

Disjoining pressure of thin films stabilized by nonionic surfactants

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Abstract

In this article an attempt is made to derive a comprehensive theory of the disjoining pressure of thin liquid films, stabilized by low molecular nonionic surfactants. We accounted for effects playing a role in the case of surfactants with spherical hydrophilic heads: (i) The thermal fluctuations of the adsorbed surfactant molecules, due to the fact that the energy of adsorption of a $-\text{CH}_2-$ group is approximately equal to the average thermal energy $k_B T$; (ii) The contribution of the collisions between molecules adsorbed on different surfaces; (iii) The restriction imposed on the fluctuation of the molecules by the presence of a second surface situated at a small distance h from the interface where the molecules are adsorbed; (iv) The volume of the hydrophilic heads, which expels part of the water molecules from the film region; (v) The equilibrium between the molecules adsorbed at the film surfaces and at the menisci surrounding the film. The adsorption on the film surfaces has two main effects. First, the concentration of solute inside the film region becomes larger than in the bulk solution and this will push the solvent toward the film thus creating an osmotic pressure (the disjoining pressure), which tends to increase the film thickness. Second, the higher concentration inside the film and the collisions between the polar heads lead to higher chemical potential, which pushes the surfactant toward the meniscus. We treated these effects by modifying adequately the Hildebrand–Scatchard theory for the osmotic pressure of concentrated solutions. The partition function of the surfactant, needed for this calculation, was found by deriving an expression for the configurational integral, based on virial expansion. The surface equations of state of Helfand, Frisch and Lebowitz and Volmer were critically analyzed and then generalized, by using the partition function obtained by virial expansion, to permit the derivation of partition functions of the surfactant molecules in the film. A simple thermodynamic approach was developed and applied to derive expressions for the disjoining pressure, Π , and the chemical potential of the surfactant molecules in the film, μ . They were used to calculate numerically Π and μ and analyze their dependence on the film thickness h and the surface coverage θ . It turned out that Π has completely different behavior above and below $h=2d$, where d is the diameter of the hydrophilic head. For thick films, with $h>2d$, the decay of Π is initially exponential (due mainly to the thermal fluctuations of the adsorbed molecules), followed by a long tail, proportional to h^{-2} , due to the contribution of the osmotic pressure of the displaced solvent molecules. At $h<2d$ the collisions between the molecules adsorbed at different surfaces are hindered, which leads to a steady decrease of the contribution due the interaction between the molecules. The overall result of these effects is the appearance of a maximum of Π at $h=2d$. It is very large (it may reach 1000 atm and even more) and depends strongly on the surfactant adsorption. To facilitate the application and the analysis of the theory, we derived several simpler asymptotic expressions. One of them is virial expansion, which is valid for small surface coverage and has the advantage of being independent of the adsorption model. The other asymptotic expression is applicable at $h>2d$, which is the region where the stabilization of the film occurs. We compared our theory with the simpler theory of Israelachvili and Wennerström. It turned out that while both theories lead to decay of Π vs. h , the numerical results and the shape of the curves are usually very different. The experimental data, which could be used to verify our theory, are scarce, but we found reasonable agreement with the data of Lyle and Tiddy for bilayers of C_{12}EO_4 . The data of Parsegian et al. for lipid bilayers also confirmed qualitatively some of our theoretical conclusions.

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1. Introduction

The advent of the DLVO theory gave tremendous thrust to Colloid Science, since it allowed quantitative interpretation of many inexplicable before phenomena observed with charged particles. Without exaggeration one may say that only then Colloid Science became truly science. The other important colloidal phenomena, stabilization of colloids by adsorption of polymers, also received adequate theoretical treatment through several theories, the most widely used being Alexander–de Gennes theory [1–3]. However, the third important phenomenon, stabilization of solid and fluid dispersions by low molecular nonionic surfactants, is by far less understood. It is customary to say that the nonionic surfactants provide “steric stabilization”. From the very definition of “steric effects” (“*Steric effects are the interaction of molecules dictated by their shape and/or spatial relationships*” [Wikipedia Encyclopedia]) it follows that by “steric stabilization” one understands direct contact and repulsion (as between hard spheres or rods) between the hydrophilic heads of the adsorbed surfactant, i.e. it is assumed that the surfactant creates kind of a fence around the particles, thus preventing their coagulation or coalescence. Whereas for ionic surfactants the DLVO theory allows the calculation of the stabilizing repulsive force and its dependence on the system parameters, such as surfactant adsorption, surface potential and electrolyte concentration, until very recently there was no theory, permitting similar calculations for the stabilizing efficiency and its dependence on the system parameters (including also surfactant concentration) for low molecular nonionic surfactants. Experimentally it was shown that lipids [4,5] and other nonionic surfactants [6] can give rise to very strong repulsion, reaching thousand atmospheres and even more, but it was attributed to “hydration forces”, a notion which we find rather obscure.

Israelachvili and Wennerström [7] were the first to suggest another possible reason for this repulsion and to do the first attempt for a simple theory. They used the hypothesis of Aniansson [8] that due to thermal fluctuations the surfactant molecules can protrude, thus creating some roughness of the interface. Israelachvili and Wennerström implicitly assumed that the film surfaces are completely covered by surfactant molecules, ordered in such a way that exactly opposite to each

molecule on one of the surfaces there is another molecule on the other surface. They oscillate and when they collide this leads to a repulsive force. The authors termed it “protrusion force”.

We agree that such force must exist but we believe that the phenomenon is much more complicated. In order to be able to describe the transition from coalescence to stability, one must account also for the fact that the surfaces may not be completely covered by surfactant. Instead, the adsorption Γ may change with the bulk concentration. If the adsorption is low, the repulsion should not be able to stabilize the film and it will rupture. If the surface coverage is not complete, the oscillating molecules can collide also with the bare opposite surface. Besides, in this case the molecules can move along the surface. Then the probability for collision and the contribution of a given collision to the repulsive force will depend in a very complicated way on the relative positions of the colliding molecules. The theory is additionally complicated by the fact that the hydrophobic tails and the hydrophilic heads of the surfactant molecules displace part of the water in the surface region – this gives rise to another contribution to the free energy of the system and thereby – to the repulsion force.

