Role of Surface Forces in the Stability of Evaporating Thin Liquid Films That Contain Surfactant Micelles

Theodor Gurkov,* Krassimir Danov,*-¹ Norbert Alleborn,† Hans Raszillier,† and Franz Durst†

*Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics, Faculty of Chemistry, University of Sofia, James Bourchier Avenue 1, Sofia 1126, Bulgaria; and ¹Lehrstuhl für Strömungsmechanik, Technische Fakultät, Friedrich-Alexander Universität Erlangen-Nürnberg, Cauerstrasse 4, D-91058 Erlangen, Germany

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We consider an evaporating liquid film which lies on a planar heated solid substrate. The film contains a dissolved surfactant at a high concentration, so that micellar aggregates exist in the bulk. Linear stability analysis of this system is performed by investigating the time evolution of the amplitude of fluctuation waves. The liquid-vapor interface is regarded as a two-dimensional continuum characterized by intrinsic viscosity, specific adsorption, and surface tension. The latter quantities depend on the instantaneous surfactant concentration of surfactant monomers (subject to fluctuation) and upon the temperature. At small Reynolds and large Peclet numbers, and for thin films, the lubrication approximation model can be applied to solve the hydrodynamic problem. In the balance of normal stress at the fluid interface, we account for the contribution of intermolecular forces. There are van der Waals, electrostatic, steric, and oscillatory structural interactions, which are described in terms of separate components of disjoining pressure. The oscillatory structural forces are due to the presence of surfactant micelles or other colloidal particles in the film. These forces turn out to have the highest magnitude, and are of great importance for the stability. We solve numerically the evolution equation for the fluctuation, thus finding the critical thickness of film rupture and the critical lateral wave number. The influence of the surfactant type and concentration and the relative significance of the particular interactions under different conditions are discussed in detail.

Key Words: evaporating thin liquid films; linear stability analysis; oscillatory structural forces; surfactant at a high concentration; interfacial viscosity; Marangoni temperature and adsorption effects.

1 INTRODUCTION

The stability of thin liquid films (with thickness in the range between 10 nm and 20 μm) has important scientific and technological implications. There are many particular systems, for example, foams and emulsions, layers obtained by coating and deposition processes, and tear films in the human eye, in which the conditions for film rupture represent the main objective of investigation. Numerous studies have been devoted to this problem, either in the geometry of free films or for liquid layers on solid substrates. Scheludko (1) suggested the idea that rupture instability results from amplification of spontaneous fluctuations in the shape of the fluid interfaces, under the action of long-range attractive van der Waals forces. The latter are always operative at small thicknesses, below ~100 nm.

A surfactant monolayer, spread on the liquid interface, is well known to damp the wave motion (2). The phenomenon is due to the fact that as the monolayer is compressed and expanded, the local variations of the adsorption lead to changes in the interfacial tension. The combination of the resulting tension gradients (Marangoni effect) with the interfacial viscous friction brings about suppression of the surface waves.

Linear stability analysis for an isothermal nondraining film on a horizontal plate was carried out by Ruckenstein and Jain (3), who accounted for the van der Waals interactions in the context of the so-called “body force” approach. A gradient of appropriate potential energy was added to the Navier-Stokes equations in the liquid film. Williams and Davis (4) proposed a nonlinear theory for the same system. The treatment was based on the fact that the unstable fluctuation disturbances had wavelengths much larger than the film thickness. Constant interfacial tension was assumed by Williams and Davis (4); i.e., the Marangoni effects were discarded. The nonlinear analysis of de Wit et al. (5) included the variation of the interfacial tension due to local changes in the surface coverage of insoluble surfactants; the interfacial viscosity was neglected in Ref. (5). The flow in a free film was compared with that of a layer on solid substrate. It was shown that the two systems were substantially different from the hydrodynamic viewpoint (5).

A comprehensive linear theory for the fluctuations in the thickness of a plane-parallel film sandwiched between two fluid phases was presented by Maldarelli (6) and Maldarelli and Jain (7), who took into account the Marangoni effects.
connected with the surfactant redistribution. In addition, the
electrostatic interactions were incorporated by utilizing the
body-force approach. Felderhof (8) also studied the linear
dynamics of free liquid films in the presence of repulsive
forces arising from the overlap of diffuse electric double
layers (however, this was done for inviscid flow). A quasi-
static approximation was commonly adopted, in the sense
of using expressions for the Maxwell stress tensor obtained
by solving the static field equations with the assumption
that the electric charge distribution corresponded to thermal
equilibrium at any moment in time.

Recently, some effort has been made to investigate the
dynamics of thin films on which insoluble surfactant (9) or
liquid drop of soluble surfactant (10, 11) is spreading. It
was found that the surfactant-induced interfacial tension gra-
dients drive Marangoni convection; the latter creates film
disturbances which cause thinning in the central region (9).
The surface diffusion of the amphiphilic substance leads to
faster spreading and suppresses the film disturbances (9).
The role of the surfactant solubility in the film phase consists
of decreasing both the disturbances and the surface concen-
tration, and inducing adsorption-driven backflow (10). Ex-
perimental results (11) compare favorably with the theoreti-
cal description of the flow.

Evaporation from or condensation onto the interface of
a wetting liquid film was found to induce a pronounced
destabilization (12–14). Danov et al. (15) demonstrated that
mass transfer toward the film phase can influence signif-
ificantly the magnitude of the interfacial corrugations.
Burelbach et al. (12) extended the nonlinear analysis of
Williams and Davis (4) by investigating the evaporative
and the thermo-capillary effects in films on a heated solid
substrate, without surfactant. The possibilities for the process
of evaporation to take place under nonequilibrium and under
quasi-equilibrium conditions were considered (12). Danov
et al. (14) studied the linear stability of the same system,
but in the presence of soluble surfactant which adsobs on
the liquid/gas boundary. The existence of interfacial viscos-
ity, the Marangoni effect connected with nonuniform adsorp-
tion, and the bulk and the surface diffusivity of amphiphilic
substances were accounted for. In principle, the dynamic
interfacial characteristics (Gibbs elasticity and instantaneous
adsorption, surface diffusivity, and viscosity) are known to
be more important factors than the value of the interfacial
tension itself (2). The surface excess of adsorbed solute
opposes the movement of the phase boundary and delays or
inhibits the appearance of instability.

The purpose of this work is to clarify the role of the
intermolecular forces for the stability of evaporating films
that contain large amounts of surfactant. We adopt the “dis-
joining pressure” approach, which means that the Navier-
Stokes equations in the bulk of the film are not supplemented
with interaction terms. Instead, the boundary conditions are
modified, and in particular the normal stress balance on the
interface includes the contribution of the surface forces.
Maldarelli (6) and Maldarelli and Jain (7) discussed the
“disjoining pressure” and the “body force” approaches in
detail; the former was found to be applicable in the case of
long wavelength disturbances (such are considered here).

When the thickness is sufficiently small, the molecular
interactions lead to changes in the chemical potential (and
of all other intensive thermodynamic properties) inside the
film, with respect to a large bulk phase of the same material.
A corresponding excess pressure may be thought to be ex-
erted on the film surfaces, in the normal direction. This is
called the “disjoining pressure,” \( P \), and is defined to be
positive for repulsion and negative for attraction (16–18).
We shall consider four different components of \( P \), due to
van der Waals, electrostatic, steric, and oscillatory structural
interactions. Whereas the first two have been studied inten-
sively, no attempt has ever been made to explore the role
of the oscillatory structural forces in the stability of films
against hydrodynamic fluctuations.

In general, whenever a surface bounds a liquid phase,
ordering is induced among the particles neighboring the wall
(19). In the case of a film, the structured regions around
the two opposing surfaces overlap, which gives rise to an
oscillatory disjoining pressure and interaction energy. The
amplitude of the latter decays exponentially with increase
in the film thickness (19). The phenomenon is particularly
pronounced in colloidal suspensions such as latexes and mi-
cellar surfactant solutions. In most practical situations one
encounters surfactant concentrations which are well above
the critical micellar concentration (CMC). Then, aggregates
(micelles) composed of amphiphilic molecules exist in the
bulk, along with the monomers (20). It has been established
experimentally that the presence of colloidal particles in liq-
uid films leads to a drastic change of behavior during the
process of thinning. The latter proceeds in a stepwise man-
ner, due to layer-by-layer destruction of the crystal-like
structure of ordered spheres inside the film. This phenome-
non, named stratification, was observed both with latexes
(21) and with surfactant micelles (22). It represents a mani-
festation of the oscillatory structural forces.

