Stability of an evaporating thin liquid film

By OLEG E. SHKLYAEV AND ELIOT FRIED

Department of Mechanical & Aerospace Engineering Washington University in St. Louis,
Campus Box 1185 St. Louis, MO 63130-4899, USA

(Received 7 June 2006)

We use a newly developed set of boundary conditions to revisit the problem of an evaporating thin liquid film. In particular, instead of the conventional Hertz–Knudsen–Langmuir equation for the evaporation mass flux we impose a more general equation expressing the balance of configurational momentum. This balance, which supplements the conventional conditions enforcing the balances of mass, momentum, and energy on the film surface, arises from a consideration of configurational forces within a thermodynamical framework. We study the influence of newly introduced terms such as the effective pressure, encompassing disjoining and capillary components, on the evolution of the liquid film. We demonstrate that this quantity affects a time-dependent base state of the evaporating film and is an important factor in applications involving liquid films with thicknesses of one or two monolayers. These factors lead to a revised understanding of the stability of an evaporating film. Dimensional considerations indicate that the most significant influence of these effects occurs for molten metals.

1. Introduction

Evaporation is a widespread phenomenon accompanying many physical processes. It plays an important role in the evolution of liquid films. The investigation of liquid films is a rapidly developing research field with a wide spectrum of engineering applications (including microfluidics, film deposition, cooling, coating, and drying). At present there are many works devoted to the investigation of different effects helping to predict or control the evolution of liquid films. Relevant problems show rich behavior and encompass many physical phenomena such as capillarity, thermocapillarity, evaporation, and van der Waals interactions. Under certain conditions, each of these effects can substantially influence the evolution of thin films. For a comprehensive review see Oron et al. 1997.

Deryagin & Churaev (1965) showed that long-range intermolecular forces are capable of initiating flow in a capillary tube and of significantly changing the rate of evaporation. It was recognized that van der Waals forces become important for the consideration of thin films of thickness less than 1000A. Sheludko (1967) showed, that for layer thickness on the order of 100A, these forces result in an instability mode and cause the rupture of the film. Criteria for the stability and rupture of a liquid film located on a solid substrate were derived by Jain & Ruckenstein (1976). Later many works investigated the combined effects of evaporation, capillary, and disjoining pressure in liquid systems with curved interfaces. Important examples of such systems include menisci and constrained vapor bubbles. A detailed review of these works is given by Wayner (1999).

A linear stability analysis of the effect of rapid evaporation on the stability of a liquid-vapor interface was performed by Palmer (1976). By means of linear and nonlinear analyses, Burelbach et al. (1988) used a single long-wave evolution equation to investigate the influence of effects such as vapor recoil, thermocapillary, and the disjoining pressure
on liquid film instabilities and rupture. Danov et al. (1998) generalized the work of Burelbach et al. (1988) to account for the presence of a nonvolatile dissolved surfactant. This work discussed the influences of the interfacial viscosity, concentration gradients, and Marangoni effects on film stability.

To describe the dynamics of a phase transformation, an additional interface condition accounting for the exchange of material between phases is required. This condition does not follow from the classical balances for mass, forces, moments, and energy. Moreover, it entails the provision of additional constitutive relations. In the literature on evaporation the Hertz–Knudsen–Langmuir equation is commonly used in this capacity. One drawback of this choice is that the derivation of the Hertz–Knudsen–Langmuir equation is based on the assumption that the mechanisms underlying evaporation depend only on the states of the liquid and vapor phases, and are independent of mass, momentum, and energy transfer (Cammenga 1980). Despite the neglect of these effects, the Hertz–Knudsen–Langmuir equation is, as Koffman et al. (1984) observe, often used without justification in continuum problems involving transfers of mass, momentum, and energy.

In this work, we consider the stability of an evaporating liquid film using instead of the Hertz–Knudsen–Langmuir equation a more general evaporation boundary condition. That condition, arises from a consideration of configurational forces within a thermodynamical framework which explicitly accounts for the mass, momentum, and energy transfer across and along the liquid-vapor interface. More importantly, it supplements the conventional conditions enforcing the balances of mass, momentum, and energy on the interface. Aside from classical term involving the difference between the temperatures of the liquid and adjacent vapor at the interface, the configurational momentum balance includes several additional terms. Among these is a term accounting for combined influence of the capillary and disjoining pressure similar to that considered previously by Ajaev & Homsy (2001) and Wayner (2002). For brevity, we refer to this as the effective pressure term. We find that a time-dependant base state of evaporating liquid film is tangibly influenced by the effective pressure term. In particular, the effective pressure strongly affects the film rupture processes and is an important factor in the consideration of liquid films with thicknesses of one or two monolayers. These factors lead to a revised understanding of the stability of an evaporating film. Parameter domains where the contributions of the newly introduced terms are important are determined.

The organization of the paper is as follows. In Section 2, we formulate the problem and present the governing equations. The time-dependent base state and the influence of the effective pressure on that state are examined in Section 3. The effect of different parameters entering the model on the linear stability of the liquid film is presented in Section 4. In Section 5 we generalize all previous results to account, in the manner of Danov et al. (1998), for the presence of a nonvolatile dissolved surfactant. Finally we summarize and briefly discuss our results in Section 6. Details of the long-wave approximation applied to derive of the evolution equations are presented in the Appendix.

2. Formulation of the one-sided problem

The system under consideration is a thin film of a viscous, incompressible liquid, resting on a horizontal solid substrate (Fig. 1). The film occupies the region between the solid boundary at $z = 0$ and a free boundary at $z = h(x,t)$. The buoyancy force is neglected and we suppose that the liquid is heated from the solid substrate and evaporates at the free surface.

We assume that the density, viscosity, and thermal conductivity of the vapor phase are much smaller that those of the liquid phase. The behavior of the system is therefore
Stability of an evaporating thin liquid film

Figure 1. Geometry of the system.

determined by the dynamics of the liquid phase and is independent of the processes in vapor phase, so that model is one-sided. Within the liquid film, the velocity, pressure (of the liquid measured relative to the pressure of vapor), and absolute temperature fields \( u \), \( p \), and \( \theta \) are governed by the Navier–Stokes, heat conduction, and continuity equations:

\[
\frac{Du}{Dt} = -\frac{1}{\rho} \nabla p + \nu \nabla^2 u, \\
\rho c \frac{D\theta}{Dt} = \kappa \nabla^2 \theta, \\
\nabla \cdot u = 0.
\] (2.1)

Here, as is usual, \( D/Dt \) is the material time derivative and \( \nabla \) is the spatial gradient operator. The liquid is characterized by the density \( \rho > 0 \), the kinematic viscosity \( \nu > 0 \), and the thermal diffusivity \( \kappa/\rho c > 0 \), with \( c \) the specific heat and \( \kappa \) the thermal conductivity. At the liquid-solid interface \( z = 0 \) we invoke the no-slip condition for the velocity field and assume that the temperature is given:

\[
u = 0, \quad \theta = \theta_s.
\] (2.2)

Letting \( \theta_s \) denote the saturation temperature (i.e., the temperature at which liquid and vapor phases are in thermodynamic equilibrium), we assume that the interfacial free energy \( \psi^x \) depends linearly on the interfacial temperature \( \theta \), so that

\[
\psi^x = \psi^x_s - \eta^x_s (\theta - \theta_s),
\] (2.3)

where \( \psi^x_s \) and \( \eta^x_s \) are the constant values of the interfacial free energy and entropy arising for \( \theta = \theta_s \). The interface conditions of Fried et al. (2006) then specialize to:

\[
J = \rho(u \cdot n - V) = \rho^v(u^v \cdot n - V), \\
\theta_s \eta_s(KV - \nabla_s \cdot u_s) = \kappa \nabla \theta \cdot n - J V^{\text{mig}}, \\
\frac{A}{6\pi h^3} + Tn \cdot n + \frac{J^2}{\rho_v} = \psi^x K, \\
Tn \cdot t = \nabla_s \psi^x \cdot t, \\
\beta_s V^{\text{mig}} = -l \left( \frac{\theta}{\theta_s} - 1 \right) - \left( p - \frac{J^2}{\rho_v} \right) + \frac{1}{2} \rho |u|^2.
\] (2.4)

Here, \( n \) and \( t \) denote the interfacial unit tangent and normal vectors, the latter being directed from the liquid into the vapor, \( K \) denotes the interfacial curvature, and \( P = \ldots \).
Oleg E. Shklyaev and Eliot Fried

$1 - n \otimes n$ denotes the interfacial projector. Also, $u$ and $u^v$ are the interfacial limits of the velocities in the liquid and vapor phases, $u^v$ is the velocity describing the evolution of the liquid-vapor interface, $V = u^v \cdot n$ is the (scalar) normal velocity of the interface, $V^{\text{mig}} = V - u \cdot n$ is the velocity of the interface relative to the liquid velocity, and $u_s = (u \cdot t)t$ is the tangential component of the velocity of the liquid at the liquid-vapor interface.

In the equations (2.4), $\nabla_s$ denotes the surface gradient. Given scalar and vector fields $f$ and $f$ defined on the surface, $\nabla_s f$ and $\nabla_s \cdot f$ can be computed using the normally constant extensions $f^c$ and $f^c$ of $f$ and $f$ via $\nabla_s f = P\nabla f^c$ and $\nabla_s \cdot f = P : \nabla f^c$. In the equations (2.4), $T = -pI + 2\rho \nu D$, where $D = \frac{1}{2}((\nabla u + (\nabla u)^\top))$ is the bulk rate-of-stretch. Also, $D$ denotes the interfacial rate-of-stretch as defined in terms of the interfacial limit of the bulk rate-of-stretch $\bar{D}$ and the projector $P$, by

$$D = P\bar{D}.$$

The parameters $l > 0$, $\alpha > 0$, $\alpha + \lambda > 0$, and $\beta_s$ are the latent heat of vaporization, the interfacial shear viscosity, the interfacial dilatational viscosity, and a modulus associated with the kinetics of attachment and detachment at the interface. Further, $A$ is the Hamaker constant—the value of which depends on the properties of the liquid and the substrate. Further, the evaporation mass flux $J$ is given by $J = -\rho V^{\text{mig}}$.

