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

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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 subsurface 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. © 1998 Academic Press

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

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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 gradients 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 concentration, and inducing adsorption-driven backflow (10). Experimental results (11) compare favorably with the theoretical 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 significantly 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 adsorbs on the liquid/gas boundary. The existence of interfacial viscosity, the Marangoni effect connected with nonuniform adsorption, 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 ''disjoining 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 exerted on the film surfaces, in the normal direction. This is called the ''disjoining pressure,'' Π, and is defined to be positive for repulsion and negative for attraction (16–18). We shall consider four different components of Π, due to van der Waals, electrostatic, steric, and oscillatory structural interactions. Whereas the first two have been studied intensively, 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 micellar 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 liquid films leads to a drastic change of behavior during the process of thinning. The latter proceeds in a stepwise manner, due to layer-by-layer destruction of the crystal-like structure of ordered spheres inside the film. This phenomenon, named stratification, was observed both with latexes (21) and with surfactant micelles (22). It represents a manifestation of the oscillatory structural forces.

In this paper we investigate the influence of structural interactions on the stability of evaporating films which contain 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 lubrication approximation is adopted for films which are much thinner than the wavelength of the unstable corrugations. Linear analysis is carried out, calculating the critical thickness 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.
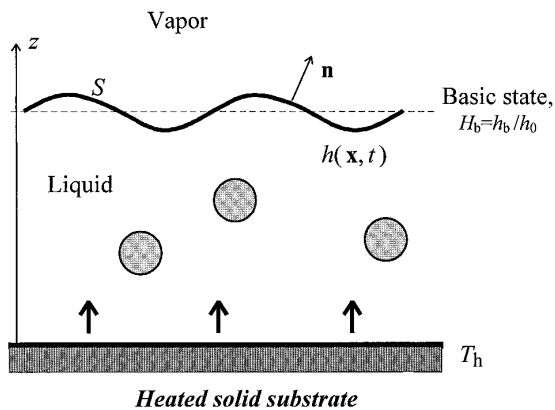
FIG. 1. Sketch of the system under consideration. The evaporating liquid film supposedly contains surfactant micelles, or other spherical particles.

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)

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

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

$$[1b]$$

Here t is time, ∇ is the spatial gradient operator, ρ 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 diffu-

sivity 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, $\mathbf{D}$,

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

where p is the pressure in the liquid phase, $\mathbf{I}$ is the three-dimensional idemfactor, $\mathbf{T}$ is the viscous part of the stress tensor, η 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

$$\mathbf{v} = \mathbf{0}, \quad T = T_{\mathrm{h}}, \quad \frac{\partial c}{\partial z} = 0. \quad [3]$$

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

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

$$\frac{\partial \Gamma}{\partial t} + \nabla_{\mathrm{s}} \cdot (\Gamma \mathbf{v}_{\mathrm{s}}) - \nabla_{\mathrm{s}} \cdot (D_{\mathrm{s}} \nabla_{\mathrm{s}} \Gamma)$$

$$= [-D\nabla c + c(\mathbf{v} - \mathbf{u}_{\mathrm{ds}})] \cdot \mathbf{n}. \quad [4b]$$

We use the following notation: ∇_{s} is the surface gradient operator, J is the mass flux due to evaporation, $\mathbf{u}_{\mathrm{ds}}$ 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), Γ is the adsorption, D_{s} is the interfacial diffusion coefficient, and $\mathbf{v}_{\mathrm{s}}$ 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

$$\mathbf{T} \cdot \mathbf{n} = \nabla_{\mathrm{s}} \cdot \mathbf{P}_{\mathrm{s}} + \left(p + \Pi - p_{\mathrm{v}} - \frac{J^2}{\rho_{\mathrm{v}}}\right)\mathbf{n}, \quad [4c]$$

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

where L is the latent heat of vaporization, λ is the thermal conductivity in the film, $\mathbf{P}_{\mathrm{s}}$ is the surface stress tensor, Π is the disjoining pressure, and ρ_{v} and p_{v} are the vapor density and pressure, respectively.

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, Π_{vW}, electrostatic, Π_{el}, steric, Π_{st}, and oscillatory structural, Π_{osc}:

$$\Pi = \Pi_{vW} + \Pi_{el} + \Pi_{st} + \Pi_{osc}. \qquad [5]$$

Most extensively studied is the role of the van der Waals component of Π; for planar films Π_{vW} is calculated by a simple explicit equation (19):

$$\Pi_{vW} = -\frac{A}{6\pi h^3} . \qquad [6]$$

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-Scriven constitutive law (2, 25):

$$\mathbf{P}_s = \sigma\mathbf{I}_s + (\eta_s^{dil} - \eta_s^{sh})(\mathbf{I}_s:\mathbf{D}_s)\mathbf{I}_s + 2\eta_s^{sh}\mathbf{D}_s, \quad [7a]$$

$$\mathbf{D}_s = \frac{1}{2}\left[(\nabla_s\mathbf{v}_s)\cdot\mathbf{I}_s + \mathbf{I}_s\cdot(\nabla_s\mathbf{v}_s)^T\right] \qquad [7b]$$

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, σ, and the intrinsic shear and dilatational surface viscosities, η_s^{sh} and η_s^{dil}, 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),

$$J = J_T(T_s - T_e), \quad \text{with } J_T = \text{constant}, \qquad [8]$$

where T_e denotes the saturation temperature at the given pressure (when the liquid and vapor would rest in equilib-

rium), T_s is the actual temperature at the fluid surface, and J_T is a solvent property that depends on T_e.