In this paper we investigate the influence of structural
interactions on the stability of evaporating films which con-
tain surfactant micelles (above the CMC). The concomitant
oscillatory disjoining pressure turns out to be high and can
lead to either stabilization or destabilization, depending on
the instantaneous film thickness and the micellar volume
fraction. In essence, we use a model and computation scheme
similar to those proposed by Danov et al. (14). The lubrica-
tion approximation is adopted for films which are much
thinner than the wavelength of the unstable corrugations.
Linear analysis is carried out, calculating the critical thick-
ness of rupture. The latter is defined as the thickness of the
basic state at which the fluctuations grow so much that the
liquid/gas interface touches the solid substrate.
2. MATHEMATICAL FORMULATION OF THE PROBLEM

We consider a thin layer of viscous liquid lying on a uniformly heated plate of infinite extension (Fig. 1). The film contains surfactant; the upper phase is gaseous and consists of solvent vapor. A continuous process of evaporation goes on, accompanied by solvent mass flux, momentum transfer, and energy consumption at the liquid/gas interface. Since the solute is nonvolatile, its concentration increases during the film thinning. However, the average adsorption hardly changes, because the total surfactant content always remains above the CMC and the interfacial layer is very close to saturation. We assume that the density of the liquid phase is independent of the composition. The viscosity may increase with time when the volume fraction of surfactant micelles in the film becomes high. The bulk solution will be treated as an incompressible Newtonian fluid. Since the thickness of film rupture is of the order of 5–10 nm, the continuum theory is applicable. We study the stability of films with initial thickness not greater than ~2 μm, hence gravity effects can be neglected.

The transport equations of mass, momentum, energy, and surfactant in the liquid (film) phase are (23)

\[
\nabla \cdot \mathbf{v} = 0, \quad \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} = \frac{1}{\rho} \nabla \cdot \mathbf{P}, \quad [1a]
\]

\[
\frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T = \nabla \cdot (a \nabla T), \quad \frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = \nabla \cdot (D \nabla c). \quad [1b]
\]

Here \( t \) is time, \( \nabla \) is the spatial gradient operator, \( \rho \) and \( T \) are the liquid density and temperature, \( \mathbf{v} \) is the average mass velocity, \( \mathbf{P} \) is the bulk stress tensor in the film, \( c \) is the concentration of surfactant monomers, \( a \) is the thermal diffusivity of the solution, and \( D \) is the bulk diffusion coefficient of the amphiphilic molecules. For Newtonian fluids the stress tensor \( \mathbf{P} \) is connected with the rate-of-strain tensor, \( \mathbf{D} \),

\[
\mathbf{P} = -\rho \mathbf{I} + \mathbf{T}, \quad \mathbf{T} = 2\eta \mathbf{D} = \eta [\nabla \mathbf{v} + (\nabla \mathbf{v})^T]. \quad [2]
\]

where \( \rho \) is the pressure in the liquid phase, \( \mathbf{I} \) is the three-dimensional identity factor, \( \mathbf{T} \) is the viscous part of the stress tensor, \( \eta \) is the shear coefficient of dynamic viscosity, and the superscript ‘T’ denotes transposition.

On the heated substrate, \( z = 0 \) (see Fig. 1), we assume a constant temperature \( T_h \) and no specific adsorption. This is equivalent to zero surfactant diffusion flux, so the boundary conditions at \( z = 0 \) are

\[
\mathbf{v} = 0, \quad T = T_h, \quad \frac{\partial c}{\partial z} = 0. \quad [3]
\]

The balances of mass and surfactant species at the film/vapor interface have the form (2, 12, 14, 24)

\[
J = \rho (\mathbf{v} - \mathbf{u}_{ab}) \cdot \mathbf{n}, \quad [4a]
\]

\[
\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\Gamma \mathbf{v}_s) - \nabla_s \cdot (D_s \nabla \Gamma) = [-D_s \nabla c + c(\mathbf{v} - \mathbf{u}_{ab})] \cdot \mathbf{n}. \quad [4b]
\]

We use the following notation: \( \nabla_s \) is the surface gradient operator, \( J \) is the mass flux due to evaporation, \( \mathbf{u}_{ab} \) is the (nonmaterial) velocity of the dividing surface \( S \), \( \mathbf{n} \) is the vector of the unit normal to \( S \), directed toward the vapor phase (Fig. 1), \( \Gamma \) is the adsorption, \( D_s \) is the interfacial diffusion coefficient, and \( \mathbf{v}_s \) is the continuous tangential velocity component of the material points at \( S \). In the boundary condition for the surfactant concentration [4b], the surface convection and diffusion are taken into account, together with the flux of monomers from the volume.

We consider the limiting case of low density, viscosity, and thermal conductivity of the gaseous phase compared with the liquid (film) phase. Consequently, the stability will be determined solely by the processes in the liquid (12). In this limit the boundary conditions for the conservation of surface-excess linear momentum and energy at \( S \) reduce to

\[
\mathbf{T} \cdot \mathbf{n} = \nabla_s \cdot \mathbf{P}_s + \left( p + \Pi - p_v - \frac{J^2}{\rho_v} \right) \mathbf{n}, \quad [4c]
\]

\[
JL = -(\lambda \nabla T) \cdot \mathbf{n}, \quad [4d]
\]

where \( L \) is the latent heat of vaporization, \( \lambda \) is the thermal conductivity in the film, \( \mathbf{P}_s \) is the surface stress tensor, \( \Pi \) is the disjoining pressure, and \( \rho_v \) and \( p_v \) are the vapor density and pressure, respectively.

FIG. 1.  Sketch of the system under consideration. The evaporating liquid film supposedly contains surfactant micelles, or other spherical particles.
There are many forces which can influence the hydrodynamic stability of thin liquid films: capillary forces, tangential stresses caused by interfacial tension gradients induced by temperature and concentration inhomogeneities (Marangoni effects), buoyancy due to temperature gradients (Bénard convection), and molecular interactions (leading to surface forces). Whereas the first three are mainly responsible for triggering the instabilities, the intermolecular forces come into play in the later stages of film evolution toward rupture. One may distinguish four major types of interactions operative in thin liquid films which are made from micellar surfactant solutions; the disjoining pressure that appears in [4c] is accordingly decomposed into the following contributions: van der Waals, $\Pi_w$, electrostatic, $\Pi_d$, steric, $\Pi_s$, and oscillatory structural, $\Pi_{osc}$:

$$\Pi = \Pi_w + \Pi_d + \Pi_s + \Pi_{osc}. \quad [5]$$

Most extensively studied is the role of the van der Waals component of $\Pi$; for planar films $\Pi_w$ is calculated by a simple explicit equation (19):

$$\Pi_w = -\frac{A}{6\pi h^3}. \quad [6]$$

Here $A$ is the Hamaker constant, and $h$ is the thickness.

When a surfactant-laden fluid interface is disturbed from equilibrium, the latter will be restored either by adsorption from the bulk solution or through surface convection driven by interfacial tension gradients (elasticity of the liquid boundary), in interplay with a specific viscous friction within the surface (the so-called Boussinesq effect). A simple rheological model of the interfacial dynamics is provided by the linear Boussinesq-Sriven constitutive law (2, 25):

$$\mathbf{P}_s = \sigma \mathbf{I}_s + (\eta^s_{sl} - \eta^s_{sh})(\mathbf{I}_s \cdot \mathbf{D}_s) \mathbf{I}_s + 2\eta^s_{sh} \mathbf{D}_s, \quad [7a]$$

$$\mathbf{D}_s = \frac{1}{2}[(\nabla \mathbf{v}_s) \cdot \mathbf{I}_s + \mathbf{I}_s \cdot (\nabla \mathbf{v}_s)^T] \quad [7b]$$

Here $\mathbf{I}_s$ is the two-dimensional idemfactor and $\mathbf{D}_s$ is the surface rate-of-strain tensor. The physical parameters characterizing the fluid boundary are the interfacial tension, $\sigma$, and the intrinsic shear and dilatational surface viscosities, $\eta^s_{sl}$ and $\eta^s_{sh}$, respectively.

In order to close the system of governing equations, one must specify the mass flux, $J$. We will apply the simplified Hertz-Knudsen constitutive relationship, which is widely used (12, 14),

$$J = J_r(T_s - T_c), \quad \text{with } J_r = \text{constant}, \quad [8]$$

where $T_c$ denotes the saturation temperature at the given pressure (when the liquid and vapor would rest in equilibrium), $T_s$ is the actual temperature at the fluid surface, and $J_r$ is a solvent property that depends on $T_s$.

Let us denote by $c_i$ the instantaneous local value of the subsurface bulk concentration of surfactant monomers ($c_i$ fluctuates around the CMC). The adsorption at the interface, $\Gamma$, is connected with $c_i$ via an isotherm (the process of adsorption is assumed to be fast enough, without substantial free energy barriers). For many different surfactants, both nonionic and ionic, below and around the CMC, it was established experimentally that the Langmuir isotherm is adequate (see, e.g., the review by Krachevsky et al. (26), and the references cited therein). Hence, we write

$$\Gamma = \frac{c_i}{c_i + c_l}, \quad [9a]$$

where $\Gamma_\infty$ is the maximum adsorption at saturation and $c_l$ is a constant parameter of the isotherm (related to the free energy of adsorption per molecule). In addition, a surface equation of state connects the interfacial tension, $\sigma$, with $\Gamma$.