That is why we adopted a different and more detailed approach. We confined ourselves with bubbles or drops, which can deform and form a planar thin film. The rest of the surface of the bubbles or drops, encircling the film, we call meniscus. The surfactant molecules adsorb on the surfaces of the film and oscillate normally to them. They interact between themselves and with the film surfaces. This interaction has two main effects: (i) The concentration of solute inside the film region becomes larger than in the bulk solution and the chemical potential of the solvent (usually water) becomes lower — this will push the solvent toward the film thus creating an osmotic pressure, which tends to increase the film thickness; (ii) The higher concentration inside the film and the collisions between the hydrophilic heads lead to higher chemical potential of the surfactant molecules in comparison with its value at the meniscus surfaces — hence, the surfactant will be pushed toward the meniscus (or will desorb, if it is soluble). The competition between these two effects determines the equilibrium repulsive force between the film surfaces. The value of this force per unit area was called by Derjaguin “disjoining pressure”, Π (see e.g. [9]). It is assumed positive, when it

leads to repulsion between the film surfaces and negative when it leads to attraction. From hydrostatic viewpoint the disjoining pressure of a planar film is equal to the difference of the normal component of the pressure tensor inside the thin film and the bulk liquid. The equilibrium disjoining pressure must be equal to the capillary pressure of the meniscus [10].

The phenomenon, described above, looks much like the usual osmotic pressure, although there are some differences. The film surfaces, which adsorb the surfactant molecules, create higher concentration in the film than in the bulk solution and in this respect they play the role of a semi-permeable membrane. The difference is that in the true osmotic equilibrium the membrane is permeable only for the solvent and is totally impermeable for the solute whereas here the solute molecules can leave the film surface and go to the meniscus or the bulk. The transport of solute molecules to the meniscus surfaces must stop when the solute chemical potentials in the film and at the meniscus become equal — hence, the membrane is in fact partly permeable for the solute. Nevertheless, the disjoining pressure due to the adsorbed molecules is a close analog of the osmotic pressure. That is why we based our theory on the theory of Hildebrand [11,12] and Scatchard [13] for the osmotic pressure of concentrated solutions.

In this theory the direct interaction between the surfactant molecules is accounted for by their partition function Q . It contains the configurational integral Z , which involves very complicated integrations over the coordinates of all interacting molecules. One way to make the problem tractable is to use the virial expansion of Z in series with respect of the adsorption, Γ , and to confine oneself only with binary collisions, i.e. to consider only the second virial coefficient. This leads to the appearance of two interaction functions: between molecules adsorbed on the same surface, f_S , and between molecules adsorbed on opposite surfaces, f_O . The total interaction function is $f = f_S + f_O$. The results obtained by virial expansion will be obviously valid only for small surface coverage. On the other hand, as already mentioned, there are numerous data on the interaction forces in lipid and surfactant bilayers, which correspond to high surface coverage (see e.g. [4–6]). The only way we found to extend our theory to large surface coverage was to assume that the expressions for the interaction function f , obtained from the virial expansion (i.e. for binary collisions), remain valid also at large surface coverage, where the collisions involve simultaneously several molecules. We are fully aware that this is a very crude approximation, but our hope is (and it seems confirmed by the data in Section 6) that this will lead at least to *qualitatively* correct results. In this respect our approach is analogous to the derivation of the two-dimensional Volmer equation of state, which is performed by transforming a partition function valid for low surface coverage in such a way, that it behaves qualitatively correct even at high coverage (for details see Sections 3 and 4). We did that by modifying appropriately the partition functions of the surface equations of state of Helfand, Frisch and Lebowitz (HFL for short) and of Volmer (see Section 3).

At this point a discussion about the terming (the definition) of this type of disjoining pressure seems pertinent. A general

principle, which must be followed, when defining a quantity, is that the definition must be phenomenological, i. e. related as little as possible with the supposed mechanism of the phenomenon. Otherwise if later one discovers that this mechanism is wrong, one must change the definition. This is what happened with the so-called “hydration forces”, which were believed to be the cause for the bilayer repulsion — as Israelachvili and Wennerström pointed out [7], it is more likely that the repulsion is due to what they called “protrusion forces”. The latter term is correct for films with thickness $h > 2d$ (where d is the diameter of the hydrophilic head), since for such films the protrusion of the surfactant molecules is mainly responsible for the repulsion. However, such definition rules out the possibility for repulsion in a film with thickness $h < 2d$, having two adsorbed layers with incomplete coverage. In this case the layers can interpenetrate and give rise to disjoining pressure even if the molecules do not perform any motion normally to the interface, i.e. do not protrude. Hence, the term “osmotic repulsion” seems more appropriate, but the “electrostatic” and the “macromolecular” forces have in fact also osmotic nature. Israelachvili [14] correctly called the “protrusion forces” also “fluctuational” but the “undulation” and the “peristaltic” forces are also fluctuational. What differs the forces, considered here, from the “undulation” and the “peristaltic” (which are related to the motion of the membrane as a whole), is the fact that *separate* particles (molecules) perform Brownian motion. Hence, probably a correct term, reflecting their nature and distinguishing them from the other forces would be “nonionic osmotic Brownian forces”. However, this definition, as well as the others, discussed above, is based on hypotheses for the mechanism. Therefore, we suggest instead the term “disjoining pressure of nonionic surfactants” to be used as a truly phenomenological definition: indeed, under “surfactants” one understands relatively *small* amphiphilic *molecules*, which makes the difference with the macromolecular stabilization, the “undulation” and the “peristaltic” forces, while the adjective “nonionic” discriminates the ionic surfactants.

The paper is organized as follows. Since we expect this paper to be read mainly by chemists, we decided to start by a Section called “Model formulation” (Section 2), where we present in a simplified form the main techniques, which will be used in the core of the paper. This includes some notions about the meaning of partition function, configurational integral and virial expansion. The complete equations for these functions for a system containing N molecules are basically simple, but have rather complicated appearance, which may hinder their understanding. To help the reader, we applied the general methods of the statistical mechanics to systems containing only 2 molecules (for adsorption) and 4 molecules (for interactions in thin films). This allowed us not only to demonstrate on these simple systems all physical effects and the methods to be used further, but also to obtain simplified forms of the main equations, derived later. Section 3 is devoted to the derivation and analysis of the configurational integrals and the virial expansions of the surface equations of state of HFL and Volmer, which we will need later to generalize our theory to systems with higher surface coverage. In Section 4.1 complete derivation of the virial expansion and the

partition function for the interacting surfactant molecules is carried out for HFL and Volmer models. The results are generalized for higher concentrations. The partition function for the solvent (water) molecules is derived in Section 4.2 by means of a generalization of the Hildebrand–Scatchard theory, whose physical foundations and applicability is also analyzed. The results from Sections 4.1 and 4.2 are used in Section 5 to derive complete expressions for the disjoining pressure of the film, Π , and the chemical potential, μ , of the adsorbed molecules. Two particular cases, constant surface coverage, θ , and constant chemical potential are considered.

The obtained results are applied to numerical calculations of Π and μ and analysis of the data in Section 6. Based on the derivation of f_s and f_o in the Appendix A, in Section 6.1 numerical calculation of the interaction function f are performed for several model surfactants and some useful asymptotic expressions are derived. In Sections 6.2 and 6.3 numerical results for constant coverage and constant chemical potential are obtained and analyzed. In Section 6.4 several relatively simple explicit analytical expressions for the disjoining pressure are derived and compared with the results of the theory of Israelachvili and Wennerström [7]. The applicability of our theory to experimental systems is discussed in Section 6.5. Section 7 is devoted to concluding remarks.