Let us denote by c_s the instantaneous local value of the subsurface bulk concentration of surfactant monomers (c_s fluctuates around the CMC). The adsorption at the interface, Γ, is connected with c_s 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 Kralchevsky *et al.* (26), and the references cited therein). Hence, we write

$$\frac{\Gamma}{\Gamma_\infty} = \frac{c_s}{c_L + c_s} , \qquad [9a]$$

where Γ_∞ 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, σ, with Γ. Thermodynamically consistent with [9a] is the Szyszkowski equation (26):

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

In [9b] $\sigma_p(T_s)$ 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 ($T_h - T_e$) is not high and the parameters A, Γ_∞, 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 $z = h(\mathbf{x}, t)$ and $z = 0$, respectively, in the coordinate system with vertical axis Oz and horizontal coordinates $\mathbf{x}$. The lateral and normal velocity components are denoted by $\mathbf{u}$ 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, $\rho h_0^2/(\eta t_d) \ll 1$, large thermal Peclet number, $at_d/h_0^2 \gg 1$, large diffusivity Peclet number, $Dt_d/h_0^2 \gg 1$, and small slope of the interface, $(\nabla_s h)^2 \ll 1$ (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 lateral characteristic length parameter, $l \gg 1$:

$$t_d \equiv \frac{\rho h_0}{J_T \Delta T} \left(1 + \frac{LJ_T h_0}{2\lambda} \right), \quad l \equiv \sqrt[4]{\frac{\sigma_0 t_d}{3\eta h_0}},$$

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

where τ, Z, and $\mathbf{X}$ are dimensionless time and space coordinates and σ_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 $\mathbf{U}$, are introduced as follows:

$$h = h_0 H, \quad p - p_v = \frac{12\eta l^2}{t_d} P,$$

$$w = \frac{h_0}{t_d} W, \quad \mathbf{u} = \frac{2lh_0}{t_d} \mathbf{U}. \quad [11]$$

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

$$\frac{T_h - T}{\Delta T} = \frac{Z}{N_{de} + H}, \quad \mathbf{U} = 3Z(Z - H)\nabla_{\parallel} P + \frac{Z}{H} \mathbf{U}_s, \quad [12a]$$

$$W = Z^2(3H - 2Z)\nabla_{\parallel}^2 P + 3Z^2 \nabla_{\parallel} P \cdot \nabla_{\parallel} H$$

$$- Z^2 \nabla_{\parallel} \cdot \left(\frac{1}{H} \mathbf{U}_s \right), \quad [12b]$$

where $\Delta T = T_h - T_e$ is a characteristic temperature difference, $\nabla_{\parallel}$ is the dimensionless horizontal projection of the spatial gradient operator ∇, $\mathbf{U}_s$ is the lateral component of the dimensionless velocity at the interface, and the pressure $P(\tau, \mathbf{X})$ 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 $H(\tau, \mathbf{X})$ and $C(\tau, \mathbf{X})$—see below.

The deviation from equilibrium at the evaporating liquid surface is measured by the parameter $N_{de} \equiv \lambda/(LJ_T h_0)$, appearing in [12a]. In the quasi-equilibrium limit, $N_{de} \ll 1$, the process of evaporation is fast and the interfacial temperature, T_s, remains practically constant and equal to the saturation temperature, T_e. 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 $T_s \approx T_h$).

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]:

$$\frac{\partial H}{\partial \tau} + \nabla_{\parallel} \cdot (H\mathbf{U}_s) = \nabla_{\parallel} \cdot (H^3 \nabla_{\parallel} P) - \frac{2N_{de} + 1}{2(N_{de} + H)}, \quad [13a]$$

$$P = \frac{N_{ml}}{4} \frac{N_{de}^2}{(N_{de} + H)^2} - \tilde{\Pi}$$

$$- \frac{1}{4} \left[1 - N_{sl} \frac{\ln(1 - N_a G)}{\ln(1 - N_a)} \right] \nabla_{\parallel}^2 H. \quad [13b]$$

Here $\tilde{\Pi}$ denotes the dimensionless disjoining pressure, $\tilde{\Pi} \equiv \Pi t_d/(12\eta l^2)$. In the context of the lubrication approximation $\nabla_{\parallel}$ may be shown to coincide with the dimensionless form of the surface gradient operator, ∇_s. The quantity N_{ml} in [13b] is defined as $N_{ml} \equiv h_0(lJ_T \Delta T)^2/(\rho_v \sigma_0)$, 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, Γ, is scaled with its value at the CMC, Γ_{CMC}, thus introducing the new variable $G = \Gamma/\Gamma_{CMC}$. The capacity of the interfacial layer is determined by the number $N_a \equiv \Gamma_{CMC}/\Gamma_\infty$; the parameter

$$N_{sl} \equiv - \frac{k_B(T_h + T_e)\Gamma_\infty}{2\sigma_0} \ln(1 - N_a)$$

represents a measure of the slope of the functional dependence of the surface tension, σ, vs. the logarithm of the surfactant concentration, c. For most types of amphiphilic molecules N_a 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 $N_a \approx 0.9$. 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

[4c] one can find the dimensionless surface velocity, $\mathbf{U}_s$. Up to the leading order, we derive

$$H\nabla_\| P + \frac{1}{3H} \mathbf{U}_s = \frac{2N_{Mt}N_{de}}{3(N_{de} + H)^2} \nabla_\| H$$

$$- \frac{2N_{Ma}}{3(1 - N_a G)} \nabla_\| G + \frac{N_{sv}}{3} \nabla_\| \cdot (G\nabla_\| \mathbf{U}_s). \quad [13c]$$

The existing gradients of interfacial temperature and adsorption give rise to variations of the surface tension (Marangoni effects). These are included in [13c] through the quantities

$$N_{Mt} \equiv -\frac{3l^2\Delta T}{4\sigma_0}\left(\frac{\partial\sigma}{\partial T}\right), \quad N_{Ma} \equiv \frac{3l^2}{8\sigma_0} k_B(T_h + T_e)\Gamma_{CMC}.$$

The classical Marangoni adsorption number is related to the Gibbs elasticity of the interfacial layer, $E_G = -\partial\sigma/\partial \ln \Gamma$ (2, 27). In our particular system Γ is always very close to Γ_{CMC}, and we assume the validity of the isotherm [9b]. Under these conditions, $E_G = k_B T_s \Gamma_{CMC}/(1 - N_a)$. The Boussinesq-Scriven constitutive law [7] leads to coupling of the dilatational and shear interfacial viscosities to give one parameter: $\eta_s = \eta_s^{dil} + \eta_s^{sh}$. The latter depends on the local surfactant coverage. A simple linear relationship may be conjectured: $\eta_s = \eta_s^m \Gamma/\Gamma_{CMC}$. The corresponding dimensionless number, which enters into [13c], is defined as $N_{sv} \equiv \eta_s^m/(\eta l^2 h_0)$.