Thermodynamically consistent with [9a] is the Szyszkowski equation (26):

$$\sigma = \sigma_s(T_s) + k_B T_s \Gamma_\infty \ln \left(1 - \frac{\Gamma}{\Gamma_\infty}\right). \quad [9b]$$

In [9b] $\sigma_s(T_s)$ is the surface tension of the pure solvent at temperature $T_s$, and $k_B$ is the Boltzmann constant. In most practical systems the temperature difference ($T_s - T_c$) is not high and the parameters $A$, $\Gamma_\infty$, and $c_l$ change insignificantly.

### 3. LUBRICATION APPROXIMATION AND SCALING OF THE MODEL

An evaporating liquid film on a solid plate is sketched in Fig. 1. The liquid/gas interface and the substrate are located at $z = h(x, t)$ and $z = 0$, respectively, in the coordinate system with vertical axis $Oz$ and horizontal coordinates $x$. The lateral and normal velocity components are denoted by $u$ and $w$. It is known that short-wave perturbations disappear faster than those of wavelengths longer than the film thickness, owing to the higher viscous dissipation and capillary damping in the former case (7, 12, 15, 24). Therefore, the long-wave approximation will be adopted here, which simplifies the task of finding a solution to our particular problem. In the context of such an approach one assumes a small Reynolds number, $\rho h_0^2/(\eta u_d) \ll 1$, large thermal Peclet number, $a_t h_0^2/\eta u_d \gg 1$, large diffusivity Peclet number, $D_d h_0^2 \gg 1$, and small slope of the interface, $(\nabla h)^2 \ll 1$ (12, 24). This set of assumptions is often called the “lubrication approximation.” The characteristic time for film thinning is denoted here by $t_d$ (see Eq. [10]), and $h_0$ is the initial thickness.
We shall use a scaling procedure very similar to that proposed originally by Danov et al. (14). The only difference will be the variable viscosity of the liquid phase: in the present analysis the viscosity may change as a function of the micellar volume fraction. In order to minimize the number of dimensionless quantities, Danov et al. (14) defined the disappearance time, $t_d$, and later characteristic length parameter, $l \gg 1$:

$$
t_d = \frac{\rho h_0}{J_2 \Delta T} \left( 1 + \frac{L J h_0}{2\lambda} \right), \quad l = \sqrt{\frac{\sigma \delta_a}{3\eta h_0}},
$$

$$
t = t_d \tau, \quad x = h_0 X, \quad z = h_0 Z, \quad [10]
$$

where $\tau$, $Z$, and $X$ are dimensionless time and space coordinates and $\sigma_0$ is the interfacial tension of the pure solvent at the initial time, $t = 0$. The scales of the velocity and pressure can be found directly from the mass and momentum transport equations [1a]. The dimensionless film thickness, $H$, pressure, $P$, and normal and lateral velocity components, $W$ and $U$, are introduced as follows:

$$
h = h_0 H, \quad p - p_e = \frac{12\eta l^2}{t_d} P, \quad w = \frac{h_0}{t_d} W, \quad u = \frac{2lh_0}{t_d} U, \quad [11]
$$

The leading-order solutions of [1a] and [1b] for the temperature and velocity distributions, which obey also the boundary conditions [3] and [4d] and the constitutive relationship [8], are

$$
\frac{T_h - T}{\Delta T} = \frac{Z}{N_{de} + H}, \quad U = 3Z(Z - H)\nabla || P + \frac{Z}{H} U_s, \quad [12a]
$$

$$
W = Z^2(3H - 2Z)\nabla || P + Z^2\nabla || P \nabla || H - Z^2\nabla || \left( \frac{1}{H} U_s \right), \quad [12b]
$$

where $\Delta T = T_b - T_c$ is a characteristic temperature difference, $\nabla ||$ is the dimensionless horizontal projection of the spatial gradient operator $\nabla$, $U_s$ is the lateral component of the dimensionless velocity at the interface, and the pressure $P(\tau, X)$ does not depend on the $Z$-coordinate. Equations [12a, b] have been derived from Eqs. [1a, b] using the lubrication approximation, which is represented by the set of assumptions listed in the beginning of this section. In addition, quasi-steady state is supposed when the distributions of velocity and temperature are sought for. This means that the time derivatives $\partial \mathbf{v} / \partial t$ in the Navier-Stokes equation [1a] and $\partial T / \partial t$ in [1b] are neglected, and the respective physical quantities, $\mathbf{v}$, $T$, depend on time only implicitly, through $H(\tau, X)$ and $C(\tau, X)$—see below.

The deviation from equilibrium at the evaporating liquid surface is measured by the parameter $N_{de} = \lambda / (L J h_0)$, appearing in [12a]. In the quasi-equilibrium limit, $N_{de} \ll 1$, the process of evaporation is fast and the interfacial temperature, $T_e$, remains practically constant and equal to the saturation temperature, $T_s$. In contrast, the case $N_{de} \gg 1$ corresponds to nonvolatile substances, almost without evaporation, when the mass flux $J$ is very close to zero (and $T_e \approx T_b$).

Leading-order equations for the shape of the dividing surface and for the pressure are obtained after inserting the general solutions [12] into the interfacial mass balance [4a], and in the normal projection of the excess linear momentum equation [4c]:

$$
\frac{\partial H}{\partial \tau} + \nabla || \cdot (HU_s) = \nabla || \cdot (H^3\nabla || P) - \frac{2N_{de} + 1}{2(N_{de} + H)}, \quad [13a]
$$

$$
P = \frac{N_{sl}}{4} \left( \frac{N_{de}^2}{(N_{de} + H)^2} - \hat{\Pi} \right) - \frac{1}{4} \left[ 1 - N_{sl} \frac{\ln(1 - N_s)}{\ln(1 - N_s)} \right] \nabla || H. \quad [13b]
$$

Here $\hat{\Pi}$ denotes the dimensionless disjoining pressure, $\hat{\Pi} = \Pi_{de} / (12\eta l^2)$. In the context of the lubrication approximation $\nabla ||$ may be shown to coincide with the dimensionless form of the surface gradient operator, $\nabla$. The quantity $N_{sl}$ in [13b] is defined as $N_{sl} = h_0 (U_2 \Delta T)^2 / (\rho \sigma_0)$, and characterizes the ratio of the linear momentum loss, caused by evaporation, to the dynamic pressure in the film phase. The last term on the right-hand side of [13b] estimates the influence of the capillary pressure on the film stability. The nondimensionalised Szyszkowski equation of state [9b] has been substituted en route during the derivation, to yield [13b]. The surfactant adsorption, $\Gamma$, is scaled with its value at the CMC, $\Gamma_{CMC}$, thus introducing the new variable $G = \Gamma / \Gamma_{CMC}$. The capacity of the interfacial layer is determined by the number $N_{sl} = \Gamma_{CMC} / \Gamma_s$; the parameter

$$
N_{sl} = - \frac{k_b (T_h + T_e) \Gamma_s}{2\sigma_0} \ln(1 - N_s)
$$

represents a measure of the slope of the functional dependence of the surface tension, $\sigma$, vs. the logarithm of the surfactant concentration, $c$. For most types of amphiphilic molecules $N_s$ is between 0.75 and 0.95, depending on the specific interactions within the adsorption monolayer (27).

A typical value of the coverage at the CMC is $N_s \approx 0.9$. For water/air interfaces $N_{sl}$ ranges from 0.5 to 0.7.

Combining the solutions [12] with the lateral component of the surface-excess linear momentum balance equation
one can find the dimensionless surface velocity, \( U_s \).  

The classical Marangoni adsorption number is related to the Gibbs elasticity of the interfacial layer, \( E_g = -\sigma T \ln \Gamma \). In our particular system \( \Gamma \) is always very close to \( \Gamma_{\text{CMC}} \), and we assume the validity of the isotherm \[9b\]. Under these conditions, \( E_g = k_B T \Gamma_{\text{CMC}} / (1 - N_s) \). The Bousinesq-Scriven constitutive law \[7\] leads to coupling of the \[13a\] \(- [13c]\) and \[15\], which allow us to investigate the respective value at the CMC, \( C_{\text{CMC}} \), and we assume the validity of the isotherm \[9b\]. Table 1 presents typical values of the physical parameters that are relevant for our problem. These data will be used below for calculations; some of them correspond to the example of material properties given by Burelbach et al. \(12\) for relatively dilute aqueous solutions.

### 4. Basic State and Linear Analysis

There is now a complete set of four governing equations, \[13a\]\(- [13c]\) and \[15\], which allow us to investigate the hydrodynamic stability of the film. The nonperturbed (basic) state is assumed to be static, \( U_s = 0 \), with a flat evaporating interface. All quantities that refer to the basic state will be designated hereafter by a subscript “b”. Burelbach et al. \(12\) obtained the respective explicit solutions for the film thickness, pressure, and mass flux. We shall use the following expressions:

\[
H_b = [N_{de}^2 + (1 + 2N_{de}(1 - \tau))^2]^{1/2} - N_{de},
\]

\[
J_b / J_r = N_{de} / (N_{de} + H_b).
\]

The time for which the film would vanish as a result of evaporation only (without any fluctuations) is called the “disappearance time,” \( t_d \); it corresponds to \( \tau = 1, H_b = 0 \). Actually, unstable disturbances in the thinning film will cause rupture at times earlier than \( t_d \). With rising \( N_{de} \) (and simultaneously diminishing \( J_r \)) the evaporation process slows down, since the solvent is then less volatile and \( J_b \) decreases.

