Instabilities of non-isothermic ultra-thin two-layer films

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Abstract. Evolution of ultra-thin bilayer films under the joint action of the van der Waals forces and Marangoni stresses in the presence of an inclined temperature gradient, is investigated. The problem is solved by means of a linear stability theory and nonlinear simulations. The linear analysis leads to the discovery of the phenomenon of “isotropization”. In the nonlinear region, the formation of ordered structures that consist of equally sized droplets moving with equal velocities and located at equal distances from each other, is revealed. The influence of the gravity on the instabilities of non-isothermic two-layer films is studied.

1. Introduction
In the past few decades, the development of microfluidics and nanotechnology led to a significant progress in the exploration of thin film flows. The dynamics of ultra-thin (but still macroscopic) films, with the thickness less than 100 nm, is of a special interest. In the case of ultra-thin films, it is necessary to take into account the long-range intermolecular forces (first of all, van der Waals forces) acting between molecules of the liquid and substrate [1]. Depending on the sign of the Hamaker constant, these forces can either stabilize the film or create a longwave instability leading to the film rupture through the formation of holes [2].

The wetting properties of the interfaces can be significantly changed by the creation of two-layer films, which reveal much richer dynamics than one-layer films [3]. The nonlinear evolution of two-layer liquid films in the presence of van-der-Waals interactions and other effects, such as evaporation, adsorption of surfactants, thermocapillary and solutocapillary effects, action of an electrostatic field, and Rayleigh-Taylor instability, has been studied [4], [5], [6], [7], [8]. Besides a rupture, the development of instabilities may lead to the formation of different morphologies including holes, droplets and even labyrinthine structures. In the present work, we have found the phenomenon of a spontaneous ordering of a droplet system under the action of an imposed inclined temperature gradient.

2. Formulation of the Problem
Consider a system of two superposed layers of immiscible liquids with different physical properties. The bottom layer rests on a solid substrate, the top layer is in contact with the adjacent gas phase. The temperature of the solid substrate is $T_s + Ax$, the temperature of the gas near the interface is assumed to be $T_g + Ax$. All the variables referring to the bottom
layer are marked by subscript 1, and all the variables referring to the top layer are marked by subscript 2. The equilibrium coordinates of interfaces are \( \hat{H}_i \), \( i = 1, 2 \). The deformable interfaces are described by equations \( z = H_1(x, y, t) \) (liquid-liquid interface) and \( z = H_2(x, y, t) \) (liquid-gas interface). The \( i \)th fluid has density \( \rho_i \), kinematic viscosity \( \nu_i \), dynamic viscosity \( \eta_i = \rho_i \nu_i \), thermal diffusivity \( \chi_i \) and heat conductivity \( \kappa_i \). The surface tension coefficients on the lower and upper interfaces, \( \sigma_1 \) and \( \sigma_2 \), are linear functions of temperature \( T \): \( \sigma_1 = \sigma_1^0 - \alpha_1 T \), \( \sigma_2 = \sigma_2^0 - \alpha_2 T \). The effect of gravity is neglected. For a heat flux on the liquid-gas interface we use an empirical condition,

\[
k_2 \frac{\partial T_2}{\partial x_i} n_{2i} = -q(T_2 - T_g - Ax),
\]

where \( q \) is the heat exchange coefficient which is assumed to be constant.

The system of equations and boundary conditions governing the problem is rather complicated. However, in the case of thin film flows, when the fluid system is thin in one direction and extended in other directions, the nonlinear model governing three-dimensional flows with a deformable interface can be drastically simplified by means of long-wavelength expansions. The longwave approach is based on the assumption that the characteristic spatial scales in the directions \( x \) and \( y \) are much larger than that in the direction \( z \). The details of the longwave approach applied to thermocapillary flows can be found in review papers [12], [13]. In the framework of the leading order approximation, which is known as lubrication approximation, pressures \( P_i \), \( i = 1, 2 \), do not depend on the transverse coordinate \( z \).

The van der Waals forces manifest themselves as external normal stresses ("disjoining pressures") imposed on each interface [1]. These pressures can be calculated using the potential energy of the van der Waals interactions

\[
\Psi(H_1, H_2) = -\frac{A_{sg} - A_{s2} - A_{g1}}{12\pi H_2^2} - \frac{A_{s2}}{12\pi H_1^2} - \frac{A_{g1}}{12\pi (H_2 - H_1)^2},
\]

where \( A_{sg}, A_{s2} \) and \( A_{g1} \) are Hamaker constants for the interactions between the solid substrate and the gas phase across the two liquid layers, between the solid substrate and an infinite layer of the liquid 2 across liquid 1, and between the gas and an infinite layer of the liquid 1 across liquid 2, correspondingly (see [7]). These Hamaker constants can be calculated on the basis of Lifshitz theory [1].

In the present paper, we consider solely the case where \( A_{sg} - A_{s2} - A_{g1} > 0 \), \( A_{s2} < 0 \), and \( A_{g1} < 0 \). That means that the effective interaction between the liquid 2/gas interface and the liquid 1/substrate interface is attractive, and it creates a van der Waals instability. However, the effective interactions between two other pairs of interfaces are repulsive, and they prevent the rupture of the layers.