In the lubrication approximation the solution of the diffusion equation [1b] is represented as a sum of uniform part, $C(\mathbf{X}, \tau)$, and a small perturbation, $C_1(\mathbf{X}, Z, \tau)/l^2$, where the bulk concentration of surfactant monomers is scaled with the respective value at the CMC, c_{CMC}. $C(\mathbf{X}, \tau)$ does not depend on the vertical coordinate Z and is equal to the dimensionless subsurface concentration. The Z-derivative of $C_1(\mathbf{X}, Z, \tau)/l^2$ is comparable in magnitude to the lateral and time derivatives of $C(\mathbf{X}, \tau)$ (24). Thus, after integrating the diffusion equation [1b] from 0 to H, using the boundary condition [3], one ends up with a result for the right-hand side of the surfactant species mass transport equation on the interface [4b]. Up to leading order we write (14)

$$-N_{Pe}\frac{\partial C_1}{\partial Z} + N_{Pe}\nabla_\| H \cdot \nabla_\| C + C\left(W - 2\mathbf{U}_s \cdot \nabla_\| H - \frac{\partial H}{\partial \tau}\right)$$

$$= -\frac{\partial}{\partial\tau}(HC) + \nabla_\| \cdot [N_{Pe}H\nabla_\| C + (H^3\nabla_\| P - H\mathbf{U}_s)C].$$

$$[14]$$

The bulk diffusion flux is scaled by using the characteristic time and length dimensions [10]; the diffusivity Peclet number acquires the form $N_{Pe} \equiv Dt_d/(l^2 h_0^2)$. Now, with the general solution [12] and with the expression for the surfactant mass flux [14], Eq. [4b] can be further transformed to read

$$\frac{\partial}{\partial\tau}(G + N_{cl}HC) + \nabla_\| \cdot [2G\mathbf{U}_s - N_{Pe}(N_{sd}\nabla_\| G$$

$$+ N_{cl}H\nabla_\| C) - N_{cl}HC(H^2\nabla_\| P - \mathbf{U}_s)] = 0, \quad [15]$$

where N_{sd} is the ratio between the surface and the bulk diffusion coefficients: $N_{sd} \equiv D_s/D$. The capacity of the liquid layer is determined by the number $N_{cl} \equiv h_0 c_{CMC}/\Gamma_{CMC}$.

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, $\mathbf{U}_s = \mathbf{0}$, 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:

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

$$\frac{J_b}{J_T\Delta T} = \frac{N_{de}}{N_{de} + H_b}. \quad [16]$$

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_T) 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_{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_{CMC}. The rest of the surfactant will be engaged in micellar aggregates (20). Consequently, $C_b = 1$ and $G_b = 1$, as the single molecules exchange between the bulk and the interface. The *instantaneous* adsorption, Γ, and subsurface monomer concentration, c, fluctuate around the corresponding values at the CMC (Γ_{CMC},

TABLE 1
Characteristic Parameters of the System

Physical quantity	Symbol	Dimension	Value(s) used
Vapor/liquid equilibrium temperature	T_e	K	373.15
Vapor density	ρ_v	kg/m^3	0.60
Liquid density	ρ	kg/m^3	960.0
Dynamic viscosity of the liquid phase	η	kg/(m·s)	2.88×10^{-4}
Thermal conductivity	λ	J/(m·s·K)	0.680
Latent heat of vaporization	L	J/kg	2.3×10^6
Evaporation mass flux coefficient (Eq. [8])	J_T	kg/(m^2·s·K)	2.960
Hamaker constant	A	J	1.15×10^{-20}
			-1.15×10^{-20}
Surface tension of the pure solvent	σ_0	N/m	0.030
Temperature coefficient of the surface tension	$(\partial\sigma/\partial T)$	N/(m·K)	-1.80×10^{-4}
Bulk diffusion coefficient of surfactant molecules	D	m^2/s	5.0×10^{-9}
Surface diffusion coefficient	D_s	m^2/s	5.0×10^{-9}
Critical micellar concentration (CMC)	c_{CMC}	mol/m^3	8.0
			0.050
Adsorption at the CMC	Γ_{CMC}	mol/m^2	3.0×10^{-6}
Surface viscosity at the CMC	η_s^m	kg/s	1.0×10^{-8}
Surface coverage at the CMC	$N_a \equiv \Gamma_{CMC}/\Gamma_\infty$	—	0.90
Surface dissociation constant of ionic amphiphiles	K_d	mol/m^3	1.16×10^2
Micellar diameter	d	m	4.8×10^{-9}
Aggregation number of micelles	N	—	67

c_{CMC}). The perturbations will be assumed to occur at fixed composition of the liquid phase. In other words, both c and c_{tot} will change, but

$$\frac{c}{c_{tot}} = \frac{c_{CMC}}{c_{tot,b}}, \quad \frac{C}{C_b} = \frac{C_{tot}}{C_{tot,b}} = C. \quad [17]$$

Here $C_{tot} = c_{tot}/c_{CMC}$ and $C_{tot,b} = c_{tot,b}/c_{CMC}$ 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}–5×10^{-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 $c_b = c_{CMC}$, $C_b = 1$. 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 **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:

$$H = H_b(1 + H_f F_0), P = P_b + P_f F_0, \mathbf{U}_s = \mathbf{U}_f F_1, \quad [18a]$$

$$G = 1 + G_f F_0, C = 1 + C_f F_0,$$

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

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

$$\tilde{\Pi}(H, C_{tot}) = \tilde{\Pi}_b(H_b, C_{tot,b})$$

$$+ \left\{ \left(\frac{\partial\tilde{\Pi}}{\partial H}\right)_b H_b H_f + \left(\frac{\partial\tilde{\Pi}}{\partial C_{tot}}\right)_b C_{tot,b} C_f \right\} F_0. \quad [19]$$

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

[13c], we are left with explicit relationships that connect the amplitudes of pressure, P_f, and velocity, $\mathbf{U}_f$, with those of shape, H_f, and total surfactant monomer fluctuation, S_f. The latter is an auxiliary quantity, defined as $S_f \equiv G_f + N_{cl}H_bC_f$. The final expressions are

$$P_f = p_hH_f + p_sS_f, \quad p_h \equiv - \frac{N_{ml}N_{de}^2H_b}{2(N_{de} + H_b)^3}$$

$$- \left(\frac{\partial \tilde{\Pi}}{\partial H}\right)_b H_b + \frac{k^2H_b}{4}(1 - N_{sl}), \quad [20a]$$

$$p_s \equiv - \frac{1}{(1 + f_s)(1 - N_a)} C_{tot,b}\left(\frac{\partial \tilde{\Pi}}{\partial C_{tot}}\right)_b, \quad [20b]$$

$$\mathbf{k} \cdot \mathbf{U}_f = u_hH_f + u_sS_f,$$

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

$$u_s \equiv \frac{H_bk^2}{1 + f_v}\left[\frac{2N_{Ma}}{(1 - N_a)(1 + f_s)} + 3H_bp_s\right], \quad [20d]$$

where the surfactant factor, $f_s \equiv N_{cl}H_b/(1 - N_a)$, is calculated using the dimensionless form of the Langmuir isotherm [9a], with $G_b = 1$. $f_v \equiv k^2N_{sv}H_b$ 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_f and S_f 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

$$\frac{dH_f}{d\tau} = a_{11}H_f + a_{12}S_f, \quad \frac{dS_f}{d\tau} = a_{21}H_f + a_{22}S_f. \quad [21]$$