We consider only the case when the total surfactant concentration in the film, \( c_{\text{tot}} \), is above the CMC. Therefore, in the nonperturbed state the individual amphiphilic molecules (the monomers which float freely in the solution) will have a constant concentration, equal to \( c_{\text{CMC}} \). The rest of the surfactant will be engaged in micellar aggregates \(20\). Consequently, \( C_0 = 1 \) and \( G_b = 1 \), as the single molecules exchange between the bulk and the interface. The instantaneous adsorption, \( \Gamma \), and subsurface monomer concentration, \( c \), fluctuate around the corresponding values at the CMC \( \Gamma_{\text{CMC}} \).
The perturbations will be assumed to occur at fixed composition of the liquid phase. In other words, both \( c \) and \( c_{\text{tot}} \) will change, but

\[
\frac{c}{c_{\text{tot}}} = \frac{c_{\text{CMC}}}{c_{\text{tot,b}}}, \quad \frac{C}{C_{\text{tot}}} = \frac{C_{\text{tot,b}}}{C_{\text{tot,b}}} = C.
\]  

[17]

Here \( C_{\text{tot}} = c_{\text{tot}}/c_{\text{CMC}} \) and \( C_{\text{tot,b}} = c_{\text{tot,b}}/c_{\text{CMC}} \) denote the dimensionless total concentrations. The assumption set forth by Eq. [17] is valid only when the characteristic time of micellization is larger than the inverse frequency of the waves (fast fluctuations). Actually, the surfactant aggregates are subject to complicated dynamic processes in the solution, involving an exchange of molecules with the bulk. Typical time scales are of the order of \( 10^{-4} - 5 \times 10^{-2} \) s [20]. It should be emphasized that our equation [15] applies for sufficiently fast fluctuations only (which is likely to be the case in reality). Correspondingly, no source terms connected with micellization were added to the transport equation for monomers, Eq. [1b] (the latter is relevant for the development of disturbances).

On the other hand, usually the thickness of the basic state of the film decreases slowly compared to the characteristic time of micellization. Therefore, we assume that in the basic state the bulk concentration of individual amphiphilic molecules remains constant and refers to micellar equilibrium, i.e., one simply writes \( c_{\text{b}} = c_{\text{CMC}} \), \( C_{\text{b}} = 1 \). In summary, the micellization processes are considered to be slower than the fluctuations but faster than the film thinning due to evaporation.

For the linear analysis of the system [13a]–[13c] and [15] we introduce small perturbations with respect to the basic state. The disturbances are in the form of surface waves with dimensionless wave vector \( \mathbf{k} \) and lateral wave functions \( F_0 = \cos (\mathbf{k} \cdot \mathbf{X}) \) and \( F_1 = \sin (\mathbf{k} \cdot \mathbf{X}) \). The perturbed physical variables (pressure, interfacial velocity and shape, adsorption, and surfactant concentration) can be represented as follows:

\[
H = H_b(1 + H_t F_0), \quad P = P_b + P_t F_0, \quad U_t = U_t F_1, \quad [18a]
\]

\[
G = 1 + G_t F_0, \quad C = 1 + C_t F_0,
\]

\[
C_{\text{tot}} = C_{\text{tot,b}}(1 + C_t F_0). \quad [18b]
\]

All fluctuation amplitudes carry the subscript “f”; they depend only upon the dimensionless time, \( \tau \). Note the specific definition of \( H_t \), relative to the film thickness in the basic state, \( H_b \), which continuously decreases owing to evaporation. The disjoining pressure, \( \Pi \), is a function of the local thickness, \( H \), and the total surfactant content, \( C_{\text{tot}} \). Accordingly, we may write

\[
\Pi(H, C_{\text{tot}}) = \Pi_b(H_b, C_{\text{tot,b}}) + \left[ \left( \frac{\partial \Pi}{\partial H} \right)_b H_t H + \left( \frac{\partial \Pi}{\partial C_{\text{tot}}} \right)_b C_{\text{tot,b}} C_t \right] F_0. \quad [19]
\]

After linearizing the boundary condition [13b] and the normal and tangential projections of the vectorial equation

<table>
<thead>
<tr>
<th>Physical quantity</th>
<th>Symbol</th>
<th>Dimension</th>
<th>Value(s) used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor/liquid equilibrium temperature</td>
<td>( T_e )</td>
<td></td>
<td>373.15</td>
</tr>
<tr>
<td>Vapor density</td>
<td>( \rho_v )</td>
<td>kg/m(^3)</td>
<td>0.60</td>
</tr>
<tr>
<td>Liquid density</td>
<td>( \rho_l )</td>
<td>kg/m(^3)</td>
<td>960.0</td>
</tr>
<tr>
<td>Dynamic viscosity of the liquid phase</td>
<td>( \eta )</td>
<td>kg/(m \cdot s)</td>
<td>( 2.88 \times 10^{-4} )</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>( \lambda )</td>
<td>J/(m \cdot s \cdot K)</td>
<td>0.680</td>
</tr>
<tr>
<td>Latent heat of vaporization</td>
<td>( L )</td>
<td>J/kg</td>
<td>( 2.3 \times 10^6 )</td>
</tr>
<tr>
<td>Evaporation mass flux coefficient (Eq. [8])</td>
<td>( J_1 )</td>
<td>kg/(m(^2) \cdot s \cdot K)</td>
<td>2.960</td>
</tr>
<tr>
<td>Hamaker constant</td>
<td>( A )</td>
<td></td>
<td>( 1.15 \times 10^{-20} )</td>
</tr>
<tr>
<td>Surface tension of the pure solvent</td>
<td>( \sigma_0 )</td>
<td>N/m</td>
<td>0.030</td>
</tr>
<tr>
<td>Temperature coefficient of the surface tension</td>
<td>( (\partial \sigma/\partial T) )</td>
<td>N/(m \cdot K)</td>
<td>( -1.80 \times 10^{-4} )</td>
</tr>
<tr>
<td>Bulk diffusion coefficient of surfactant molecules</td>
<td>( D )</td>
<td>m(^2)/s</td>
<td>( 5.0 \times 10^{-9} )</td>
</tr>
<tr>
<td>Surface diffusion coefficient</td>
<td>( D_s )</td>
<td>m(^2)/s</td>
<td>( 5.0 \times 10^{-9} )</td>
</tr>
<tr>
<td>Critical micellar concentration (CMC)</td>
<td>( c_{\text{CMC}} )</td>
<td>mol/m(^3)</td>
<td>8.0</td>
</tr>
<tr>
<td>Adsorption at the CMC</td>
<td>( \Gamma_{\text{CMC}} )</td>
<td>mol/m(^2)</td>
<td>( 3.0 \times 10^{-6} )</td>
</tr>
<tr>
<td>Surface viscosity at the CMC</td>
<td>( \eta_s )</td>
<td>kg/s</td>
<td>( 1.0 \times 10^{-8} )</td>
</tr>
<tr>
<td>Surface coverage at the CMC</td>
<td>( N_c )</td>
<td></td>
<td>—</td>
</tr>
<tr>
<td>Surface dissociation constant of ionic amphiphiles</td>
<td>( K_d )</td>
<td>mol/m(^3)</td>
<td>( 1.16 \times 10^{2} )</td>
</tr>
<tr>
<td>Micellar diameter</td>
<td>( d )</td>
<td>m</td>
<td>( 4.8 \times 10^{-9} )</td>
</tr>
<tr>
<td>Aggregation number of micelles</td>
<td>( N )</td>
<td></td>
<td>67</td>
</tr>
</tbody>
</table>
and on the wave number, the coefficients of the problem [21] depend on time, $H_t$, and total surfactant monomer fluctuation, $S_t$. The latter is an auxiliary quantity, defined as $S_t = G_t + N_c H_t C_t$. The final expressions are

$$
P_t = p_h H_t + p_b S_t, \quad p_h = -\frac{N_{at} N_{de}^2 H_b}{2(N_{de} + H_b)^3} - \frac{\partial \Pi}{\partial H} \bigg|_{H_b} + \frac{k^2 H_b}{4} (1 - N_a), \quad [20a]
$$

$$
p_s = -\frac{1}{(1 + f_s)(1 - N_a)} C_{ion,b} \left( \frac{\partial \Pi}{\partial C_{ion}} \right)_{H_b}, \quad [20b]
$$

$$
k \cdot U_t = u_h H_t + u_s S_t,
$$

$$
u_h = \frac{H_b k^2}{1 + f_s} \left[ \frac{3 p_h - 2 N_{at} N_{de}}{(N_{de} + H_b)^3} \right], \quad [20c]
$$

$$
u_s = \frac{H_b k^2}{1 + f_s} \left[ \frac{2 N_{de}}{(1 - N_a)(1 + f_s)} + 3 H_b p_s \right], \quad [20d]
$$

where the surfactant factor, $f_s = N_c H_b/(1 - N_a)$, is calculated using the dimensionless form of the Langmuir isotherm [9a], with $G_b = 1$. $f_s = k^2 N_c H_b$ is the interfacial viscosity factor, and $k^2 = \mathbf{k} \cdot \mathbf{k}$ is the squared modulus of the wave vector. No time derivatives are present in [20]. The temporal evolution of $H_t$ and $S_t$ may be determined after substitution of the perturbations [18] into the surface mass and species transport equations, [13a] and [15]. The subsequent linearisation of the resulting system yields

$$
\frac{dH_t}{d\tau} = a_{11} H_t + a_{12} S_t, \quad \frac{dS_t}{d\tau} = a_{21} H_t + a_{22} S_t. \quad [21]
$$