2. Model formulation

There are numerous nonionic surfactants used as stabilizers: different compounds with oxyethylene chain but different structure such as polyoxyethylene alcohols, esters, mercaptans etc., as well as compounds with different hydrophilic chain such as polysaccharides [15–24]. Since the structure of the surfactant molecule plays substantial role in our theory, we will confine ourselves only with the simplest type of nonionic surfactants, the polyoxyethylene alcohols. We will assume that their molecules consist of a spherical hydrophilic head with radius R and a hydrophobic tail, which is a cylinder with radius s and length L .

The liquid film, stabilized by a nonionic surfactant, is a three-dimensional system. The head of the adsorbed molecules can move in the film volume $V^f = Ah$, where A is the film area and h is the film thickness. Since the surfactant molecules are adsorbed, the film basically consists of two adsorbed monolayers, but the molecules adsorbed on one of the surfaces can interact also with the other surface or with the molecules adsorbed on it. That is why it is pertinent to begin the description of the model of such films by a discussion of adsorbed layers.

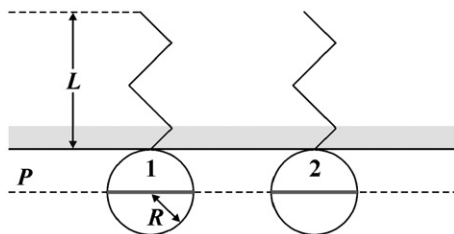


Fig. 1. Sketch of surfactant molecules adsorbed at a surface with a radius of the hydrophilic head R and a length of the hydrophobic tail L .

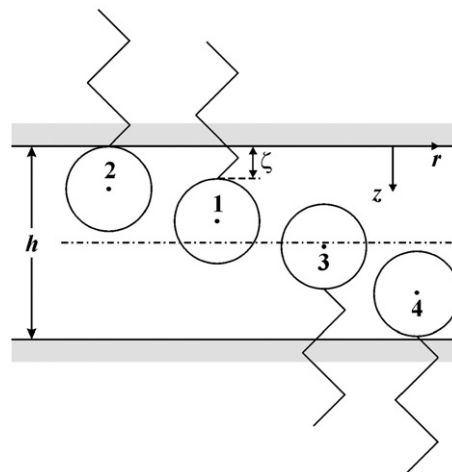


Fig. 2. Sketch of surfactant molecules adsorbed at the film surfaces. The molecules 1, 2, 3 and 4 can move along the interface and normally to it and collide between themselves.

Most theories of surfactant layers assume that the centers of the hydrophilic heads lie in a plane P (see Fig. 1) and move only along this plane, which is assumed usually parallel to the dividing surfaces between the two phases (to simplify the expressions we will consider the liquid of the lower phase, usually water, as solvent and the upper, hydrophobic phase, is usually air or oil). The effect of the solvent is disregarded, so that the molecules are effectively replaced by discs of zero thickness (shown by thick line in Fig. 1). Since in this model the collisions occur only at the equators of the hydrophilic heads, the radius of the disc, R , is the only geometrical parameter entering the expressions for the two-dimensional pressure, $\Delta\sigma$, and for the chemical potential, μ .

The real picture of the monolayer is different in many respects (see the upper part of Fig. 2 above the dashed–dotted line). The adsorbed molecules are not fixed in a plane, but they can perform thermal motion also in direction, z , which is perpendicular to the interface. If the tails of the molecules are perpendicular to the interface and their hydrophilic heads are at a distance ζ from it (as shown for molecule 1 in Fig. 2), their energy will be increased by $\Delta u(\zeta) = w_l \zeta$ with respect to the energy at $\zeta = 0$ (w_l is the energy of transfer of unit length of the hydrophobic chain, assumed linear, from the lower phase to the upper phase). According to Boltzmann equation, the probability to find the head of the molecule at a distance, ζ , is proportional to $\exp(-\zeta/\delta_s) d\zeta$, where T is the temperature, k_B is the Boltzmann constant. The average immersion depth $\delta_s \equiv k_B T / w_l$ is of the order of 1 Å (more precisely from the data of Tanford [25] for w_l , one finds $\delta_s = 0.875$ Å for the interface water/oil and $\delta_s = 1.16$ Å for water/air [26]). On the other hand, the molecules 1 and 2 can move along the interface and interact with lateral energy u_{12} , which depends on the distances ζ_1 , ζ_2 and the radial distance, r_{12} , between them. Then, the probability to find a molecule 2 at a distance r_{12} from molecule 1 is proportional to $\exp[-u_{12}/(k_B T)] dA_1 dA_2$, where dA_1 and dA_2 are the respective area elements (A is the area of the monolayer). It is convenient to choose the position of molecule 1 as zero of the radial

coordinate r_{12} , so that $dA_1 dA_2 = dA_1 \times (2\pi r_{12} dr_{12})$. Then the product

$$dP = \exp \left[-\frac{\Delta u(\zeta_1) + \Delta u(\zeta_2) + u_{12}(\zeta_1, \zeta_2, r_{12})}{k_B T} \right] d\zeta_1 d\zeta_2 (2\pi r_{12} dr_{12}) dA_1 \quad (2.1)$$

will be proportional to the probability to find the molecules 1 and 2 in positions ζ_1 and ζ_2 and at a radial distance r_{12} from each other. The integral of dP over all possible values of the variables A_1 , ζ_1 , ζ_2 and r_{12}

$$Z_2 = \int_{(A)} \int_{\zeta_1=0}^L \int_{\zeta_2=0}^L \int_{r_{12}=0}^{\infty} dP \quad (2.2)$$

is proportional to the sum of all such probabilities, i.e. it is proportional to the total probability for all possible configurations of the molecules 1 and 2, consistent with the restrictions of constant temperature, T , and total number of molecules, N . In the case under consideration here, $N=2$ (hence, the subscript 2 on Z) and the upper limit of ζ is set equal to the length L of the hydrophobic tail of the molecule, because at $\zeta > L$ the molecules are no longer adsorbed. Z is called configurational integral and is related to that part of the free energy of the system, F_{int} , which accounts for the interactions in the system (for more rigorous discussion the reader is referred to Chapter 1 of [27]):

$$F_{\text{int}} = -k_B T \ln Z. \quad (2.3)$$

It is convenient to introduce in Z the so-called Mayer function

$$f_{12} \equiv \exp \left(-\frac{u_{12}}{k_B T} \right) - 1 \quad (2.4)$$

If one considers only repulsive energy, i.e. if only the so-called hard-core interactions are effective, then $u_{12} \rightarrow +\infty$ and $f_{12} = -1$ when the surfactant molecules overlap and $u_{12} = 0$ and $f_{12} = 0$ if the molecules are not overlapping. Therefore, the integral containing f_{12} will be different from 0 only when the molecules 1 and 2 overlap at least in one point.