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

$$a_{11} = \frac{(2N_{de} + 1)(N_{de} + 2H_b)}{2H_b(N_{de} + H_b)^2} - u_h - k^2H_b^2p_h,$$

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

$$a_{21} = -N_{cl}\frac{(2N_{de} + 1)(N_{de} + 2H_b)}{2(N_{de} + H_b)^2} - 2u_h,$$

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

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, τ_c, that refers to an initial amplitude $H_f(0)$. For a single perturbation mode with wave number k the film will rupture at the moment τ_r, when the corrugated liquid/gas interface just touches the solid substrate; i.e., $H_f(\tau = \tau_r) = 1$. Then, the minimum of τ_r for all possible wave numbers k gives the critical time, τ_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, $H_f(0)$, and the initial thickness of the basic state, h_0, have values chosen by us. In other words, h_0 and $H_f(0)$ are free parameters of the model. However, the total surfactant monomer fluctuation at time zero, $S_f(0)$, 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 ω is the initial increment/decrement. With such a type of functional dependence, the set of equations [21] transforms into a dispersion relationship for ω. There are two solutions, but we choose the greater one, ω_r:

$$\omega_r = \frac{1}{2}\{a_{11}(0) + a_{22}(0)$$

$$+ \sqrt{[a_{11}(0) - a_{22}(0)]^2 + 4a_{12}(0)a_{21}(0)}\}. \quad [23]$$

Let us denote by k_0 the wave number at which $\omega_r = 0$. Then, the initially unstable waves ($\omega_r > 0$) are those with $0 < k^2 < k_0^2$. For each k the initial condition for S_f that leads to faster film rupture is $S_f(0) = a_{21}(0)H_f(0)/[\omega_r - a_{22}(0)]$. Some typical curves $\omega_r(k)$ 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 1×10^{-4}. The derivatives $(\partial\tilde{\Pi}/\partial H)_b$, $(\partial\tilde{\Pi}/\partial C_{tot})_b$ 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 $\tilde{\Pi}$ 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 $H_f(\tau)$, $S_f(\tau)$ over a small time interval $\Delta\tau$ by solving Eqs. [21] with *constant coefficients, a_{ij}, taken in the middle of the time interval (at $\tau + \Delta\tau/2$). 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, Γ, 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 Γ 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}–5×10^{-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 $c_b = c_{CMC}$, $C_b = 1$.

(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, $A_{solid/liquid/gas}$, can be conveniently represented as a combination of other constants that correspond to simpler systems:

$$A_{solid/liquid/gas}$$
$$= \frac{1}{2}(A_{liquid/gas/liquid} - A_{solid/gas/solid} + A_{solid/liquid/solid}). \quad [24]$$

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 $A_{PVC/water/gas} = -1.15 \times 10^{-20}$ 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: $A_{PTFE/water/gas} = +0.265 \times 10^{-20}$ J. In the latter case there is van der Waals attraction. Obviously, the interactions are sensitive to the chemical nature of the materials, and
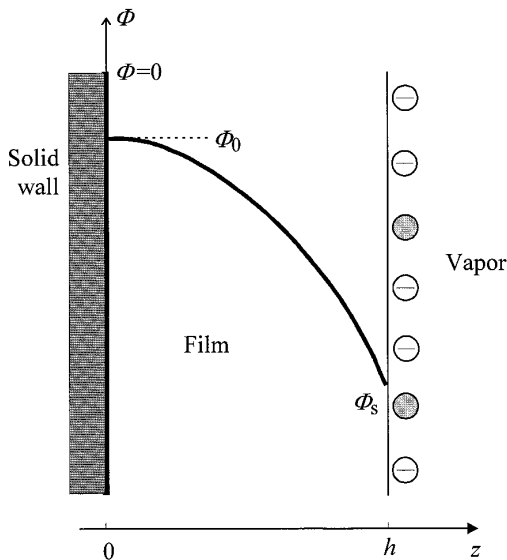
FIG. 2. Schematic diagram of the electric potential inside the film. The liquid/gas interface is charged because of adsorbed ionic surfactant molecules that may be partially dissociated.

Π_{vW} can even change sign. In our analysis we shall use both positive and negative values of A.

5.2. Electrostatic Forces

The liquid/gas interface may carry electric charges, due to the presence of an adsorbed layer of ionic surfactant. It will be assumed here that no specific adsorption of ions takes place on the solid substrate. The respective boundary condition for the electric potential, Φ, at the uncharged plane $z = 0$ is $(\partial\Phi/\partial z)_{z=0} = 0$. The shape of the function $\Phi(z)$ is sketched in Fig. 2. It now becomes evident that the problem for finding Φ is mathematically equivalent to the analogous problem in a *symmetric* liquid film whose thickness is equal to $2h$. The latter configuration has been well studied (17, 19, 26), and we can apply some results directly. Thus, the disjoining pressure, Π_{el}, obeys the following equation (17):

$$\Pi_{el} = 2k_B T c_{el,0}[\cosh(\phi_0) - 1]. \qquad [25]$$

The dimensionless potential at the solid wall, ϕ_0, is defined as $\phi_0 \equiv e\Phi_0/(k_B T)$, where $\Phi_0 \equiv \Phi(z = 0)$ (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-

neous volume phase. Then, the concentration $c_{el,0}$ will be purely fictitious, as there is no such place in the film where $\Phi = 0$. Nevertheless, $c_{el,0}$ can be found and Eq. [25] is useful (see below).

