



# Stability of evaporating two-layered liquid film in the presence of surfactant—I. The equations of lubrication approximation

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**Abstract**—In this study we consider the stability of horizontal two-layered liquid film attached to a heated solid substrate. The film can contain surfactant that is soluble in both liquid phases. The evaporation of solvent from the upper film is also taken into account. Thus, the two-layered film can exhibit both thermocapillary and Marangoni instabilities coupled with the effect of solvent mass loss. The problem is solved in the framework of the lubrication approximation. We derive a system of partial differential equations describing the evolution of long-wave disturbances in the presence of surfactant and evaporation. Appropriate rescaling is proposed and a numerical analysis of the dimensionless groups for particular system of water-light oil film upon a horizontal PVC plate is performed. The model allows one to investigate the role of different factors on the film stability: the surfactant concentration and distribution coefficient, the critical concentrations of micellization, the surface viscosities, the adsorption isotherms of the surfactant at the liquid surfaces and the intensity of evaporation. Based on this model the full linear analysis of the stability is given in Part II [see Danov *et al.* (1997b) *Chem. Engng Sci.*, submitted]. The non-linear effects are also taken into account in Part III [see Paunov *et al.* (1997) *Chem. Engng Sci.* submitted], where these effects are studied numerically for a particular case of PVC/tetrachlorethane/water/vapour system. © 1998 Elsevier Science Ltd. All rights reserved.

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## 1. INTRODUCTION

The problem for the stability of thin liquid films represents both scientific and technological interest. Practically, most of the industrial application of surfactants include thin films in foams, emulsions, wetting and coating films (cf. Adamson, 1976; Kralchevsky *et al.*, 1996). The mechanism of arising of instabilities in thin liquid films can be rather different depending on the particular factors. In general, due to thermal or other fluctuations the film surfaces are disturbed. When the film is thin enough, the attractive disjoining pressure can amplify the fluctuation and can cause the film rupture (see Maldarelli and Jain, 1988). The liquid interfaces can be additionally destabilised by processes like evaporation or conden-

sation of vapour at the interface (cf. Hatzivramidis, 1992).

Levich (1962) has shown that when surfactant is present at the interface the surface waves are effectively suppressed due to the elastic properties of the deformed surfactant monolayer. Prosperetti and Plesset (1984) demonstrate that for a single liquid interface the high intensive evaporation can strongly increase the interfacial instabilities with growth times less than a millisecond.

There are numerous contributions to the stability analysis of thin liquid films in the literature. Linear stability analysis of the fluctuations of the thickness of stationary quasi-equilibrium plane-parallel thin liquid film between two different phases is performed by Maldarelli and Jain (1988). The authors derived a dispersion relation which includes the influence of the van der Waals and electrostatic interactions and Marangoni effect due to the surfactant redistribution. Ivanov and Dimitrov (1988) investigated the stability

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of a thin foam plane-parallel film during the process of its drainage.

Edwards *et al.* (1991) performed linear stability analysis of surfactant stabilised wetting film. They establish that the surface diffusivity and viscosity, Gibbs elasticity and instantaneous adsorption are more important factors than the value of the surface tension itself. The inclusion of non-linear effects may be of particular significance to the predicted rupture time (cf. Williams and Davis, 1982).

Non-linear stability problems of surfactant free evaporating/condensing thin liquid films have been reported by Davis (1987), Burelbach *et al.* (1988) and Joo *et al.* (1991). Their results show that both the evaporation and condensation amplify the instabilities at the film surfaces. Danov *et al.* (1997a) extended the work of Burelbach *et al.* (1988) for the case of surfactant containing wetting film in the presence of evaporation. These authors investigate the influence of the surface viscosity and elasticity, the surfactant concentration, bulk and surface diffusivity of surfactant and the intensity of evaporation on the film stability. Hatzivramidis (1992) reports results for the influence of surfactant on the film stability in the case when the surfactant adsorption is kinetically controlled. Stability analysis of down-flowing multilayer liquid films has been performed by Kao (1968) and Kliakhandler and Sivashinsky (1995). However, the possible effects due to the presence of surfactant and evaporation of solvent have not been considered. For detailed review of the literature on the stability of coating films we recommend Burelbach *et al.* (1988) and Danov *et al.* (1997a).

In this study we deal with the problem of the stability of an evaporating two-layered liquid film that contains soluble surfactant. The film is attached to a heated solid substrate. In Section 2 the model of Danov *et al.* (1997a) is extended by taking into account the presence of a second liquid layer. We investigate the evolution of long waves on the both liquid interfaces by using lubrication approximation. Thus, the evolution equations for the film thicknesses and the surfactant concentration are derived and re-scaled (Sections 3 and 4). The respective dimensionless numbers that appear in the problem are defined in a similar way as in the paper of Danov *et al.* (1997a), which allows one to keep them fixed during the process of evaporation, when both the temperature and the surfactant concentration change. In Section 5 we perform numerical analysis of the dimensionless groups for particular system: water-light oil film on a horizontal PVC substrate. Note that in the paper of Burelbach *et al.* (1988) and related works the authors performed parametric studies of the film stability by varying the values of the dimensionless groups. However, in our case the variation of some dimensionless numbers at fixed values of the other ones seems to be incorrect, because there is no real physical system that corresponds exactly to each combination of dimensionless numbers. In order to avoid this, we perform a parametric study of the stability of particular systems by

varying their physical parameters. In this respect, we present the numerical results for the stability of particular systems with evaporation and surfactant in the next two parts of this study which are separate papers. The *linear stability analysis* of water-light oil film is a subject of the second part of this study [cf. Danov *et al.* (1997b)]. *Non-linear analysis* of the stability of a two-layered liquid film of heavy oil and water is performed in the third part (cf. Paunov *et al.*, 1997). We believe that this work will contribute to a better understanding of the processes of appearing and growing of instabilities in multilayered films in real conditions and to clarify the role of the surfactants in these phenomena.

## 2. MATHEMATICAL FORMULATION OF THE PROBLEM

In this study we consider the problem for the stability of evaporating two-layered film attached to an uniformly heated wall. The film is formed from two completely immiscible phases (1 and 2) and contains surfactant which is soluble in both liquid phases. The upper film is evaporating, so there is solvent mass loss, momentum transfer, and energy consumption at the vapour-liquid interface. For the sake of simplicity, we will accept that the density and the bulk viscosity of the phases do not change due to the process of evaporation. We will consider only films of thickness less than  $20\ \mu\text{m}$ , which allows us to neglect the gravity effects (cf. Danov *et al.*, 1997a). When the films are thin enough, the interaction between the film interfaces affects strongly the film stability and has to be taken into account.

In general, lateral variations in the film surface tension can be induced by both fluctuations in the surfactant adsorption and the temperature due to evaporation. The resulting Marangoni instability causes flow in the film core and perturbs both the surfactant and temperature distribution (cf. Levich, 1962). The physical picture is complicated by the additional contribution of the disjoining pressure in the film in the enhancing (or quenching) of the film shape fluctuation. That is why the correct analysis of the film shape fluctuations requires the simultaneous consideration of the heat and mass transfer as well as the flow induced in the film.

### 2.1. Transport equations in the bulk phases

For incompressible surfactant solutions the transport equations of mass, momentum, energy, and species in the bulk phases are (cf. Levich, 1962; Landau and Lifshitz, 1984)

$$\nabla \cdot \mathbf{v}_k = 0, \quad \frac{\partial \mathbf{v}_k}{\partial t} + (\mathbf{v}_k \cdot \nabla) \mathbf{v}_k = \frac{1}{\rho_k} \nabla \cdot \mathbf{P}_k \quad (1)$$

$$\frac{\partial T_k}{\partial t} + (\mathbf{v}_k \cdot \nabla) T_k = \nabla \cdot (a_k \nabla T_k),$$

$$\frac{\partial c_k}{\partial t} + (\mathbf{v}_k \cdot \nabla) c_k = \nabla \cdot (D_k \nabla c_k). \quad (2)$$

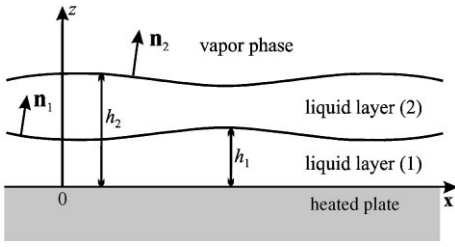


Fig. 1. The physical configuration of the two-layered film on a heated plate.

Here the subscript  $k = 1, 2$  corresponds to the lower and upper liquid layer (see Fig. 1),  $t$  the time,  $\nabla$  the spatial gradient operator,  $\rho_k$ ,  $T_k$  and  $c_k$  are the liquid density, temperature and surfactant concentration,  $\mathbf{v}_k$  the average mass velocity,  $\mathbf{P}_k$  the liquid pressure tensor,  $a_k$  the thermal diffusivity of the solution, and  $D_k$  the surfactant bulk diffusion coefficient. Below we assume that  $a_k$  and  $D_k$  are constant during the film thinning and the solutions can be treated as incompressible Newtonian fluids. Then the pressure tensor  $\mathbf{P}_k$  reads

$$\mathbf{P}_k = -p_k \mathbf{I} + \mathbf{T}_k, \quad \mathbf{T}_k = \eta_k [\nabla \mathbf{v}_k + (\nabla \mathbf{v}_k)^T]. \quad (3)$$

In eq. (3)  $p_k$  is the pressure in the liquid,  $\mathbf{I}$  the unit operator,  $\mathbf{T}_k$  the viscous stress tensor, the superscript T denotes transposition, and the dynamic viscosity  $\eta_k$  will be considered constant.

