Role of Surface Diffusion for the Drainage and Hydrodynamic Stability of Thin Liquid Films

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The dynamics of thin liquid films is analyzed taking into account the dependence of the surface diffusion coefficient of the adsorbed surfactant molecules on the density of the adsorption layer. The analysis shows that the Gibbs elasticity disappears from the final equations describing the drainage and hydrodynamic stability of thin liquid films. Thus from a theoretical viewpoint, no correlation between the Gibbs elasticity and the dynamic properties of the thin foam and emulsion films is expected. This conclusion is valid also for a variety of other dynamic processes (in a quasi-stationary regime) where the concentration Marangoni effect is important, such as the motion of drops and bubbles in a liquid medium, and rheology of foams and emulsions. The theory predicts that the main factors governing these processes are (i) the density of the adsorption layer and (ii) the surface friction coefficient of the adsorbed molecules.

1. Introduction

The important role of the particle interactions for the dynamic processes in concentrated dispersions is well recognized. The effect of these interactions on processes such as diffusion, sedimentation, electrophoresis, as well as on the rheological properties of concentrated dispersions has been intensively studied during the past decades.[1−22] In particular, it was shown that the particle interactions led to the appearance of two different types of diffusion coefficients: the collective diffusion coefficient, D_{BC} (usu-

ally denoted in the literature by D_C), and the self-diffusion coefficient, D_{BS} (usually denoted by D_S).[23] The collective diffusion coefficient, D_{BC}, is defined through Fick's law and characterizes the propagation of a concentration front in a nonhomogeneous suspension

$$\mathbf{J} = -D_{BC}\nabla c \tag{1.1}$$

where c is the number particle concentration and $\mathbf{J}$ is the diffusion flux. The self-diffusion coefficient, D_{BS}, characterizes the motion of an individual (tracer) particle and is conventionally defined by the expression

$$D_{BS} = \frac{1}{3}\int_0^\infty \langle \mathbf{V}_p(0)\cdot\mathbf{V}_p(t)\rangle \, \mathrm{d}t \tag{1.2}$$

where $\mathbf{V}_P$ is the particle velocity and t is time.

For infinitely diluted suspensions, these two coefficients converge to a value, D_{B0}, which is related to the hydrodynamic friction of the particle, β_{B0}, by the Einstein relation[24]

$$D_{B0} = kT/\beta_{B0} \tag{1.3}$$

For spherical particles $\beta_{B0} = 6\pi\eta a$ (η is dynamic viscosity of the fluid, a is particle radius), and the diffusion coefficient is given by the Stokes−Einstein formula

$$D_{B0} = kT/6\pi\eta a \tag{1.4}$$

For nonspherical particles and molecules, eq 1.4 can still be applied but an effective hydrodynamic radius, $\bar{a}$, has to be used.

It was rigorously shown[1−21] that D_{BC} and D_{BS} depend in a rather different way on the particle concentration. Thus for a relatively diluted suspension of hard spheres,

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(23) The following notation is used throughout the paper: The first letter in the subscript shows whether the bulk (B) or surface (S) diffusion coefficient is considered, whereas the second letter might be C (for collective diffusion), S (for self-diffusion), or 0 (for the diffusion coefficient of a single particle). One should not mistake the notation used for the surface collective diffusion coefficient, D_{SC}, with the notation for the bulk self-diffusion coefficient, D_{BS} (both are denoted in the literature by D_S).
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D_{BC} increases[2,8] while D_{BS} decreases[10,11] with the volume fraction of the particles. An expression for D_{BC}, valid at an arbitrary particle concentration, was derived[2,3,5] by generalizing the Einstein approach to systems of interacting particles:

$$D_{BC} = \frac{1}{(1 - \phi)\beta_B(\phi)}\left(\frac{\partial\mu}{\partial\ln\phi}\right)_{T,p} = D_{B0}\frac{K_B(\phi)}{(1 - \phi)}\left(\frac{\partial\mu/kT}{\partial\ln\phi}\right)_{T,p} \quad (1.5)$$

where ϕ is the particle volume fraction, $\beta_B(\phi)$ is the friction coefficient, and the dimensionless mobility function,[2] $K_B(\phi)$, is defined as

$$\beta_B(\phi) = \beta_{B0}/K_B(\phi) \quad (1.6)$$

For infinitely dilute suspensions ($\phi \to 0$), D_{BC} tends to D_{B0}, because $\mu(\phi,T) = \mu_0(T) + kT\ln\phi$ and $K_B(\phi) \to 1$. At finite concentrations, $K_B(\phi)$ accounts for the changes in the hydrodynamic friction between the fluid and the particles (created by the hydrodynamic interactions between the particles), while the gradient of the chemical potential gives the thermodynamic force. For suspensions of hard spheres, Batchelor[2] showed that the leading term for the hydrodynamic interactions is $K_B(\phi) \approx 1 - 6.55\phi$, while for the thermodynamic ones it is known[25] to be

$$\frac{1}{1-\phi}\left(\frac{\partial\mu/kT}{\partial\ln\phi}\right)_{T,p} \approx 1 + 8\phi$$

Combining these two terms together, Batchelor[2] obtained $D_{BC} = D_{B0}(1 + 1.45\phi)$, which shows that neither of them can be neglected.