The coefficients of the problem [21] depend on time, $\tau$, and on the wave number, $k$, in the following complicated manner:

$$
a_{11} = \frac{(2 N_{de} + 1)(N_{de} + 2 H_b)}{2 H_b (N_{de} + H_b)^3} - u_h - k^2 H_b^2 p_h, \quad [22a]
$$

$$a_{12} = -u_s - k^2 H_b^2 p_s, \quad [22a]
$$

$$a_{21} = -N_c \left( \frac{(2 N_{de} + 1)(N_{de} + 2 H_b)}{2(N_{de} + H_b)^2} - 2 u_h \right), \quad [22b]
$$

$$a_{22} = -2 u_s - k^2 N_c \frac{N_{at} + f_s}{1 + f_s}. \quad [22b]
$$

It should be noted that the derivatives of the disjoining pressure, which occur in [20a] and [20b], refer to the basic state. Hence they are easily calculated from the analysis of the intermolecular forces acting in plane-parallel film geometry.

The time dependence of the nonperturbed state affects the wavelength at which the fluctuation has a maximum increment at a given moment. Following the idea of linear stability analysis of a draining thin liquid film (7), we shall define the critical rupture time, $\tau_c$, that refers to an initial amplitude $H_t(0)$. For a single perturbation mode with wave number $k$ the film will rupture at the moment $\tau_c$, when the corrugated liquid/gas interface just touches the solid substrate; i.e., $H_t(\tau = \tau_c) = 1$. Then, the minimum of $\tau_c$ for all possible wave numbers $k$ gives the critical time, $\tau_c$. The corresponding dimensionless thickness of the basic state is called here the “critical film thickness,” $H_c = H_b(\tau_c)$.

In order to solve the linear system of equations [21], one needs initial conditions. The initial amplitude of the thickness fluctuation, $H_t(0)$, and the initial thickness of the basic state, $h_0$, have values chosen by us. In other words, $h_0$ and $H_t(0)$ are free parameters of the model. However, the total surfactant monomer fluctuation at time zero, $S_t(0)$, is not an independent quantity. It can be found by means of an asymptotic analysis at $\tau \to 0$ (14). We assume that the perturbation amplitudes are proportional to the exponential time factor $\exp(\omega \tau)$, where $\omega$ is the initial increment/decrement. With such a type of functional dependence, the set of equations [21] transforms into a dispersion relationship for $\omega$. There are two solutions, but we choose the greater one, $\omega_i$:

$$
\omega_i = \frac{1}{2} \left\{ a_{11}(0) + a_{22}(0) \right\} + \sqrt{(a_{11}(0) - a_{22}(0))^2 + 4a_{12}(0)a_{21}(0)}. \quad [23]
$$

Let us denote by $k_0$ the wave number at which $\omega_i = 0$. Then, the initially unstable waves ($\omega_i > 0$) are those with $0 < k^2 < k_0^2$. For each $k$ the initial condition for $S_t$ that leads to faster film rupture is $S_t(0) = a_{21}(0) H_t(0)/[\omega_i - a_{22}(0)]$. Some typical curves $\omega_i(k)$ are shown below. The very long waves ($k \ll 1$) are unstable owing to thermal effects connected with evaporation: in the thinner part of the film the interfacial temperature is higher, which accelerates the vaporization and the thickness decreases even faster.

Numerical solution of the problem [21] (which represents a set of two ordinary differential equations) is obtained by using Runge-Kutta fourth-order scheme with dimensionless time step $1 \times 10^{-4}$. The derivatives $\partial \Pi/\partial H_b$, $\partial \Pi/\partial C_{ion,b}$ in [20a] and [20b] are also found numerically. Some difficulties connected with the stability of the procedure may arise at high surfactant concentrations, when the derivatives of $\Pi$ become very large and the set [21] is rendered stiff. In such cases we apply another computational scheme, whose idea is to increment the functions $H_t(\tau)$, $S_t(\tau)$ over a small time interval $\Delta \tau$ by solving Eqs. [21] with constant coefficients, $a_i$, taken in the middle of the time interval ($\tau + \Delta \tau/2$). This method has improved
convergence, especially for stiff systems, as described elsewhere (14).

Before considering in detail the influence of particular molecular interactions, it is instructive to summarize the main assumptions of our hydrodynamic model:

(i) We neglect the temperature dependence of the density, \( \rho = \rho(T) \) (i.e., Bénard convection is discarded). Such a simplification is acceptable because the effect due to the temperature dependence of the interfacial tension, \( \sigma(T) \), is much more important in thin films, as discussed by Edwards et al. (2). Similarly, the other material properties like viscosity, diffusion coefficient, and adsorption, are supposed not to be functions of \( T \).

(ii) The lubrication approximation is adopted, which is reasonable for thin films, in the sense of very small thickness compared to the wavelength of the relevant fluctuation disturbances. Inherent to this model treatment are the assumptions of small Reynolds number (negligible inertia), large Peclet numbers (predominant diffusion of heat and species, insignificant convective transfer), and small slope of the surface.

(iii) The adsorption, \( \Gamma \), is always supposed to correspond to local equilibrium of the interface with the (fluctuated) subsurface monomer concentration, \( c \). In other words, the physical process of adsorption is regarded as fast enough, without substantial free energy barriers. Such a view is supported by the experimentally confirmed fact that the exchange of individual surfactant monomers, which float freely in the bulk solution, with the molecules engaged in big aggregates (micelles) is really very rapid (20). The characteristic times fall in the range of nanoseconds to microseconds (20). This is the so-called fast relaxation process (20). The rate of exchange of molecules between a large interface and the adjacent subsurface zone should be of the same order of magnitude. The above reasoning justifies the applicability of the equilibrium isotherm, Eq. [9a], to connect \( \Gamma \) with \( c \) even in the fluctuated state.

(iv) The formation and disintegration of micelles as distinct objects involve a mechanism which is actually a sequence of many steps (each representing an exchange of one molecule). The overall sequence (perceived as creation or disappearance of one micelle as a whole) has been identified as a slow relaxation process, whose characteristic time is of the order of \( 10^{-4} \cdots 5 \times 10^{-2} \) s (20). In the context of our model, it is natural to consider the micellization to be slower than the fluctuations in the film. For this reason, the local disturbances are assumed to occur at constant composition; i.e., the concentrations of the monomers and micelles fluctuate proportionally (Eq. [17]), as no micellar equilibrium succeeds to establish. Correspondingly, no source term connected with micellization is included in the mass balance equation of surfactant monomers, Eq. [1b], which is relevant for the development of fluctuations.

On the other hand, the thinning of the basic state of the film is usually slower than the characteristic time of micellization. Therefore, we assume that in the basic state the bulk concentration of individual amphiphilic molecules remains constant and refers to micellar equilibrium; i.e., it is simply \( c_0 = c_{\text{CMC}}, \ C_0 = 1 \).

(v) We reason that there is no specific adsorption of any substance on the solid substrate. With the surfactant this premise gives the boundary condition [3], and with the ionic species it leads to zero slope of the potential: \( (\partial \Phi / \partial z)_{z=0} = 0 \) — see Section 5.2.

5. CONTRIBUTIONS OF MOLECULAR INTERACTIONS TO THE DISJOINING PRESSURE

5.1. Van der Waals Forces

We accept the simple expression [6] for the description of the van der Waals disjoining pressure in a plane-parallel film, as done by other authors (7, 14). Equation [6] does not take into account the electromagnetic retardation (19). In other words, the parameter \( A \) (the Hamaker constant) is assumed to be independent of \( h \). The rigorous theory predicts that \( A \) should fall progressively with increasing \( h \) (28). For our purpose it is not necessary to include this effect because, as will be shown below, the van der Waals interactions start to influence the stability of evaporating films only at very small thicknesses, when the corrections due to retardation are insignificant.