## 2.2. Boundary conditions

In order to close the system of eqs (1)–(3), in this section we consider the boundary conditions at the heated wall,  $z=0$ , at the liquid–liquid interface,  $z=h_1$ , and at the liquid–vapour interface,  $z=h_2$  (see Fig. 1). The respective constitutive relations are discussed below.

At the film boundary  $z=0$  (see Fig. 1), we assume no relative motion of the wall, constant temperature  $T_h$  and no specific adsorption, which is equivalent to zero surfactant diffusion flux. The boundary conditions at  $z=0$  are

$$\mathbf{v}_1 = \mathbf{0}, \quad T_1 = T_h, \quad \frac{\partial c_1}{\partial z} = 0. \quad (4)$$

Across the film–vapour interface  $z=h_2$ , we require conservation of mass, surface-excess linear momentum, energy, and interfacial species mass. We consider the limiting case of small vapour density, viscosity and thermal conductivity comparable to the respective liquid layer parameters. By this way, the problem in the vapour phase can be eliminated and the stability problem for the film can be solved separately [detail explanation is given by Burelbach *et al.* (1988) and Danov *et al.* (1997a)]. Levich (1962), Burelbach *et al.* (1988), Slattery (1990) and Edwards *et al.* (1991) showed that in this limit the

boundary conditions simplify to

$$J = \rho_2 (\mathbf{v}_2 - \mathbf{u}_2) \cdot \mathbf{n}_2 \quad (5)$$

$$\mathbf{T}_2 \cdot \mathbf{n}_2 = \nabla_S \cdot \mathbf{S}_2 + \left( p_2 + \Pi_2 - p_v - \frac{J^2}{\rho_v} \right) \mathbf{n}_2 \quad (6)$$

$$JL = -(\lambda_2 \nabla T_2) \cdot \mathbf{n}_2 \quad (7)$$

$$\begin{aligned} \frac{\partial \Gamma_2}{\partial t} + \nabla_S \cdot (\Gamma_2 \mathbf{u}_2) - \nabla_S \cdot (\mathbf{B}_2 \nabla_S \Gamma_2) \\ = [-D_2 \nabla c_2 + c_2 (\mathbf{v}_2 - \mathbf{u}_2)] \cdot \mathbf{n}_2. \end{aligned} \quad (8)$$

The notation appearing in these equations is as follows:  $\mathbf{u}_2$  the velocity of the liquid–vapour interface,  $\mathbf{n}_2$  the unit normal (see Fig. 1),  $\nabla_S$  is the surface gradient operator,  $\mathbf{S}_2$  is the interfacial pressure tensor,  $\Pi_2$  is the disjoining pressure,  $p_v$  and  $\rho_v$  are the vapour pressure and density,  $J$  is the mass flux due to the evaporation,  $L$  is the specific heat of vaporisation,  $\lambda_2$  is the thermal conductivity of the liquid.  $\Gamma_2$  is the adsorption, and  $B_2$  is the interfacial diffusion coefficient.

At the liquid–liquid interface  $z=h_1$ , the kinematic and dynamic boundary conditions are

$$\frac{\partial h_1}{\partial t} + (\mathbf{u}_1 \cdot \nabla_S) h_1 = \mathbf{v}_1 \cdot \mathbf{n}_1 = \mathbf{v}_2 \cdot \mathbf{n}_2, \quad \mathbf{v}_1 = \mathbf{v}_2 \quad (9)$$

$$(\mathbf{T}_1 - \mathbf{T}_2) \cdot \mathbf{n}_1 = \nabla_S \cdot \mathbf{S}_1 + (p_1 + \Pi_1 - p_2 - \Pi_2) \mathbf{n}_1 \quad (10)$$

where  $\mathbf{u}_1$  is the velocity of the liquid–liquid interface,  $\mathbf{n}_1$  is the unit normal (see Fig. 1),  $\mathbf{S}_1$  is the interfacial pressure tensor,  $\Pi_1$  and  $\Pi_2$  are the disjoining pressures in films 1 and 2, respectively.

The conservation of energy across the liquid–liquid interface leads to the expression for continuity of the heat flux, i.e.

$$(\lambda_1 \nabla T_1 - \lambda_2 \nabla T_2) \cdot \mathbf{n}_1 = 0, \quad T_1 = T_2 = T_{1s} \quad (11)$$

where  $T_{1s}$  is the temperature at the interface.

The local change of the interfacial species mass is compensated by the interfacial convection, by diffusion and by the diffusion fluxes from both the contiguous phases. Thus, the boundary condition for the mass balance of surfactant at the liquid–liquid interface reads (cf. Levich, 1962)

$$\begin{aligned} \frac{\partial \Gamma_1}{\partial t} + \nabla_S \cdot (\Gamma_1 \mathbf{u}_1) - \nabla_S \cdot (\mathbf{B}_1 \nabla_S \Gamma_1) \\ = (D_2 \nabla c_2 - D_1 \nabla c_1) \cdot \mathbf{n}_1 \end{aligned} \quad (12)$$

at  $z=h_1$ . In eq. (12)  $\Gamma_1$  is the adsorption at interface 1 and  $B_1$  is the respective surface diffusion coefficient.

In order to close the system (5)–(8), one has to write the constitutive equations for the mass flux  $J$ , for the latent heat of vaporisation  $L$ , for the disjoining pressure  $\Pi_k$ , for the adsorption  $\Gamma_k$  and for the interfacial pressure tensor  $\mathbf{S}_k$ , ( $k=1, 2$ ). The expression for the solvent mass flux  $J$  is given by the kinetic theory and is used by many authors (cf. Plesset, 1952, Palmer, 1976)

$$J = J_T (T_{2s} - T_s), \quad \text{with } J_T = \text{const}, \quad \text{and } L = \text{const}. \quad (13)$$

Here  $T_{2s}$  is the temperature of the liquid–vapour interface,  $T_s$  is the equilibrium saturation temperature,  $J_T$  and  $L$  depend on the molecular weight and on the saturation temperature.

Various surface forces which can influence the hydrodynamic stability of thin liquid films (van der Waals, electrostatic, depletion, etc.)—see e.g. Maldarelli and Jain (1988) and Israelachvili (1992). Actually, the latter depends on the film composition, the contamination of electrolytes, etc. Here we will investigate only the role of van der Waals interactions, therefore the disjoining pressure in the two layers can be written in the form

$$\Pi_1 = -\frac{A_1}{6\pi h_1^3} - \frac{A_i}{6\pi h_2^3}, \quad \Pi_2 = -\frac{A_2}{6\pi(h_2 - h_1)^3} - \frac{A_i}{6\pi h_2^3}. \quad (14)$$

This is the case when the film contains no electrolyte and the surfactant is non-ionic, otherwise additional contributions to the disjoining pressure should be taken into account. In eq. (14),  $A_1$ ,  $A_2$  and  $A_i$  are the respective complex Hamaker constants of the layers 1 and 2, defined by the expressions (cf. Israelachvili, 1992)

$$\begin{aligned} A_1 &= A_{s2} - A_{s1} - A_{12} + A_{11}, \\ A_2 &= A_{v1} - A_{v2} - A_{12} + A_{22} \\ A_i &= A_{vs} - A_{v1} - A_{s2} + A_{12}. \end{aligned} \quad (15)$$

Hence the Hamaker constants for solid/vacuum/liquid is  $A_{sk}$ , for vapour/vacuum/liquid is  $A_{vk}$ , for liquid/vacuum/liquid is  $A_{kk}$ , where  $k = 1, 2$ , for vapour/vacuum/solid is  $A_{vs}$ , and for liquid1/vacuum/liquid 2 is  $A_{12}$ . Note that in this case the van der Waals pressure can have a non-monotonic behaviour as a function of the film thickness which depends on the values of the Hamaker constants.

Let us consider some disturbance of the interface of an equilibrium surfactant solution. The surface dynamics will try to restore the equilibrium, either by adsorption from bulk phase, or by surface convection, driven by the gradient of interfacial tension (elasticity of the interface) in interplay with a specific interfacial viscous friction (the Boussinesq effect). A simple rheological model of the interface dynamics is provided by the linear Boussinesq–Scriven constitutive law (cf. Boussinesq, 1913; Scriven, 1960)

$$\begin{aligned} \mathbf{S}_k &= \sigma_k \mathbf{I}_{s,k} + (\eta_k^{\text{dil}} - \eta_k^{\text{sh}})(\mathbf{I}_{s,k} : \mathbf{D}_k) \mathbf{I}_s + 2\eta_k^{\text{sh}} \mathbf{D}_k \\ \mathbf{D}_k &= \frac{1}{2} [(\nabla_s \mathbf{u}_k) \cdot \mathbf{I}_{s,k} + \mathbf{I}_{s,k} \cdot (\nabla_s \mathbf{u}_k)^T], \quad k = 1, 2 \end{aligned} \quad (16)$$

where  $\mathbf{I}_{s,k}$  is the surface idemfactor,  $\mathbf{D}_k$  and  $\sigma_k$  are the surface rate of deformation tensor and the interfacial tension of the film interface  $k$ , respectively;  $\eta_k^{\text{sh}}$  and  $\eta_k^{\text{dil}}$  are the interfacial shear and dilatational viscosities (cf. Edwards *et al.*, 1991).