The dependence of the *surface* diffusion coefficient on the density of the surfactant adsorption layers has practically remained out of the scope of the researchers so far. We are aware of one article[26] where this effect is incorporated in the theory of foam film thinning. However, the analysis in ref 26 has to be completed with an account for the hydrodynamic interactions between the adsorbed molecules. That is why in the present study we modify the approach used in the literature for description of the bulk diffusion and make a more comprehensive analysis of the role of intermolecular interactions in the surface diffusion.

The article is organized as follows. In section 2 we derive expressions for the dependence of the surface diffusion coefficient on the density of the surfactant adsorption layer. In section 3 we analyze the process of liquid film thinning. The surface mobility of the adsorbed molecules is discussed in section 4, and the conclusions are summarized in section 5. As Supporting Information (available via Internet or upon request from the authors), we briefly outline the theory of bulk diffusion to demonstrate the main effects leading to the dependence of D_{BC} on ϕ.

2. Surface Diffusion of Uncharged Surfactant Molecules

An expression for the concentration dependence of the surface collective diffusion coefficient, D_{SC}, of adsorbed molecules can be derived by following an approach, similar to that used previously[2,5] for bulk diffusion. Note that D_{SC} is expected to depend strongly on the surfactant concentration even at low bulk concentrations, because the

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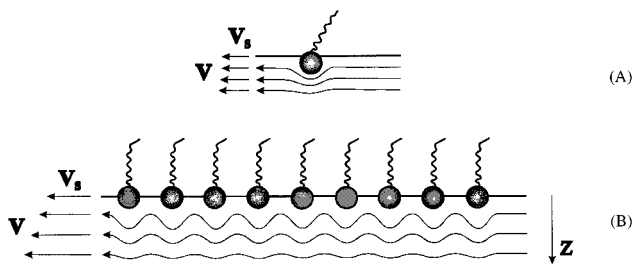

Figure 1. Schematic presentation of the streamlining of adsorbed surfactant molecules by a fluid substrate: (A) single molecule; (B) dense adsorption layer. The adsorbed molecules are considered immobile (held by fictitious external forces of an average magnitude, **f**), whereas the fluid is moving with velocity **V**(z). The surface velocity of the fluid, $\mathbf{V}_S$, is defined in the equimolecular dividing surface, $\mathbf{V}_S \equiv \mathbf{V}(0)$.

density of the molecules in the adsorption layers is typically much higher.

Let us outline first several differences between the bulk solutions and the interfacial adsorption layers: (i) The adsorption layer cannot be considered as a two-dimensional (2D) incompressible fluid. (ii) The surface concentrations, Γ_i, of the surfactant ($i = 1$) and of the fluid ($i = 0$) are considered as excess quantities with respect to the bulk concentrations and their values depend on the choice of the dividing surface (the interfacial tension of planar interfaces does not depend on the choice of the dividing surface[27]). In the following, we work with the so-called equimolecular surface, where the excess of the solvent molecules is zero, i.e., $\Gamma_0 = 0$. (iii) The perturbations in the surfactant adsorption are related to variations of the surface tension (which is a 2D analogue of the bulk pressure) through the Gibbs−Duhem equation for the surface.

The thermodynamic force acting on the surfactant molecules is given by the gradient of the surface chemical potential $\mu_{S,1}$

$$\mathbf{f}_S = -\nabla\mu_{S,1} \quad (2.1)$$

and the terminal velocity of the surfactant molecules is calculated by equilibrating the thermodynamic and surface friction forces

$$\mathbf{f}_{fr} = -\beta_S(\Gamma_1)\mathbf{V}_S \quad (2.2)$$

where $\beta_S(\Gamma_1)$ is the surface friction coefficient, whose meaning is the following: assume that surfactant molecules of density Γ_1 are kept immobile by external forces, **f**, in a 2D array, where the molecules have acquired statistically averaged equilibrium positions (determined by the intermolecular forces); assume also that the fluid substrate moves with an average surface velocity, $\mathbf{V}_S$, defined in the plane of the equimolecular dividing surface; then each molecule feels a friction force $\mathbf{f}_{fr}$, which is equal in magnitude (in average) to the external force, **f**. From the values of **f** and $\mathbf{V}_S$, one determines $\beta_S(\Gamma_1)$, eq 2.2. This definition shows that (i) β_S might strongly depend on the density of the adsorption layer, because the adsorbed molecules change the hydrodynamic flow distribution, see Figure 1, and (ii) β_S depends on the interactions between the molecules indirectly (the intermolecular forces determine the arrangement of the molecules in the adsorption layer). A more detailed discussion of the dependence β_S vs Γ_1 is given in section 4 below.

(27) Ono, S.; Kondo, S. Molecular Theory of Surface Tension in Liquids. In *Handbuch der Physik*; Springer: Berlin, 1960. Vol. X.