It is reasonable to work in the approximation of thick films, which in the present context means $\kappa h \gg 1$. The Debye length, κ^{-1}, characterises the effective width of the double electric layer around the charged surface. According to its definition, the parameter κ is connected with $c_{el,0}$ (17),

$$\kappa^2 = \frac{8\pi e^2 c_{el,0}}{\epsilon k_B T}, \qquad [26]$$

where ϵ is the dielectric permittivity of the medium. Typical values of κ^{-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 $\kappa h \gg 1$ 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 semiinfinite liquid phase) with the same surface potential, Φ_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 Φ_1, has an analytical solution. The standard electrostatic theory (17, 19, 26) then yields a relationship between ϕ_0 and ϕ_s,

$$\tanh\left(\frac{\phi_0}{8}\right) = \tanh\left(\frac{\phi_s}{4}\right)\exp(-\kappa h), \qquad [27]$$

where $\phi_s \equiv e\Phi_s/(k_B T)$.

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),

$$SK \overset{K_d}{\leftrightarrow} S^- + K^+, \qquad [28]$$
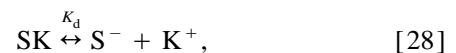
which involves the neutral species SK and the ions S^- residing on the interface. The counterions K^+ that can be exchanged are located near the surface, where their bulk concentration is $c_{el,0}\exp(-\phi_s)$. We define the degree of dissociation, α_s, connected with the ''reaction constant'' K_d:

$$\alpha_s = \frac{1}{1 + \dfrac{c_{el,0}}{K_d} \exp(-\phi_s)} . \qquad [29]$$

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

$$-\frac{e}{k_B T \kappa} \frac{d\Phi}{dz}\bigg|_{z=h} = \sqrt{2[\cosh(\phi_s) - \cosh(\phi_0)]}$$

$$= \frac{\kappa}{2c_{el,0}} \alpha_s \Gamma. \qquad [30]$$

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

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

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

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 $c_{el,0}\exp[-e\Phi/(k_B T)]$ is the local concentration of K^+ species at the place where the potential is Φ. Straightforward application of the classical electrostatic theory leads to the following connection between $c_{el,0}$ and c_{el},

$$\frac{c_{el}}{c_{el,0}} = \cosh \phi_0 - \frac{\sqrt{2}}{\kappa h} \left\{ \sqrt{\cosh \phi_0 + 1} \right.$$

$$\times E\left(\arcsin\sqrt{\frac{\cosh \phi_s - \cosh \phi_0}{\cosh \phi_s - 1}}, \sqrt{\frac{2}{\cosh \phi_0 + 1}}\right)$$

$$\left. + \frac{2\sqrt{\cosh \phi_s - \cosh \phi_0}}{1 - \exp(-\phi_s)} \right\}, \qquad [32]$$

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

The liquid phase in our system may have a complex composition, containing salt, A^-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 ex-

perimental 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

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

The degree of micellar dissociation, α_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 α_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, ϕ_s, ϕ_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_{tot} and c_{AK}, as the amount of dissolved material is conserved in the process of film thinning. Then, Π_{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 $\kappa h \gg 1$ 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_s (cf. Eq. [9a]). The latter circumstance is supported by available experimental evidence (see, e.g., the review by Kralchevsky *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.
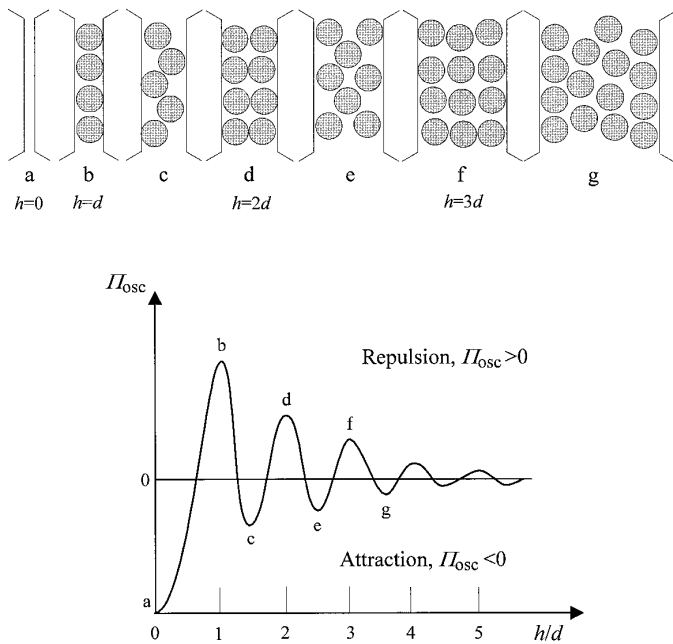
FIG. 3. Qualitative illustration of the oscillatory structural component of disjoining pressure, engendered by partial ordering of spheres which are confined between the two surfaces of a thin film.

Let L be the threshold thickness at which the steric interaction becomes operative. The repulsive force will be described by means of a model expression for the respective disjoining pressure component,

$$\Pi_{st} = A_{ster}\left[\exp\left(-2\pi\frac{h}{L}\right) - \exp(-2\pi)\right], \quad [34]$$

at $h < L$. This is written by analogy with Alexander-de Gennes' theory for grafted polymer brushes (19). In the original treatment, the coefficient in Eq. [34] was identified as $A_{ster} = 100\ k_BT\Gamma^{3/2}$ (19). Here we shall assume that L is of the order of the effective micellar diameter, d_{eff}. The assumption is plausible for low volume fractions in the liquid phase, $\varphi < \pi/(3\sqrt{3}) \approx 0.6046$, smaller than the limiting value for one flat layer of hard spheres tightly packed between two walls. The role of the steric interactions in film stability will be considered below with different numbers for A_{ster}.

5.4. Oscillatory Structural Forces

The physical origin of these forces was discussed in detail in the book by Israelachvili (19) (see also the introduction of this paper). An illustration of the dependence $\Pi_{osc}(h)$, and its connection with the partial ordering of spheres in the film, is shown in Fig. 3. Rigorous theoretical studies of the phenomenon were carried out by computer simulations and numerical solutions of the integral equations of statistical

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, Π_{osc}. The result was

$$\Pi_{osc} = P_0\cos\left(\frac{2\pi h}{d_1}\right)\exp\left(\frac{d^3}{d_1^2 d_2} - \frac{h}{d_2}\right), \quad [35a]$$

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,

$$P_0 = \rho k_BT\frac{1 + \varphi + \varphi^2 - \varphi^3}{(1 - \varphi)^3}, \quad [35b]$$

where φ is the volume fraction and ρ 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:

$$\frac{d_1}{d} = \sqrt{\frac{2}{3}} + 0.23728\Delta\varphi + 0.63300(\Delta\varphi)^2, \quad [35c]$$