The bulk subsurface concentration  $c_{ks}$ , ( $k = 1, 2$ ) is related to the surfactant adsorption at the interface via the adsorption isotherm. In addition, the inter-

facial tension is connected to the absorption by means of the respective interfacial equation of state. Typical for most of the surfactant solution below and close to the critical micelles concentration are the Langmuir (1918) isotherm and the Frumkin (1925) equation of state

$$\begin{aligned} \frac{\Gamma_k}{\Gamma_{k,\infty}} &= \frac{c_{ks}}{b_k + c_{ks}}, \quad \sigma_k = \sigma_{k,p}(T_{ks}) \\ &+ k_B T_{ks} \Gamma_{k,\infty} \ln \left( 1 - \frac{\Gamma_k}{\Gamma_{k,\infty}} \right), \quad (k = 1, 2). \end{aligned} \quad (17)$$

Here  $\Gamma_{k,\infty}$  is the saturation adsorption at the film interface  $k$ ,  $b_k$  is a constant concentration parameter of the adsorption isotherm, related to the energy of adsorption per molecule,  $c_{1s}$  is the subsurface concentration of the surfactant from layer 1;  $c_{2s}$  is the respective concentration from layer 2;  $\sigma_{k,p}(T_{ks})$  is the interfacial tension of the pure solvent at temperature  $T_{ks}$ , and  $k_B$  is the Boltzmann constant. In most systems of practical interest the relative temperature difference  $T_h - T_s$  is not very high and the parameters  $b_k$ , and  $\Gamma_{k,\infty}$  can be considered that change insignificantly.

In addition, the condition for adsorption/desorption equilibrium of the surfactant

$$m_1 c_{1s} = m_2 c_{2s}, \quad m_1 = \frac{\partial \Gamma_1}{\partial c_1}, \quad m_2 = \frac{\partial \Gamma_1}{\partial c_2} \quad (18)$$

takes place, where  $m_1$  and  $m_2$  are the surfactant equilibrium constants. As a rule,  $m_1 \neq m_2$  even for identical surfactants because of the different properties of the fluid in the separate layers (cf. Adamson, 1976; Lucassen-Reynders, 1981).

### 3. LUBRICATION APPROXIMATION

Let us choose the coordinate system so that the plane  $z = 0$  to coincide with the surface of the solid substrate (see Fig. 1). The vapour–liquid interface and the liquid–liquid interface are located at  $z = h_2(\mathbf{x}, t)$  and  $z = h_1(\mathbf{x}, t)$ , respectively, with  $\mathbf{x}$  being the lateral coordinate. The lateral and vertical velocity components are denoted by  $\mathbf{v}_{k,\parallel}$  and  $w_k$ , ( $k = 1, 2$ ). Levich (1962), Maldarelli and Jain (1988) and Ivanov and Dimitrov (1988) showed that the short wave perturbations disappear faster due to the higher viscous dissipation of energy and by capillary damping, than those of wavelengths longer than the film thickness. Therefore, the long wave approximation will be applied to the solution of the problem in sequel. The general assumptions are:

- (i) small Reynolds number,  $\max[\rho_1 h_1^2 / (\eta_1 t_f), \rho_2 (h_2 - h_1)^2 / (\eta_2 t_f)] \ll 1$ ;
- (ii) small thermal Peclet number,  $\max[h_1^2 / a_1 t_f, (h_2 - h_1)^2 / a_2 t_f] \ll 1$ ;
- (iii) small diffusive Peclet number,  $\max[h_1^2 / D_1 t_f, (h_2 - h_1)^2 / D_2 t_f] \ll 1$ ;
- (iv) small slope of the interfaces,  $(\nabla_s h_1)^2 \ll 1$  and  $(\nabla_s h_2)^2 \ll 1$ .

These numbers are defined using the characteristic time of disturbance evolution  $t_f$ .

### 3.1. Solution of the problem in the bulk phases

From eq. (2) and boundary conditions (4), (7), (11) and (13) we can calculate the leading order solution for the temperature distribution, for the interfacial temperature and for the mass flux due to the evaporation. These expressions read

$$T_1 = T_h - (T_h - T_{1s}) \frac{z}{h_1}, \quad T_2 = T_{1s} - (T_{1s} - T_{2s}) \times \frac{z - h_1}{h_2 - h_1} \quad (19)$$

$$T_{1s} = T_s + \Delta T \frac{\lambda_1 + LJ_T(h_2 - h_1)\lambda_{12}}{\lambda_1 + LJ_T(h_2 - h_1)\lambda_{12} + LJ_T h_1} \quad (20)$$

$$T_{2s} = T_s + \Delta T \frac{\lambda_1}{\lambda_1 + LJ_T(h_2 - h_1)\lambda_{12} + LJ_T h_1} \quad (21)$$

$$J = \frac{\lambda_1 J_T \Delta T}{\lambda_1 + LJ_T(h_2 - h_1)\lambda_{12} + LJ_T h_1} \quad (22)$$

where the dimensionless ratio between the thermal conductivities of the two liquids is  $\lambda_{12} = \lambda_1/\lambda_2$  and the temperature difference is  $\Delta T = T_h - T_s$ .

The solution of eq. (1) in the framework of lubrication approximation with boundary condition (4) for the pressure and lateral component of the velocity yields

$$p_k = p_k(\mathbf{x}, t), \quad (k = 1, 2) \quad (23)$$

$$\mathbf{v}_{1,\parallel} = \frac{z(z - h_1)}{2\eta_1} \nabla_{\parallel} p_1 + \frac{z}{h_1} \mathbf{u}_1 \quad (24)$$

$$\mathbf{v}_{2,\parallel} = \frac{(z - h_1)(z - h_2)}{2\eta_2} \nabla_{\parallel} p_2 + \frac{h_2 - z}{h_2 - h_1} \mathbf{u}_1 + \frac{z - h_1}{h_2 - h_1} \mathbf{u}_2. \quad (25)$$

If we substitute expressions (24) and (25) into the continuity equation (1) and integrate the resulting equations with the boundary conditions (4) and (9), then the distribution of the vertical velocity component in the liquid layers can be obtained in the framework of the lubrication approximation

$$\begin{aligned} w_1 &= \frac{z^2}{12\eta_1} (3h_1 - 2z) \nabla_{\parallel}^2 p_1 + \frac{z^2}{4\eta_1} \nabla_{\parallel} p_1 \cdot \nabla_{\parallel} h_1 \\ &\quad - \frac{z^2}{4} \nabla_{\parallel} \left( \frac{1}{h_1} \right) \mathbf{u}_1 \\ w_2 &= \frac{\partial h_1}{\partial t} + \mathbf{u}_1 \cdot \nabla_{\parallel} h_1 - \frac{z^3 - h_1^3}{6\eta_2} \nabla_{\parallel}^2 p_2 \\ &\quad + \frac{z^2 - h_1^2}{4\eta_2} \nabla_{\parallel} \cdot [(h_1 + h_2) \nabla_{\parallel} p_2] \\ &\quad - \frac{z - h_1}{2\eta_2} \nabla_{\parallel} \cdot (h_1 h_2 \nabla_{\parallel} p_2) \end{aligned} \quad (26)$$

$$\begin{aligned} & - \frac{z^2 - h_1^2}{2} \nabla_{\parallel} \cdot \left[ \frac{1}{h_2 - h_1} (\mathbf{u}_2 - \mathbf{u}_1) \right] \\ & - (z - h_1) \nabla_{\parallel} \cdot \left( \frac{h_2}{h_2 - h_1} \mathbf{u}_1 - \frac{h_1}{h_2 - h_1} \mathbf{u}_2 \right). \end{aligned} \quad (27)$$

In eqs (26) and (27),  $\nabla_{\parallel}$  is the lateral projection of the spatial gradient operator, which in the leading order is equal to the surface gradient operator (cf. Edwards *et al.*, 1991).