Combining eqs 2.1 and 2.2, and using $\mathbf{f}_s = -\mathbf{f}_{fr}$, we derive the following expression for the surfactant flux at the interface in the laboratory frame of reference:

$$\mathbf{j}_S = \Gamma\mathbf{V}_S = -\frac{\Gamma_1}{\beta_S(\Gamma_1)}\nabla\mu_{S,1} \qquad (2.3)$$

If we consider a perturbation of the surfactant adsorption Γ_1 at a fixed temperature, eq 2.3 can be written in the form

$$\mathbf{j}_S = -\frac{\Gamma_1}{\beta_S(\Gamma_1)}\left(\frac{\partial\mu_{S,1}}{\partial\Gamma_1}\right)_T\nabla\Gamma_1 \qquad (2.4)$$

Comparing eq 2.4 to Fick's law for the surface flux of the surfactant

$$\mathbf{j}_S = -D_{SC}\nabla\Gamma_1 \qquad (2.5)$$

we obtain the following expressions for the surface diffusion coefficient D_{SC}

$$D_{SC} = \frac{1}{\beta_S(\Gamma_1)}\left(\frac{\partial\mu_{S,1}}{\partial\ln\Gamma_1}\right)_T = D_{S0}K_S(\Gamma_1)\left(\frac{\partial\mu_{S,1}/kT}{\partial\ln\Gamma_1}\right)_T \qquad (2.6)$$

where $D_{S0} = kT/\beta_{S0}$ is the surface diffusion coefficient of an isolated adsorbed molecule, β_{S0} is the corresponding friction coefficient, and $K_S(\Gamma_1)$ is the dimensionless surface mobility coefficient, which accounts for the variations of the friction of a molecule in the adsorption layer, as compared to β_{S0}. Similar formula was derived recently in ref 26, but the dependence of the hydrodynamic friction on the adsorption was ignored, $K_S(\Gamma_1) = 1$. As discussed by the end of section 1, both types of factors (thermodynamic and hydrodynamic) are important and neither of them could be neglected in the general consideration.

Assuming a local thermodynamic equilibrium (which requires a small Peclet number in the appropriate diffusion length scale[5]), we have the following Gibbs−Duhem equation for the interface

$$\nabla\sigma = -\Gamma_1\nabla\mu_{S,1} \qquad (2.7)$$

where σ is the interfacial tension. Substituting eq 2.7 into eq 2.3 we derive

$$\mathbf{j}_S = \frac{1}{\beta_S(\Gamma_1)}\nabla\sigma \qquad (2.8)$$

which can be written also in the following equivalent forms:

$$\mathbf{j}_S = \frac{1}{\beta_S(\Gamma_1)}\left(\frac{\partial\sigma}{\partial\Gamma_1}\right)_T\nabla\Gamma_1 = -\frac{kT}{\beta_S(\Gamma_1)}\frac{E_G}{kT\Gamma_1}\nabla\Gamma_1 = \\ -D_{S0}K_S(\Gamma_1)\frac{E_G}{kT\Gamma_1}\nabla\Gamma_1 \qquad (2.9)$$

where $E_G = -(\partial\sigma/\partial\ln\Gamma_1)_T$ is the Gibbs elasticity of the adsorption layer. Therefore, for the surface collective diffusion coefficient we finally derive

$$D_{SC} = D_{S0}K_S(\Gamma_1)\frac{E_G}{kT\Gamma_1} \qquad (2.10)$$

Equation 2.10 demonstrates again that D_{SC} depends on the adsorption Γ_1 through two types of factors: (i) the interactions between the adsorbed molecules, expressed by the term $E_G/kT\Gamma_1$, and (ii) the change of the hydro-
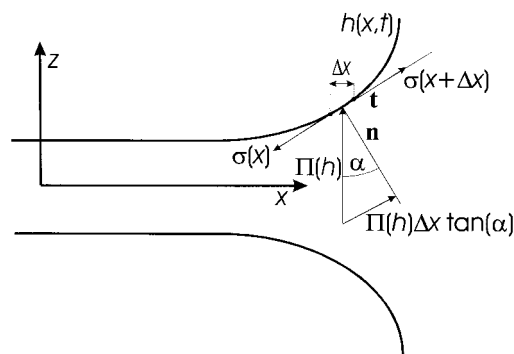

Figure 2. Schematic presentation of the profile of a thin liquid film and the forces acting on a surface element, Δx.

dynamic surface mobility of the adsorbed molecules, expressed by $K_S(\Gamma_1)$.

3. Effect of Surfactant on Thin Film Drainage and Hydrodynamic Stability

The consideration below is made for a thin liquid film of thickness, h, which may depend on time and the local coordinate (see Figure 2). For clarity, the analysis is made for a film of translational symmetry (infinite in one direction) but the main formulas are presented for circular films as well. The consideration is made for diffusion-controlled adsorption, when a local equilibrium between the adsorption layer and the subsurface layer is assumed.

The drainage and the hydrodynamic stability of thin liquid films are both analyzed by a common hydrodynamic approach.[28−32] In this section we briefly outline the key steps of this approach and analyze how the concentration dependence of the surfactant diffusion coefficients affects the final results.