The system of the boundary conditions (2.4) has two differences from that discussed by Burelbach et al. (1988). The first difference is the term $\theta_s \eta_x (K V - \nabla_s \cdot u_s)$ in the equation (2.4) accounting for the transport of energy along the liquid-vapor interface. The second difference is the form of the configurational momentum balance (2.4). The second and the third terms on the right-hand side of (2.4) represent the effective pressure, also accounting for a vapor recoil, and the kinetic energy. Influence of the effective pressure on the dynamics of an evaporating meniscus is discussed by Wayner (1999). The goal of this paper is to investigate the influence of the entropy flux along the interface and the effective pressure on the stability of the evaporating film. In the lubrication approximation utilized in this paper the terms $KV$ and $\frac{1}{2}\rho |u|^2$ turn out to be small and do not contribute to the leading-order problem.

2.1. Scaling of the model

Letting $h_0$ denote a characteristic measure of the film thickness (e.g., the initial, undisturbed thickness of the film), we introduce the following dimensionless variables

$$\tilde{x} = \frac{x}{h_0}, \quad \tilde{t} = \frac{\nu t}{h_0^2}, \quad \tilde{u} = \frac{h_0 u}{\nu}, \quad \tilde{h} = \frac{h}{h_0}, \quad \tilde{p} = \frac{h_0^2 \bar{p}}{\rho \nu^2},$$

$$\tilde{J} = \frac{L h_0 J}{\kappa \Delta \theta}, \quad \tilde{\theta} = \frac{\theta - \theta_s}{\Delta \theta}, \quad \tilde{\psi} = \frac{\psi}{\psi_s}, \quad \tilde{\eta} = \frac{\eta}{\eta_s},$$

where

$$L = \frac{l}{\rho}$$

denotes the latent heat per unit mass and

$$\Delta \theta = \theta_b - \theta_s$$
denotes the temperature drop between the base and the free surface of the film. This scaling gives rise to the following dimensionless numbers:

\[ \text{Pr} = \frac{\rho c \nu}{\kappa}, \quad M = \frac{\rho \eta c \Delta \theta}{2 \kappa \nu}, \quad D = \frac{\rho \nu}{\rho}, \quad C = \frac{\eta \Delta \theta}{\psi_x}, \]

\[ \Sigma = h_{0} \psi_x, \quad \Pi = \frac{-A}{6 \pi h_{0} \rho \nu^2}, \quad E = \frac{\kappa \Delta \theta}{\rho \nu L}, \quad N = \frac{\eta \nu \theta_s}{h_{0} \kappa \Delta \theta}, \]

\[ A_1 = \frac{\beta_s \kappa \theta_s}{\rho h \lambda}, \quad A_2 = \frac{\rho \nu^2 \theta_s}{h_0^3 \Delta \theta}, \quad \bar{\alpha} = \frac{\alpha}{\rho \nu h_0}, \quad \bar{\lambda} = \frac{\lambda}{\rho \nu h_0}. \]

Here: \( \text{Pr} \) and \( M \) are Prandtl and Marangoni numbers; \( D \) is the ratio of the density of the vapor phase to that of the liquid phase; \( C \) and \( \Sigma \) are the capillary and the reverse capillary numbers; \( \Pi \) is the dimensionless Hamaker constant; \( E \) is the evaporation number; \( N \) is a parameter which accounts for the energy flux along the interface; \( A_1 \) characterizes how far is the system from thermodynamic equilibrium; \( A_2 \) accounts for the magnitude of the effective pressure; and \( \bar{\alpha} \) and \( \bar{\alpha} + \bar{\lambda} \) are the dimensionless shear and dilatational viscosities.

Dropping the superposed tildes from the dimensionless variables (2.5), the scaled bulk evolution equations following from (2.1) are:

\[ \frac{Du}{Dt} = -\nabla p + \nabla^2 u \]

\[ \text{Pr} \frac{D\theta}{Dt} = \nabla^2 \theta, \]

\[ \nabla \cdot u = 0; \]

the dimensionless boundary conditions on the substrate following from (2.2) are:

\[ u = 0, \quad \theta = 1; \]

the conditions at the liquid-vapor interface following from (2.4) are:

\[ EJ = (u \cdot n - V), \]

\[ N (KV - \nabla_s \cdot u_s) = \nabla \theta \cdot n + J, \]

\[ \frac{\Pi}{h^3} - p + 2Du \cdot n = -\frac{E^2 J^2}{D} + \Sigma K (1 - C\theta), \]

\[ -Dn \cdot t = \frac{M}{\text{Pr} \kappa}, \quad \nabla_s \theta \cdot t, \]

\[ A_1 J = \theta + A_2 \left( p - \frac{1}{2} u^2 - E^2 D^{-1} J^2 \right). \]

Assuming that the horizontal scale of the liquid motion is significantly larger than the vertical one and that the time evolution is slow enough, a long-wave approximation can be applied. Writing \( X, Z, U \) and \( W \) for the long-wave dimensionless counterparts of \( x, z, u \) and \( w \); \( P, \Theta, \) and \( H \) for the variables corresponding to dimensionless pressure, temperature, and the film thickness, we derive the leading-order equations following the procedure described by Williams & Davis (1982). Details of the derivation are given in
the Appendix. The leading-order dimensionless problem consists of: bulk equations

\[-P_X + U_{ZZ} = 0,\]
\[-P_Z = 0,\]
\[\theta_{ZZ} = 0,\]
\[U_X + W_Z = 0;\]

boundary conditions at the solid substrate

\[W = 0, \quad U = 0, \quad \Theta = 1;\]  

and boundary conditions at the liquid-vapor interface \(Z = H(X, T)\)

\[\bar{E}J = -H_T - H_X U + W,\]
\[\bar{N}V_X = -\Theta_Z - J,\]
\[P = \bar{E}^2 \bar{D}^{-1} J^2 + \frac{\bar{\Pi}}{H^3} - \bar{\Sigma} H_{XX},\]
\[\frac{1}{2} U_Z + \frac{M}{F} (\Theta_X + H_X \Theta_Z) = 0,\]
\[A_1 J = \Theta + \bar{A}_2 (P - \bar{E}^2 \bar{D}^{-1} J^2).\]

Equations (2.9)\_2,3 indicate that, to leading order, the pressure \(P\) is independent of the vertical coordinate \(Z\) and the temperature \(\Theta\) is a linear function of \(Z\). Applying the boundary condition (2.11)\_3 at \(Z = H\), we obtain

\[P = \bar{E}^2 \bar{D}^{-1} J^2 + \frac{\bar{\Pi}}{H^3} - \bar{\Sigma} h_{XX},\]
\[\Theta = 1 + c_1 Z,\]

where \(c_1\) depends on \(X\) and \(T\). Integration of (2.9)\_1,4 gives explicit representations

\[U(Z) = \frac{P_X}{2} Z(Z - H) + \frac{V}{H} Z,\]
\[W(H) = \frac{P_{XX}}{12} H^3 + \frac{P_X}{4} H^2 H_X - \frac{1}{2} V_X H + \frac{1}{2} V H_X,\]

for the velocity components \(U\) and \(W\) in terms of the unknown height \(H\) and unknown horizontal component \(V\) of the liquid velocity at the interface. Expressing the pressure \(P\) in the equation (2.11)\_5 through the equation (2.11)\_3 we obtain

\[A_1 J = \Theta - \bar{A}_2 \left( \bar{\Sigma} H_{XX} - \frac{\bar{\Pi}}{H^3} \right),\]

which determines the constant \(c_1\) as

\[c_1(J) = \left[ A_1 J - 1 + \bar{A}_2 \left( \bar{\Sigma} H_{XX} - \frac{\bar{\Pi}}{H^3} \right) \right] \frac{1}{H}.

To simplify notation we return to the original variables. To the leading-order, the solution to the problem (2.9)-(2.11) splits into two subsystems. The first subsystem, which
determines how $u$, $w$, and $\theta$ depend on $z$ has the form

$$u(z) = \frac{p_x}{2} z (z - h) + \frac{V}{h} z,$$

$$w(h) = \frac{p_{xx} h^3}{12} + \frac{p_x h^2 h_x^2}{4} - \frac{1}{2} V_x h + \frac{1}{2} V h_x, \quad (2.12)$$

$$\theta(z) = 1 + \left[ A_1 J - 1 + A_2 \left( \Sigma h_{xx} - \frac{\Pi}{h^3} \right) \right] \frac{z}{h}.$$

From (2.12), knowledge of $p$, $h$, $V$, and $J$ is sufficient to determine $u$, $w$, and $\theta$. The second subsystem determines the long wave evolution of the system and has the form

$$p = E^2 D^{-1} J^2 + \frac{\Pi}{h^3} - \Sigma h_{xx}$$

$$EJ = -h_t + \frac{1}{12} (p_x h^3)_x - \frac{1}{2} (V h)_x,$$

$$NV_x = \left[ 1 - A_1 J - A_2 \left( \Sigma h_{xx} - \frac{\Pi}{h^3} \right) \right] \frac{1}{h} - J,$$

$$\frac{p_x h}{2} + \frac{V}{h} + 2 M^{-1} P^{-1} \left[ A_1 J_x + A_2 \left( \Sigma h_{xxx} + 3 h_x \right) \right] = 0.$$

This set of equations represents a closed system for the unknown variables $p$, $h$, $V$, and $J$. In the system (2.13), the term with coefficient $A_2$ introduces capillary and disjoining pressure effects into the energy and momentum balance equations (2.13). It is important to note that in the momentum balance the dimensionless numbers $M A_1 / P$ and $M A_2 \Sigma / P$ accounting for mass flux and capillary pressure are both independent of the scale $h_0$ of the film thickness.