Let us now comment on the value of \( A \) for the system under consideration, which is of type solid/liquid/gas (Fig. 1). The compound Hamaker constant, \( A_{\text{solid/liquid/gas}} \), can be conveniently represented as a combination of other constants that correspond to simpler systems:

\[
A_{\text{solid/liquid/gas}} = \frac{1}{2} \left( A_{\text{liquid/gas/liquid}} + A_{\text{solid/gas/solid}} + A_{\text{solid/liquid/solid}} \right). \tag{24}
\]

The interactions in the gaseous phase may be neglected because of the low density. Many experimental data and theoretical estimates of \( A \) are available in the literature for different substances interacting across vacuum or across a liquid phase. We shall utilize the information collected in the book by Israelachvili (19). Thus, for the particular example of aqueous films on polystyrene or polyvinylchloride (PVC) plates, Eq. [24] yields \( A_{\text{PVC/water/gas}} = -1.15 \times 10^{-20} \) J. The negative value of \( A \) means that the van der Waals forces are repulsive. In contrast, if we take polytetrafluoroethylene (PTFE) as a solid substrate, then a positive compound Hamaker constant would result: \( A_{\text{PTFE/water/gas}} = +0.265 \times 10^{-20} \) J. In the latter case there is van der Waals attraction. Obviously, the interactions are sensitive to the chemical nature of the materials, and
The dimensionless potential at the solid wall, \( \Phi \).

For example, let \( S \) be the surfactant ions and the counterions, respectively. We shall consider also the presence of an inorganic salt, \( A^-K^+ \), with the same cation \( K^+ \).

The quantity \( c_{el,0} \) in Eq. [25] represents the total electrolyte content at a point where \( \Phi = 0 \), i.e., in the bulk of an imaginary solution which would rest in electro-chemical equilibrium with the film. In reality, however, the evaporating liquid layer may not be in equilibrium with any homoge-

\[ \Pi_{el} = 2k_B T c_{el,0} [\cosh (\phi_0) - 1]. \]  

[25]

\( \phi_0 \) is defined as \( \phi_0 = e\Phi_0/(k_B T) \), where \( \Phi_0 = \Phi(z = 0) \) (Fig. 2), and \( e = 4.8 \times 10^{-10} \) CGSE is the elementary charge. We assume that only monovalent electrolyte is dissolved in the film. For example, let \( S^- \) and \( K^+ \) be the surfactant ions and the counterions, respectively. We shall consider also the presence of an inorganic salt, \( A^-K^+ \), with the same cation \( K^+ \). The quantity \( c_{el,0} \) in Eq. [25] represents the total electrolyte content at a point where \( \Phi = 0 \), i.e., in the bulk of an imaginary solution which would rest in electro-chemical equilibrium with the film. In reality, however, the evaporating liquid layer may not be in equilibrium with any homoge-

\[ \kappa^2 = \frac{8\pi e^2 c_{el,0}}{\epsilon k_B T}, \]  

[26]

where \( \epsilon \) is the dielectric permittivity of the medium. Typical values of \( \kappa^{-1} \) are below 1 nm for electrolyte concentrations above 0.1 mol/L. For our particular system of evaporating film (in its basic state), the validity of the condition \( kh \gg 1 \) is maintained during the whole process of thinning, until the moment of rupture. In this framework, the electrostatic problem is simplified considerably by introducing the assumption originally proposed by Verwey and Overbeek (29): \( \Phi_0 \approx 2\Phi_1(h) \). Here \( \Phi_1(h) \) denotes the potential at a distance \( h \) from a single charged interface (bounding a semi-infinite liquid phase) with the same surface potential, \( \Phi_s \), as that in the case of a film (cf. Fig. 2). For planar geometry the nonlinear Poisson-Boltzmann equation, which is to be satisfied by \( \Phi_1 \), has an analytical solution. The standard electrostatic theory (17, 19, 26) then yields a relationship between \( \phi_0 \) and \( \phi_s \):

\[ \tanh \left( \frac{\phi_0}{8} \right) = \tanh \left( \frac{\phi_s}{4} \right) \exp(-\kappa h), \]  

[27]

Another useful equation follows from the boundary condition that establishes a link between the charge and the potential at the liquid/gas interface. One should account for the partial dissociation of the polar heads of the adsorbed surfactant molecules. Even when the monomers in the bulk are fully ionized, a closely packed surface layer is likely to exhibit a degree of dissociation considerably lower than 100%. This effect has been studied mostly with ionic micelles (30). We accept the notion of existing "chemical" equilibrium (19),

\[ \text{SK} \leftrightarrow S^- + K^+, \]  

[28]

which involves the neutral species SK and the ions \( S^- \) residing on the interface. The counterions \( K^+ \) that can be exchanged are located near the surface, where their bulk concentration is \( c_{el,0} \exp(-\phi_s) \). We define the degree of dissociation, \( \alpha_s \), connected with the "reaction constant" \( K_d \):

**FIG. 2.** Schematic diagram of the electric potential inside the film. The liquid/gas interface is charged because of adsorbed ionic surfactant molecules that may be partially dissociated.
\[
\alpha_s = \frac{1}{1 + \frac{c_{el,0}}{K_d} \exp(-\phi_s)}.
\]

Thus, the surface charge is equal to \((- e\alpha_s \Gamma)\) and the electrostatic boundary condition at \(z = h\) acquires the form

\[
- \frac{e}{k_B T} \frac{d\phi}{dz} \bigg|_{z=h} = \sqrt{2} \left[ \cosh(\phi_s) - \cosh(\phi_0) \right].
\]

\[
= \frac{\kappa}{2 c_{el,0}} \alpha_s \Gamma.
\]

The next task is to find \(c_{el,0}\). This can be accomplished by considering the material balances of the ions in the film:

\[
K^+: \quad c_{el,0} \int_0^h \exp\left( -\frac{e\phi}{k_B T} \right) dz = c_{el} + \alpha_s \Gamma, \quad [31a]
\]

\[
S^- + A^-: \quad c_{el,0} \int_0^h \exp\left( \frac{e\phi}{k_B T} \right) dz = c_{el} h. \quad [31b]
\]

The real concentration of electrolyte in the liquid layer is denoted here by \(c_{el}\), which is a known quantity (see below). Validity of the Boltzmann law is always assumed, so that \(c_{el,0} \exp\left( -e\phi/(k_B T) \right)\) is the local concentration of \(K^+\) species at the place where the potential is \(\Phi\). Straightforward application of the classical electrostatic theory leads to the following connection between \(c_{el,0}\) and \(c_{el}\),

\[
\frac{c_{el}}{c_{el,0}} = \cosh \phi_0 - \frac{\sqrt{2}}{k_B h} \left\{ \sqrt{\cosh \phi_0 + 1} \right. \\
\times \left. \operatorname{E} \left( \arcsin \sqrt{\frac{\cosh \phi_s - \cosh \phi_0}{\cosh \phi_s - 1}}, \sqrt{\frac{2}{\cosh \phi_0 + 1}} \right) \\
+ \frac{2 \sqrt{\cosh \phi_s - \cosh \phi_0}}{1 - \exp(-\phi_s)} \right\}, \quad [32]
\]

where \(\operatorname{E}(\varphi, m) = \int_0^\varphi \sqrt{1 - m^2 \sin^2 \psi} \, d\psi\) is the elliptic integral of second kind.

The liquid phase in our system may have a complex composition, containing salt, \(\Lambda^+ \cdot K^-\), surfactant monomers, \(S^-\), and also micelles which are partially dissociated and have released some counterions, \(K^+\). Such solutions have been studied and the question of how to find the ionic strength has been discussed. In general, it was established that the charged micelles themselves should not be included explicitly, as they contribute in an intricate manner to the screening of the electrostatic interactions between two film surfaces or colloidal particles. Richetti and Kékicheff (31) fitted experimental results for the interaction force vs. separation distance between adsorption layers of surfactant in solutions above the CMC. It was found that the effective ionic strength of the surfactant is determined solely by the completely dissociated monomers plus the counterions released from the micelles. Using Eq. [3] of Richetti and Kékicheff (31), we may write for our particular system

\[
c_{el} = c_{AK} + \frac{1}{2} \left[ 2 c_{CMC} + \alpha_m (c_{tot} - c_{CMC}) \right]. \quad [33]
\]

The degree of micellar dissociation, \(\alpha_m\), can be rationalized again with the help of the concept of a "reaction," Eq. [28]. Since the actual concentration of the counterions \(K^+\) in the film volume is practically equal to \(c_{el}\), an estimate for \(\alpha_m\) may be extracted from the relationship \(\alpha_m = K_m/(K_m + c_{el})\). The dissociation constant \(K_m\) has a meaning analogous to \(K_d\).

There is now a set of three nonlinear equations, [27], [30], and [32], which contain three unknowns, \(\phi_s\), \(\phi_0\), and \(c_{el,0}\). This set is solved numerically for arbitrary values of the film thickness in the basic state, \(h\). Of course, the overall electrolyte content, \(c_{el}\), is a function of \(h\) through \(c_{el} \) and \(c_{AK}\), as the amount of dissolved material is conserved in the process of film thinning. Then, \(\Pi_{el}\) is readily obtained from Eq. [25].