The surfactants influence the dynamic properties of thin films in several ways: (1) by creating the concentration Marangoni effect, (2) by surface viscous effects, and (3) by changing the disjoining pressure, which accounts for the interaction between the two film surfaces. The tangential stress balance for the film surfaces can be written in general terms as[32]

$$-||T_{nt}||\Delta S = \text{tangential surface forces} + \\ \text{surface viscous forces} \qquad (3.1)$$

where $||T_{nt}||$ is the jump of the bulk tangential stress on the surface, i.e., this is the tangential force created by the bulk solution on the surface, and ΔS is the area of the surface element. This force is compensated by the tangential surface forces (including the gradient of the surface tension and the tangential projection of the disjoining pressure) and the surface viscous stress. For simplicity, in our consideration below we do not consider the surface viscous effects, which might be important in many cases. The viscous stresses can be incorporated into this consideration in a straightforward manner, without changing any of the main conclusions drawn in the article.[32]

The contribution of the surface tension gradient to the tangential force balance, eq 3.1, is $f_{surf} = (\partial\sigma/\partial x)\Delta S$. The

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(31) Levich, V. G. *Physicochemical Hydrodynamics*; Prentice Hall: Englewood Cliffs, NJ, 1962; Chapters XI−XII.
(32) Edwards, D. A.; Brenner, H.; Wasan, D. T. *Interfacial Transport Processes and Rheology*; Butterworth Heinemann: Oxford, 1991; Chapters III, V, and XIII.

contribution of the disjoining pressure to this balance can be calculated by using the Derjaguin approximation,[33] which is valid when the two surfaces are very close to each other and their slope is small, $(\partial h/\partial x)^2 \ll 1$. The Derjaguin approximation states that the force acting on a surface element is equal to $\Pi(h(x))\Delta S$, where $\Pi(h)$ is the disjoining pressure in an infinite planar film of thickness h equal to the local thickness of the curved film (the remaining parameters are the same as those of the curved film, see Figure 2). This force is directed perpendicularly to the x-axis, outward from the film. Note that the force is *not* directed normally to the film surfaces, because otherwise it could not compensate the variation of the surface tension, created by the disjoining pressure, in an equilibrium thin film.[34] Note also that $\Delta S = L\Delta x/\cos(\alpha) \approx L\Delta x$, where $L\Delta x$ is the projection of the film area on the x-direction and α is the slope of the film surface, $\tan(\alpha) = \partial h/\partial x \ll 1$. Thus we obtain $f_t = \Pi(h)\Delta S(\partial h/\partial x)$ for the tangential component of the force created by the disjoining pressure, whereas the normal component of this force is $f_t = \Pi(h) \cos(\alpha)\Delta S \approx \Pi(h)\Delta S$. Combining the contributions of the disjoining pressure and of the surface tension gradients, we obtain the following expression for the tangential force balance on the film surface

$$-||T_{nt}|| = \frac{\partial \sigma}{\partial x} + \Pi \frac{\partial h}{\partial x} \quad (3.2)$$

In the case of equilibrium films, when the bulk tangential stresses are zero, the latter equation gives the known expressions for the surface tension and the running slope angle as functions of the disjoining pressure.[34]

If hydrodynamic processes occur in the film, the local surface tension depends on both the surfactant concentration (which is perturbed by the hydrodynamic flow in the film) and the disjoining pressure. To extract the effect of the surfactant concentration, we assume that the surface is in a *local* thermodynamic equilibrium, viz., the Gibbs–Duhem equation can be used[30,34]

$$d\sigma = -\Gamma_1 \, d\mu_{1,S} - \Pi \, dh \quad (3.3)$$

Combining eqs 3.2 and 3.3, we derive the following expression for the jump of the bulk viscous stress

$$||T_{nt}|| = \Gamma_1 \frac{\partial \mu_{1,S}}{\partial x} \quad (3.4)$$

The right-hand side of eq 3.4 expresses the so-called *concentration Marangoni effect*. Note that the effect of the disjoining pressure does not appear in eq 3.4, and only the effect of the surfactant adsorption has remained. In other words, only the gradients of the surface tension created by variations of Γ_1 must be taken into account when calculating the Marangoni term.

For thin films, one can calculate the gradients of the surface tension, created by variations of Γ_1, from the equations of surfactant conservation in the film interior and on the surface. By integrating these equations across the film and using the equation of fluid conservation, one obtains the following expression for the balance of surfactant in a given small element of length dx in the film (see Figure 2)[30,31]

(33) Derjaguin, B. V.; Churaev, N. V.; Muller, V. M. In *Surface Forces*; Nauka: Moscow, 1986; Chapter 2 [in Russian].
(34) Ivanov, I. B.; Kralchevsky, P. A. In *Thin Liquid Films*; Ivanov, I. B., Ed.; Marcel Dekker: New York, 1988.

$$\frac{\partial}{\partial t}\left(\Gamma_1 + \int_0^h c_1 \, dz\right) + \frac{\partial}{\partial x}\left(\Gamma_1 U_S + \int_0^h c_1 V_x \, dz\right) = \frac{\partial}{\partial x}\left(D_{SC}\frac{\partial \Gamma_1}{\partial x} + \int_0^h D_{BC}\frac{\partial c_1}{\partial x} \, dz\right) \quad (3.5a)$$

where the z-coordinate is perpendicular to the x-axis, V_x is the x-component of the fluid velocity in the film, and $U_S \equiv V_x|_{z=h}$ is the surface tangential velocity of the fluid at the film surface. The terms under the time derivative represent the total amount of surfactant on the surface and in the bulk at point x, the other terms on the left-hand side represent the convective fluxes on the surface and in the bulk of the film, and the terms on the right-hand side present the respective diffusion fluxes. For circular films, this equation acquires the form