When there is no entropy transport along the film surface and the effective pressure is neglected, so that $N = A_2 = 0$, the system (2.13) can be reduced to a single evolution equation of the form

$$h_t + \frac{E}{A_1 + h} + \left[ \left( \frac{2 E^2 h^3}{3 D(A_1 + h)^3} + \frac{\Pi}{h} + \frac{M A_1 h^2}{P(A_1 + h)^2} \right) h_x + \frac{\Sigma h^3 h_{xxx}}{3} \right] x = 0.$$

This equation was studied in detail by Burelbach et al. (1988). For this reason in the following analysis we focus our attention on influences of the entropy transport ($N \neq 0$) and the effective pressure ($A_2 \neq 0$) terms on the film evolution and stability.

### 3. Base state

The base state of the evaporating film is time-dependent. Assuming that changes in film thickness occur only due to evaporation and that otherwise the film is motionless ($u = 0$) with properties independent of the $x$-coordinate (so that all derivatives with respect of $x$ vanish), we rewrite the governing equations (2.7)_{1,2} in the form:

$$\hat{\rho} = 0,$$

$$Pr \hat{\theta}_t = \hat{\theta}_{zz}. \quad (3.1)$$

Since $u = 0$, the incompressibility equation (2.7)_{3} is trivially satisfied. Here a superposed hat is used to denote a variable describing the time-dependent base state. The boundary
condition (2.7) on the substrate reduces to

\[ \hat{\theta} = 1; \quad (3.2) \]

at the liquid-vapor interface the boundary conditions (2.8) become

\[
\begin{align*}
E \hat{J} &= -\hat{h}_t, \\
\hat{J} &= -\hat{\theta}_z, \\
\hat{p} &= E^2 D^{-1} \hat{j}^2 + \frac{\Pi}{h^3}, \\
A_1 \hat{J} &= \hat{\theta} + \frac{A_2 \Pi}{h^3}.
\end{align*}
\]

Equation (3.1) has exponentially decaying time-dependent solutions. To solve the stability problem we will use perturbations in the form of the normal modes which may grow exponentially in time. We therefore consider such a quasi-static limit of the base state problem (3.1)–(3.3), for which the slow evolution of the base state may be neglected relative to exponentially growing perturbations developing on top of the base state. This can be achieved in the following two cases.

(I) First is the case \( E \ll 1 \) of slow evaporation but Prandl number \( Pr \) of \( O(1) \). It is then convenient to make the transformation \((z, t) \mapsto (z, Et)\) and seek a solution in powers of \( E \):

\[
\begin{align*}
\hat{p} &= E^{-1}(p_0 + E p_1 + \cdots), \\
\hat{\theta} &= \theta_0 + E \theta_1 + \cdots, \\
\hat{J} &= J_0 + E J_1 + \cdots.
\end{align*}
\]

Assuming that \( D, \Pi, \) and \( A_2 \) can be represented as \( D = E^3 \bar{D}, \Pi = E \bar{\Pi}, \) and \( A_2 = \bar{A}_2 / E \), where \( \bar{D} \sim \bar{\Pi} \sim \bar{A}_2 \sim O(1) \), the resulting leading order system is:

\[
\begin{align*}
p_{0z} &= 0, \\
\theta_{0zz} &= 0, \\
\theta_0 &= 1, \\
J_0 &= -\hat{h}_t, \\
J_0 &= -\theta_0, \\
p_0 &= E^3 D^{-1} J_0^2 + \frac{E \Pi}{h^3}, \\
A_1 J_0 &= \theta_0 + \frac{A_2 \Pi}{h^3}.
\end{align*}
\]

(II) Second is the case \( Pr \ll 1 \) of small Prandtl number but evaporation number \( E \) of \( O(1) \). This case is relevant to molten metals, for which the Prandtl number has order ranging between \( 10^{-3} \) and \( 10^{-2} \). Under these circumstances, the solution can be sought in powers of \( Pr \):

\[
\begin{align*}
\hat{p} &= Pr^{-1}(p_0 + Pr p_1 + \cdots), \\
\hat{\theta} &= \theta_0 + Pr \theta_1 + \cdots, \\
\hat{J} &= J_0 + Pr J_1 + \cdots.
\end{align*}
\]

Assuming that \( D = Pr \bar{D}, \Pi = Pr \bar{\Pi}, \) and \( A_2 = \bar{A}_2 / Pr \), where \( \bar{D} \sim \bar{\Pi} \sim \bar{A}_2 \sim O(1) \), we
Stability of an evaporating thin liquid film

arrive at:

\[ p_0_z = 0, \]
\[ \theta_0_z = 0, \]
\[ z = 0 : \theta_0 = 1, \]
\[ z = \hat{h}(t) : \]
\[ EJ_0 = -\hat{h}_t, \]
\[ J_0 = -\theta_0_z, \]
\[ p_0 = Pr E^2 D^{-1} J_0^2 + \frac{Pr \Pi}{h^3}, \]
\[ A_1 J_0 = \theta_0 + \frac{A_2 \Pi}{h^3}. \]

(3.5)

To the leading order, the solution to the systems (3.4) and (3.5) can be represented in the original variables as:

\[ \hat{h}_t = -\frac{1 + \frac{A_2 \Pi}{h(t)^3}}{A_1 + h(t)} E, \]
\[ \hat{J}(t) = -\hat{h}_t/E, \]
\[ \hat{\theta}(t) = 1 - \hat{J}(t)z, \]
\[ \hat{\rho}(t) = E^2 D^{-1} \hat{J}(t)^2 + \frac{\Pi}{h(t)^3}. \]

(3.6)

Typical values of the Hamaker constant are usually small. According to Wayner (1998), the Hamaker constants for water, ethanol, and benzene are \( 3.7 \cdot 10^{-20} \text{J}, 3.6 \cdot 10^{-20} \text{J}, \) and \( 5 \cdot 10^{-20} \text{J} \) respectively. If we neglect the dimensionless parameter \( A_2 \Pi, \) which is small (for water, \( A_2 \Pi \sim 10^{-5} \)) in comparison to 1 in the numerator of the equation (3.6), the base state takes the simple form \( \hat{h}(t) = -A_1 + \sqrt{(A_1 + 1)^2 - 2Et} \) investigated by Burelbach et al. (1988). Note that the solution to (3.6) does not satisfy the arbitrary initial temperature distribution across the layer and has a singularity at the disappearance time \( t_d \) when \( A_1 = 0 \) and \( h = 0. \) Burelbach et al. (1988) addressed these issues and showed that nevertheless the solution provides a good approximation in the intermediate time regime. Also we can see that the entropy flux characterized by \( N \) does not affect the base state (3.6).

The equation (3.6)_1 suggests that, for small enough film thickness \( h, \) the base state is influenced by the disjoining pressure term proportional to \( A_2. \) Depending on the properties of the liquid and the underlying substrate, we can expect cases where the film partially (\( \Pi > 0 \)) or completely (\( \Pi < 0 \)) wets the substrate. For \( \Pi > 0 \) the film ruptures once it thins to a certain critical thickness. The evolution of the film thickness in the base state according to the equation (3.6)_1 is presented in the Figure 2a with dotted lines. All parameters except \( A_2 \) are for water. In this case increasing \( A_2 \) reduces \( t_d. \) Note that the effect is small. To demonstrate it, we took \( A_2 = 100. \) For water \( A_2 \) is \( \sim 0.01. \) Our choice is therefore unrealistically large and is made only to suggest what may happen for other substances. The solution shown with the dashed line indicates the demarking case \( A_2 = 0. \)

Burelbach et al. (1988) \( (A_2 = 0 \text{ in (3.6)}_1) \) showed that, the vertical velocity \( \hat{h}_t \) behaves as \( \hat{h}_t \sim 1/(A_1 + h) \) when \( h \to 0. \) Therefore in the limiting case of \( A_1 = 0 \) the lubrication approximation breaks down. In contrast to this, the evolution equation (3.6)_1 shows that,
Figure 2. a) Evolution of the film thickness for different parameters $A_2$. $A_2 = 20$, $A_2 = 100$ (dotted lines); $A_2 = -20$, $A_2 = -100$ (solid lines). Time is measured in the units of disappearance time for the case $A_2 = 0$ (dashed line). b) Film thickness as the function of the parameter $A_2$: $h^* = (-A_2\Pi)^{1/3}$ for $\Pi = 1 \times 10^{-4}$ (dotted line), $\Pi = 1 \times 10^{-3}$ (dashed line), $\Pi = 1 \times 10^{-2}$ (solid line).

in the presence of nonvanishing effective pressure, the expression for $h_t$ is always singular, even for the cases when $A_1 \neq 0$, and that changes in the base state occur even faster. Specifically, $h_t \sim A_2/(A_1 + h)h^3$ as $h \to 0$. The reduction of the disappearance time due to the disjoining pressure imposes even stricter limitations on the range in which the lubrication approximation is valid. Also, this result demonstrates the importance of the effective pressure term in problems of the nonlinear film evolution leading to rupture.