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

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. Π_{osc} is calculated from Eq. [35a] and is inserted into Eq. [5]. Π_{osc} depends on the thickness, h, both explicitly and implicitly (through φ). 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 = $ constant.) The magnitude of Π_{osc}
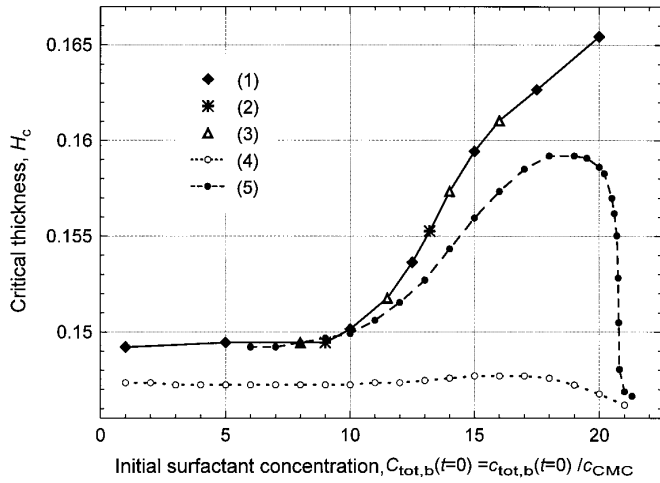
FIG. 4. Role of the surfactant concentration in the film stability. $d_{eff} = d = 4.8$ nm, $h_0 = 50$ nm. (1) Full diamonds: calculations accounting for the direct electrostatic interactions due to adsorbed ionic surfactant on the film/gas interface, in the presence of inorganic salt (1 CMC); (2) asterisks: as for (1), but without added salt; (3) open triangles: no electrostatic interactions are considered (nonionic surfactant). Such is the case also with (4) and (5). (1–3, and 5): $\Delta T = 0.10°C$; (4): $\Delta T = 10.0°C$. (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.

increases with rising φ. We determine the volume fraction φ at each value of h using the equation $\rho = (c_{tot} - c_{CMC})/N$, where N represents the aggregation number of the micelles. We take $N = 67$ (which holds for sodium dodecyl sulfate).

Some discussion is needed for the case of ionic surfactants. The charged micelles experience electrostatic interactions and, therefore, are not exactly hard spheres. Nevertheless, they can be represented as such by taking into account the Debye counterion atmosphere (31, 33). We define the effective diameter

$$d_{eff} = d_{core} + 2\kappa^{-1}, \qquad [36]$$

which is identified with d in [35]. d_{core} denotes the hydrodynamic diameter of the micelles themselves, measured, for instance, by dynamic light scattering; κ^{-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 η 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 $\varphi < 0.63$.

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 (Π_{el}). With ionic amphiphiles, however, a change of concentration leads to a change of the Debye screening length, κ^{-1}. This in turn will affect Π_{osc}, through d_{eff} and the particle volume fraction, φ. In order to exclude the indirect impact on Π_{osc}, all calculations in Fig. 4 were performed without taking into account the Debye atmosphere as part of the effective micellar diameter: $d_{eff} = d_{core} = d$ was assumed. Now, if we look at cases (1–3) in Fig. 4, it becomes evident that the electrostatic forces are negligible. Irrespective of the presence of added salt, the points lie on the same curve, which also describes the case with no electrostatics at all. The reason for such behavior is that if the film contains micelles then Π_{el} is always much smaller in absolute value than Π_{osc}.

Figure 4 presents also data for a higher temperature difference, $\Delta T = 10.0°C$ (curve 4). Here, the destabilizing effect of the surfactant is virtually nonexistent. Indeed, in this situation the thermal instabilities due to evaporation dominate and the other factors are of little importance. Similar trends were observed by Burelbach et al. (12) and Danov et al. (14).
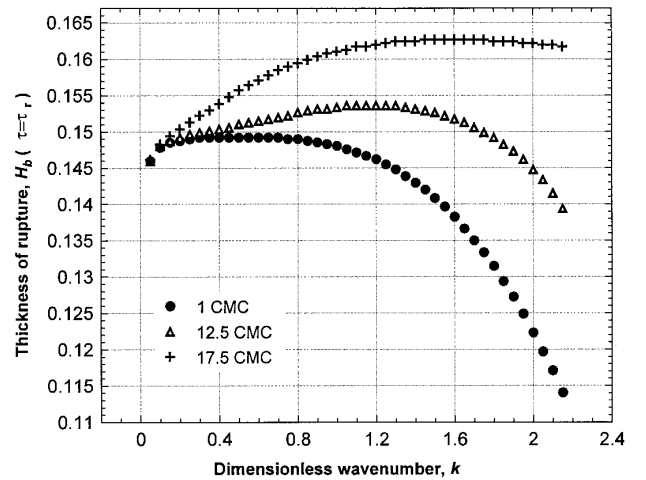

FIG. 5. Dependence of the critical film thickness upon the wave number of the fluctuation, calculated at three different surfactant concentrations. The conditions are the same as in Fig. 4, case 3.
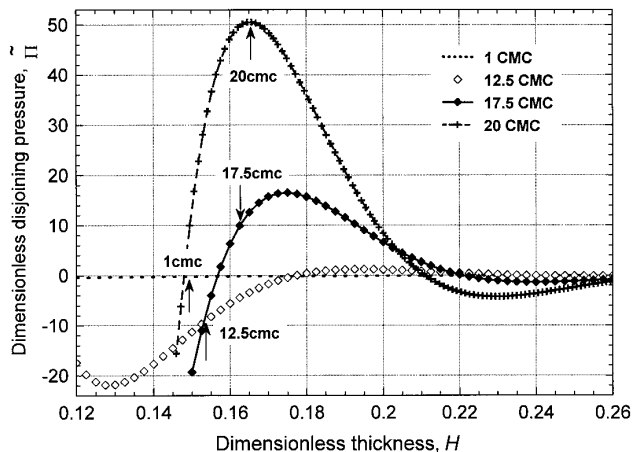
FIG. 6. Disjoining pressure in the basic state, at different initial concentrations of nonionic surfactant. $d = 4.8$ nm, $h_0 = 50$ nm, $\Delta T = 0.10°C$. The arrows point to the critical thickness of film rupture.