Let us formulate the mathematical model in the non-dimensional form. The natural vertical length scale is the initial thickness of the lower layer, \( H_1^0 \). We fix the horizontal length scale, \( L^* \), as

\[
L^* = (H_1^0)^2 \sqrt{\frac{6\pi \sigma_1^0}{|A_{sg}|}},
\]

which is convenient for the analysis of the instability induced by intermolecular forces [7]. We choose

\[
r^* = \frac{\eta_1 (L^*)^4}{\sigma_1^0 (H_1^0)^3}
\]

as a time scale and

\[
p^* = \frac{\sigma_1^0 H_1^0}{(L^*)^2}
\]

as a pressure scale.
Governing equations look as follows:

\[ h_{1\tau} + \nabla \cdot \mathbf{q}_1 = 0, \quad h_{2\tau} + \nabla \cdot \mathbf{q}_2 = 0, \quad (5) \]

\[ \mathbf{q}_1 = f_{11} \nabla p_1 + f_{12} \nabla p_2 + \mathbf{q}_1^T, \quad \mathbf{q}_2 = f_{21} \nabla p_1 + f_{22} \nabla p_2 + \mathbf{q}_2^T, \quad (6) \]

where \( h_j = H_j/H_1^0, \quad p_j = P_j/p^*, \quad j = 1, 2, \)

\[ f_{11} = \frac{1}{3} h_1^3, \quad f_{12} = -\frac{1}{2} h_1^2(h_2 - h_1), \quad f_{21} = \frac{1}{6} h_1^3 - \frac{1}{2} h_1^2 h_2, \]

\[ f_{22} = (h_2 - h_1) \left[ h_1^2 \left( \frac{1}{2} - \frac{\eta}{3} \right) + h_1 h_2 \left( -1 + \frac{2\eta}{3} \right) - \frac{\eta h_2^2}{3} \right]. \]

The contributions of disjoining pressures are included:

\[ p_1 = -\nabla^2 h_1 - \sigma \nabla^2 h_2 + w_1(h_1, h_2), \quad (7) \]

\[ p_2 = -\sigma \nabla^2 h_2 + w_2(h_1, h_2), \quad (8) \]

\[ w_1 = \frac{a_0 - a_1 - a_2}{h_2^3} + \frac{a_1}{h_1^3}, \quad (9) \]

\[ w_2 = \frac{a_0 - a_1 - a_2}{h_2^3} + \frac{a_2}{(h_2 - h_1)^3}. \quad (10) \]

The non-dimensional expressions for the fluxes generated by the thermocapillary effect are:

\[ \mathbf{q}_1^T = \frac{M_{\perp}}{2} h_1^2 \nabla \{ d(Bi h_1 - \alpha \kappa) \} - \frac{M_{\parallel}}{2} (1 + \alpha) h_1^2 \mathbf{e}_x. \quad (11) \]

\[ \mathbf{q}_2^T = \frac{M_{\perp}}{2} (-h_2^2 \nabla (d \eta \alpha \kappa) + (2h_2 - h_1) h_1 \nabla \{ d(Bi h_1 - \alpha(1 - \eta)) \}) - \frac{M_{\parallel}}{2} [\eta \alpha h_2^2 + (1 + \alpha - \eta \alpha) h_1(2h_2 - h_1)] \mathbf{e}_x. \quad (12) \]

Here

\[ M_{\perp} = \frac{\alpha_1(T_s - T_g)}{\sigma_1^0} \left( \frac{L^*}{H_1^0} \right)^2, \quad \quad (13) \]

\[ M_{\parallel} = \frac{\alpha_1AL^*}{\sigma_1^0} \left( \frac{L^*}{H_1^0} \right)^2 \quad (14) \]

are the modified transverse and longitudinal Marangoni numbers, correspondingly,

\[ Bi = \frac{qH_1^0}{\kappa_2} \quad (15) \]

is the Biot number, and

\[ d = [\kappa + Bi(1 - \kappa)h_1 + Bih_2]^{-1}, \quad (16) \]

\[ \eta = \eta_1/\eta_2, \quad \kappa = \kappa_1/\kappa_2, \quad \sigma = \sigma_2/\sigma_1, \quad \alpha = \alpha_2/\alpha_1, \quad \]

\[ a_0 = \text{sign}(A_{sg}), \quad a_1 = \frac{A_{g2}^{-}}{|A_{sg}|}, \quad a_2 = \frac{A_{g1}^{-}}{|A_{sg}|}. \quad (17) \]

The system of equations (5) contains ten nondimensional parameters: \( M_{\perp}, M_{\parallel}, Bi, \sigma, \alpha, \eta, \kappa, a_0, a_1, \) and \( a_2. \)
First, let us consider the linear stability of a parallel thermocapillary flow with flat interfaces \( h_1 = 1, h_2 = h \). The growth rate \( \lambda(k) \) of a disturbance with a wavevector \( k = (k_x, k_y) \) is determined by the dispersion relation \( \det(N - \lambda I) = 0 \), where \( I \) is a 2×2 unit matrix, and

\[
N = k^2 A + k^4 B + M_1 k^2 C + i k_x M_\parallel D.
\]