$$\frac{\partial}{\partial t}\left(\Gamma_1 + \int_0^h c_1 \, dz\right) + \frac{1}{r}\frac{\partial}{\partial r}(r\Gamma_1 U_S + r\int_0^h c_1 V_r \, dz) = \frac{1}{r}\frac{\partial}{\partial r}\left(rD_{SC}\frac{\partial \Gamma_1}{\partial r} + r\int_0^h D_{BC}\frac{\partial c_1}{\partial r} \, dz\right) \quad (3.5b)$$

where r is the radial coordinate. Note that the film thickness $h = h(x,t)$ or $h(r,t)$ in eq 3.5 is a function of both time and spatial coordinate. The equation for conservation of the fluid is[31]

$$\frac{\partial h}{\partial t} = \frac{\partial}{\partial x}(\int_0^h V_x \, dx)$$

or

$$\frac{\partial h}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}(r\int_0^h V_r \, dz) \quad (3.6)$$

for circular films.

For very thin films, the integrals in the z-direction can be taken under the assumption that the surfactant concentration is almost constant across the film, i.e., equal to the subsurface concentration, $c_{1,S}$: $\int_0^h c_1 \, dz \approx c_{1,S}h$ and $\int_0^h c_1 V_x \, dz \approx c_{1,S}\int_0^h V_x \, dz$ (another approach, which is based on expansion of the surfactant concentration in series around the equilibrium concentration and gives equivalent results, is presented in refs 28 and 30). Under this assumption, eq 3.5a converts into

$$\frac{\partial}{\partial t}(\Gamma_1 + c_{1,S}h) + \frac{\partial}{\partial x}(\Gamma_1 U_S + c_{1,S}\int_0^h V_x \, dz) = \frac{\partial}{\partial x}\left(D_{SC}\frac{\partial \Gamma_1}{\partial x} + D_{BC}h\frac{\partial c_{1,S}}{\partial x}\right) \quad (3.7)$$

Then we can use eqs 1.5 and 2.6 and express the diffusion fluxes in terms of the derivatives of the surface and bulk chemical potentials

$$\frac{\partial}{\partial t}(\Gamma_1 + c_{1,S}h) + \frac{\partial}{\partial x}(\Gamma_1 U_S + c_{1,S}\int_0^h V_x \, dz) = \frac{\partial}{\partial x}\left(\frac{\Gamma_1}{\beta_S}\frac{\partial \mu_{1,S}}{\partial x} + \frac{hc_{1,S}}{(1 - \phi_{1,S})\beta_B}\frac{\partial \mu_1}{\partial x}\right) \quad (3.8)$$

For diffusion-controlled adsorption, the surface and the subsurface layers are in a local thermodynamic equilibrium ($\mu_{1,S} = \mu_1$), and we derive (see also eq 3.3)

$$\frac{\partial}{\partial t}(\Gamma_1 + c_{1,S}h) + \frac{\partial}{\partial x}\left(\Gamma_1 U_S + c_{1,S}\int_0^h V_x\,dz\right) =$$
$$-\frac{\partial}{\partial x}\left\{\left(D_{S0}K_S(\Gamma_1) + D_{B0}\frac{K_B(\phi_1)}{1-\phi_1}h\frac{c_{1,S}}{\Gamma_1}\right)\frac{1}{kT}\left(\frac{\partial\sigma}{\partial x} + \Pi\frac{dh}{dx}\right)\right\} \tag{3.9}$$

Two approximations, commonly used in the literature at this stage, are as follows:[30] (i) the deviations of the surfactant adsorption and concentration from their equilibrium values are small, and (ii) the time derivatives of the adsorption, Γ_1, and of the subsurface concentration are negligible, that is, the convection fluxes are compensated by the diffusion ones (so-called "quasi-stationary regime" of film thinning). Under these assumptions we obtain (see also eq 3.6)

$$\Gamma_{1,eq}U_S =$$
$$-\left(D_{S0}K_S(\Gamma_{1,eq}) + D_{B0}\frac{K_B(\phi_{1,eq})}{1-\phi_{1,eq}}h\frac{c_{1,eq}}{\Gamma_{1,eq}}\right)\frac{1}{kT}\left(\frac{\partial\sigma}{\partial x} + \Pi\frac{dh}{dx}\right) \tag{3.10}$$

where $\Gamma_{1,eq}$ and $c_{1,eq}$ are the respective equilibrium values of the adsorption and of the bulk surfactant concentration. In the case of a circular film, the x-derivatives in eq 3.10 must be replaced by derivatives with respect to the radial coordinate, r. From eq 3.10, we can express the surface force acting on the interface, which is needed for calculating the jump of the tangential stress in eq 3.2

$$-\left(\frac{\partial\sigma}{\partial x} + \Pi\frac{dh}{dx}\right) =$$
$$\frac{U_S kT\Gamma_{1,eq}}{\left(D_{S0}K_S(\Gamma_{1,eq}) + D_{B0}\dfrac{K_B(\phi_{1,eq})}{1-\phi_{1,eq}}h\dfrac{c_{1,eq}}{\Gamma_{1,eq}}\right)} =$$
$$\frac{U_S\Gamma_{1,eq}}{\left(\dfrac{1}{\beta_S(\Gamma_{1,eq})} + \dfrac{hc_{1,eq}}{(1-\phi_{1,eq})\beta_B(\phi_{1,eq})\Gamma_{1,eq}}\right)} \tag{3.11}$$

The comparison of eqs 3.2, 3.4, and 3.11 shows that we succeeded in expressing the concentration Marangoni effect through the surface velocity, U_S, and the equilibrium properties of the surfactant solution.