### 3.2. Compatibility equations and surface-excess linear momentum boundary conditions

After substitution of the expressions for the vertical velocity components (26) and (27) into the surface mass balance and kinematic equations (5) and (9) the so-called compatibility problem is derived

$$\frac{\partial h_1}{\partial t} + \nabla_{\parallel} \cdot \left( \frac{h_1}{2} \mathbf{u}_1 \right) = \nabla_{\parallel} \cdot \left( \frac{h_1^3}{12\eta_1} \nabla_{\parallel} p_1 \right) \quad (28)$$

$$\begin{aligned} & \frac{\partial (h_2 - h_1)}{\partial t} + \nabla_{\parallel} \cdot \left[ \frac{h_2 - h_1}{2} (\mathbf{u}_1 + \mathbf{u}_2) \right] \\ & = \nabla_{\parallel} \cdot \left[ \frac{(h_2 - h_1)^3}{12\eta_2} \nabla_{\parallel} p_2 \right] - \frac{J}{\rho_2}. \end{aligned} \quad (29)$$

From the surface-excess linear momentum equations (6) and (10) and the general solution for the lateral velocity component (26) and (27), the normal and tangential stress boundary conditions at the interfaces simplify to

$$p_1 + \Pi_1 = p_2 + \Pi_2 - \sigma_1 \nabla_{\parallel}^2 h_1 \quad (30)$$

$$p_2 = p_v + \frac{J^2}{\rho_v} - \Pi_2 - \sigma_2 \nabla_{\parallel}^2 h_2 \quad (31)$$

$$\begin{aligned} & \frac{h_1}{2} \nabla_{\parallel} p_1 + \frac{\eta_1}{h_1} \mathbf{u}_1 + \frac{h_2 - h_1}{2} \nabla_{\parallel} p_2 - \frac{\eta_2}{h_2 - h_1} (\mathbf{u}_2 - \mathbf{u}_1) \\ & = \nabla_{\parallel} \sigma_1 + \nabla_{\parallel} \cdot (\eta_1^s \nabla_{\parallel} \mathbf{u}_1) \end{aligned} \quad (32)$$

$$\begin{aligned} & \frac{h_2 - h_1}{2} \nabla_{\parallel} p_2 + \frac{\eta_2}{h_2 - h_1} (\mathbf{u}_2 - \mathbf{u}_1) \\ & = \nabla_{\parallel} \sigma_2 + \nabla_{\parallel} \cdot (\eta_2^s \nabla_{\parallel} \mathbf{u}_2) \end{aligned} \quad (33)$$

where the Boussinesq–Scriven constitutive law (16) leads to the coupling of the dilatational and shear interfacial viscosities effect in one interfacial viscosity parameter, defined by  $\eta_k^s = \eta_k^{dil} + \eta_k^{sh}$ , ( $k = 1, 2$ ).

### 3.3. Interfacial species transport equation

To obtain the interfacial total species transport equation in the lubrication approximation we sum eqs (8) and (12). The result reads

$$\begin{aligned} & \frac{\partial}{\partial t} (\Gamma_1 + \Gamma_2) + \nabla_{\parallel} \cdot (\Gamma_1 \mathbf{u}_1 + \Gamma_2 \mathbf{u}_2 - B_1 \nabla_{\parallel} \Gamma_1 - B_2 \nabla_{\parallel} \Gamma_2) \\ & = (D_2 \nabla c_2 - D_1 \nabla c_1) \cdot \mathbf{n}_1 |_{z=h_1} \\ & \quad - [D_2 \nabla c_2 - c_2 (\mathbf{v}_2 - \mathbf{u}_2)] \cdot \mathbf{n}_2 |_{z=h_2} \end{aligned} \quad (34)$$

The diffusion fluxes in eq. (34) can be calculated from the diffusion equations (2). In the framework of the lubrication approximation the surfactant concentration  $c_2$  is a sum of a uniform part,  $c_{2s}(\mathbf{x}, t)$ , and a small perturbation,  $c_{2,f}(\mathbf{x}, z, t)$ .  $c_{2s}(\mathbf{x}, t)$  does not depend on the vertical coordinate  $z$  and it is equal to the subsurface concentration, and the  $z$ -derivative of  $c_{2,f}(\mathbf{x}, z, t)$  is comparable with the lateral and time derivatives of the subsurface concentration (cf. Ivanov and Dimitrov, 1988). Then the diffusion equation (2) can be written in the following form:

$$\begin{aligned} \frac{\partial c_{2s}}{\partial t} + (\mathbf{v}_{2,\parallel} \cdot \nabla_{\parallel}) c_{2s} - \nabla_{\parallel} \cdot (D_2 \nabla_{\parallel} c_{2s}) \\ = \frac{\partial}{\partial z} \left( D_2 \frac{\partial c_{2,f}}{\partial z} \right). \end{aligned} \quad (35)$$

After integrating the diffusion equation (35) from  $h_1$  to  $h_2$ , using the solution (25), the leading order of the diffusion fluxes from the liquid phase 2 appearing in eq. (34) becomes

$$\begin{aligned} (D_2 \nabla c_2) \cdot \mathbf{n}_2|_{z=h_2} - (D_2 \nabla c_2) \cdot \mathbf{n}_1|_{z=h_1} = (h_2 - h_1) \frac{\partial c_{2s}}{\partial t} \\ + \left[ \frac{h_2 - h_1}{2} (\mathbf{u}_1 + \mathbf{u}_2) - \frac{(h_2 - h_1)^3}{12\eta_2} \nabla_{\parallel} p_2 \right] \cdot \nabla_{\parallel} c_{2s} \\ - \nabla_{\parallel} \cdot [D_2 (h_2 - h_1) \nabla_{\parallel} c_{2s}]. \end{aligned} \quad (36)$$

It is important to note that the subsurface surfactant concentrations in the layer 2 at the liquid–vapour interface and at the liquid–liquid interface are equal.

Similarly, we represent the surfactant concentration  $c_1$  as a sum of uniform part,  $c_{1s}(\mathbf{x}, t)$ , and small perturbation,  $c_{1,f}(\mathbf{x}, z, t)$ .  $c_{1s}(\mathbf{x}, t)$  does not depend on the vertical coordinate  $z$  and it is equal to the subsurface concentration, and the  $z$ -derivative of  $c_{1,f}(\mathbf{x}, z, t)$  is comparable with the lateral and time derivatives of the subsurface concentration. Then the diffusion equation (2) can be rewritten in the form analogous to eq. (35):

$$\frac{\partial c_{1s}}{\partial t} + (\mathbf{v}_{1,\parallel} \cdot \nabla_{\parallel}) c_{1s} - \nabla_{\parallel} \cdot (D_1 \nabla_{\parallel} c_{1s}) = \frac{\partial}{\partial z} \left( D_1 \frac{\partial c_{1,f}}{\partial z} \right). \quad (37)$$

After integrating the diffusion equation (37) from 0 to  $h_1$ , using the solution (24), the leading order of the diffusion fluxes from the liquid phase 1 appearing in eq. (34) is derived to be

$$\begin{aligned} (D_1 \nabla c_1) \cdot \mathbf{n}_1|_{z=h_1} = h_1 \frac{\partial c_{1s}}{\partial t} + \left( \frac{h_1}{2} \mathbf{u}_1 - \frac{h_1^3}{12\eta_1} \nabla_{\parallel} p_1 \right) \\ \times \nabla_{\parallel} c_{1s} - \nabla_{\parallel} \cdot (D_1 h_1 \nabla_{\parallel} c_{1s}). \end{aligned} \quad (38)$$

Finally, after substituting eqs (36) and (38) into the interfacial total species transport equation (34), using the compatibility equations (28) and (29) and the condition for adsorption/desorption equilibrium (18),

we obtain

$$\begin{aligned} \frac{\partial}{\partial t} (\Gamma_1 + \Gamma_2) + \nabla_{\parallel} \cdot (\Gamma_1 \mathbf{u}_1 + \Gamma_2 \mathbf{u}_2 - B_1 \nabla_{\parallel} \Gamma_1 - B_2 \nabla_{\parallel} \Gamma_2) \\ = - \frac{\partial}{\partial t} [(h_2 - h_1 + m_{21} h_1) c_{2s}] + \nabla_{\parallel} \cdot \{ [D_2 (h_2 - h_1) \\ + m_{21} D_1 h_1] \nabla_{\parallel} c_{2s} \} \\ - \nabla_{\parallel} \cdot \left\{ \left[ \frac{h_2 - h_1}{2} (\mathbf{u}_1 + \mathbf{u}_2) - \frac{(h_2 - h_1)^3}{12\eta_2} \nabla_{\parallel} p_2 \right. \right. \\ \left. \left. + m_{21} \left( \frac{h_1}{2} \mathbf{u}_1 - \frac{h_1^3}{12\eta_1} \nabla_{\parallel} p_1 \right) \right] c_{2s} \right\} \end{aligned} \quad (39)$$

where the dimensionless ratio between the surfactant equilibrium constants is  $m_{21} = m_2/m_1$ .

The non-linear problem for the stability and evolution of the two-layer film on the heated wall contains three partial differential equations with time and space derivatives (28), (29) and (39), four differential equations only with space derivatives (30)–(33), and non-linear algebraic equations (17), (18) and (20)–(22). This model is a generalisation of the results of Danov *et al.* (1997a) for the case of evaporating two-layered film on a solid substrate in the presence of surfactant in both liquid phases.

#### 4. SCALING OF THE MODEL

The viscous scales of Williams and Davis (1982), which are appropriate to isothermal layers, are not typical for our problem. That is why we use an appropriate scaling of the governing system which is consistent with lubrication theory in our case. We use the following parameters when defining the respective dimensionless groups:

- (i) the thickness,  $h_0$ , of the upper liquid layer and the ratio of the thicknesses of the lower and upper layers,  $h_{12}$ , at the initial time  $t = 0$ ;
- (ii) the disappearance time  $t_d$ , defined as

$$t_d \equiv \frac{\rho_2 h_0}{J_T \Delta T} \left( 1 + \frac{1}{2\mathcal{K}} + \frac{h_{12}}{\mathcal{K} \lambda_{12}} \right). \quad (40)$$

Equation (40) is obtained after integration of eq. (29) with the assumption of the absence of any fluctuations. Here, the dimensionless parameter  $\mathcal{K}$  is a measure for the degree of non-equilibrium at the evaporating interface

$$\mathcal{K} = \frac{\lambda_2}{L J_T h_0}. \quad (41)$$

The physical meaning of the disappearance time is discussed in the next section.