Let us finally discuss the assumption that the concentration of surfactant monomers does not depend on the \(z\)-coordinate (up to the leading order). This was used when solving the hydrodynamic problem (at the end of Section 3), and may be expected to fail with ionic surfactants because of the influence of the electric potential. In fact, the film is thick, so that the requirement \(kh \gg 1\) is met. Hence, the dependence \(c(z)\) will be negligible in the interior of the film and will be appreciable only in a narrow zone very close to the fluid interface. On the other hand, the Langmuir adsorption isotherm can be considered to hold with the bulk value of \(c\) instead of the true subsurface concentration, \(c\). (cf. Eq. [9a]). The latter circumstance is supported by available experimental evidence (see, e.g., the review by Kratchevsky et al. (26) and references cited therein). These arguments justify the applicability of our analysis even to systems with ionic surfactants.

5.3. Steric Repulsion

We shall take into account the possibility of the appearance of steric interactions at sufficiently small thickness of the film in its basic state. The adsorbed surfactant molecules often possess voluminous hydrophilic heads, e.g., when the polar part of the amphiphile consists of oxyethylene chains. The latter may overlap at close approach of two layers packed with surfactant. Our films always contain micelles that are pressed (and deformed) between the surfaces when the separation distance is very small.
mechanics. For the sake of estimates, Israelachvili (19) proposed an analytical expression in which both the oscillatory period and the decay length of the forces were set equal to the particle diameter, $d$. This oversimplified expression was proved to be unsatisfactory (32), as the experimental data with stratifying films give indications of an appreciable dependence of the oscillatory period and decay length on the particle volume fraction. In order to obtain a quantitatively correct equation, Kralchevsky and Denkov (32) adopted a semi-empirical approach. They analyzed the more sophisticated theories of other authors, and succeeded in constructing a convenient explicit equation for the calculation of the oscillatory structural contribution to the disjoining pressure, $\Pi_{osc}$. The result was

$$\Pi_{osc} = P_0 \cos \left( \frac{2\pi h}{d_1} \right) \exp \left( \frac{d_3^2 - h}{d_2} \right), \quad [35a]$$

for $h > d$. Here $h$ is the film thickness, $d$ denotes the diameter of the particles, and $P_0$ is the osmotic pressure in the film interior. It should be emphasized that Eq. [35a] is valid only for hard spheres. $P_0$ may be found from the Carnahan-Starling equation,

$$P_0 = \frac{\rho k_B T}{1 + \varphi + \varphi^3 - \varphi^3} (1 - \varphi^3), \quad [35b]$$

where $\varphi$ is the volume fraction and $\rho$ is the number density of the particles in the solution: $\rho = 6\varphi/(\pi d^3)$ (32).

The oscillatory period, $d_1$, and the decay length, $d_2$, are determined by empirical relationships:

$$\frac{d_1}{d} = \sqrt{\frac{5}{3}} + 0.23728\Delta\varphi + 0.63300(\Delta\varphi)^3, \quad [35c]$$

$$\frac{d_2}{d} = \frac{0.48663}{\Delta\varphi} - 0.42032; \quad \Delta\varphi = \frac{\pi}{3\sqrt{2}} - \varphi. \quad [35d]$$

The maximum solid content with three-dimensional close packing of rigid spheres is $\varphi_{max} = \pi/(3\sqrt{2}) \approx 0.7405$. Kralchevsky and Denkov (32) tested the numerical results yielded by Eqs. [35] against the outcome from the statistical mechanical theories of other authors. Reasonably good agreement was reported.

The considerations outlined above are utilized in this paper to study the impact of the oscillatory structural forces on the instabilities in an evaporating film which contains micelles. $\Pi_{osc}$ is calculated from Eq. [35a] and is inserted into Eq. [5]. $\Pi_{osc}$ depends on the thickness, $h$, both explicitly and implicitly (through $\varphi$). That is why the maxima of the curve $\Pi_{osc}(h)$ will not be positioned at $h = d, 2d, 3d$, etc., as drawn in Fig. 3. (Note that Fig. 3 shows a simplified graph, for $d_1 \approx d$ and $\varphi = \text{constant}.$) The magnitude of $\Pi_{osc}$
6. NUMERICAL RESULTS AND DISCUSSION

In Fig. 4 we plot the computed critical thickness of film rupture as a function of the initial surfactant concentration ($h_0 = 50$ nm). Each point was obtained by scanning through all possible wavenumbers of unstable modes, $k$, finding the maximum value of $H_c$. A typical dependence of the rupture thickness upon $k$ is shown in Fig. 5. With rising concentration $H_c$ is observed to increase (Figs. 4 and 5), which means more pronounced instability. This may seem surprising, because a large amount of surfactant is commonly believed to stabilize the film. An explanation of our peculiar finding is given below. It is connected with the role of the micelles, i.e., with the oscillatory structural forces.

We wanted to check the influence of the electrostatic interactions ($\Pi_{el}$). With ionic amphiphiles, however, a change of concentration leads to a change of the Debye screening length, $\kappa^{-1}$. This in turn will affect $\Pi_{osc}$, through $d_{eff}$ and the direct electrostatic interactions due to adsorbed ionic surfactant on the particle volume fraction, $\varphi$. In order to exclude the indirect impact on $\Pi_{osc}$, all calculations in Fig. 4 were performed as for (1), but without added salt; (2) open triangles: no electrostatic interactions are considered (nonionic surfactant). Such is the case also with (4) and (5). (1–3, and 5): $\Delta T = 0.10^\circ$; (4): $\Delta T = 10.0^\circ$. (1–3): Constant viscosity of the bulk liquid in the film is assumed; (4 and 5): the viscosity increases with the volume fraction, according to the hard-sphere model.

![Image](image.png)

**FIG. 4.** Role of the surfactant concentration in the film stability. $d_{eff} = d_{core} + 2\kappa^{-1}$, which is identified with $d$ in [35]. $d_{core}$ denotes the hydrodynamic diameter of the micelles themselves, measured, for instance, by dynamic light scattering; $\kappa^{-1}$ is the Debye screening length.

Another matter of concern is the rheological behavior of the liquid in the film: as the evaporation proceeds the solution becomes increasingly more concentrated, and this will affect the viscosity. Insofar as the micelles are regarded as hard spheres, it is reasonable to adopt the corresponding semiempirical equation which describes the effective viscosity of the suspension: $\eta_{eff} = \eta(1 - \varphi/0.63)^{-2}$ (28). Here $\eta$ refers to the pure solvent. The expression is valid for both neutral and charged particles (provided that $\kappa d \gg 1$). Of course, it will be applied for $\varphi < 0.63$.

![Image](image.png)

**FIG. 5.** Dependence of the critical film thickness upon the wave number of the fluctuation, calculated at three different surfactant concentrations. The conditions are the same as in Fig. 4, case 3.
Curves 4 and 5 in Fig. 4 are calculated with the changing viscosity of the liquid phase, \( \eta_{\text{eff}} \), taken into account. No influence of \( \eta_{\text{eff}} \) upon \( H_t \) is seen for initial concentrations below \( \sim 10 \) CMC (curve 5), but at higher surfactant contents (up to 20 CMC) the increased viscosity partially compensates for the unfavorable effect of the micelles. The stability rises sharply beyond 20 CMC (curve 5), when the fluid in the film becomes very viscous (e.g., at 21 CMC \( \varphi \approx 0.59 \) just before rupture, and \( \eta_{\text{eff}} \approx 248 \eta \)). At \( \Delta T = 10^\circ \text{C} \), in the concentration range above 18 CMC, the critical thickness \( H_t \) is also observed to diminish (curve 4 in Fig. 4), but in this case the effect is suppressed by the intensive evaporation. The fact that high values of \( \eta_{\text{eff}} \) promote the film stability is discussed below in view of the time evolution of the fluctuation amplitude (Fig. 13).

Let us now explore the behavior of the total disjoining pressure, \( \Pi \) (see Eq. [5]), during the film thinning, under the conditions of Fig. 4 (cases 1–3). The results are plotted in dimensionless form in Fig. 6 as a function of the thickness in the basic state. The moment of rupture is indicated by arrows on the curves. There is a positive slope of considerable magnitude, \( (d\Pi/dH)_b > 0 \), for initial concentrations in the range 12.5–17.5 CMC. This form of the dependence \( \Pi_b \) is due to the oscillatory structural forces, which bring about film destabilization (compare with Fig. 4). In the literature, the positive slope of the disjoining pressure vs. thickness has been recognized to enhance the fluctuation disturbances (7). In our case the effect is caused by the micelles and is highly sensitive to the instantaneous conditions in the film, because \( \Pi_{\text{osc}} \) is an oscillating function.

From Fig. 6 it is seen that for 20 CMC \( (d\Pi/dH)_b \approx 0 \) at rupture; for even higher initial surfactant concentrations stabilization may be expected, since \( (d\Pi/dH)_b \) is then negative in a wide range of \( H \). Indeed, \( (d\Pi/dH)_b < 0 \) leads to damping of the interfacial corrugations, as will be discussed below (Figs. 10, 13).