The application of this approach to the model with planar adsorbed layer (Fig. 1) is easy, since in this case the integrals over ζ and r_{12} can be taken separately. One must assume however, that the molecules all the time remain in the same plane, i.e. that the plane itself moves, which means that all molecules must move in z -direction in a coordinated way. By substituting Eqs. (2.1) and (2.4) into Eq. (2.2) and by assuming that the maximum distance at contact is $d=2R$, one obtains:

$$Z_2 = A^2 \delta_s^2 \left(1 - 4 \frac{\alpha}{A} \right) \quad (2.5)$$

where $\alpha = \pi R^2$. When deriving Eq. (2.5), we have neglected with respect to unity the term proportional to $\exp(-L/\delta_s)$, because L/δ_s is large. By means of Eq. (2.5) one can calculate the chemical potential, μ , which in turn can be used to derive the adsorption isotherm. One finds so, that the adsorption constant is proportional to δ_s . That is why δ_s can also be called effective thickness of the adsorption layer [26].

In practically all papers on surfactant adsorption and surface layers the transfer energy w_l is disregarded, i.e. it is implicitly assumed zero. If one does it, instead of Eq. (2.5), one obtains:

$$Z_2 = A^2 L^2 \left(1 - 4 \frac{\alpha}{A} \right) \quad (2.6)$$

This means that the effective thickness of the adsorbed layer in this model is assumed equal to $L \gg \delta_s$ (such assumption was done in [28]), which leads to significantly larger value of the adsorption constant for a given value of the adsorption energy. On the contrary, if the adsorption energy is calculated from the measured adsorption constant, the result obtained from this model will be lower than the true value by $k_B T \ln(L/\delta_s)$. For a typical surfactant with 10–12 carbon atoms this gives 2 to 3 $k_B T$ units, which is roughly equal to the transfer energy of 2 to 3 CH_2 - groups.

In the general case, after substitution of Eqs. (2.1) and (2.4) into Eq. (2.2) and performing the integration over ζ in the first integral and over A_1 , one obtains:

$$Z_2 = A^2 \delta_s^2 + 2\pi A \int_{\Omega_c} \exp \left(-\frac{\zeta_1 + \zeta_2}{\delta_s} \right) f_{12} r_{12} d\zeta_1 d\zeta_2 dr_{12} \quad (2.7)$$

where Ω_c is the contact region of integration, inside which $f_{12} = -1$. The integral in Eq. (2.7) will lead again to some collision area, α_c , but it will not be exactly equal to α . Indeed, the collision region of the integration, Ω_c , in Fig. 2 depends obviously on the geometry of the surfactant molecule, so that the collision area, α_c , will depend not only on R , but also (as a result of the integration) on the length, L , and the energy, w_l (see Section 6.1).

The situation with the film is similar, but now we must account also for the possibility of collision of the molecules 1 and 2 with molecules on the other surface. To illustrate the main steps involved in deriving the general equations for a film with N molecules at each interface (see Section 4) it is enough to consider in addition to the molecules 1 and 2, two more molecules, 3 and 4, at the lower interface, as in Fig. 2. All four molecules can collide by moving both in z and r directions as it is obvious from Fig. 2. The integration over ζ must be carried out only in the film region, i.e. the upper limit of ζ in the integral, Eq. (2.2), must be changed to $h-2R$ to account for the fact that the hydrophilic heads cannot penetrate into the opposite interface. In the configurational integral there will be four energies $\Delta u(\zeta)$ and two energies of lateral interaction between the molecules on the same surfaces, u_{12} and u_{34} . Besides, there will be four more energies of interaction between molecules on the opposite surfaces: u_{13} , u_{14} , u_{23} and u_{24} . Upon integration, the collisions between the molecules adsorbed on the same surface lead to two identical integrals. Similarly, the collisions between molecules adsorbed on the opposite surfaces lead to four other identical integrals. Therefore, for the purpose of illustration less cumbersome equations will be obtained if one considers only one energy of a given type, say u_{12} and u_{13} . Then, there will be two Mayer functions, f_{12} and f_{13} , so that

$$\begin{aligned} \exp \left(-\frac{u_{12} + u_{13}}{k_B T} \right) &= (1 + f_{12})(1 + f_{13}) \\ &= 1 + f_{12} + f_{13} + f_{12}f_{13} \end{aligned} \quad (2.8)$$

The product $f_{12}f_{13}$, corresponding to simultaneous collision of the three molecules, dramatically complicates the integration. Hence, it is usually neglected, i.e. only binary collisions are accounted for. This restricts the result to low surface concentrations. As a result of the substitution of Eq. (2.8) into Eq. (2.2), two types of integrals, similar to the one in Eq. (2.7), will appear in the expression for Z_4 : the ones containing f_{12} correspond to lateral collisions between molecules, adsorbed at the *same* surface, and the other ones containing f_{13} account for collisions between the molecules, adsorbed on the *opposite* surfaces. The integration over all coordinates then leads to:

$$Z_4 = A^4 \delta_f^4 (1 + S_S + S_O), \quad \delta_f = \delta_s \left[1 - \exp\left(\frac{d-h}{\delta_s}\right) \right] \quad (2.9)$$

where S_S and S_O denote respectively the contribution of the collisions between the molecules at the *same* surface and at the *opposite* surfaces and δ_f plays the role of counterpart of δ_s for a film. In Section 3 the procedures, described above, are generalized for an interface with N adsorbed molecules and in Section 4 — for a film with total number of $2N$ molecules (N on each interface).

The second important shortcoming of the model of planar monolayer of discs, as in Fig. 1, is that it disregards the fact that the surfactant molecules are material objects: their hydrophilic heads are not discs with zero volume and the hydrophobic tails are not threads of zero diameters. They displace part of the water molecules from the surface region, thus altering the free energy of the water, F_W . The total free energy of the monolayer, F_{tot} , will also depend on this effect and must be represented as sum of the contributions of the water, F_W , and the surfactant molecules, F . The latter is calculated from the configurational integral, Z , whose meaning was illustrated above and the exact derivation is given in Section 4.

For the free energy of the water we used a simple expression (see Section 4), proposed by Hildebrand and Scatchard [11–13], which apparently is the same as for an ideal gas. In fact there are two important differences: (i) in the case of an ideal gas no intermolecular interaction is accounted for, whereas the partition function per water molecule, q_W , in the films or the adsorbed layers and the adsorbed layers contains the full configurational integral for condensed water; (ii) for an ideal gas the volume, V , is an external parameter, which can take any value, whereas the volume of the film, V^f , must be equal to the sum of the volumes, occupied by the water and the solute molecules in the film. For more details see Section 4.

