 0 \quad [\text{A.4a}]$$

where $[a] = a_v - a_l$ (a_v and a_l represent the quantity a evaluated on the vapor and liquid side, respectively), $\mathbf{u} = (u, w)$ and $w_{R(\xi)} = Dh/Dt = h_t + uh_x$, becomes, for the system depicted in figure 1b,

$$[\rho(w - h_t - uh_x)] = J. \quad [\text{A.4b}]$$

The r.h.s. of [A.4b] is given (Palmer 1976) by

$$J = \beta(T - T_s). \quad [\text{A.4c}]$$

The jump condition for linear momentum at the interface is

$$[\rho\mathbf{u}(\mathbf{u} \cdot \boldsymbol{\xi} - w_{R(\xi)}) - \mathbf{T} \cdot \boldsymbol{\xi}] = 2H\sigma\boldsymbol{\xi} + \nabla_l\sigma, \quad [\text{A.5}]$$

with $2H = (1/R_1 + 1/R_2)$ and $\nabla_l = (\mathbf{t} \times \boldsymbol{\xi} \partial_t - \boldsymbol{\tau} \times \boldsymbol{\xi} \partial_x) / \boldsymbol{\xi} \cdot (\mathbf{t} \times \boldsymbol{\tau})$ (Joseph 1976), where $(\boldsymbol{\xi}, \mathbf{t}, \boldsymbol{\tau})$ is a right-handed coordinate system. With the assumption that the vapor density and viscosity are negligible when compared to the corresponding liquid properties, [A.5] written in terms of its normal and tangential component yields

$$J^2 \rho_v^{-1} - p + 2\mu[(1-h_x^2)w_z - h_x(u_z + w_x)](1+h_x^2)^{-1} = \sigma h_{xx}(1+h_x^2)^{-3/2} \quad [\text{A.6a}]$$

and

$$-\mu[(u_z + w_x)(1-h_x^2) + 2h_x(w_z - u_x)](1+h_x^2)^{-1} = \sigma_T(T_x + h_x T_z)(1+h_x^2)^{-1/2}, \quad [\text{A.6b}]$$

respectively.

Finally, the energy jump condition (Slattery 1981)

$$[\rho(U + \frac{1}{2}u^2)(\mathbf{u} \cdot \boldsymbol{\xi} - w_{K(\xi)}) + \mathbf{q} \cdot \boldsymbol{\xi} - \mathbf{u} \cdot (\mathbf{T} \cdot \boldsymbol{\xi})] = 0, \quad [\text{A.7a}]$$

with the assumption that the jump in kinetic energy is negligible, becomes

$$J\lambda + k(T_z - h_x T_x) = 0. \quad [\text{A.7b}]$$

APPENDIX B

Following Levich (1962), the flux of the surfactant at the interface is given by

$$j = \nabla_s \cdot (\Gamma \mathbf{u}) = (\Gamma u)_x. \quad [\text{B.1}]$$

If the assumption is made that the rate-determining process is adsorption/desorption of surfactant at the interface, this flux can also be written as

$$j = A(c_0, \Gamma) - D(\Gamma) \approx A(c_0, \Gamma_0) - D(\Gamma_0) - \left[\left(\frac{\partial D}{\partial \Gamma} \right)_{\Gamma_0} - \left(\frac{\partial A}{\partial \Gamma} \right)_{\Gamma_0} \right] (\Gamma - \Gamma_0). \quad [\text{B.2a}]$$

The first two terms of the r.h.s. cancel because of equilibrium $\Gamma_0 = \Gamma_0(c_0)$ and [B.2a] becomes

$$j = -\alpha(\Gamma - \Gamma_0). \quad [\text{B.2b}]$$

With the proper non-dimensionalization (after dropping “ \sim ”) and with the long-wavelength approximation

$$u = u_0 + qu_1 + O(q^2); \quad \Gamma = \Gamma_0 + q\Gamma_1 + O(q^2), \quad [\text{B.3}]$$

where dimensionless $\Gamma_0 = 1$, [B.1] and [B.2b] yield

$$u_{0\xi} = -\epsilon\Gamma_1, \quad [\text{B.4a}]$$

where $\epsilon = \alpha h_0^2/\nu$ and

$$(u_0\Gamma_1)_\xi + u_{1\xi} = 0. \quad [\text{B.4b}]$$