For the case $\Pi < 0$, van der Waals forces are able to prevent further evaporation when the film reaches the critical thickness (as determined by the case $\Pi > 0$) and liquid film forms a thin layer that covers the substrate without rupturing. A discussion of the situation when the van der Waals forces suppress evaporation from the adsorbed liquid film in systems where the liquid completely wets the substrate is given by Moosman & Homny (1980) and by Wayner (1999) for a meniscus. The evolution of the film thickness base state for the case $\Pi < 0$ is shown with solid lines in Figure 2a. At the moment $t^*$ when the disjoining pressure suppresses evaporation, a new stationary state solution (“adsorbed layer”) is achieved. We determine such a solution by setting $h_t$ in (3.6) equal to zero. This solution is characterized by zero mass flux, constant temperature across the layer, and pressure given by the disjoining pressure:

\[
h^* = (-A_2\Pi)^{1/3},
J^* = 0,
\theta^* = 1,
p^* = \frac{\Pi}{(h^*)^3} = \frac{1}{-A_2}.
\] (3.7)

Depending on the parameters characterizing the liquid and the substrate, the thickness of this stationary layer thickness $h^*$ on the parameter $A_2$ is shown in Figure 2b for different values of the dimensionless Hamaker constant $\Pi$. Even though the relative magnitudes of the coefficients $A_2$ and $\Pi$ are small, the figure shows that we can expect to obtain a film thickness of one or few monolayers. To see explicitly which physical variables affect the thickness $h$ of the layer (3.7)_1, we use dimensional units to give:

\[
h = \left(\frac{-A\theta_s}{6\pi h_0^3 l \Delta \theta}\right)^{1/3}.
\]
Stability of an evaporating thin liquid film

<table>
<thead>
<tr>
<th>Variable</th>
<th>Units</th>
<th>Water</th>
<th>Sodium</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_s$</td>
<td>K</td>
<td>373</td>
<td>1156</td>
</tr>
<tr>
<td>$\Delta \theta$</td>
<td>K</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>$\rho$</td>
<td>kg/m$^3$</td>
<td>960</td>
<td>750</td>
</tr>
<tr>
<td>$\nu$</td>
<td>m$^2$/s</td>
<td>$3 \cdot 10^{-7}$</td>
<td>$2 \cdot 10^{-7}$</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>J/m s K</td>
<td>0.68</td>
<td>48</td>
</tr>
<tr>
<td>$c$</td>
<td>J/kg K</td>
<td>4166</td>
<td>1280</td>
</tr>
<tr>
<td>$L$</td>
<td>J/kg</td>
<td>$2.3 \cdot 10^6$</td>
<td>$4.24 \cdot 10^6$</td>
</tr>
<tr>
<td>$\eta_s$</td>
<td>N/m K</td>
<td>$1.8 \cdot 10^{-4}$</td>
<td>$0.94 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>$\psi_s$</td>
<td>N/m</td>
<td>$5.89 \cdot 10^{-2}$</td>
<td>$1.2 \cdot 10^{-1}$</td>
</tr>
<tr>
<td>$A$</td>
<td>J</td>
<td>$10^{-20}$</td>
<td>$10^{-21}$</td>
</tr>
<tr>
<td>$\beta_s$</td>
<td>kg/m$^2$s</td>
<td>$10^6$</td>
<td>$10^6$</td>
</tr>
</tbody>
</table>

**Table 1.** Material properties of water and molten sodium. Parameters are taken near the boiling temperature.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Water</th>
<th>Sodium</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$5.2 \times 10^{-3}$</td>
<td>0.55</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$1.5 \times 10^{-2}$</td>
<td>0.054</td>
</tr>
<tr>
<td>$D$</td>
<td>$6.25 \times 10^{-4}$</td>
<td>$3.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>$E$</td>
<td>0.010</td>
<td>0.15</td>
</tr>
<tr>
<td>$M$</td>
<td>0.18</td>
<td>$1.2 \times 10^{-4}$</td>
</tr>
<tr>
<td>$N$</td>
<td>0.30</td>
<td>0.022</td>
</tr>
<tr>
<td>$Pr$</td>
<td>1.76</td>
<td>0.004</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>6.81</td>
<td>40</td>
</tr>
<tr>
<td>$\Pi$</td>
<td>$6.1 \times 10^{-4}$</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

**Table 2.** Dimensionless parameters at $h_0 = 100A$.

This expression agrees with estimate for the adsorbed film thickness obtained by Wayner (1999). We see that for $A < 0$ the thickness $h$ increases with the saturation temperature $\theta_s$ and the magnitude $|A|$ of the dimensional Hamaker constant. Also $h$ decreases with the latent heat of evaporization and with increasing values of the initial temperature difference $\Delta \theta$ across the layer.

The results of this section show that, since the base state is independent of the horizontal coordinate, the structure is not affected by the entropy flux along the surface. The influence of the effective pressure increases toward the disappearance time. In the absence of the effective pressure the base state is insensitive to the sign of the Hamaker constant and, therefore, there is a degeneracy with respect to the cases when liquid partially or absolutely wets the substrate. The presence of the effective pressure alleviates this degeneracy and leads to a rich spectrum of solutions that evolve from the base state.
4. Linear stability of the film

To investigate the stability of the system (2.13) we perturb the time-dependent base state in the form

\begin{align*}
    h(t, x) &= \hat{h}(t) + H(t)e^{ikx}, \\
    J(t, x) &= \hat{J}(t) + J(t)e^{ikx}, \\
    V(t, x) &= iV(t)e^{ikx}, \tag{4.1}
\end{align*}

where \( k \) is the wave number, and obtain an ordinary differential equation

\[ \frac{\dot{H}}{H} = F(t, k, A_1, A_2, D, E, M, Pr, N, \Pi, \Sigma) \tag{4.2} \]

describing the evolution of disturbances to the interface. Integrating (4.2) over \( t \) from \( t = 0 \) to \( t = t^* \), with \( t^* < t_d \), we have

\[ H(t^*) = H(0) \exp(\sigma(t^*)t^*), \]

where

\[ \sigma(t^*) = \frac{1}{t^*} \int_0^{t^*} F(t, k, A_1, A_2, D, E, M, Pr, N, \Pi, \Sigma) \, dt \]

is an effective growth rate which is calculated numerically. We also assume that there exists a limiting case of a time-independent base state, frozen at the instant \( t = 0 \). For this case, \( \hat{h} \) and \( \hat{J} \) in (4.1) are taken as \( \hat{h} = 1 \) and \( \hat{J} = (1 + A_2\Pi)/(A_1 + 1) \) and we use the following expression for the growth rate:

\[ \omega = \frac{\dot{H}}{H} = F(0, k, A_1, A_2, D, E, M, Pr, N, \Pi, \Sigma). \tag{4.3} \]

Numerical experiments performed with different parameter values showed that the evaporation number \( E \) exerts a significant influence on stability. To demonstrate this influence, we plot in Figure 3 the effective growth rate \( \omega \) for increasing values of \( E \), taking all other dimensionless parameters for water (Table 2). The parameter sequence \( E = 0.03, E = 0.04, E = 0.05 \) corresponds to three pairs of dispersion curves with increasing maximal growth rate \( \omega \). Each pair consists of a solid and a dashed curve. Figure 3a shows the influence of the evaporation number on the entropy transport on the surface as determined by the dimensionless number \( N \). This influence is given by the difference between the solid and dashed curves in each pair. The dashed curves indicate cases with \( N = A_2 = 0 \); the solid curves show cases with \( N = 0.3 \) and \( A_2 = 0 \). In the same way, Figure 3b shows the influence of the evaporation number \( E \) on the effective pressure. The dashed curves indicate cases with \( N = A_2 = 0 \); the solid curves show the cases with \( N = 0 \) and \( A_2 = 0.015 \).

The results presented in Figure 3 indicate that the effects of the entropy transport along the surface as well as the effective pressure on the stability of the liquid film (as given by the difference between the solid and the dashed curves in each pair) both increase with increasing evaporation number \( E \). The values of \( E \) used to demonstrate this effect are somewhat larger than the actual value \( E = 0.01 \) of the evaporation number for water. According to our discussion of the base state in Section 3, large evaporation numbers make it impossible to use the slow evaporation limit, which is relevant for regular fluids when the evaporation number obeys \( E \ll 1 \) and the Prandtl number is of \( O(1) \). To proceed with our analysis we therefore use the alternative type of base state valid for circumstances where the Prandtl number obeys \( Pr \ll 1 \) and the evaporation number is of \( O(1) \). Molten metals seem to be good candidates for this purpose. As the data in Tables 2 and 3 shows, they have small Prandtl numbers and relatively large evaporation numbers \( E \).
Figure 3. Three pairs of the dispersion curves for increasing values of the evaporation number \( E = 0.03, E = 0.04, \) and \( E = 0.05 \) correspondingly. a) Change due to the influence of \( N \). Dashed curve indicate cases with \( N = A_2 = 0 \), solid curves show cases with \( N = 0.3 \) and \( A_2 = 0 \). b) Change due to the influence of \( A_2 \). Dashed curve shows the case \( N = A_2 = 0 \). Solid curves show the case \( N = 0 \) and \( A_2 = 0.015 \).

<table>
<thead>
<tr>
<th>Material</th>
<th>( E = \frac{\kappa \Delta \theta}{\rho_v L} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.001</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.0005</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.189</td>
</tr>
<tr>
<td>Lead</td>
<td>0.022</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.098</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.075</td>
</tr>
</tbody>
</table>

Table 3. Evaporation number for molten metals (\( \Delta \theta = 1K \)).

As representative example of a molten metal, we consider molten sodium. A detailed description of the properties of sodium and potassium is given by Foust (1972). The configurational momentum balance contains the modulus \( \beta_s \) associated with the kinetics of attachment and detachment at the interface. This modulus enters the dimensionless parameter \( A_1 \). To make reasonable estimates of the magnitude of \( \beta_s \), we used experimental data relating the evaporating mass flux \( J \) with the pressure deviation \( p - p_v \), where \( p_v \) is the pressure of the vapor phase. Substituting these data into the truncated version

\[
\beta_s = \frac{\rho}{J} \left( p - \frac{J^2}{\rho_v} \right)
\]

of the configurational momentum balance (2.4)_6, we obtained rough estimates for \( \beta_s \). Experimental data obtained by Yang et al. (1994) and Fedkin et al. (2005) give \( \beta_s \) values on the order of \( 10^6 \text{kg/m}^2\text{s} \) and \( 10^5 \text{kg/m}^2\text{s} \), respectively. These values agree with estimates for coefficient \( A_1 \) utilized by Ajaev & Homsey (2001).

The influences of dimensionless parameters on the dispersion curves are presented in Figure 4 for molten sodium (Table 2). Figure 4a demonstrates the influence of the surface entropy flux as characterized by the dimensionless parameter \( N \). The solid line represents the behavior of the growth rate \( \omega \) for the parameter \( N = N_{\text{sod}} \) for molten sodium. The dashed line shows the case \( N = 0 \) of no entropy flux along the liquid-vapor interface. The dotted line shows the case \( N = N_{\text{sod}}/2 \). The dynamics of these changes demonstrate that the increase of the entropy flux on the film surface decreases the maximal growth rate. The corresponding wave number slowly decreases while the cutoff wave number slowly increases and thereby broadens the interval of unstable modes.