(iii) The characteristic scale,  $l$ , of the lateral fluctuations, which is defined below is used for the scaling of the lateral coordinates.

We will define the dimensionless time  $\tau$  and the dimensionless lateral coordinates  $\mathbf{X}$  as follows:

$$t = t_d \tau, \quad \mathbf{x} = h_0 l \mathbf{X}. \quad (42)$$

Then the dimensionless liquid layer thicknesses  $H_k$ , pressure  $P_k$ , and lateral interfacial velocity  $\mathbf{U}_k$ , ( $k = 1, 2$ ) read

$$h_1 = h_0 H_1, \quad h_2 - h_1 = h_0 H_2, \quad p_k = \frac{12\eta_k l^2}{t_d} P_k, \\ \mathbf{u}_k = \frac{2lh_0}{t_d} \mathbf{U}_k. \quad (43)$$

If we substitute the definitions (40)–(43) into the compatibility equations (28) and (29), using solution (22), we arrive at the system

$$\frac{\partial H_1}{\partial \tau} + \nabla_{\parallel} \cdot (H_1 \mathbf{U}_1) = \nabla_{\parallel} \cdot (H_1^3 \nabla_{\parallel} P_1) \quad (44) \\ \frac{\partial H_2}{\partial \tau} + \nabla_{\parallel} \cdot [H_2 (\mathbf{U}_1 + \mathbf{U}_2)] = \nabla_{\parallel} \cdot (H_2^3 \nabla_{\parallel} P_2) \\ - \frac{2\mathcal{K} + 1 + 2h_{12}\lambda_{21}}{2(\mathcal{K} + H_2 + H_1\lambda_{21})} \quad (45)$$

where  $\lambda_{21} = 1/\lambda_{12} = \lambda_2/\lambda_1$  is the inverse ratio of the layer thermal conductivities.

Another group of dimensionless parameters is connected with the interfacial properties and it is independent of the local changes of temperature. The capacities of the interfaces and the liquid layers are determined by the numbers  $\mathcal{G}_k$  and  $\mathcal{Z}_k$ ; a measure of a log-concentration slope of the interfacial tensions are defined by  $\mathcal{S}_k$  ( $k = 1, 2$ ):

$$\mathcal{G}_k = \frac{\Gamma_{k, \text{CMC}}}{\Gamma_{k, \infty}}, \quad \mathcal{Z}_1 = \frac{h_{12} h_0 c_{1, \text{CMC}}}{\Gamma_{1, \text{CMC}}}, \quad \mathcal{Z}_2 = \frac{h_0 c_{2, \text{CMC}}}{\Gamma_{2, \text{CMC}}}, \\ \mathcal{S}_k = - \frac{k_B \Gamma_{k, \infty} (T_h + T_s)}{2\sigma_{k,0}} \ln(1 - \mathcal{G}_k). \quad (46)$$

The notation appearing in this definitions is as follows:  $\Gamma_{k, \text{CMC}}$  the adsorption at the critical micelles concentration,  $c_{k, \text{CMC}}$ ;  $\sigma_{k,0}$  the pure solvent interfacial tension at the initial time  $t = 0$ . For all types of surfactant,  $\mathcal{G}_k$  changes from 0.75 to 0.95 depending on the specific molecular interactions at the interface. Only for very strong repulsion between the head of surfactant molecules  $\mathcal{G}_k$  reaches 0.75; the typical value of  $\mathcal{G}_k$  is about 0.9. The values of  $\mathcal{S}_k$  for water–air interfaces are in the range from 0.5 to 0.7, but for most surfactants it is about 0.5. The corresponding values for water–oil interfaces can be larger from 0.5 to 0.9. For a given layer thickness  $\mathcal{Z}_k$  can change by several orders of magnitudes from one type of species to another; its magnitude increases with the increase of the initial thickness (cf. Lucassen-Reynders, 1981).

We will introduce the dimensionless adsorption  $G_k$  and subsurface concentration  $C$  scaling by the corresponding values at the critical micelles concentration, i.e.

$$G_k = \frac{\Gamma_k}{\Gamma_{k, \text{CMC}}}, \quad C = \frac{c_{2s}}{c_{2, \text{CMC}}}. \quad (47)$$

Then from definitions (46) and (47), the dimensionless form of the equations of state (17) becomes

$$\frac{\sigma_k}{\sigma_{k,0}} = \frac{\sigma_{k,p}}{\sigma_{k,0}} - \mathcal{S}_k \frac{2T_{ks}}{T_h + T_s} \frac{\ln(1 - \mathcal{G}_k G_k)}{\ln(1 - \mathcal{G}_k)}, \quad (k = 1, 2) \quad (48)$$

and the dimensionless form of the Langmuir isotherms are

$$G_1 = \frac{C}{(1 - \mathcal{G}_1) C_{12} m_{12} + C \mathcal{G}_1}, \quad G_2 = \frac{C}{1 + C \mathcal{G}_2 - \mathcal{G}_2}, \\ C_{12} = \frac{c_{1, \text{CMC}}}{c_{2, \text{CMC}}}. \quad (49)$$

The characteristic parameter,  $l$ , of the lateral fluctuation length we introduce as the ratio between the capillary and pressure dimensions appearing in the normal stress boundary condition (31) at the evaporating interface

$$l = 4 \sqrt{\frac{\sigma_{2,0} t_d}{3\eta_2 h_0}}. \quad (50)$$

(cf. Danov *et al.*, 1997a). Then the ratio between van der Waals disjoining pressure and the loss of interfacial linear momentum due to evaporation to the dynamic pressure in the liquid phase 2 are estimated, respectively, by the dimensionless numbers  $\mathcal{W}_2, \mathcal{W}_i$  (called van der Waals number below) and  $\mathcal{E}$ . We will use the following definitions for these dimensionless parameters:

$$\mathcal{W}_2 = \frac{A_2 l^2}{4\pi\sigma_{2,0} h_0^2}, \quad \mathcal{W}_i = \frac{A_i l^2}{4\pi\sigma_{2,0} h_0^2}, \quad \mathcal{E} = \frac{h_0 (l J_T \Delta T)^2}{\sigma_{2,0} \rho_v}. \quad (51)$$

The dimensionless form of the normal stress boundary condition (31) at the evaporating interface becomes

$$P_2 = \frac{\mathcal{E}}{4} \frac{\mathcal{K}^2}{(\mathcal{K} + H_2 + H_1 \lambda_{21})^2} + \frac{\mathcal{W}_2}{6H_2^3} + \frac{\mathcal{W}_i}{6(H_1 + H_2)^3} \\ - \frac{1}{4} \left[ 1 - \mathcal{S}_2 \frac{\ln(1 - \mathcal{G}_2 G_2)}{\ln(1 - \mathcal{G}_2)} \right] \nabla_{\parallel}^2 (H_2 + H_1) \quad (52)$$

where the vapour pressure  $p_v$  is taken to be zero. The corresponding boundary condition at the liquid–liquid interface (30) is

$$\eta_{12} P_1 = P_2 + \frac{\mathcal{W}_1}{6H_1^3} - \frac{\mathcal{W}_2}{6H_2^3} - \frac{\sigma_{12}}{4} \\ \times \left[ 1 - \mathcal{S}_1 \frac{\ln(1 - \mathcal{G}_1 G_1)}{\ln(1 - \mathcal{G}_1)} \right] \nabla_{\parallel}^2 H_1 \quad (53)$$

where the van der Waals number, dimensionless ratio between the viscosities and the interfacial tensions are defined by

$$\mathcal{W}_1 = \frac{A_1 l^2}{4\pi\sigma_{2,0} h_0^2}, \quad \eta_{12} = \frac{\eta_1}{\eta_2}, \quad \sigma_{12} = \frac{\sigma_{1,0}}{\sigma_{2,0}}. \quad (54)$$

In eqs (52) and (53) the leading order of the dimensionless equations of state (48) is used.

The thermal Marangoni effects are included in the Marangoni number  $\mathcal{M}_k$ . The influence of interfacial rheology is measured by Boussinesq and surfactant Marangoni numbers, defined through the Gibbs elasticities of the interfaces. For the present investigation these classical numbers are not convenient, because the Gibbs elasticity changes by eight orders of magnitude with the increase of surfactant concentration from low values to CMC. Therefore, scaling of the tangential stress boundary conditions (32) and (33) are performed with interfacial viscosity numbers  $\mathcal{V}_k$  and adsorption elasticity numbers  $\mathcal{A}_k$ , which do not depend on the bulk surfactant concentration. The experimental results obtained by surface waves methods show that the dependence of the interfacial viscosity on the surfactant concentration is analogous to that of the bulk viscosity of concentrated dispersions: the interfacial viscosity increases to  $\eta_{k,\max}^s$  at concentrations close to CMC and after that it decreases again and reaches a plateau. However, close and above CMC, the film interfaces become tangentially immobile and the further increasing of the surfactant concentration does not influence the film stability. Therefore, we use below a simple linear relation between the interfacial viscosity and the adsorption, i.e.  $\eta_k^s = \eta_{k,\text{CMC}}^s \Gamma_k / \Gamma_{k,\text{CMC}}$ , where  $\eta_{k,\text{CMC}}^s$  is the interfacial viscosity at the corresponding critical micelles concentration.