Although the direct electrostatic forces, \( \Pi_0 \), turn out to be insignificant, the addition of an inorganic salt influences the hydrodynamic stability. The effective volume fraction of the micelles changes via \( \kappa^{-1} \) and \( d_{\text{eff}} \), Eq. [36]. Consequently, the magnitude of \( \Pi_{\text{osc}} \) will decrease with rising electrolyte content, since the ionic atmosphere around the micellar aggregates shrinks. Figure 7 illustrates this idea. In general, films with an ionic surfactant are less stable (\( H_t \) is higher) compared to nonionic amphiphiles with the same diameter of the “bare” micelles, \( d_{\text{core}} \). The effect is easily understood in view of the fact that \( d_{\text{eff}} \gg d_{\text{core}} \), and the destabilizing oscillatory disjoining pressure is greater with an ionic surfactant. In the presence of a large amount of salt \( d_{\text{osc}} \gg \kappa^{-1} \), \( d_{\text{eff}} \approx d_{\text{core}} \) and the two curves in Fig. 7 necessarily converge. Below \( \sim 0.1 \) CMC the concentration of added salt becomes much smaller than that of the surfactant, which is itself an electrolyte.

Figure 8 presents the results for the critical thickness of rupture as a function of the diameter \( d \) of spherical particles inside the film. Typically, \( H_t \) has values of about 0.1–0.2 (see also Figs. 4, 5, 7, 12), which means that the critical rupture time, \( \tau_{\text{eff}} \), falls in the range 0.92 ± 0.83 (with \( N_{\text{osc}} \approx 2.0 \), cf. Eq. [16] and Table 1). Hence, the disappearance time, \( \tau_0 \), defined by Eq. [10], provides a relevant scale for the order of magnitude of the time elapsed from the initial state, with thickness \( h_0 \), until the occurrence of rupture.

The increase in \( H_t \) for larger \( d \) (Fig. 8) is due to the impact of \( \Pi_{\text{osc}} \). However, if one plots the time evolution of the fluctuation wave amplitude, \( H_{\Pi} \), of the most unstable mode, some interesting effects will be discovered (Fig. 9). For \( d = 5 \) nm, \( H_{\Pi} \) grows monotonously. In contrast, the curve for \( d = 6.5 \) nm demonstrates the existence of a time period when the disturbance is damped. It is easy to rational-
FIG. 8. Role of the micellar size in the stability of films containing a nonionic surfactant. $h_0 = 50$ nm, $\Delta T = 0.10^\circ$C; the initial surfactant concentration is equal to 10 CMC.

FIG. 9. Time dependence of the fluctuation wave amplitude for films with a nonionic surfactant. The wavenumbers are $k = 2.15$ for $d = 6.5$ nm and $k = 0.950$ for $d = 5.0$ nm (the most unstable modes); $h_0 = 50$ nm, $\Delta T = 0.10^\circ$C.

FIG. 10. Disjoining pressure isotherms in the basic state, corresponding to the two curves in Fig. 9.

FIG. 11. Dependence of the film stability on the initial thickness, $h_0$, $d = 4.8$ nm, $\Delta T = 0.10^\circ$C; the initial concentration of nonionic surfactant is equal to 10 CMC. (1): $A = -1.15 \times 10^{-29}$ J; (2 and 3): $A = +1.15 \times 10^{-29}$ J. (1 and 2): $c_{CMC} = 8.0$ mol/m$^3$; (3): $c_{CMC} = 5 \times 10^{-2}$ mol/m$^3$.

ize this behavior if we compare Fig. 9 with the functional dependence $\Pi(\tau)$. The latter is drawn in Fig. 10 with the same parameters as in Fig. 9. When $d = 5$ nm the disjoining pressure decreases with time; i.e. $(d\Pi/dH)_{h_0} > 0$, up to the moment of rupture, $\tau = 0.87$. The stabilizing branch of the curve (Fig. 10) cannot be reached. On the other hand, the slope of $\Pi$ vs. $\tau$ for $d = 6.5$ nm switches over from wave damping (in the interval $0.74 < \tau < 0.8$) to destabilization (for $\tau > 0.8$). Thus, the peculiar dependence of $H_l(\tau)$ is explained.

From the data plotted in Fig. 11, it follows that the films with higher initial thickness, $h_0$, are very unstable. A similar conclusion was also drawn by Danov et al. (14). The effect of the van der Waals disjoining pressure is investigated by changing the sign of the Hamaker constant, $A$. Comparing cases 1 and 2 in Fig. 11, we observe that $\Pi_{hw}$ has an influence only for extremely thin films: $h_0 \leq 10$ nm. The attraction ($A > 0$) is connected with destabilization, as might be expected. A 160-fold decrease in the CMC renders the thicker films less unstable (curve 3 in Fig. 11).

Figure 12 illustrates the role of the steric repulsion. We vary the constant $A_{stc}$ (see Eq. (34)) by several orders of magnitude. The stronger the steric interaction, the lower the critical thickness of rupture, and the more stable the films. There is also a pronounced effect of shift of the most unstable modes to small wavenumbers, $k$, as $A_{stc}$ increases. Only very long waves may grow when excess repulsion is operative, then the lateral gradients of the physical variables (pressure, interfacial tension, etc.) become insignificant. The evaporation appears to be the predominant factor in destabilization.

The time evolution of the fluctuation in the film thickness, $H_l$, is shown in Fig. 13a for a high initial surfactant concentration. The concomitant change of the bulk liquid viscosity
In general, thicker films are less stable than thinner films. Steric and van der Waals interactions play a role only at very small thicknesses. Repulsion brings stabilization, as might be expected.

It is worth pointing out the existence of interdependence between the influences of various factors. Thus, for example, the temperature difference, $\Delta T$, and the viscosity in the liquid film, $\eta_{\text{eff}}$, modify the impact of the surfactant concentration on the stability (Fig. 4); the Hamaker constant, $A$, and the value of the CMC influence the dependence of the critical thickness of rupture, $H_c$, on the initial thickness, $h_0$ (Fig. 11).

With ionic surfactants the direct electrostatic forces between the two film surfaces are always negligible, because in the presence of micelles $\Pi_d$ is much smaller in absolute value than the direct electrostatic force (according to the hard sphere model) is plotted in Fig. 13b.

There is a marked difference in the behavior of the disturbances with $k = 1.50$ for 10, 30, and 50 times the CMC. The system with 10 CMC is unstable, as $H_f$ increases monotonically until rupture ($H_f = 1$). At 30 CMC there is partial damping of the wave amplitude, but ultimately the film cannot survive. A different kind of development is observed at 50 CMC. The fluctuation first grows, but subsequently is damped and finally dies out (Fig. 13a). Moreover, the viscosity in the film simultaneously rises considerably (Fig. 13b), since the particle volume fraction approaches the limiting value of 0.63. The film eventually solidifies and is stable. Therefore, unlike relatively low surfactant concentrations (between 1 and 20 CMC), sufficiently high concentrations bring about film stabilization.

### 7. CONCLUSIONS

We have carried out a linear stability analysis of evaporating liquid films on a solid substrate. The role of different molecular interactions (van der Waals, electrostatic, steric, oscillatory structural) was the main subject of the investigation, which was based on the disjoining pressure approach. It is demonstrated that the oscillatory structural forces, $\Pi_{\text{osc}}$, are most important for the evolution of hydrodynamic fluctuations in films containing colloidal particles (systems with surfactant micelles are considered here). At a relatively low volume fraction instability is promoted, and stable films may be expected only at a sufficiently high surfactant content. In the latter case the viscosity of the liquid phase rises too much, and at the same time the disturbances disappear under the influence of the oscillatory structural interaction. With increasing temperature difference ($\Delta T$) the thermal effects become predominant and suppress the impact of other factors. In general, thicker films are less stable than thinner films. Steric and van der Waals interactions play a role only at very small thicknesses. Repulsion brings stabilization, as might be expected.

It is worth pointing out the existence of interdependence between the influences of various factors. Thus, for example, the temperature difference, $\Delta T$, and the viscosity in the liquid film, $\eta_{\text{eff}}$, modify the impact of the surfactant concentration on the stability (Fig. 4); the Hamaker constant, $A$, and the value of the CMC influence the dependence of the critical thickness of rupture, $H_c$, on the initial thickness, $h_0$ (Fig. 11).

With ionic surfactants the direct electrostatic forces between the two film surfaces are always negligible, because in the presence of micelles $\Pi_d$ is much smaller than absolute...
value than $\Pi_{\text{osc}}$. Addition of an inorganic electrolyte leads to shrinkage of the Debye counterion atmosphere around the particles, thus decreasing the effective volume fraction. Consequently, the magnitude of the oscillatory forces diminishes. The latter can either enhance or damp the fluctuation amplitude, depending on the instantaneous film thickness and the micellar content.

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