Figure 4b demonstrates the influence of the effective pressure as characterized by the
Figure 4. The influence of the surface entropy and the effective pressure on the dispersion curve. 

(a) \( A_2 = 0 \) for all curves. \( N = 0 \) (dashed curve), \( N = 0.011 \) (dotted curve), \( N = 0.022 \) (solid curve).

(b) \( N = 0 \) for all curves. \( A_2 = 0 \) (dashed curve), \( A_2 = 0.025 \) (dotted curve), \( A_2 = 0.05 \) (solid curve).

dimensionless parameter \( A_2 \). The solid line represents the behavior with the parameter \( A_2 = (A_2)_{\text{sod}} \) for molten sodium. The dashed line shows the case \( A_2 = 0 \) for which the effective pressure is absent. The dotted line shows the case \( A_2 = (A_2)_{\text{sod}}/2 \). Increasing \( A_2 \) narrows the interval of the unstable modes and decreases the maximal growth rate. We therefore observe that the effective pressure exerts a stabilizing influence on a film of molten sodium.

The stabilizing influence of the surface entropy flux and the effective pressure seems reasonable if we recall that both effects arise from dissipative mechanisms (Fried et al. 2006). Another quantity strongly affecting the stability results is the parameter \( A_1 \), describing how far the system is from the saturation equilibrium. To examine the changes this parameter causes, we use dimensionless parameters for the molten sodium and plot in Figure 5 the growth rate \( \omega \) for three different values of \( A_1 \). The increasing parameter sequence \( A_1 = 0.6, A_1 = 1, A_1 = 1.4 \), corresponds to three pairs of curves with decaying maximal growth rate \( \omega \). The solid curves represent the cases with \( N = A_2 = 0 \). The solid curves show the case with \( N = 0.0022 \) and \( A_2 = 0 \). The dashed curves represent the cases with \( N = 0 \) and \( A_2 = 0.01 \) (Figure 5a) and the case with \( N = 0 \) and \( A_2 = 0 \) (Figure 5b). We see that \( A_1 \) exerts a strong stabilizing influence on the system. With \( A_1 \) increasing, the maximal effective growth rate decays and the cutoff wave number decreases. The relative influence (difference between the solid and dashed curves in the corresponding pictures) of the surface entropy flux (Figure 5a) and the effective pressure (Figure 5b) decreases as the parameter \( A_1 \) increases. This result implies that the effective pressure and the surface entropy flux along the surface both exert considerable influence on the stability of a molten metal film only when the film is far enough from saturation equilibrium.

It is interesting to examine how the characteristic thickness \( h_0 \) of the film influences the stability of the system. For this purpose, we fix parameters that characterize the physical properties of the system independent of \( h_0 \) and study the impact of varying \( h_0 \). In so doing, we consistently recalculate all dimensionless parameters depending on \( h_0 \). The behavior of the dimensional maximal growth rate \( w_m \) (in units of s\(^{-1}\), where \( w_m \) is maximized over the range of unstable wave numbers) is shown in Figure 6a for three particular cases. The dashed line indicates the dependence with no surface entropy flux and no effective pressure \((N = A_2 = 0)\). The dotted line shows the case \( A_2 = 0 \) and \( N = 0.022 \), for which only the influence of the surface entropy flux is taken into account. The solid line demonstrates the case \( A_2 = 0.015 \) and \( N = 0 \), for which only the effective pressure is taken into account. We see that the stabilizing influence of the effective pressure (difference between the solid and the dashed lines) is stronger than that of the surface entropy flux (difference between the solid and the dotted lines). Moreover,
the maximal growth rate $\omega_m$ is not a monotonic function of $h_0$. In the case of the presence of the effective pressure only (the solid curve) the largest value of $\omega_m$ corresponds to larger initial film thicknesses $h_0$ relative to the case $A_2 = 0$, $N = 0.022$ (the dashed curve). On its own, the surface entropy flux (the dotted curve) moves the maximal growth rate $\omega_m$ to the thinner initial film thicknesses $h_0$. The figure also shows that both effects are important for the stability of molten metal films with thickness of 5–30nm. Films of such thicknesses are common in applications such as welding (Winkler & Amberg 2005).

Similarly in the Figure 6b, we consider the change in stability that results when the dimensional temperature difference $\Delta \theta$ across the film changes from 0 to 10K. We fix parameters that characterize the physical properties of the system independent of $\Delta \theta$ and study the impact of varying $\Delta \theta$ recalculating all dimensionless parameters depending on $\Delta \theta$. For this purpose, the initial film thickness remains fixed at $h_0 = 100$ Å. The dashed lines represents the case of zero surface entropy flux ($N = 0$) and zero effective pressure ($A_2 = 0$). The dotted line shows the case with $A_2 = 0$ and $N = 0.022$. The solid line represents the case $A_2 = 0.015$ and $N = 0$. Again, we see the strong stabilizing influence of both effects relative to the case $N = A_2 = 0$. As the temperature difference across the layer increases, the influences of the effective pressure and the entropy flux become more important.

From the base state time behavior (Figure 2), we expect the influence of all considered effects to increase as the instant $t_d$ of disappearance is approached. The effective growth rate $\sigma(t^*)$ as a function of the wave number is shown in Figure 7 at three different instants.
of time. We see that, in contrast to the results presented by Burelbach et al. (1988), the maximal growth rate is not a monotonic function of time for chosen parameter values. As $t$ tends to $t_d$, the cutoff wave number increase—i.e., the interval of the unstable modes becomes wider and the system becomes more unstable. Figure 7 demonstrates that, for the chosen parameters, the stability of the base state (3.6) does not change significantly for $t < t_d$. The effect is made evident on comparing the results for $\sigma$ ($t \neq 0$) shown in Fig. 7 to the results for $\omega$ ($t = 0$) shown with the solid curve ($A_2 = 0.05$) in the Fig. 4b. Therefore the influences of the effective pressure and the entropy flux along the surface therefore remain important for all stages of the base state evolution. The stability results for $\sigma$ quantitatively alter the corresponding results for $\omega$ presented in Figures 3–6 without inducing a qualitative change of the reported effects.

The results of this section reveal that, for the parameter values considered, the surface entropy flux, governed by $N$, and the effective pressure, governed by $A_2$, stabilize the liquid layer. The film stability is more sensitive to variations of the effective pressure than to the surface entropy flux. In particular, the effective pressure term strongly affects the cutoff wave number. The strong stabilizing effect of the effective pressure may be explained by the presence of the additional (relative to the case $A_2 = 0$) capillary terms in the energy balance (2.13) and in the tangential momentum balance (2.13). Capillarity suppresses short waves and shifts the cutoff wave number in the direction of long waves as shown in the Figure 4b. Also we see that the parameter $A_1$ characterizing the closeness of the system to the saturation equilibrium exerts a substantial influence.

5. Stability of the film with surfactant

In this section we consider the influence of the interfacial energy flux and the effective pressure on the stability of at liquid film consisting of a volatile solvent and a nonvolatile surfactant. A stability analysis for water-like liquids and common surfactants is given by Danov et al. (1998). Based on the foregoing results, we focus here on molten metals. For such liquids, dopants such as oxygen and sulfur play roles analogous to surfactants in conventional liquids and, as such, are commonly referred to as surfactants (Winkler & Amberg 2005). In this case, we assume that the expression (2.3) for the surface energy $\psi^x$ has the form

$$\psi^x = \psi^x_s - \mu_s n^x - n^x_s (\theta - \theta_s),$$

where the chemical potential $\mu$ is defined as $\mu = \partial \psi^x / \partial n$ and $\mu_s$ is its constant value at $\theta = \theta_s$. The presence of the surfactant introduces additional terms into the system (2.4)
and the interface conditions (Fried et al. 2006) become:

\[ J = \rho (u \cdot n - V) = \rho \psi (u^s \cdot n - V), \]

\[ \theta_s \eta_s^e (KV - \nabla_s \cdot u_s) = \kappa \nabla \theta \cdot n - l^\text{mig}, \]

\[ A \frac{1}{6 \pi h^3} + T_n \cdot n + \frac{J^2}{\rho_v} = \psi^x K + (\nabla_s \cdot (2\alpha \mathbb{D} + \lambda (\text{tr} \mathbb{D})\mathbb{P})) \cdot n, \]

\[ T_n \cdot t = (\nabla_s \psi^x + \nabla_s \cdot (2\alpha \mathbb{D} + \lambda (\text{tr} \mathbb{D})\mathbb{P})) \cdot t, \]

\[ \beta_s V^\text{mig} = -l \left( \frac{\theta}{\theta_s} - 1 \right) - \left( p - \frac{J^2}{\rho_v} \right) - \psi_s \left( \frac{n}{n_s} - 1 \right) + \frac{1}{2} \rho |u|^2, \]

\[ \tilde{n}^x + n^x (\nabla_s \cdot u_s - KV) = \kappa^x \nabla_s \cdot (\nabla_s n^x) - \kappa_n (\nabla n) \cdot n - n V^\text{mig}. \]

Here the time derivative $$\tilde{n}^x$$ accounts for the surface molecular density change at the interface $$z = h(x, t)$$. Given a normally constant extension of a surface field $$\varphi$$ (Cermelli et al. 2005), $$\tilde{\varphi}$$ can be related to the spatial time-rate of $$\varphi$$ via $$\tilde{\varphi} = \varphi_t + u_s \cdot \nabla_s \varphi$$.