3. Partition functions of adsorbed monolayers

The exact calculation of the partition function of thin films is a very complicated task. For this reason we will start with the calculation of the partition function of a single adsorbed monolayer.

The general formula for the partition function, Q , of a three dimensional system of interacting undistinguishable molecules is [27]:

$$Q = \frac{1}{N!} \left(\frac{q_0}{\Lambda^3} \right)^N \quad Z \approx \left(\frac{q_0 e}{\Lambda^3 N} \right)^N Z \quad (3.1)$$

where N is the number of molecules, q_0 is the partition function for a single molecule, Λ is the de Broglie thermal wave length, Z is the configurational integral and e is the Neper number. Note that in Eq. (3.1) we replaced $N!$ by the approximation $N! \approx (N/e)^N$. If U is the total interaction energy of the system, then

$$Z = \int \dots \int \exp\left(-\frac{U}{k_B T}\right) dV_1 \dots dV_N \quad (3.2)$$

where $dV_k = dz_k dA_k$ is the volume element of the k -th molecule ($k=1, 2, \dots, N$) with a vertical coordinate z_k and area element dA_k .

If the energy, U , is pair-wise additive, there are two main components in the interaction energy of the adsorbed molecules: (i) the energy, u_{ij} , due to interaction between two molecules i and j ; (ii) the interaction energy u of a single molecule with the two phases, forming the interface.

Since the adsorbed molecules can perform thermal motion normal to the interface, u depends on the degree of immersion of the molecule in the water phase (see Section 2). Assuming for simplicity that the tail of the molecule is always perpendicular to the interface, the immersion can be characterized only by the distance ζ (Fig. 2). Then one can write [26]:

$$u(\zeta) = -E_{\text{ads}} + w_l \zeta \quad (3.3)$$

where w_l is the energy of transfer per unit length of the hydrophobic chain (assumed linear) from the water to the upper phase, E_{ads} is the adsorption energy, i.e. the transfer energy of the whole hydrophobic chain from the water phase to the upper phase. Based on the sketch of a paraffinic chain, done by Tanford [25], one can represent the transfer energy of the paraffinic chain as sum of the transfer energy of one $-\text{CH}_2-$ group, w_c , times the number of these groups, n_c , plus the transfer energy of the cap (assumed planar with area A_c), due to the terminal $-\text{CH}_3-$ group. One must add to this the surface free energy, due to the disappearance, during the adsorption, of a portion of the interface with area, A_c , equal to the cross-sectional area of the chain. Thus, $E_{\text{ads}} = w_c n_c + (w_s + \sigma_{\text{HW}}) A_c$, where w_s is the energy of transfer per unit area and σ_{HW} is the interfacial tension between the water and the hydrophobic phase [26].

Upon inserting Eq. (3.3) into Eq. (3.2), a factor, $\exp[NE_{\text{ads}}/(k_B T)]$, will appear. To simplify the terminology we will use in Eq. (3.1) instead of q_0 a new partition function *per molecule*:

$$q = q_0 \exp\left(\frac{E_{\text{ads}}}{k_B T}\right) \quad (3.4)$$

In this way we formally change the configurational integral, Z , which will depend now on all interaction energies besides the adsorption energy, E_{ads} .

It is customary to assume that the surfactant molecules are situated in the same plane and when their hydrophilic head come at a distance equal to their diameter $d=2R$, they repeal each other as hard discs. Then, one represents the interaction energy, u_{ij} , as sum of two components, which are functions of the radial

distance, r_{ij} , between the molecules: short-range strong repulsion and long-range weak interaction with energy $|u_{ij}^{\text{int}}| < k_B T$:

$$|u_{ij}| \gg k_B T \quad \text{at} \quad r_{ij} \leq d \quad \text{and} \quad u_{ij} = u_{ij}^{\text{int}} \quad \text{at} \quad r_{ij} > d \quad (3.5)$$

With some additional assumptions (analogous to those used to derive van der Waals equation of state, see e.g. Ref. [29]) one obtains the familiar equation of state [30]:

$$\frac{\Delta\sigma}{k_B T} = \frac{\Gamma}{1-2\alpha\Gamma} - \frac{\beta\alpha}{2} \Gamma^2 \quad (3.6)$$

where $\Delta\sigma$ is the two-dimensional pressure, $\Gamma = N/A$ is the adsorption, $\alpha = \pi R^2$ is the true area occupied by a molecule. The repulsive term in Eq. (3.6) (the first of the right hand side) was proposed on qualitative considerations by Volmer [31]. Since the addition of the interaction term with β makes the equation an exact two-dimensional analog of the famous equation of van der Waals, it is often called also van der Waals equation of state. Depending on whether or not we are using the term with β , we will call it either Volmer or van der Waals equation.

The factor $\beta\alpha/2$ is equal to the integral of $-u_{ij}^{\text{int}}/(k_B T)$ from the contact distance $r_{ij} = d$ to infinity. This follows from the two terms virial expansion of the equation of state [27], which accounts only for binary collisions:

$$\begin{aligned} \frac{\Delta\sigma}{k_B T} &\approx \Gamma + B_2 \Gamma^2 \quad \text{and} \\ B_2 &= \pi \int_0^\infty \left[1 - \exp\left(-\frac{u_{ij}}{k_B T}\right) \right] r_{ij} dr_{ij} \end{aligned} \quad (3.7)$$

With the potential given by Eq. (3.5), for small absolute values of $u_{ij}^{\text{int}}/(k_B T)$, it yields:

$$B_2 = 2\alpha + \frac{4\alpha}{k_B T} \int_1^\infty u_{ij} x dx \quad \text{and} \quad x = r_{ij}/d. \quad (3.8)$$

The integral (3.8) depends on the parameters of the interaction energy, u_{ij}^{int} , which in principle includes the interaction between the surfactant molecules as a whole, i.e. this involves both the hydrophobic tails and the hydrophilic heads. For the most common case, attractive London interaction with an absolute value of the attraction energy of two molecules at contact, u_0 , and $u_{ij}^{\text{int}} = -u_0/x^6$, simple calculations lead to:

$$B_2 = 2\alpha - \alpha \frac{u_0}{k_B T} \quad (3.9)$$

Comparing Eq. (3.7) with this value of B_2 with the analogous expansion of Eq. (3.6) in terms of $\alpha\Gamma$, one finds that β is simply $2u_0/k_B T$.