The dimensionless form of the tangential stress boundary condition (32), using solution (20) and the Frumkin equation of state (17) becomes

$$\begin{aligned} \eta_{12} H_1 \nabla_{\parallel} P_1 + \frac{\eta_{12}}{3H_1} \mathbf{U}_1 + H_2 \nabla_{\parallel} P_2 - \frac{1}{3H_2} (\mathbf{U}_2 - \mathbf{U}_1) \\ = -\frac{2\mathcal{M}_1}{3} \nabla_{\parallel} \left( \frac{\mathcal{K} + H_2}{\mathcal{K} + H_2 + H_1 \lambda_{21}} \right) \\ - \frac{2\mathcal{A}_1}{3(1-G_1\mathcal{G}_1)} \nabla_{\parallel} G_1 + \frac{\mathcal{V}_1}{3} \nabla_{\parallel} \cdot (G_1 \nabla_{\parallel} \mathbf{U}_1) \end{aligned} \quad (55)$$

where the dimensionless parameters are defined by

$$\begin{aligned} \mathcal{M}_1 = -\frac{3l^2 \Delta T}{4\sigma_{2,0}} \left( \frac{\partial \sigma_1}{\partial T} \right)_0, \quad \mathcal{A}_1 = \frac{3l^2 k_B}{4\sigma_{2,0}} \frac{T_h + T_s}{2} \Gamma_{1,\text{CMC}}, \\ \mathcal{V}_1 = \frac{\eta_{1,\text{CMC}}^s}{\eta_2 h_0 l^2}. \end{aligned} \quad (56)$$

The corresponding tangential stress boundary condition (33) at the evaporating interface reads

$$\begin{aligned} H_2 \nabla_{\parallel} P_2 + \frac{1}{3H_2} (\mathbf{U}_2 - \mathbf{U}_1) \\ = -\frac{2\mathcal{M}_2}{3} \nabla_{\parallel} \left( \frac{\mathcal{K}}{\mathcal{K} + H_2 + H_1 \lambda_{21}} \right) \\ - \frac{2\mathcal{A}_2}{3(1-G_2\mathcal{G}_2)} \nabla_{\parallel} G_2 + \frac{\mathcal{V}_2}{3} \nabla_{\parallel} \cdot (G_2 \nabla_{\parallel} \mathbf{U}_2) \end{aligned} \quad (57)$$

where the dimensionless numbers appearing in eq. (57) are

$$\begin{aligned} \mathcal{M}_2 = -\frac{3l^2 \Delta T}{4\sigma_{2,0}} \left( \frac{\partial \sigma_2}{\partial T} \right)_0, \quad \mathcal{A}_2 = \frac{3l^2 k_B}{4\sigma_{2,0}} \frac{T_h + T_s}{2} \Gamma_{2,\text{CMC}}, \\ \mathcal{V}_2 = \frac{\eta_{2,\text{CMC}}^s}{\eta_2 h_0 l^2}. \end{aligned} \quad (58)$$

Finally, the dimensionless form of the interfacial total species transport equation (39) is obtained to be

$$\begin{aligned} \frac{\partial}{\partial \tau} (\Gamma_{12} G_1 + G_2) + \nabla_{\parallel} \cdot [2\Gamma_{12} G_1 \mathbf{U}_1 + 2G_2 \mathbf{U}_2 \\ - \mathcal{B}(\Gamma_{12} \mathbf{I}_1 \nabla_{\parallel} G_1 + \mathbf{I}_2 \nabla_{\parallel} G_2)] \\ = -\mathcal{L}_2 \frac{\partial}{\partial \tau} [(H_2 + m_{21} H_1) C] + \mathcal{B} \mathcal{L}_2 \nabla_{\parallel} \\ \times [(H_2 + m_{21} D_{12} H_1) \nabla_{\parallel} C] - \mathcal{L}_2 \nabla_{\parallel} \cdot \{ [H_2 (\mathbf{U}_1 + \mathbf{U}_2) \\ - H_2^2 \nabla_{\parallel} P_2 + m_{21} (H_1 \mathbf{U}_1 - H_1^2 \nabla_{\parallel} P_1)] C \} \end{aligned} \quad (59)$$

where the dimensionless ratio between the adsorption at the CMC and diffusion coefficients of the liquid phases, and the bulk and surface diffusivity parameters are

$$\Gamma_{12} = \frac{\Gamma_{1,\text{CMC}}}{\Gamma_{2,\text{CMC}}}, \quad D_{12} = \frac{D_1}{D_2}, \quad \mathcal{B} = \frac{D_2 t_d}{h_0^2 l^2}, \quad \mathcal{N}_k = \frac{B_k}{D_2}. \quad (60)$$

The dimensionless form of the non-linear problem for the stability and evolution of the two-layer film on the heated wall contains the partial differential equations (44), (45) and (59) with time and space derivatives, the differential equations (52), (53), (55) and (57) only with space derivatives, and non-linear algebraic equations (49). We will use these equations later when performing the stability analysis in the next parts Danov *et al.* (1997b) and Paunov *et al.* (1997).

## 5. DIMENSIONLESS GROUPS ANALYSIS

In order to elucidate the effects of the different parameters on the magnitude of the dimensionless groups appeared in the problem for the stability of the evaporating two-layered film, we will use a particular physical system. The upper and vapour phases consist of a light organic material, for example, hexane ( $\text{C}_6\text{H}_{14}$ ) or heptane ( $\text{C}_7\text{H}_{16}$ ). The lower phase is water solution of surfactant and the heated substrate is a polymeric material, e.g. polystyrene or polyvinylchloride (PVC). For the sake of brevity, we will refer to the above system as P/W/H/V. The physical parameters of heptane and hexane are given by Daubert and Danner (1989) and they are illustrated in Tables 1 and 2.

Using the formula of Plesset (1952), the saturation temperature  $T_s$ , the vapour density, and the latent heat of evaporation  $L$ , we calculated the value of the coefficient  $J_T$ , appearing in eq. (13). Thus, for hexane we obtain:  $T_s = 342$  K,  $\rho_v = 3.182$  kg/m<sup>3</sup>,  $L = 3.35$



Table 1. The physical parameters of the water and hexane at the hexane saturation temperature  $T_s = 342\text{ K}$

	Water	Hexane
$M$	18	86.18
$\rho$ (kg/m <sup>3</sup> )	989.1	612.6
$\eta$ (Pa s)	$4.08 \times 10^{-4}$	$1.88 \times 10^{-4}$
$\nu$ (m <sup>2</sup> /s)	$4.125 \times 10^{-7}$	$3.069 \times 10^{-7}$
$\lambda$ (J/(msK))	0.658	0.138

Table 2. The physical parameters of the water and heptane at the heptane saturation temperature  $T_s = 371\text{ K}$

	Water	Hexane
$M$	18	100.3
$\rho$ (kg/m <sup>3</sup> )	960.0	605.6
$\eta$ (Pa s)	$2.88 \times 10^{-4}$	$1.62 \times 10^{-4}$
$\nu$ (m <sup>2</sup> /s)	$3.00 \times 10^{-7}$	$2.657 \times 10^{-7}$
$\lambda$ (J/(msK))	0.679	0.140

$\times 10^5\text{ J/kg}$ , and  $J_T = 6.85\text{ kg}/(\text{sK m}^2)$ . For heptane we derive:  $T_s = 371\text{ K}$ ,  $\rho_v = 3.432\text{ kg/m}^3$ ,  $L = 3.16 \times 10^5\text{ J/kg}$ , and  $J_T = 6.65\text{ kg}/(\text{sK m}^2)$ . In both cases, the saturation temperature is lower than the water saturation temperature and the lighter liquid has the greater vapour density

We estimate the values of the Hamaker constants, appearing in eq. (14), by using the following average values for the Hamaker constants available from Israelachvili (1992):  $4 \times 10^{-20}\text{ J}$  for water/vacuum/water film,  $7.5 \times 10^{-20}\text{ J}$  for PVC/vacuum/PVC, and  $1.2 \times 10^{-20}\text{ J}$  for PVC/water/PVC. Therefore, the Hamaker constant for PVC/vacuum/water is calculated to  $5.15 \times 10^{-20}\text{ J}$ . The values of the Hamaker constants for water/octane/air is  $0.52 \times 10^{-20}\text{ J}$  and for octane/water/air it is  $-0.24 \times 10^{-20}\text{ J}$ . Using these parameters we calculate the respective Hamaker

constants for water/vacuum/octane to be  $4.22 \times 10^{-20}\text{ J}$  and for octane/vacuum/octane to be  $4.74 \times 10^{-20}\text{ J}$ . There are no data available for the Hamaker constant for polystyrene/vacuum/hexane, polystyrene/vacuum/heptane, PVC/vacuum/hexane or PVC/vacuum/heptane. That is why we used the formula  $A_{s2} \approx \sqrt{A_{ss}A_{22}}$  from Israelachvili (1992) to estimate them. The calculated result is  $5.96 \times 10^{-20}\text{ J}$  for PVC/vacuum/octane film. Here we assume that the van der Waals interaction in hexane, heptane and octane layers is similar. Finally, for the Hamaker constants, appearing in our problem we obtain:  $A_1 = 5.9 \times 10^{-21}\text{ J}$  and  $A_2 = 5.2 \times 10^{-21}\text{ J}$  which are positive (attraction), and  $A_i = -9.3 \times 10^{-21}\text{ J}$  which is negative (repulsion).