The right-hand side of the normal and tangential momentum balances (5.1) and (5.1) acquire additional terms accounting for the influence of the surface viscosity. The right-hand side of the configurational momentum balance (5.1) acquires the term $$-\psi(n/n_s - 1)$$ showing an explicit dependence on the molecular density. Besides that, the system involves the additional equation, (5.1), describing the balance between the bulk and surface molecular densities. We scale the bulk molecular density $$n$$, the surface molecular density $$n^x$$, and the chemical potential according to

\[ \tilde{n} = \frac{n}{n_s}, \quad \tilde{n}^x = \frac{n^x}{n_s}, \quad \tilde{\mu} = \frac{\mu}{\mu_s}, \]

where $$n_s$$ and $$n^x_s$$ are saturation values of the molecular density and surface molecular density. This gives rise to the following additional dimensionless parameters:

\[ A_3 = \frac{\psi_s \theta_s}{\Delta \theta}, \quad M_n = \frac{h_0 \mu_s n^x_s c}{2 \kappa \nu}, \quad P_n = \frac{\nu}{\kappa_n}, \quad P_{n^x} = \frac{h_0 \nu}{\kappa^x_n}, \quad b = \frac{n_s h_0}{n_s^x}, \quad \Omega = \frac{\xi}{2 \rho \nu h_0}. \] (5.3)

Here: $$A_3$$ is the surfactant activity; $$M_n$$ is molecular density Marangoni number; $$P_n$$ and $$P_{n^x}$$ are bulk and surface molecular density Prandtl numbers; $$b$$ is the ratio of the bulk and the interface saturation concentrations; and $$\Omega$$ is the dimensionless interfacial viscosity. $$\kappa_n$$, $$\kappa^x_n$$ and $$\xi$$ are the surfactant bulk diffusivity, the surfactant interface diffusivity and the interfacial viscosity correspondingly. Typical parameters characterizing surfactant can be found in the following works (Table 4): the values of $$\eta_s^e$$, $$\psi^x$$, $$n^x_s$$, $$\kappa_n$$, and $$\kappa_{n^x}$$ for sulfur are taken from Winkler & Amberg (2005); the values of $$n_s$$, $$\xi$$, and $$n_\infty$$ are taken from Danov et al. (1998). Estimates for $$\psi_s$$ and $$\mu_s$$ are made on the basis of data provided by Tanaka & Gubbins (1992). The associated dimensionless numbers resulting for $$h_0 = 100$$Å and $$\Delta \theta = 2$$ are given in Table 5.

When the surfactant is present, the system of dimensionless equations (2.7)–(2.8) governing the dynamics of liquid should be complemented with the equation for the transfer of the bulk molecular density $$n$$. In dimensionless form, the bulk transport equation is

\[ P_n \frac{Dn}{Dt} = \nabla^2 n. \]

On the substrate, we require that $$\partial n/\partial z = 0$$. On the liquid–vapor interface, we impose the conditions representing the dimensionless counterparts to the equations (5.1). To close the system of equations we have to add the sorption isotherm relating $$n^x$$ and $$n$$. 


Following the approach of Jensen & Grotberg (1993) and looking for the molecular density solution in the form \(n(x, z, t) = n^0(x, t) + \epsilon^2 n^1(x, z, t)\) (where \(\epsilon\) is an appropriate small parameter), we find that, to the leading order, the solution to the system describing the evolution of the thin film with the surfactant splits into two subsystems. The first subsystem, which determines how \(u, w, and \theta\) depend on \(z\), has the form
\[
\begin{align*}
  u(z) &= \frac{p_x}{2} z(z - h) + \frac{\mathcal{V}}{h} z, \\
  w(h) &= \frac{p_{xx}}{12} h^3 + \frac{p_x}{4} h^2 x - \frac{1}{2} \mathcal{V} x h + \frac{1}{2} \mathcal{V} h_x, \\
  \theta(z) &= 1 + \left( A_1 J - 1 - A_2 \left( \Sigma h_x - \frac{\Pi}{h^3} \right) - A_3 (n - 1) \right) \frac{z}{h}.
\end{align*}
\] (5.4)

From (5.4), knowledge of \(p, h, \mathcal{V}, J, and n\) is sufficient to determine \(u, w, and \theta\). The second subsystem, determines the long wave evolution of the system and has the form
\[
\begin{align*}
  p &= E^2 D^{-1} J^2 + \frac{\Pi}{h^3} - \Sigma h_x, \\
  E J &= -h_t + \frac{1}{12} (p_x h^3)_x - \frac{1}{2} (\mathcal{V} h)_x, \\
  N \mathcal{V} x &= \left( 1 - A_1 J - A_2 \left( \Sigma h_x - \frac{\Pi}{h^3} \right) + A_3 (n - 1) \right) \frac{1}{h} - J, \\
  \frac{p_x h}{2} + \frac{\mathcal{V}}{h} x + \frac{2 M_n}{\mathcal{P}_n} n_x + \frac{2 M}{\mathcal{P}_n} \left( A_1 J_x + A_2 \left( \Sigma h_{xx} + \frac{3 \Pi h_x}{h^4} \right) - A_3 n_x \right) &= 2 \Omega \left( \mathcal{V} x n^x + \mathcal{V} n^x_x \right),
\end{align*}
\] (5.5)

\[
\begin{align*}
  (n^x + b H n)_t + \left( \mathcal{V} n^x - \frac{b}{\mathcal{P}_n} n^x_x - b n \left( \frac{p_x h^3}{12} - \frac{\mathcal{V} h}{2} \right) - \frac{b h n_x}{\mathcal{P}_n} \right)_x &= 0, \\
  n^x &= \frac{n}{n + n_\infty}.
\end{align*}
\]

Equation (5.5)_6 represents the dimensionless sorption isotherm, where \(n_\infty\) is reference value of \(n\). To investigate the stability of the system (5.5) we perturb the time-dependent base state, as characterized by \(\hat{h}, \hat{J}, \hat{p}, \hat{n}, \hat{n}^x\), and obtain a system
\[
\begin{align*}
  \hat{H}(t) &= F[H(t), n(t)], \\
  \hat{n}(t) &= G[H(t), n(t)],
\end{align*}
\] (5.6)
of linear equations for the surface shape and the molecular density perturbation amplitudes.

### 5.1. Base state

In addition to the equations (3.3), the base state includes the condition \((\hat{n}^x + b \hat{n} \hat{h})_t = 0\) imposing surfactant balance in the film (Danov et al. 1998). The leading order solutions for variables \(J, \hat{\theta}, \hat{p}\) retain the form given by the equations (3.6)\_2,3,4, but the film thickness and the surface molecular density become:
\[
\begin{align*}
  \hat{h}_t &= \frac{1 + \Delta \Pi}{\hat{h}(t)^3} + A_3 (\hat{n} - 1) \\
  A_1 + \hat{h}(t), \\
  \hat{n}^x(t) &= \frac{1}{2} \left( 1 + \Lambda + b n_\infty \hat{h}(t) - \sqrt{\left( b n_\infty \hat{h}(t) + 1 + \Lambda \right)^2 - 4 \Lambda} \right),
\end{align*}
\] (5.7)
where \( \Lambda = \dot{h}^x(0) + b\dot{n}(0)\dot{n}(0) \) is a constant defined by the initial values at \( t = 0 \). Note that the energy flux characterized by \( N \) does not affect the base state (5.7).

The equation (5.7) for the evolution of the film thickness explicitly includes the influence of the surfactant activity \( A_3 \). The actual value of \( A_3 \) is usually small (Table 5). To obtain a qualitative understanding of the effect of the surfactant on the evolution of the base state, we therefore used much larger values of \( A_3 \). Fig. 8 shows the increase of the disappearance time \( t_d \) (when \( h = 0 \) in the case when liquid partially wets the substrate) as the surfactant activity \( A_3 \) increases. In the case when the liquid completely wets the substrate, the stationary state corresponding to the layer adsorbed by the substrate is

\[
h^* = \left( \frac{-A_3\Pi}{1 + A_2/(n^* - 1)} \right)^{1/3}.
\]

5.2. Stability

To study the influence of the energy flux and the effective pressure, we limit the stability analysis to the simple case of a quasistatic base state. Taking the base state \( \dot{h} = 1 \) and \( \dot{n} = \dot{n}(0) \) and assuming that \( H \sim e^{\omega t} \) and \( n \sim e^{\omega t} \), we obtain a dispersion relation of the form

\[
\omega = \omega(k, A_1, A_2, A_3, D, E, M, M_n, Pr, P_n, P_n^x, N, \Pi, \Sigma, b, \Omega).
\]

Due to the small value of \( A_3 \), we did not observe a significant influence of this parameter on the film stability. The influence of the coefficient \( A_2 \) associated with the effective

<table>
<thead>
<tr>
<th>Variable</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta_s )</td>
<td>N/m K</td>
<td>( 4.3 \times 10^{-4} )</td>
</tr>
<tr>
<td>( \psi_s )</td>
<td>N/m</td>
<td>1.9</td>
</tr>
<tr>
<td>( \psi_s )</td>
<td>J/mol</td>
<td>( 10^2 )</td>
</tr>
<tr>
<td>( n_s )</td>
<td>mol/m²</td>
<td>( 1.3 \times 10^{-5} )</td>
</tr>
<tr>
<td>( n_s )</td>
<td>mol/m³</td>
<td>0.1</td>
</tr>
<tr>
<td>( \xi )</td>
<td>mPa s</td>
<td>( 10^{-5} )</td>
</tr>
<tr>
<td>( n_{\infty} )</td>
<td>mol/m³</td>
<td>( 10^{-1} )</td>
</tr>
<tr>
<td>( \mu_s )</td>
<td>J/mol</td>
<td>( 10^2 )</td>
</tr>
<tr>
<td>( \kappa_n )</td>
<td>m²/s</td>
<td>( 4.3 \times 10^{-8} )</td>
</tr>
<tr>
<td>( \kappa_{n^x} )</td>
<td>m²/s</td>
<td>( 1.7 \times 10^{-8} )</td>
</tr>
</tbody>
</table>

Table 4. Material properties.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_3 )</td>
<td>( 1.8 \times 10^{-4} )</td>
</tr>
<tr>
<td>( M )</td>
<td>( 5.7 \times 10^{-4} )</td>
</tr>
<tr>
<td>( M_n )</td>
<td>( 8.6 \times 10^{-3} )</td>
</tr>
<tr>
<td>( N )</td>
<td>0.1</td>
</tr>
<tr>
<td>( P_n )</td>
<td>4.6</td>
</tr>
<tr>
<td>( P_{n^x} )</td>
<td>( 1.2 \times 10^{-7} )</td>
</tr>
<tr>
<td>( b )</td>
<td>( 10^{-4} )</td>
</tr>
<tr>
<td>( \Omega )</td>
<td>( 3 \times 10^6 )</td>
</tr>
<tr>
<td>( \Sigma )</td>
<td>633</td>
</tr>
</tbody>
</table>

Table 5. Dimensionless parameters at \( h_0 = 100 \) Å and \( \Delta \theta = 2 \).
Figure 8. Film thickness evolution for different $A_3$: $A_3 = 0$ (dashed line), $A_3 = 0.1$ (dotted line), $A_3 = 0.2$ (solid line). Other parameters were taken $A_1 = 0.005$, $A_2 = 0$, $E = 0.01$, $b = 0.001$, $n^z = 0.1$, $n_\infty = 0.1$.