Helfand, Frisch and Lebowitz (abbreviated henceforth to HFL) derived a different surface equation of state, accounting almost exactly for the hard-core repulsion [32]. By adding to their hard-core result a long-range term $\beta\alpha\Gamma^2/2$ [26], one obtains:

$$\frac{\Delta\sigma}{k_B T} = \frac{\Gamma}{(1-\alpha\Gamma)^2} - \frac{\beta\alpha}{2} \Gamma^2 \quad (3.10)$$

The configurational integrals, corresponding to the equations of state, Eqs. (3.6) and (3.10), can be derived by using the fundamental equation of an adsorbed layer with a single surfactant at constant T :

$$dF = -\Delta\sigma dA + \mu dN \quad (3.11)$$

where A is the interfacial area, μ is the surface chemical potential of the surfactant and F is the free energy. Since only Z in Eq. (3.1) depends on the area A , it can be calculated by integrating the equation:

$$\left(\frac{\partial \ln Z}{\partial A} \right)_N = \frac{\Delta\sigma}{k_B T} \quad (3.12)$$

For $\Delta\sigma$ given by Eq. (3.10) the exact result is:

$$Z^{\text{HFL}} = \left[(A - \alpha N) \exp\left(-\frac{\alpha N}{A - \alpha N} + \frac{\beta \alpha N}{2A}\right) \right]^N. \quad (3.13)$$

For small adsorptions, $\Gamma = N/A$, and $\beta = 0$ this yields

$$\ln Z^{\text{HFL}} = N \ln(A - \alpha N) - \frac{\alpha N^2}{A - \alpha N} \approx N \ln A - \frac{\alpha N^2}{A} - \frac{\alpha N^2}{A} \quad (3.14)$$

The first two terms in the last equation stem from the logarithmic term in Eq. (3.14). This fact suggests that if one takes the sum of the second and the third terms in the right (which gives $2\alpha N^2/A$), one could introduce another approximate form of the configurational integral, Z , by writing (with $\beta = 0$):

$$\ln Z \approx \ln[(A - 2\alpha N)^N] \approx N \ln A - 2 \frac{\alpha N^2}{A} \quad (3.15)$$

By substitution of this expression in Eq. (3.12), one obtains exactly the first, repulsive term in Eq. (3.6). Therefore, one can conclude that the configurational integral, corresponding to Eq. (3.6), must have the form:

$$Z^V = \left[(A - 2\alpha N) \exp\left(\frac{\beta \alpha N}{2A}\right) \right]^N \quad (3.16)$$

From the way we derived the configurational integral (3.16) it should be obvious that the respective Eq. (3.6), just as its three-dimensional analog, is not much more than a useful interpolation formula, rather than an exact equation. In fact the repulsive part of Eq. (3.6) can be derived by means of rigorous statistical thermodynamics for adsorption on a line — then it is exact, but only for adsorption on a line, rather than on an interface [32–34].

The expressions (3.13) and (3.16) were derived under the assumption that the molecules in the adsorbed layer are infinitely thin discs, moving only in two dimensions, parallel to the interface. In reality, the molecules can fluctuate normally to the interface. As it was demonstrated in Section 2, then the configurational integral involves also integration over the normal coordinate, z , and this will lead to the appearance in the expressions for Z of a factor, containing the effective thickness of the adsorbed layer, δ_s . For systems, containing N molecules, the respective factor will be δ_s^N [26]. Besides, if the

molecules are not discs, but three-dimensional objects, the lateral collisions between them will lead to an expression for α different from πR^2 (see Section 6.1).

4. Partition functions of the film

The film contains two substances: water (subscript “W”) and surfactant (no subscript). We will consider now separately the partition functions of each of them and in the next section will see how to use them in order to calculate the free energy and the other thermodynamic functions of the film.

While an adsorbed layer in principle can be considered as a layer of discs of zero thickness, so that the presence of the solvent can be ignored (as demonstrated in Section 2), a thin liquid film is always a bulk system and the solvent (water), in which the surfactant is dissolved, must be accounted for in the thermodynamic equations. The simplest assumption, which can be made, is that the total free energy of the film, F_{tot} , is a sum of the contributions of the water, F_W , and the surfactant, F :

$$F_{\text{tot}} = F_W + F = -k_B T \ln Q_{\text{tot}} \quad (4.1)$$

According to Eq. (4.1), this means that the total partition function, Q_{tot} , must be a product of the respective partition functions:

$$Q_{\text{tot}} = Q_W Q \quad (4.2)$$

which can be calculated separately.

4.1. Partition function for the surfactant

The partition function for the surfactant, Q , is defined by equations, analogous to Eqs. (3.1) and (3.2), with the following differences: it must be written for $2N$ molecules (numbered 1 to N for one of the surfaces and $N+1$ to $2N$ for the other) and the integrations must be carried out over the film volume, V^f . That is why we will denote it by Z_{2N} .

We will make two important approximations:

- (i) We will assume that the total energy is pair-wise additive and the intermolecular potential, u_{ij} , depends on z_i, z_j and the radial distance r_{ij} :

$$U = \sum_{1 \leq k \leq 2N} u(z_k) + \sum_{1 \leq i < j \leq 2N} u_{ij}(z_i, z_j, r_{ij}) \quad (4.3)$$

- (ii) Just as in the derivation in Section 2 we will account initially only for binary collisions, i.e. we will assume that the degree of surface coverage, $\alpha N/A$, is small (on a later stage we will generalize the results for higher degree of coverage). In addition, in the beginning we will neglect the long-range interaction energy, u_{ij}^{int} , but will account for it in the final results. Then Eqs. (4.2) and (4.3) lead to the analog of Eq. (3.1) for a film:

$$Q = \left(\frac{qe}{A^3 N} \right)^{2N} Z_{2N} \quad (4.4)$$

Note that instead of $(2N)!$ we used $(N!)^2 \approx (N/e)^{2N}$, since the molecules at the two surfaces are distinguishable. Besides, when integrating over z one must account for the fact that the hydrophilic head cannot penetrate beyond the film surface, which means that the center of the hydrophilic head, z , can be situated only in the range $R \leq z \leq h - R$.

We will use the following notations

$$\varphi(\zeta) \equiv \exp\left(-\frac{\zeta}{\delta_s}\right), \quad f_{ij}(z_i, z_j, r_{ij}) \equiv \exp\left(-\frac{u_{ij}}{k_B T}\right) - 1 \quad (4.5)$$

where the function φ stems from Eq. (3.3) and the Mayer functions, f_{ij} , depend on the distance between the surfactant molecules. As explained in Section 2 for hard-core interactions: $f_{ij} = -1$ if the respective molecules are overlapping; $f_{ij} = 0$ if they are not overlapping. With the notations (4.5) the configurational integral becomes

$$Z_{2N} = \int \dots \int \prod_{1 \leq k \leq 2N} \varphi(\zeta_k) \prod_{1 \leq i < j \leq 2N} (1 + f_{ij}) dV_1^f \dots dV_{2N}^f. \quad (4.6)$$

Assumption (ii) for binary collisions means that no products of two or more Mayer functions must be kept. Thus:

$$\prod_{1 \leq i < j \leq 2N} (1 + f_{ij}) \approx 1 + \sum_{1 \leq i < j \leq N} f_{ij} + \sum_{N+1 \leq i < j \leq 2N} f_{ij} + \sum_{1 \leq i \leq N} \sum_{N+1 \leq j \leq 2N} f_{ij} \quad (4.7)$$