Under the same assumptions (small deviation from equilibrium and quasi-stationary regime of film thinning) an equivalent formula was derived earlier,[29,30] which includes the collective diffusion coefficients of the surfactant

$$-\left(\frac{\partial\sigma}{\partial x} + \Pi\frac{dh}{dx}\right) = \frac{U_S E_G}{\left[D_{SC} + D_{BC}h\left(\dfrac{\partial c_1}{\partial\Gamma_1}\right)_{eq}\right]} \tag{3.12}$$

Expression 3.12 has been used by Ivanov and co-workers[29,30] to solve a variety of problems concerning the drainage and the hydrodynamic stability of thin liquid films. The continuity eq 3.6, the Navies−Stokes equation in the lubrication approximation, and eqs 3.2 and 3.12 with the respective boundary conditions (which depend on the specific problem under consideration) were used to determine the fluid velocity, the pressure distribution in the film, and its profile, i.e., to solve the entire hydrodynamic problem. Just for example, Radoev et al.[28] found that the drainage velocity, $V_{DR} \equiv -dh/dt$, of a planar foam film in the presence of water-soluble surfactant can be expressed by the formula

$$\frac{V_{DR}}{V_{Re}} = 1 + b + \frac{h_s}{h} \tag{3.13}$$

where

$$b \equiv 3\eta D_{BC}/h_a E_G$$
$$h_s \equiv 6\eta D_{SC}/E_G$$

and

$$h_a \equiv \partial\Gamma_{1,eq}/\partial c_{1,eq}$$

The coefficients b and h_s account for the influence of the bulk and surface diffusion on the film thinning rate; h_a accounts for the surface activity of the surfactant. The Reynolds velocity of thinning, V_{Re}, of a circular planar film between two tangentially immobile surfaces is given by the expression

$$V_{Re} = \frac{2h^3(P_c - \Pi)}{3\eta R^2} \tag{3.14}$$

where R is the film radius and P_c is the capillary pressure film meniscus. Therefore, the effect of the surfactant on the velocity of film thinning is expressed by E_G, D_{BC}, D_{SC}, h_a, and Π. Note, however, that the dependence of the surface and bulk diffusion coefficients on the surfactant concentration has not been taken into account in refs 28−32.

The comparison of eqs 3.11 and 3.12 shows that the dependence of the diffusion coefficients on the surfactant concentration (eqs 1.5 and 2.10) leads to the disappearance of the Gibbs elasticity in the tangential stress balance (Marangoni effect)−E_G is replaced by the term $kT\Gamma_{1,eq}$ in eq 3.11. The actual reason for this result is D_{SC} is also proportional to the Gibbs elasticity (eq 2.10). Similarly, the term $(\partial c_1/\partial\Gamma_1)_{eq}$ is replaced by $c_{1,eq}/\Gamma_{1,eq}$, due to the concentration dependence of D_{BC}. On the other side, note the different definitions of the diffusion coefficients entering eqs 3.11 and 3.12. The diffusion coefficients in eq 3.11 are the "single molecule" diffusion coefficients, D_{B0} and D_{S0}, which do not depend on the surfactant concentration. On the contrary, the diffusion coefficients in eq 3.12 are the full collective diffusion coefficients, which depend on the surfactant concentration.

One can see that eq 3.11 can be formally derived from eq 3.12 by the substitutions:

$$D_{BC} \rightarrow D_{B0}\frac{K_B(\phi_1)}{(1-\phi_1)}, \qquad D_{SC} \rightarrow D_{S0}K_S(\Gamma_1) \tag{3.15a}$$

$$E_G \rightarrow kT\Gamma_1, \qquad \partial c_1/\partial\Gamma_1 \rightarrow c_1/\Gamma_1 \tag{3.15b}$$

Therefore, all known equations for the thin film dynamics and stability, obtained under the same assumptions,[28−30] remain valid if the substitutions, eqs 3.15, are made and the proper definitions of the diffusion coefficients are used. For instance, the coefficients accounting for the effect of surfactant on the rate of film thinning, eq 3.13, acquire the form

$$b \equiv \frac{3\eta D_{B0}K_B(\phi_1)}{h_a kT\Gamma_{1,eq}(1-\phi_1)} \tag{3.16}$$

$$h_s \equiv \frac{6\eta D_{S0} K_S(\Gamma_{1,eq})}{kT\Gamma_{1,eq}}$$

$$h_a \equiv \Gamma_{1,eq}/c_{1,eq}$$

Note also that b, h_s, and h_a are expected to be independent of the solvent viscosity, η, because D_{b0} and D_{S0} are inversely proportional to η.

Let us mention here that the film can be considered in a local equilibrium if the Peclet number $Pe = hV_x/D_B \sim RV_{DR}/D_B \ll 1$. For typical values ($R \sim 1$ mm, $V_{DR} \sim 1$ nm/s, $D_B \sim 10^{-9}$ m²/s), one estimates $Pe \sim 10^{-3}$, which shows that the diffusion is fast enough to ensure a local equilibrium in the thinning film.