Figure 9. Change in the dispersion curve due to the change of a) the effective pressure $A_2$ ($N = 0$): $A_2 = 0$ (dashed curve), $A_2 = 0.05$ (solid curve). The initial surface molecular density $n^z = 0.1$. b) the surface energy flux $N$ ($A_2 = 0$): $N = 0$ (dashed curve), $N = 0.1$ (solid curve). Three pairs correspond to the initial surface molecular density $n^z = 0$, $n^z = 10^{-4}$, and $n^z = 10^{-3}$.

Pressure on the stability of the film with the surfactant is shown in Fig. 9a. The solid line shows the dispersion curve for $A_2 = 0.05$ and the dashed line shows the case $A_2 = 0$. This result is qualitatively the same as for the case of the surfactant-free film (Section 4, Fig. 4b). Increasing $A_2$ exerts a stabilizing influence on the system. Also, we see that with surfactant, shown in Fig. 9a (the initial surface molecular density $n^z = 0.1$), the growth rate $\omega$ is substantially lower than that for the surfactant-free case $n^z = n = 0$ shown in Fig. 4b. This indicates the stabilizing influence of the surfactant. The influence of the effective pressure (difference between the solid and the dashed lines) was found to be appreciable for all investigated values of the initial surface molecular density $n^z(0)$ and other parameters corresponding to molten metals.

Fig. 9b shows the influence of the surface energy flux (difference between the solid and the dashed lines) for $n^z(0) = 0$ (upper pair of curves), $n^z(0) = 10^{-4}$ (middle pair of curves), and $n^z(0) = 10^{-3}$ (lower pair of curves). The solid lines show the dispersion curve for $N = 0$ and the dashed lines show the case $N = 0$. Aside from the stabilizing influence of the surfactant, we see that as $n^z$ grows the dashed and solid curves get closer, indicating a decreasing influence of the parameter $N$ on the stability. At $n^z = 10^{-3}$, the curves almost merge, indicating the negligible influence of $N$. An explanation might be found in the fact that the interfacial viscosity and, hence, the dissipation, increases with $n^z$. Entropy transport along the interface therefore slows with increasing $n^z$.

The calculations of this section demonstrate that the influence of the effective pressure (difference between the dashed and the solid lines in the Fig. 9a), governed by $A_2$, on the stability of the thin film remains significant even in the presence of the surfactant.
But the results presented in the Fig. 9b indicate that increasing amount of the surfactant suppresses the energy flux along the interface, governed by $N$.

6. Summary

An analysis of the linear stability of the evaporating thin liquid film has been performed. The model used in our analysis accounts for: (i) the influence of the energy flux along the film surface; (ii) the influence of the effective pressure consisting of disjoining and capillary contributions. The results reveal conditions under which these two effects are important. We find that these effects have a small influence for liquids like water and ethanol, for which the evaporation number $E$ is small. The effects turn out to be appreciable for liquids with relatively large ($E \sim 0.1$) evaporation number and with small ($Pr \ll 1$) Prandtl number. In particular, we show that, for molten metals such as sodium, a consideration of the effective pressure substantially affects the values of growth rate and cutoff wave numbers. When the surface energy transport and effective pressure are negligible, our model reduces to that of Burelbach et al. (1988) and, at $N = A_2 = 0$, we recover their results.

We observe the stabilizing influences of the effective pressure for parameter values corresponding to molten metals. This result follows from the fact that this effect arises from additional dissipative mechanisms associated with the corresponding terms (Fried et al. 2006). Specifically, we demonstrate that consideration of the effective pressure makes it possible to observe the influence of the disjoining pressure on the film evolution close to the instant of rupture. The analysis of the base state shows that, for a liquid partially wetting the substrate, the disjoining pressure shortens the evolution time of the evaporating film—the thickness of which changes from the initial value to zero. When the liquid completely wets the substrate, rupture does not occur and the film evolves into the stationary state representing a thin liquid layer adsorbed onto the substrate. This result for a thin film is similar to that obtained by Moosman & Homsy (1980) for an evaporating meniscus. The expression for the thickness of the adsorbed layer obtained in our work agrees with the estimate obtained by Wayner (1999). Thus, we demonstrate that the presence of the effective pressure removes the degeneracy of the evolution of the base state with respect to the cases when a liquid partially or completely wets the substrate.

Calculations performed by Burelbach et al. (1988) revealed limitations of the lubrication approximation near the disappearance time $t_d$. At $t_d$, when the thickness $h$ vanishes, the vertical velocity becomes large according to $h_t \sim 1/(A_1 + h)$ (if $A_1 = 0$), which contradicts to the lubrication approximation. The results of our analysis show that (i) the film thickness $h$ change is always singular and follows $h_t \sim A_2 \Pi/(A_1 + h) h^3$ for small $h$, even for the case $A_1 \neq 0$; (ii) the change in the film thickness $h$ occurs even faster than predicted by Burelbach et al. (1988). This reflects the influence of the disjoining pressure.

The thin film rupture times calculated by Williams & Davis (1982) and Yiantsios & Higgins (1991) by means of linear and nonlinear theories are of the same order of magnitude. Even though the rupture time determined by nonlinear theory is shorter than that obtained by linear analysis, they give qualitatively the same estimates. For this reason we leave investigation of the influence of the energy flux on the surface and the effective pressure on the nonlinear evolution of thin film for later consideration.

Our calculations also show that, whereas the presence of a nonvolatile dissolved surfactant on the film interface suppresses the energy flux along the surface, the effective pressure remains an important factor affecting film stability.
Acknowledgement

This work was supported by DOE. We thank V. Ajaev, X. Chen, S. Davis, G. Homsy, M. Miksis, and A. Shen for helpful discussions.

Appendix A. Long-wave approximation

Here we provide some details of how the equations (2.7), the boundary conditions (2.7) and (2.8) can be reduced to (2.9)–(2.11). We adopt a rectangular Cartesian basis \{e_1, e_3\}, where the outward normal \(n\), tangent vector \(t\) to the surface, curvature \(K\), and velocity are given by

\[
\begin{align*}
    n &= \frac{-h_x e_1 + e_3}{(1+h_x^2)^{1/2}}, \\
    t &= \frac{e_1 + h_x e_3}{(1+h_x^2)^{1/2}}, \\
    K &= \frac{h_{xx}}{(1+h_x^2)^{3/2}}, \\
    u &= u e_1 + w e_3,
\end{align*}
\]

with \(h_x\) denoting the derivative of \(h\) with respect to the horizontal coordinate \(x\). Taking into consideration that

\[
\frac{Dh}{Dt} = h_x u^i + h_t = w^i
\]

(where the superscript “i” indicates the interface), we find expressions for the normal velocity \(V\), the migrational velocity \(V^{\text{mig}}\), and the product \(KV\) of curvature and normal velocity as

\[
\begin{align*}
    V &= u^i \cdot n = \frac{-h_x u^i + w^i}{(1+h_x^2)^{1/2}}, \\
    V^{\text{mig}} &= V - u \cdot n = \frac{h_x u - w + h_t}{(1+h_x^2)^{1/2}}, \\
    KV &= \frac{h_t h_{xx}}{(1+h_x^2)^2}.
\end{align*}
\]

Assuming that the horizontal scale of the liquid motion is significantly larger than the vertical one and that the time evolution is slow enough, we apply a long-wave approximation. Following Williams & Davis (1982) we take the dimensionless wave number \(k\) to be a small parameter. According to this choice we apply the change of variables

\[
x = \frac{X}{k}, \quad z = Z, \quad t = \frac{T}{k}
\]

and expand all variables in powers of \(k\):

\[
\begin{align*}
    u &= U + kU_1 + \cdots, & w &= k(W + kW_1 + \cdots), & p &= k^{-1}(P + kP_1 + \cdots), \\
    \theta &= \Theta + k\theta_1 + \cdots, & J &= J + kJ_1 + \cdots.
\end{align*}
\]