The total number of terms in the first two sums is $N(N-1)/2 \approx N^2/2$ and in the last sum it is N^2 . Then, upon substitution of Eq. (4.7) into Eq. (4.6), the respective Mayer functions will lead to the following three typical integrals:

$$Z_Z = \prod_{1 \leq k \leq 2N} \int_{V^f} \varphi(\zeta_k) dz_k dA_k \quad (4.8)$$

$$Z_S = \prod_{3 \leq k \leq 2N} \int_{V^f} \varphi(\zeta_k) dz_k dA_k \int_{V^f} \int_{V^f} \varphi(\zeta_1) \varphi(\zeta_2) f_{12} dz_1 dz_2 dA_1 dA_2 \quad (4.9)$$

$$Z_O = \left[\prod_{2 \leq k \leq N} \int_{V^f} \varphi(\zeta_k) dz_k dA_k \right]^2 \times \int_{V^f} \int_{V^f} \varphi(\zeta_1) \varphi(\zeta_{N+1}) f_{1N+1} dz_1 dz_{N+1} dA_1 dA_{N+1} \quad (4.10)$$

The subscript “S” stands for “same surface” and “O” — for “opposite surface”. Since the molecules and the surfaces are identical, each of the Mayer functions in the first and in the second sum in Eq. (4.7) will lead to the integral Z_S , and in the third sum all Mayer functions will lead to Z_O . Having in mind the number of terms in each sum (see above), we thus obtain:

$$Z_{2N} = Z_Z + (Z_S + Z_O) N^2. \quad (4.11)$$

With the exception of the last integrals in Eqs. (4.9) and (4.10) (the ones over $dz_1 dz_2 dA_1 dA_2$ in Z_S and over $dz_1 dz_N$

$+1dA_1dA_{N+1}$ in Z_O) it is easy to perform the integrations over the other variables to obtain:

$$\begin{aligned} Z_Z &= (A\delta_f)^{2N}, & Z_S &= (A\delta_f)^{2N} I_S, \\ Z_O &= (A\delta_f)^{2N} I_O \end{aligned} \quad (4.12)$$

where

$$\delta_f(h) = \delta_s \Psi(h), \quad \Psi(h) \equiv 1 - \exp\left(-\frac{d-h}{\delta_s}\right) \quad (4.13)$$

and

$$I_S = \frac{1}{\delta_f^2 A} \int_R^{h-R} \varphi(\zeta_1) \left[\int_{V^f} \varphi(\zeta_2) f_{12} dA_2 dz_2 \right] d\zeta_1 \quad (4.14a)$$

$$I_O = \frac{1}{\delta_f^2 A} \int_R^{h-R} \varphi(\zeta_1) \left[\int_{V^f} \varphi(\zeta_{N+1}) f_{1N+1} dA_{N+1} dz_{N+1} \right] d\zeta_1 \quad (4.14b)$$

Eqs. (4.14a) and (4.14b) can be presented as

$$I_S = -4 \frac{\alpha}{A} f_S(h) \quad \text{and} \quad I_O = -4 \frac{\alpha}{A} f_O(h) \quad (4.15)$$

where f_S and f_O are complicated dimensionless functions of the film thickness, h . Therefore,

$$\begin{aligned} Z_{2N} &= (A\delta_f)^{2N} \left(1 - 4\alpha f \frac{N^2}{A} \right) \quad \text{and} \\ f(h) &\equiv f_S(h) + f_O(h) \end{aligned} \quad (4.16)$$

The logarithm of the first equation in Eq. (4.16), divided by 2 (for each surface) for small values of $\alpha N/A$ is

$$\frac{1}{2} \ln Z_{2N} \approx N \ln \delta_f + N \ln A - 2\alpha f \frac{N^2}{A}. \quad (4.17)$$

Eq. (4.17), which is a virial expansion, must be compared with Eq. (3.14), but one must add to the latter a term $M \ln \delta_s$ to account for the vertical fluctuations of the molecules (see the comments at the end of Section 3). The two expressions differ only by the terms containing the functions $f(h)$ and $\ln(\delta_f/\delta_s)$. Therefore, if one replaces α by $\alpha f(h)$ and looks at the latter as some modified area of the molecule, it seems reasonable to assume that, depending on the adsorption model, Eqs. (3.13) and (3.16) (with $2N$ instead of N and with factor δ_f) can be used as configurational integrals:

$$Z_{2N}^{\text{HFL}} = \left[\delta_f A \left(1 - \frac{\alpha f N}{A} \right) \exp \left(-\frac{\alpha f N}{A - \alpha f N} + \frac{\beta_f \alpha N}{2A} \right) \right]^{2N} \quad (4.18)$$

$$Z_{2N}^V = \left[\delta_f A \left(1 - \frac{\alpha_v f N}{A} \right) \exp \left(\frac{\beta_f \alpha_v N}{2A} \right) \right]^{2N} \quad (4.19)$$

This procedure is based on the assumption that the expressions for $f(h)$, derived in Section 6.1 for binary collisions, remains valid for multiple collisions, which quantitatively is certainly not true, but there is hope that qualitatively it will lead to reasonable results. In

this respect the present procedure is analogous to the procedure used in Section 3, where the expression (3.16) for the configurational integral for the equation of van der Waals was derived by generalizing the result, valid for low surface coverage (with only binary collisions), to systems with higher surface coverage. The quantity $\alpha_v = 2\alpha$, having the meaning of excluded area, is analogous to the excluded volume in the three-dimensional equation of van der Waals. As Landau and Lifshitz [29] recommended, at large densities it must be determined from the fit of the experimental data and should not be considered as a true value of the volume (or area, in the case of adsorption) of the molecule.

The calculation of the interaction term due to the energy u_{ij}^{int} for a film is very complicated. The result depends on the geometry of the surfactant molecules, on the parameters of the London interactions head–head, tail–tail and head–tail in the water and oil, respectively. These calculations will lead to an explicit dependence of the long-range interaction parameter on the film thickness, h . Therefore, in principle β for a monolayer is different from β_f for a thin film and $\beta_f = \beta_f(h)$. In the case of surfactant molecules with large hydrophilic heads one can assume that $\beta_f \approx \beta$. We believe that such assumption is permissible, since for the models of non-localized adsorption, such as HFL and Volmer models, there are no rigorous arguments that the interaction term must be $\beta \alpha I^2/2$ [26]. That is why usually β is considered as an empirical constant, which we will also assume.