The surface parameters at the liquid–vapour interface do not depend on the surfactant concentration and they are as follows: for hexane–vapour interface,  $\sigma_{2,p} = 1.323 \times 10^{-2}\text{ N/m}$  and  $\partial\sigma_2/\partial T = -9.95 \times 10^{-5}\text{ N/(mK)}$ ; and for heptane–vapour interface,  $\sigma_{2,p} = 1.247 \times 10^{-2}\text{ N/m}$  and  $\partial\sigma_2/\partial T = -9.3 \times 10^{-5}\text{ N/(mK)}$ . The corresponding interfacial parameters at the hexane–water interface are  $\sigma_{1,p} = 5.113 \times 10^{-2}\text{ N/m}$  and  $\partial\sigma_1/\partial T = -6.95 \times 10^{-5}\text{ N/(mK)}$  and at the heptane–water interface they are  $\sigma_{1,p} = 4.644 \times 10^{-2}\text{ N/m}$  and  $\partial\sigma_1/\partial T = -9.80 \times 10^{-5}\text{ N/(mK)}$ . For the different surfactant types, typical parameters such as, ionic, non-ionic and high molecular weight are reported by Danov *et al.* (1997a).

The numerical results for the dimensionless parameters, appearing in the non-linear problem for wave evolution are illustrated in Figs. 2–9. The degree of non-equilibrium number  $\mathcal{N}$  depends only on the initial evaporating film thickness  $h_0$  and it decreases in four orders of magnitude when  $h_0$  increases from 5 nm to 20  $\mu\text{m}$  (see Fig. 2). Just the opposite is the influence of interfacial linear momentum due to evaporation. It increases with increase of  $h_0$  and temperature difference (see Fig. 4). The evaporation number  $\mathcal{E}$  decreases more than 10 times, when thickness of the water film

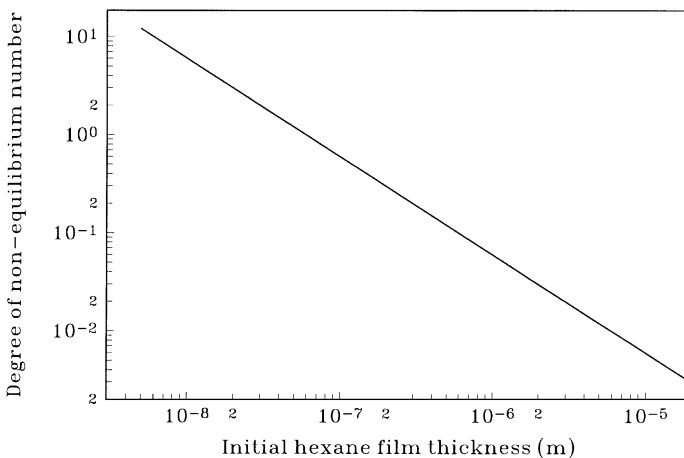
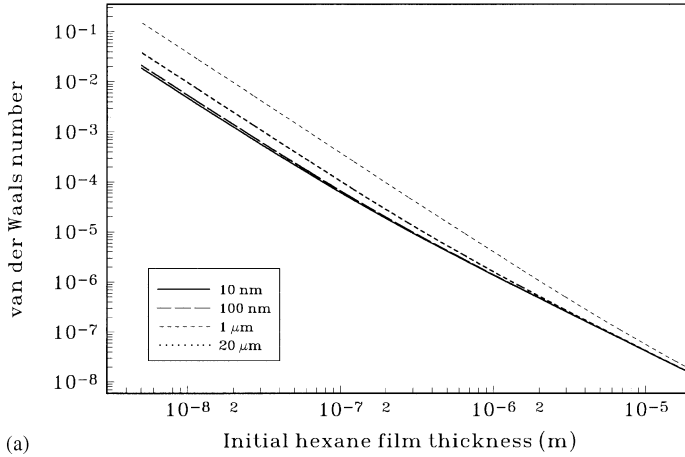


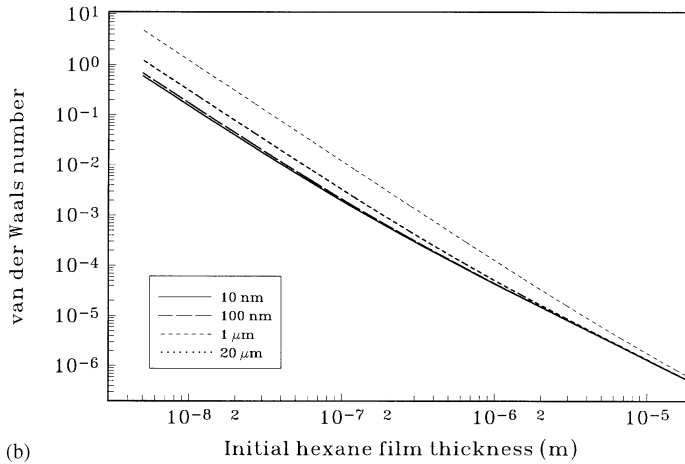
Fig. 2. Dependence of the degree of non-equilibrium number  $\mathcal{N}$  on the initial hexane film thickness  $h_0$ .

$\Delta T = 10^\circ\text{C}$



(a)

$\Delta T = 0.01^\circ\text{C}$



(b)

Fig. 3. Dependence of the van der Waals number  $\mathcal{W}_1$  on the initial hexane film thickness  $h_0$  for temperature difference (a)  $\Delta T = 10^\circ\text{C}$ , (b)  $\Delta T = 0.01^\circ\text{C}$ .

(A) -  $\Delta T = 10^\circ\text{C}$

(C) -  $\Delta T = 0.1^\circ\text{C}$

(B) -  $\Delta T = 1^\circ\text{C}$

(D) -  $\Delta T = 0.01^\circ\text{C}$

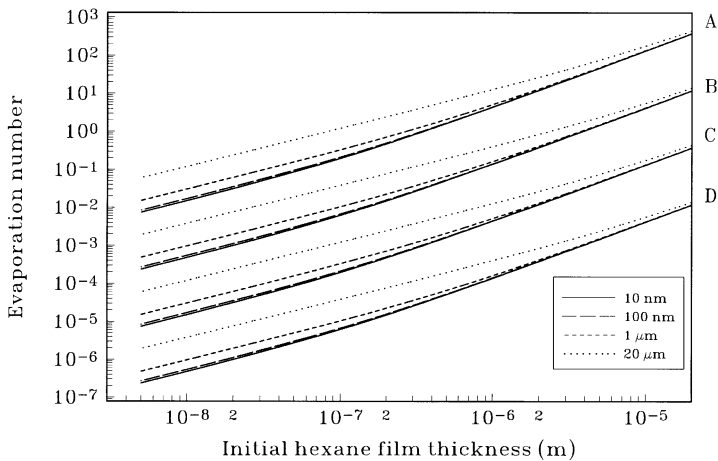


Fig. 4. Dependence of the evaporation number  $\mathcal{E}$  on the initial hexane film thickness for different thicknesses of the water  $h_w$  film and temperature differences  $\Delta T$ .

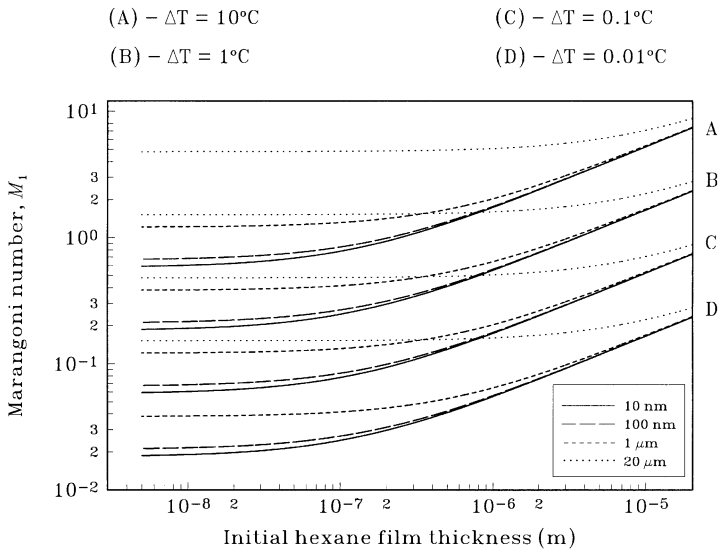


Fig. 5. Dependence of the temperature Marangoni number  $\mathcal{M}_1$  (water/hexane interface) on the initial hexane film thickness for different thicknesses of the water  $h_w$  film and temperature differences  $\Delta T$ .