Curves 4 and 5 in Fig. 4 are calculated with the changing viscosity of the liquid phase, η_{eff}, taken into account. No influence of η_{eff} upon H_c is seen for initial concentrations below ~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 $\eta_{eff} \approx 248 \eta$). At $\Delta T = 10°C$, in the concentration range above 18 CMC, the critical thickness H_c 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 η_{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, Π (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, $(d\tilde{\Pi}/dH)_b > 0$, for initial concentrations in the range 12.5–17.5 CMC. This form of the dependence $\tilde{\Pi}(H_b)$ 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 Π_{osc} is an oscillating function. From Fig. 6 it is seen that for 20 CMC $(d\tilde{\Pi}/dH)_b \approx 0$ at rupture; for even higher initial surfactant concentrations stabilization may be expected, since $(d\tilde{\Pi}/dH)_b$ is then negative in a wide range of H. Indeed, $(d\tilde{\Pi}/dH)_b < 0$ leads to

damping of the interfacial corrugations, as will be discussed below (Figs. 10, 13).

Although the direct electrostatic forces, Π_{el}, turn out to be insignificant, the addition of an inorganic salt influences the hydrodynamic stability. The effective volume fraction of the micelles changes via κ^{-1} and d_{eff}, Eq. [36]. Consequently, the magnitude of Π_{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_c is higher) compared to nonionic amphiphiles with the same diameter of the "bare" micelles, d_{core}. The effect is easily understood in view of the fact that $d_{eff} > d_{core}$, and the destabilizing oscillatory disjoining pressure is greater with an ionic surfactant. In the presence of a large amount of salt $d_{core} \gg \kappa^{-1}$, $d_{eff} \approx d_{core}$ and the two curves in Fig. 7 necessarily converge. Below ~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_c has values of about $0.1 \div 0.2$ (see also Figs. 4, 5, 7, 12), which means that the critical rupture time, τ_c, falls in the range $0.92 \div 0.83$ (with $N_{de} \approx 2.0$, cf. Eq. [16] and Table 1). Hence, the disappearance time, t_d, 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_c for larger d (Fig. 8) is due to the impact of Π_{osc}. However, if one plots the time evolution of the fluctuation wave amplitude, H_f, of the most unstable mode, some interesting effects will be discovered (Fig. 9). For $d = 5$ nm, H_f 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-
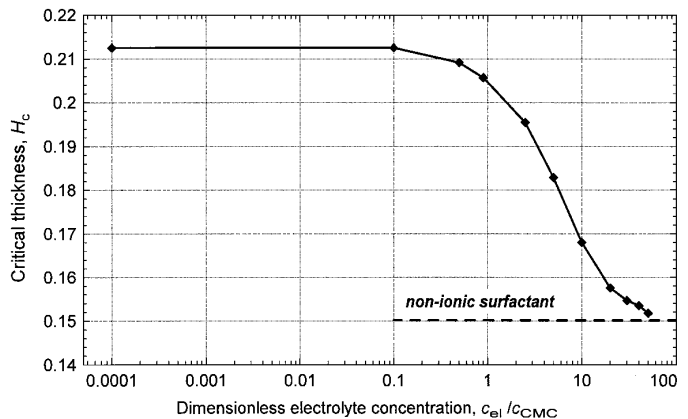

FIG. 7. Role of the inorganic electrolyte in the stability of films containing micelles of ionic surfactant. The addition of salt causes shrinking of the Debye atmosphere whose width is κ^{-1}. $d_{eff} = d_{core} + 2\kappa^{-1}$, $d_{core} = 4.8$ nm, $h_0 = 50$ nm, $\Delta T = 0.10°C$. The initial surfactant concentration (here and in Figs. 8–10) is equal to $10\, c_{CMC}$.

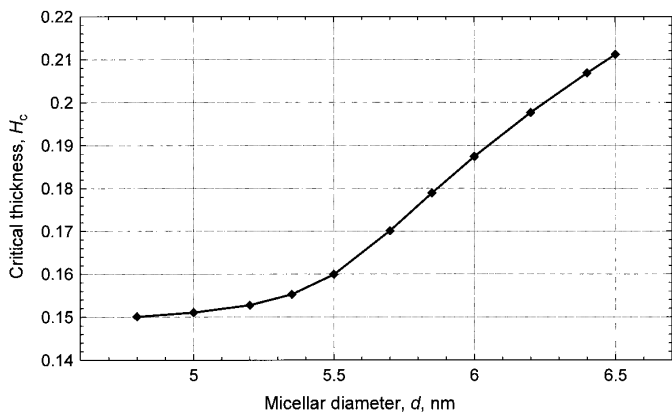**FIG. 8.** Role of the micellar size in the stability of films containing a nonionic surfactant. $h_0 = 50$ nm, $\Delta T = 0.10°C$; the initial surfactant concentration is equal to 10 CMC.

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

ize this behavior if we compare Fig. 9 with the functional dependence $\tilde{\Pi}(\tau)$. 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. $(d\tilde{\Pi}/dH)_b > 0$, up to the moment of rupture, $\tau \approx 0.87$. The stabilizing branch of the curve (Fig. 10) cannot be reached. On the other hand, the slope of $\tilde{\Pi}$ vs. τ 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 $H_f(\tau)$ 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 Π_{vw} 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_{ster} (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_{ster} 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_f, is shown in Fig. 13a for a high initial surfactant concentration. The concomitant change of the bulk liquid viscosity
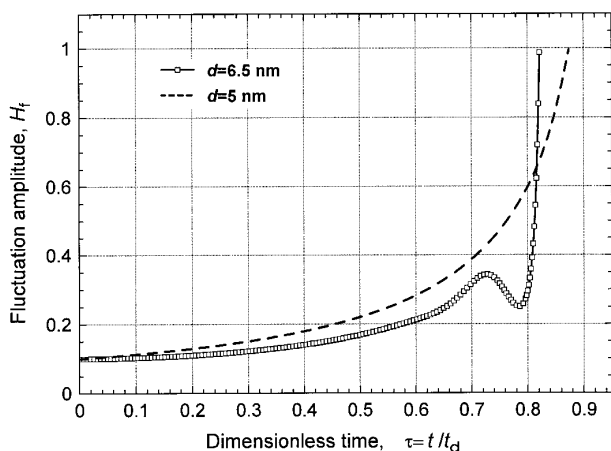