The main conclusion from the above analysis is that the Gibbs elasticity and the term $\partial\Gamma_1/\partial c_1$ disappear from the expressions describing the film dynamics. Since the surfactant solutions are diluted in most cases, the bulk factor, $K_B(\phi_1)/(1 - \phi_1)$, can be typically taken as unity. Thus the main physicochemical quantities governing the drainage and the hydrodynamic stability of thin films are the surfactant adsorption, Γ_1, and the surface mobility factor $K_S(\Gamma_1)$.

The above conclusion remains valid for single interfaces as well—the Gibbs elasticity will disappear from the equations describing the concentration Marangoni effect (in a quasi-stationary regime), because the gradient of the surface tension, which is the driving force for the surface diffusion, and the surface collective diffusion coefficient are both linearly proportional to E_G. Additionally, for single interfaces the hydrodynamic problem requires one to find the surfactant distribution in the vicinity of the interface. For this purpose one can use a model profile for the surfactant concentration[35-37] or a concentration boundary layer.[36]

Note that the quasi-stationary approximation might be inadequate for description of some dynamic processes, i.e., the time derivatives cannot be neglected in the equation describing the surfactant balance on the surface (see, e.g., eq 3.9). The analysis of such systems is much more complex, and one cannot predict in advance whether the Gibbs elasticity will cancel out from the final equations as in the quasi-stationary model.

4. Discussion of the Surface Friction Function, $\beta_S(\Gamma_1)$

The analysis performed above shows that the function $\beta_S(\Gamma_1)$ plays an important role in the dynamics of interfaces and thin liquid films. Nevertheless, we are not aware of any study where this function has been investigated theoretically or experimentally. That is why in this section we briefly discuss the expected qualitative behavior of $\beta_S(\Gamma_1)$ and suggest some (imaginary at the present) experiments for its determination. Since $\beta_S(\Gamma_1) = \beta_{S0}/K_S(\Gamma_1)$, we first consider the friction coefficient of a single (isolated) adsorbed molecule, β_{S0}; the influence of the other adsorbed molecules on the friction coefficient, expressed by the function $K_S(\Gamma_1)$, is discussed afterward (see Figure 1).

At least in principle, β_{S0} can be determined by available experimental techniques in a straightforward manner. Since β_{S0} is related to the surface diffusion coefficient by

the Einstein relation

$$D_{S0} = kT/\beta_{S0} \qquad (4.1)$$

any method for measuring the surface diffusivity of adsorbed molecules should provide the necessary information, if very diluted adsorption layers are studied (such that the interactions between the adsorbed molecules are negligible). This could be, for instance, the so-called FRAP method[17,38] (fluorescence recovery after photobleaching) if its sensitivity is high enough. On the other hand, the value of β_{S0} could be roughly estimated (within the correct order of magnitude) from the bulk diffusion coefficient or from the dimensions of the molecule. If one assumes that the bulk and surface diffusion coefficients, D_{S0} and D_{B0}, do not differ very much (which is probably correct), then one can estimate β_{S0} from eq 4.1. Alternatively, one can assume that the diffusivity of the adsorbed molecule is similar to that of a sphere or disk of similar dimensions, placed on the surface.[39,40] For typical surfactants of low molecular mass, one may expect $\beta_{S0} \sim 10^{-11}$ N·s/m.

To determine the function $K_S(\Gamma_1)$ is a much more difficult task. Qualitatively, one may expect that $K_S(\Gamma_1)$ is a monotonically decreasing function of Γ_1, because the hydrodynamic friction should increase with the density of the adsorption layer. At high surface densities, $K_S(\Gamma_1)$ should tend to zero, because only aqueous molecules participating in the hydration shells of the surfactant heads remain in the adsorption layer (these molecules are much less mobile than the molecules in free water). This limit corresponds to tangentially immobile surfaces (cf. eq 3.10).

The rigorous theoretical approach to determine $K_S(\Gamma_1)$ would require solving the hydrodynamic problem for the streaming of the fluid along a 2D array of immobile adsorbed molecules, whose mutual positions reflect the intermolecular interactions. This is a formidable theoretical task. The experimental determination of $K_S(\Gamma_1)$ is also difficult, because the surface diffusion in a nonhomogeneous adsorption layer is always accompanied by surface convection (created by gradients of σ). Hence the interpretation of data obtained by any experimental method, based on measuring the surfactant transport along the surface, should explicitly separate the effects of the surface convection and diffusion.

To illustrate this difficulty, let us describe an imaginary experiment that would give the values of $\beta_S(\Gamma_1)$. The experiment consists of the following: (1) The velocity of a surface longitudinal wave created by small gradients of Γ_1 is measured. Since the adsorption perturbation causes a gradient of surface tension, $\nabla\sigma$, the wave velocity in the laboratory frame of reference would depend both on the diffusion and convection on the surface. (2) To extract the convective contribution to the wave propagation, one should determine independently the velocity of the fluid in the equimolecular dividing surface, e.g., by laser Doppler anemometry (more precisely, the fluid velocity in a set of points close to the surface should be measured and extrapolated toward the equimolecular dividing surface). The difference between the velocity of the fluid in the surface layer and the averaged surfactant velocity would give the contribution of the surface diffusion in the overall

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surface transport of surfactant. (3) Finally, from $\nabla\sigma$ (supposedly known) one can calculate the friction coefficient (see eq 2.8). Obviously, the above "direct" experiment is rather complex, and we do not know whether the available experimental setups have the necessary accuracy to give reliable results. We describe this experiment in detail only because it demonstrates rather well the possible difficulties and clarifies some of the concepts related to the surface friction functions.