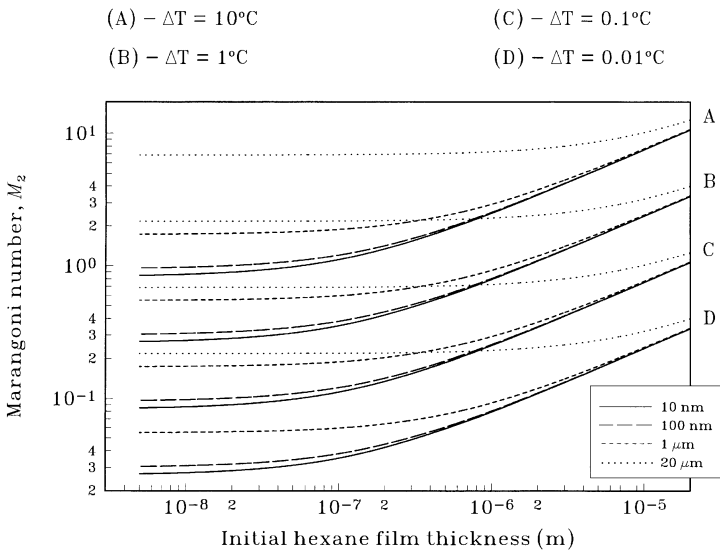


Fig. 6. Dependence of the temperature Marangoni number  $\mathcal{M}_2$  (hexane/vapour interface) on the initial hexane film thickness for different thicknesses of the water  $h_w$  film and temperature differences  $\Delta T$ .

(which is below the hexane film) increases from 5 nm to 20  $\mu\text{m}$ . This effect is more pronounced for thicker evaporating films. The influence of the intermolecular forces (van der Waals forces) are significant for lower temperature difference [compare Figs. 3(a) and (b)], when the van der Waals number increases 100 times. When the thermal capacity of the water film increases and the initial film thickness  $h_0$  decreases, the van der Waals number can reach greater values than these of the evaporation number, and comparable values with these of the degree of non-equilibrium number. It is interesting to note that the magnitudes of the temperature Marangoni numbers  $\mathcal{M}_1$  and  $\mathcal{M}_2$  are

comparable in all cases (see Figs 5 and 6). With increase of the water film thermal capacity, the temperature difference and the initial hexane film thickness  $h_0$ , the influence of interfacial mobility on the film stability increases. The effect on interfacial mobility due to the interfacial temperature gradients for thicker water layer  $h_w$  is more pronounced, and it has a simple physical explanation: with increase of  $h_w$  the disappearance time  $t_d$  and the characteristic wavelength  $l$  increase [see eqs (40) and (50)], which leads to greater values of the temperature Marangoni numbers [see eqs (56) and (58)]. The dependence of the adsorption number  $\mathcal{A}_1$  and the interfacial viscosity

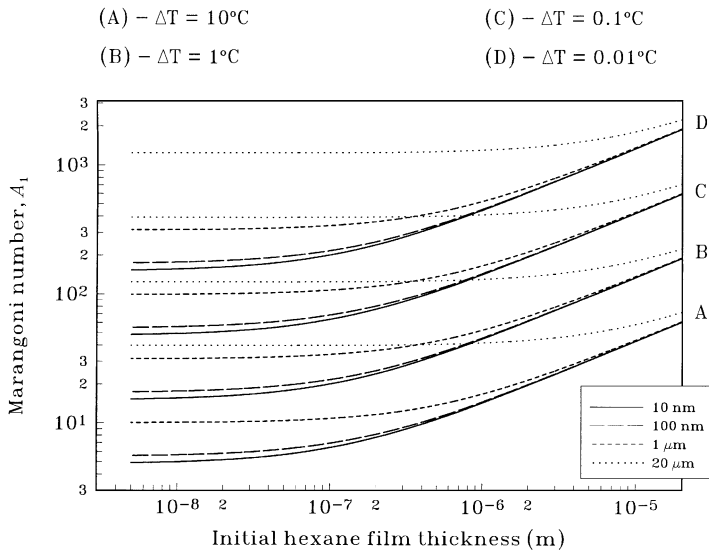


Fig. 7. Dependence of the surfactant Marangoni number  $\mathcal{A}_1$  (water/hexane interface) on the initial hexane film thickness for different thicknesses of the water  $h_w$  film and temperature differences  $\Delta T$ .

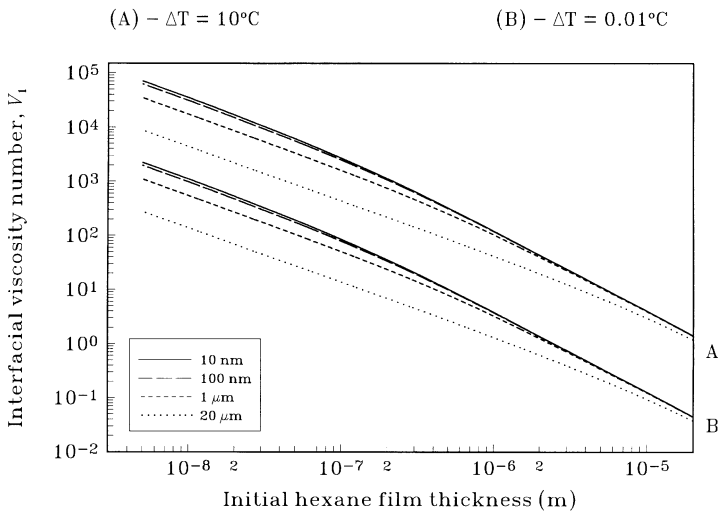


Fig. 8. Dependence of the interfacial viscosity number  $\mathcal{V}_1$  (water/hexane interface) on the initial hexane film thickness for different thicknesses of the water  $h_w$  film and temperature differences  $\Delta T$ .

number  $\mathcal{V}_1$  for typical values for a non-ionic surfactants are plotted in Figs 7 and 8. It is shown that the interfacial viscosity plays an important role for thinner films and greater temperature differences, which is exactly the opposite to the effect of interfacial elasticity. Finally, the greater the temperature difference and the lower the water film thermal capacity suppress the surfactant diffusivity (see Fig. 9).

The corresponding computations for heptane showed that the behaviour and magnitude of the dimensionless parameters are very close to those of the hexane phase.

## 6. CONCLUSIONS

We have developed a theoretical model that allows one to investigate the stability of evaporating two-layered liquid film attached to a heated solid substrate in the presence of surfactant. The model accounts for the instabilities due to surface tension gradients created by fluctuations in the temperature and the surfactant distribution, coupled by the solvent mass loss. Additionally, the role of the van der Waals surface force is also taken into account.

The model is a subject of the following restrictions: (i) small Reynolds number; (ii) small thermal Peclet

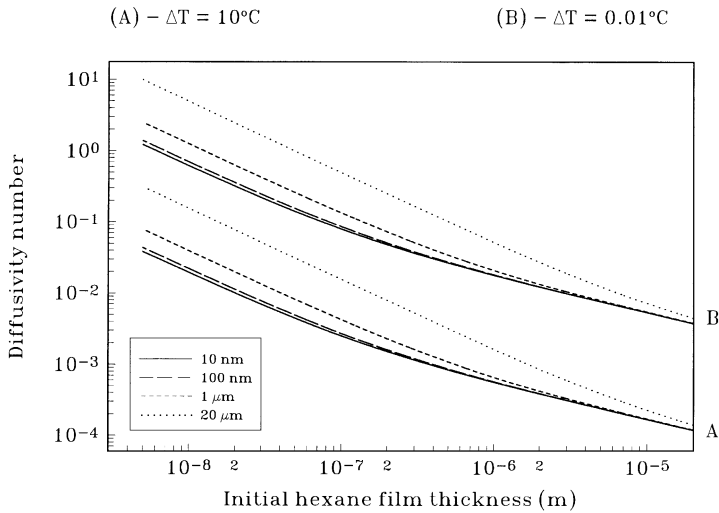


Fig. 9. Dependence of the diffusion number  $\mathcal{D}$  on the initial hexane film thickness for different thicknesses of the water  $h_w$  film and temperature differences  $\Delta T$ .

numbers, (iii) small diffusive Peclet numbers; and (iv) small slope of the interface (long waves). The theory we developed here is a result from the application of the lubrication approximation to the governing equations and allows one to investigate the evolution of the two thin liquid layers in the film and to study the influence of evaporation and surfactant on the film stability.

Four types of dimensionless groups appear in the final form of the governing equations. The first one is connected to the evaporation effects, whilst the second one gives the thermal Marangoni effect on the stability. The last two are related to the effects of the surfactant and of the surface forces on the film stability. Thus, our model allows one to investigate quantitatively the influence of the following physical parameters: bulk viscosity, surface viscosity, surface elasticity, adsorption isotherm of surfactant, CMC of the surfactant in the two liquid films, the surfactant concentration, the intensity of the evaporation, the ratio of the film thicknesses, the role of the solid substrate (in the Hamaker constant), etc.

Numerical analysis of the behaviour and magnitude of the dimensionless groups is performed in this part of the study. The linear stability analysis of the same physical system is a subject of the second part of this study (cf. Danov *et al.*, 1997b). Non-linear analysis of the stability of two-layered film of heavy oil and water is performed in the third part (cf. Paunov *et al.*, 1997).

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