The 2×2 matrices in the right-hand side of (18), which do not depend on the wavevector \( k \), describe the influence of van der Waals forces \( (A) \), surface tension \( (B) \), transverse heating \( (C) \) and longitudinal heating \( (D) \). In the absence of the thermocapillary flow \( (M_\parallel = 0) \), the growth rate \( \lambda = \lambda(k^2) \) does not depend on the orientation of the wavevector. In the case \( \beta = k_x M_\parallel / M_\perp k^2 = O(1) \) the growth rate depends significantly on the wavevector orientation. Let us emphasize that this is a peculiarity of a two-layer system, because in the case of a one-layer system \( D \) would be a number rather than a matrix, and the term containing \( k_x \) does not influence the growth rate. However, an asymptotic analysis of the dispersion relation in the limit \( \beta \gg 1 \) shows that in the leading orders \( \lambda \sim i k_x M_\parallel \lambda_1 + k^2 \lambda_2 + \ldots \), where \( \lambda_1 \) and \( \lambda_2 \) are real coefficients that do not depend on \( k \). Thus, we come to the following paradoxical situation. The longitudinal component of the temperature gradient is the only factor that violates the rotational symmetry of the problem. However, when this component is sufficiently large, the isotropy of the problem is partially restored (the real part of the growth rate is isotropic in the leading order, while the imaginary part is not isotropic), except the region of nearly longitudinal structures that have small \( \beta \) even for large \( M_\parallel \).

The investigation of the film evolution under the joint action of the thermocapillary stresses and intermolecular forces governed by full nonlinear equations (5)-(12) has been fulfilled by means of nonlinear simulations. Evolution equations (5) have been discretized by central differences for spatial derivatives and solved using an explicit scheme. Periodic boundary conditions have been applied on the boundaries of the computational region. Initial conditions for \( h_j, j = 1, 2 \) have been chosen in such a way that the mean value of \( h_1(X,Y,0) \) was equal to 1 and the mean value of \( h_2(X,Y,0) \) was equal to \( h \), where \( h > 1 \). Small random deviations of \( h_j(X,Y,0) \) from their mean values were imposed using a code creating pseudo-random numbers. The computations have been performed in the region \( 240 \times 240 \) using the grid \( 400 \times 400 \).

3. Numerical Results

We have observed numerous types of film dynamics. A typical scenario of the film decomposition due to the instability induced by the van der Waals forces includes the creation of a disordered array of droplets connected by a thin two-layer film. These droplets are subject to coarsening. Under the action of a transverse heating, \( M_\perp \neq 0 \), the dependence of the liquid-liquid interface height on the distance from the droplet center becomes non-monotonic, so that this interface resembles a “volcano”. In the absence of a longitudinal heating, \( M_\parallel = 0 \), the droplets do not move; the coarsening takes place due to the coalescence of large droplets caused by their growth, and the disappearance of small droplets. In the presence of a longitudinal component of the temperature gradient, the shape of the liquid-liquid interface beneath the droplets is strongly asymmetric: the crater-like depression is shifted to the front part of the droplet, while in its back part a high elevation is observed. The coarsening of droplets is accelerated by their drift due to the thermocapillary flow.

Surprisingly, under certain conditions we observe the formation of ordered structures that consist of equally sized droplets moving with equal velocities and located at equal distances from each other. Let us emphasize that the ordered droplets system is not a result of a casual monodispersity of droplets due to a specific choice of initial conditions, but a result of a natural evolution of the systems to its stable configuration. The same ordered system of droplets has been obtained from different initial conditions. Note that the deformation of the gas/liquid interface is much stronger than that of the liquid/liquid interface.
Outside the region of parameters corresponding to perfectly ordered structures, we observe a
dynamical regime of “splashes” which is characterized by the coexistence of several “immortal”
big droplets and a number of small droplets that are ejected by big droplets, grow with time
and finally coalesce with big droplets.

Some more regimes have been found in simulations, e.g., oblique traveling waves and
modulated longitudinal structures.

Under the action of the gravity forces, the ordered system of droplets is destroyed and
transforms through intermediate unstable stages to a new stable configurations of the vertical
stripes or the inclined stripes.

In conclusion, we have considered the evolution of a two-layer film under a joint action of
thermocapillary effect and intermolecular forces in the case of an inclined temperature gradient.
The governing equations have been derived in the lubrication approximation. It is found that for
sufficiently large values of the horizontal temperature gradient, the real part of the linear growth
rate does not depend on the direction of the wavenumber, except the case of nearly longitudinal
disturbances (phenomenon of ”isotropization”). Numerous types of nonlinear evolution regimes
have been observed, among them ordered systems of droplets, “splashes”, oblique waves, and
modulated longitudinal structures. The influence of the gravity on the instabilities of non-
isothermic two-layer films is investigated.

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