FIG. 9. Time dependence of the fluctuation wave amplitude for films with a nonionic surfactant. The wavenumbers are $k = 2.15$ for $d = 6.5$ nm and $k = 0.950$ for $d = 5.0$ nm (the most unstable modes); $h_0 = 50$ nm, $\Delta T = 0.10°C$.
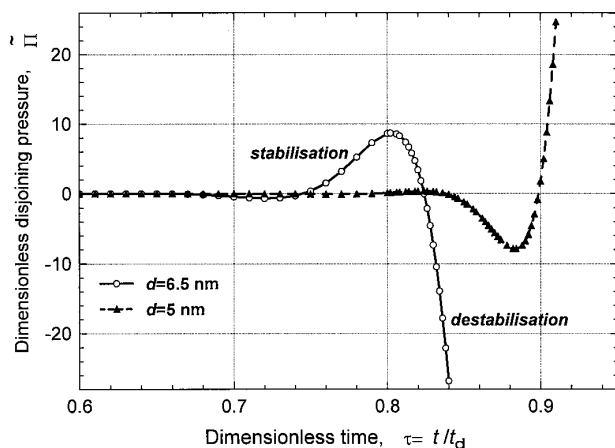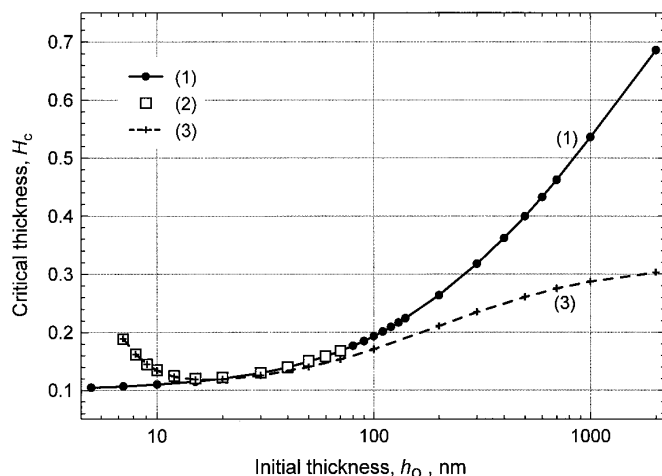

FIG. 11. Dependence of the film stability on the initial thickness, h_0. $d = 4.8$ nm, $\Delta T = 0.10°C$; the initial concentration of nonionic surfactant is equal to 10 CMC. (1): $A = -1.15 \times 10^{-20}$ J. (2 and 3): $A = +1.15 \times 10^{-20}$ J. (1 and 2): $c_{CMC} = 8.0$ mol/m^3; (3): $c_{CMC} = 5 \times 10^{-2}$ mol/m^3.
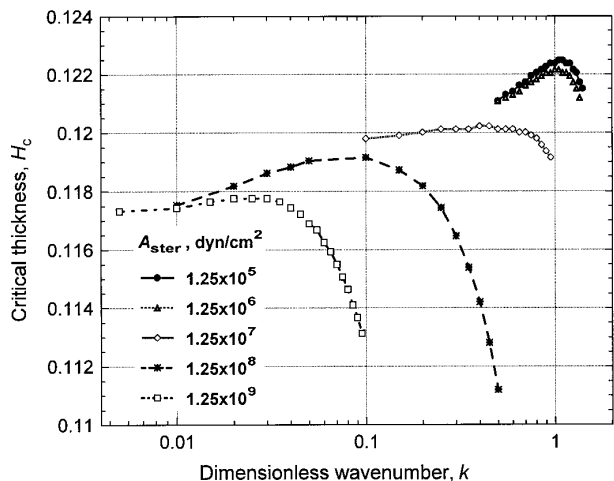
FIG. 12. Role of steric interactions in the film stability. $A = +1.15 \times 10^{-20}$ J, $d = 6$ nm, $h_0 = 20$ nm; the initial concentration of nonionic surfactant is equal to 10 CMC.

(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 monotonously 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, Π_{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 (ΔT) the thermal effects become predominant and suppress the impact of other fac-

tors. 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, ΔT, and the viscosity in the liquid film, η_{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 Π_{el} is much smaller in absolute
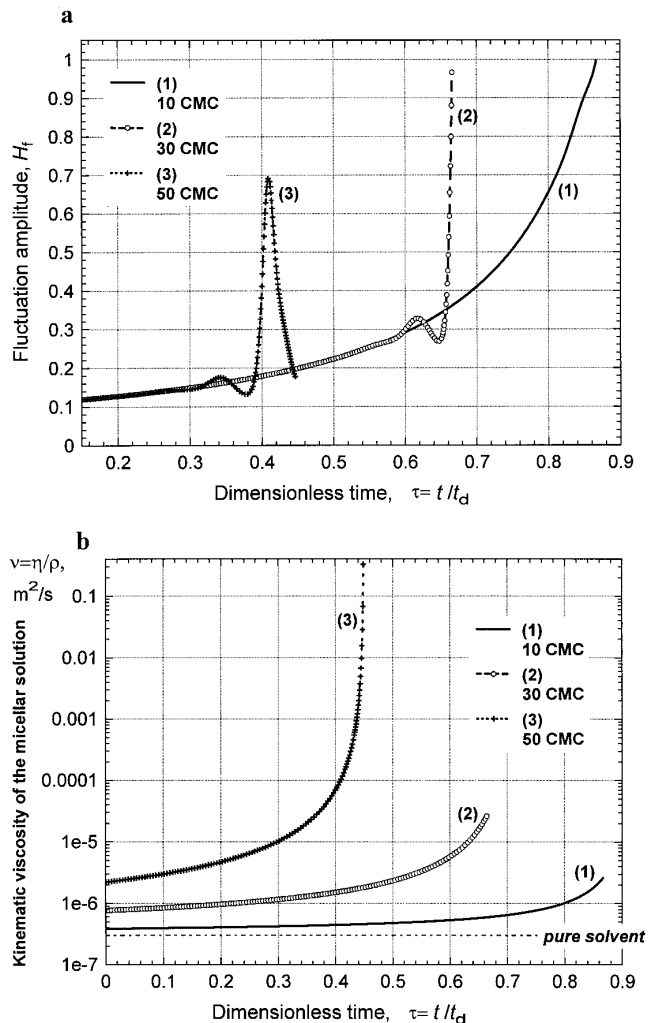

FIG. 13. Role of the surfactant concentration in the time evolution of instabilities in the film. $\Delta T = 0.10°C$, $h_0 = 120$ nm, $d = 6$ nm (nonionic surfactant). (a) Time dependence of the fluctuation wave amplitude for wave number $k = 1.50$. (b) Concomitant change in the bulk viscosity of the micellar solution, as the film thins due to evaporation and the particle volume fraction inside increases.

value than Π_{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.

ACKNOWLEDGMENT

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