Here \(u\), \(w\), \(p\), \(\theta\), \(J\), and \(h\) are functions of variables \(x\), \(z\), and \(t\), whereas their long-wave counterparts \(U\), \(W\), \(P\), \(\Theta\), \(J\), and \(H\) are functions of \(X\), \(Z\), and \(T\). To the leading order, the normal, tangent vectors and the curvature are

\[
\begin{align*}
    n &= -kH_x e_1 + e_3 + o(k), \\
    t &= e_1 + kH_x e_3 + o(k), \\
    K &= k^2 H_{XX} + o(k^2).
\end{align*}
\]
Using these expressions we calculate gradients of the normal and tangent vectors, projector $\mathbb{P}$, bulk rate of stretch $D$ and surface velocity $u_s$ as

$$\nabla n = -k^3 H_X X e_1 e_1 - k^3 H_X H_X e_3 e_1 + o(k^3),$$

$$\nabla t = -k^3 H_X H_X e_1 e_1 + k^2 H_X e_3 e_1 + o(k^3),$$

$$\mathbb{P} = e_1 e_1 + kH_X e_1 e_3 + kH_X e_3 e_1 + o(k),$$

$$D = \frac{1}{2} (2kU_X e_1 e_1 + (U_Z + k^2 W_X)e_1 e_3 + (U_Z + k^2 W_X)e_3 e_1 + 2kW_Z e_3 e_3) + o(k^2),$$

$$u_s = \mathbb{P} u = (U + k^2 (H_X W - H_X W)) e_1 + kH_X U e_3 + o(k^2).$$

Using the expression (A 2)

$$\text{for the}
\begin{equation}
\begin{aligned}
K & = k^3 H_T H_X \times \sigma + o(k^3), \\
\nabla \cdot u_s = & \mathbb{P} : \nabla u_s = k(U_X + H_X U_Z) + o(k), \\
D & = \mathbb{P} D \mathbb{P} = k(U_X + H_X U_Z) e_1 e_1 + k^2 H_X (U_X + H_X U_Z) e_1 e_3 + \\
& + k^2 H_X (U_X + H_X U_Z) e_3 e_1 + o(k^2), \\
2Dn \cdot n & = -2k(U_X + U_Z H_X) + o(k^2), \\
2Dn \cdot t & = U_Z + o(k).
\end{aligned}
\end{equation}
$$

To calculate the projection of the surface divergence $\nabla_s \cdot (2\alpha \mathbb{D} + \lambda(\mathbb{T} \Delta \mathbb{D}) \mathbb{P})$ onto the normal direction in the momentum balance equation (5.1) we note that

$$\nabla \cdot (\nabla_s \cdot (2\alpha \mathbb{D} + \lambda(\mathbb{T} \Delta \mathbb{D}) \mathbb{P}) = \mathbb{P} : \nabla ((2\alpha \mathbb{D} + \lambda(\mathbb{T} \Delta \mathbb{D}) \mathbb{P})^\top n) - (2\alpha \mathbb{D} + \lambda(\mathbb{T} \Delta \mathbb{D}) \mathbb{P}) : \nabla n.$$

Since $(2\alpha \mathbb{D} + \lambda(\mathbb{T} \Delta \mathbb{D}) \mathbb{P})^\top n = 0$, we have to calculate only the second term, which is

$$2\alpha \mathbb{D} + \lambda(\mathbb{T} \Delta \mathbb{D}) \mathbb{P} = (2\alpha + \lambda) k(U_X + H_X U_Z) e_1 e_1 + o(k).$$

Using the expression (A 2) for the $\nabla n$ we obtain

$$(2\alpha \mathbb{D} + \lambda(\mathbb{T} \Delta \mathbb{D}) \mathbb{P}) : \nabla n = o(k^2),$$

which gives the projection of the surface divergence onto the normal direction

$$\nabla \cdot (\nabla_s \cdot (2\alpha \mathbb{D} + \lambda(\mathbb{T} \Delta \mathbb{D}) \mathbb{P})) = o(k^2).$$

To the leading order this term does not contribute in the normal component of the momentum balance equation (5.1). The tangential component of the surface divergence entering the equation (5.1) is

$$\mathbb{t} \cdot (\nabla_s \cdot (2\alpha \mathbb{D} + \lambda(\mathbb{T} \Delta \mathbb{D}) \mathbb{P}) = \mathbb{P} : \nabla((2\alpha \mathbb{D} + \lambda(\mathbb{T} \Delta \mathbb{D}) \mathbb{P})^\top \mathbb{t}) - (2\alpha \mathbb{D} + \lambda(\mathbb{T} \Delta \mathbb{D}) \mathbb{P}) : \nabla \mathbb{t}.$$

Direct calculation shows that,

$$(2\alpha \mathbb{D} + \lambda(\mathbb{T} \Delta \mathbb{D}) \mathbb{P})^\top \mathbb{t} = \xi n^2 k(U_X + H_X U_Z) e_1 + o(k),$$

$$(2\alpha \mathbb{D} + \lambda(\mathbb{T} \Delta \mathbb{D}) \mathbb{P}) : \nabla \mathbb{t} = o(k^4).$$
In the expressions (A 7) we follow Danov et al. (1998) and assume that the interfacial viscosity $2\alpha + \lambda$ arises only due to the presence of the surfactant $n^x$ on the surface and is therefore $2\alpha + \lambda = \xi n$. Calculation of the first term in right-hand side of (A 6) gives
\[
P : \nabla \left( (2\bar{\alpha} \mathbb{D} + \bar{\lambda}(\text{tr} \mathbb{D})P) \right) t = k^2 \xi n^x (U_X + H_X U_Z) + \xi n^x k^2 \left[ (U_{XX} + H_{XX} U_Z + H_X U_{ZX}) + H_X (U_{XZ} + H_X U_{ZZ}) \right] + o(k^2). \quad (A 8)
\]

Using the explicit expression (2.12) for the velocity component $U$, we can calculate the following identities
\[
U_X + H_X U_Z = V_X,
\]
\[
U_{XX} + H_{XX} U_Z + 2H_X U_{ZX} + H_X^2 U_{ZZ} = V_{XX}.
\]

Finally we obtain the tangential component of the surface divergence in equation (5.1) as
\[
t \cdot \left( \nabla_s \cdot (2\bar{\alpha} \mathbb{D} + \bar{\lambda}(\text{tr} \mathbb{D})P) \right) = k^2 \xi (V_{XX} n^x + V_X n^x X) + o(k^2). \quad (A 9)
\]

Note that, in the surfactant-free case $n^x = 0$ and
\[
t \cdot \left( \nabla_s \cdot (2\bar{\alpha} \mathbb{D} + \bar{\lambda}(\text{tr} \mathbb{D})P) \right) = 0.
\]

To the leading order the governing equations (2.7) become
\[
-P_X + U_{ZZ} = 0, \\
-P_Z = 0, \\
\Theta_{ZZ} = 0, \\
U_X + W_Z = 0; \quad (A 10)
\]
the boundary conditions (2.7) reduce to
\[
W = 0, \quad U = 0, \quad \Theta = 1; \quad (A 11)
\]

further using the expressions (A 4) we can now rewrite the boundary conditions on liquid-vapor interface (2.8) as
\[
E(J + kJ_1) = k(-h_T - h_X U + W),
\]
\[
kN \mathbb{V}_X = -\Theta_Z - J,
\]
\[
\frac{k\Pi}{h^3} - P - 2k^2 \mathbb{V}_X = -kE^2 D^{-1} J^2 + k^3 \Sigma h_{XX} (1 - C \Theta),
\]
\[
-\frac{1}{2} U_Z = kM Pr^{-1} (\Theta_X + h_X \Theta_Z),
\]
\[
A_1 J = \Theta + A_2 \left( \frac{P}{k} - \frac{1}{2} (U^2 + k^2 W^2) - E^2 D^{-1} J^2 \right). \quad (A 12)
\]

To retain the physical effects important for our analysis, we adopt the scales
\[
E = k\bar{E}, \quad D = k^3 \bar{D}, \quad A_1 = \bar{A}_1, \quad A_2 = k \bar{A}_2,
\]
\[
N = \frac{\bar{N}}{k}, \quad M = \frac{\bar{M}}{k}, \quad \Omega = \frac{\bar{\Omega}}{k}, \quad \Pi = \frac{\bar{\Pi}}{k}, \quad \Sigma = \frac{\bar{\Sigma}}{k^3},
\]
where the quantities with superposed bars are assumed to be order of $O(1)$ as $k \to 0$. 

Finally, noting that
\[ k^3 \Sigma (1 - C \theta) = \Sigma - k^2 M Pr^{-1} \theta = \Sigma + O(k^2), \]
we may reduce the system (A 12) to
\[ \bar{E} J = -h_T - h_X U + W, \]
\[ \bar{N} \bar{V}_X = -\bar{\Theta} Z - J, \]
\[
\frac{\Pi}{k^3} - P = -\bar{E}^2 \bar{D}^{-1} J^2 + \Sigma h_{XX},
\]
\[ \frac{1}{2} U_Z = \bar{M} Pr^{-1} (\Theta_X + h_X \Theta_Z), \]
\[ A_1 J = \Theta + \bar{A}_2 \left( P - \bar{E}^2 \bar{D}^{-1} J^2 \right). \]  

REFERENCES


Moosman, S. & Homsy, G.M. Evaporating menisci of wetting fluids. J. Colloid Interface Sci. 73, 212–223.


<table>
<thead>
<tr>
<th>No.</th>
<th>Authors</th>
<th>Title</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1026</td>
<td>Liu, M., K. J. Hsia, and M. Sardela Jr.</td>
<td>In situ X-ray diffraction study of electric field induced domain switching and phase transition in PZT-5H— <em>Journal of the American Ceramic Society</em> (submitted)</td>
<td>May 2003</td>
</tr>
<tr>
<td>No.</td>
<td>Authors</td>
<td>Title</td>
<td>Date</td>
</tr>
<tr>
<td>-----</td>
<td>----------------------------------</td>
<td>----------------------------------------------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>No.</td>
<td>Authors</td>
<td>Title</td>
<td>Date</td>
</tr>
<tr>
<td>------</td>
<td>-------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>No.</td>
<td>Authors</td>
<td>Title</td>
<td>Date</td>
</tr>
<tr>
<td>-----</td>
<td>--------------------------------</td>
<td>------------------------------------------------------------------------------------------------</td>
<td>----------</td>
</tr>
<tr>
<td>1092</td>
<td>Natrajan, V. K., E. Yamaguchi, and K. T. Christensen</td>
<td>Statistical and structural similarities between micro- and macro-scale wall turbulence—Microfluidics and Nanofluidics (submitted)</td>
<td>Apr. 2006</td>
</tr>
</tbody>
</table>