A more plausible approach for determination of $K_S(\Gamma_1)$ would be to measure directly the surface tension $\sigma(x,t)$ during a dynamic process, related to a surface transfer of surfactant in a container of well-defined geometry (e.g., Langmuir trough[36,41,42]), and to calculate the velocity of the fluid in the substrate by solving the Navier–Stokes equations. Calculations of this type typically require some model assumptions to be made for solving the hydrodynamic problem, and only a rigorous analysis combined with comparison to real experimental data would clarify whether this approach is feasible. It is worth mentioning that such measurements, $\sigma(x,t)$, were performed already by Panaiotov et al.[41,42] in a Langmuir trough for other purposes. However, the surface diffusion was neglected in refs 41 and 42, because it is probably a second-order effect for the specific problem considered there.

Another promising experimental approach is to develop further the procedure, suggested by Manev et al.[43] and used by Valkovska and Danov,[26] for calculating the surface diffusion coefficient from experimental data for the rate of thinning of foam films, eqs 3.13 and 3.14. Experiments at various surfactant concentrations could provide the necessary information for $\beta_S(\Gamma_1)$, if the adsorption isotherm $\Gamma_1(c_1)$ and the disjoining pressure isotherm Π are known.

Let us note at the end that although the functions $\beta_S(\Gamma_1)$ and $K_S(\Gamma_1)$ are monotonic, the dependence of the collective diffusion coefficient, D_{SC}, might be a nonmonotonic function of Γ_1, because it includes also a contribution from the Gibbs elasticity, E_G (see eq 2.10), which has a different functional dependence (theoretically, E_G is calculated from the surface equation of state of the adsorption layer, whereas experimentally E_G is determined from surface tension isotherms). Similar nonmonotonic dependence of the bulk diffusion coefficient, D_{BC}, on the volume fraction of suspended particles was predicted in various studies.[15,16,21]

6. Conclusions

Following an approach, similar to that used for description of the bulk diffusion in concentrated suspensions, we have derived expressions for the surface collective diffusion coefficient, D_{SC}, of adsorbed molecules, eqs 2.6 and 2.10. It is shown that D_{SC} depends on the density of the adsorption layer, Γ_1, via two types of factors: (i) the interactions between the adsorbed molecules, which lead to a thermodynamic factor $E_G/kT\Gamma_1$, where E_G is the Gibbs elasticity of the adsorption layer, and (ii) the hydrodynamic interactions between the adsorbed molecules, which can be expressed by the hydrodynamic mobility factor $K_S(\Gamma_1)$; see Figure 1.

An analysis of the role of surface diffusion in the dynamics of film thinning and rupture is performed, taking into account the concentration dependence of the bulk and surface diffusion coefficients. A new expression is derived, eq 3.11, which relates the surface stress with the surface velocity. This expression can be used to solve a variety of particular problems following a standard procedure, developed earlier by Ivanov and co-workers.[29,30] The analysis shows that the final results remain functionally the same, if the material parameters, which account for the surfactant properties, are properly modified—see eqs 3.13, 3.15, and 3.16.

The most interesting conclusion from the study is that the Gibbs elasticity, E_G, disappears from the tangential stress balance describing the concentration Marangoni effect (eq 3.4), if the concentration dependence of the surface diffusion coefficient is taken into account (and the process can be considered as quasi-stationary); see eq 3.11. The actual reason for this result is that the gradient of Γ_1 (which is the driving force for the surface diffusion) and the surface collective diffusion coefficient are both linearly proportional to E_G. Instead of E_G, a thermodynamic term $kT\Gamma_1$ appears in the final equations; see, e.g., eq 3.16. Thus from a theoretical viewpoint, no direct correlation between the Gibbs elasticity and the dynamic properties of thin foam and emulsion films is expected. This conclusion is not limited to the processes in thin liquid films and is valid also for a variety of other dynamic processes, which are driven by the concentration Marangoni effect—motion of drops and bubbles in a fluid, rheology of emulsions and foams, etc. In addition, if diffusion-controlled adsorption is assumed, the so-called adsorption thickness, $h_a = \partial c_1/\partial\Gamma_1$, is replaced by the term c_1/Γ_1 in the final equations, due to the concentration dependence of the bulk diffusion coefficient.

The surface mobility factor, $K_S(\Gamma_1)$, is expected to play an important role even at low bulk concentrations of surfactant (when the bulk mobility factor $K_B \approx 1$), because the surfactant molecules are typically much more densely packed in the adsorption layer than in the bulk. Theoretical estimates or experimental measurement of $K_S(\Gamma_1)$ are, therefore, important to quantify the effect of surfactants on the film dynamics and stability; see section 4.

Supporting Information Available: Bulk diffusion of uncharged surfactant molecules (derivation of eq 1.5). This material is available free of charge via the Internet at http://pubs.acs.org.

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