4.2. Partition function for the water molecules

In their theory of solutions of molecules of finite size Hildebrand [11,12] and Scatchard [13] (see also Ref. [35]) suggested expressions for the partition functions for the water, Q_W , and for the solute, Q , which correspond to that for ideal two-component gas:

$$Q_W = \left(\frac{q_W eV}{A^3 N_W} \right)^{N_W} \quad \text{and} \quad Q = \left(\frac{q eV}{A^3 N} \right)^N \quad (4.20)$$

where V is the volume of the solution, N_W and N are the numbers of the respective molecules and q_W and q are considered as molecular partition functions, which do not depend on V , N_W and N . In this section N denotes the total number of solute molecules in a volume V , whereas until now we used this notation for the number of molecules adsorbed on a single interface. There should be no confusion of these notations, since the film is also a bulk system (of volume V^f) in which the number of molecules $2N$ (N from each interface) is exact analog of the number of molecules N in the system considered in the present section.

The main difference between gases and liquid solutions is their compressibility. In the case of gases the volume, V , is a free external parameter, which can be changed arbitrarily. In the case of liquid solutions (incompressible fluids) V is subjected to the following restriction:

$$V = v_W N_W + v N \quad (4.21)$$

where v_W and v are the volumes of the respective molecules. Although this is beyond the scope of the present article, we will give a modified and very simple derivation of the equation of

Hildebrand–Scatchard for the osmotic pressure of the solution, Π_{osm} , since this will show the validity of their result. This is important also for our further derivation. For simplicity we will neglect as usual the long-range interactions.

Imagine that the solution is contained in a cylinder, one end of which is closed by a piston and the other end — by a porous membrane, fully permeable for the water molecules and impermeable for the solute. The cylinder is immersed in a reservoir with pure water and constant temperature, T . If the pressure inside and outside the cylinder is the same, the chemical potential of the water inside the cylinder will be lower. Then the water will start moving into the cylinder through the membrane. This can be prevented by applying on the piston a suitably chosen pressure p . By changing the pressure p (at constant particle number N) one can vary the volume V of the solution. Therefore, the fundamental equation of the system will be (at constant T):

$$dF_{\text{tot}} = -pdV + \mu_W dN_W + \mu dN \quad (4.22)$$

where μ is the chemical potential of the solute. The chemical potential of the water, μ_W , is constant and equal to that in the reservoir. At constant N the last term in the right hand side of Eq. (4.22) is zero and the second term therein can be eliminated by means of Eq. (4.21) to obtain (at constant temperature T):

$$dF_{\text{tot}} = \left(\frac{\mu_W}{v_W} - p \right) dV. \quad (4.23)$$

By using Eqs. (4.1) and (4.20) one can obtain a statistical expression for F_{tot} as a function of V , N_W and N . However, because of the restriction (4.21) N_W is not an independent variable and must be expressed through V and N in the obtained expression for F_{tot} . The latter is then differentiated with respect to V to yield the derivative $(\partial F_{\text{tot}} / \partial V)_{N_s}$, which must be set equal to the thermodynamic expression for the same derivative following from Eq. (4.23). The result reads:

$$\frac{1}{k_B T} \left(p - \frac{\mu_W}{v_W} \right) = \frac{1}{v_W} \ln \left(\frac{q_W v_W e}{\Lambda^3} \right) - \frac{1}{v_W} \ln(1 - \Phi) - \frac{\Phi}{v_W} + \frac{\Phi}{v} \quad (4.24)$$

where the volume fraction of the solute molecules is defined as $\Phi \equiv vN/V$. If the cylinder were filled with pure solvent, its pressure at equilibrium would have been equal to the pressure in the reservoir, p_0 , and the chemical potential of the water molecules, μ_W , must be the same (as in the solution) at equilibrium. Hence, by setting $\Phi=0$ Eq. (4.24) is reduced to:

$$\frac{1}{k_B T} \left(p_0 - \frac{\mu_W}{v_W} \right) = \frac{1}{v_W} \ln \left(\frac{q_W v_W e}{\Lambda^3} \right) \quad (4.25)$$

By subtracting Eq. (4.25) from Eq. (4.24) one arrives at the equation of Hildebrand–Scatchard [11–13]:

$$\frac{\Pi_{\text{osm}}}{k_B T} = -\frac{1}{v_W} \ln(1 - \Phi) - \frac{\Phi}{v_W} + \frac{\Phi}{v} \quad (4.26)$$

where the osmotic pressure $\Pi_{\text{osm}} \equiv p - p_0$ is defined as the excess pressure to be exerted on the piston to maintain the equilibrium.

The result in Eq. (4.26) is identical with the respective expression of Flory–Huggins for polymer solutions (see Eqs. (21–16) and (21–18) in [27] with $\chi=0$ and $M=v/v_W$) derived by means of rather complicated statistical mechanics. This confirms the correctness of the approach of Hildebrand and Scatchard. One of the reasons why this simple approach works so well is that what we are looking for is not the free energy of the water *per se*, but only its change in the solution in comparison to its value in the pure bulk water.

One question that can come to mind is: since the molecules (particles) are usually much larger than the water molecules, is it permissible to look at the solvent as a continuous, structureless medium and to neglect it altogether. In this case the variables of the thermodynamic system will be only V and N . By means of Eqs. (4.1), (4.20) and (4.23) it can be shown that such assumption leads to:

$$\frac{\Pi_{\text{osm}}}{k_B T} = \frac{\Phi}{v} = \frac{N}{V} \quad (4.27)$$

which is the van't Hoff equation. It is valid only for ideal solutions, i.e. for point size molecules. Another possible assumption is to use as volume V for the water molecules in the expression for Q_W , see Eq. (4.20), the so-called “free volume”, which is defined as the volume non-occupied by the solute. According to Eq. (4.21) this free volume is $V_W = v_W N_W$, which reduces Q_W to

$$Q_W = \left(\frac{q_W v_W e}{\Lambda^3} \right)^{N_W} \quad (4.28)$$

Eq. (4.28) must be used together with the restriction (4.21). Calculations, similar to the ones above for the general case, lead again to Eq. (4.27), i.e. with this assumption the effect of the water is again disregarded.

For the solute molecules Hildebrand and Scatchard used Q in the simple form, Eq. (4.20), valid for an ideal gas. That is why it led only to the contribution $k_B T \Phi / v$ to the osmotic pressure, see Eqs. (4.26) and (4.27). Therefore, if one wants to use other, more sophisticated models for the solute molecules, it is sufficient to calculate the respective partition function, Q , and its contribution, F , to the free energy and to add the latter to the respective expression, related to the water, in order to obtain the total free energy, F_{tot} . For example, the simplest way to account for the finite size of the solute molecules in their partition function, Q , is to replace in Eq. (4.20) the volume V by the free volume *for the surfactant molecules*: $V - vN$. Simple calculations show that this leads to following expression:

$$\frac{\Pi_{\text{osm}}}{k_B T} = -\frac{1}{v_W} \ln(1 - \Phi) - \frac{\Phi}{v_W} + \frac{\Phi}{v} \frac{1}{1 - \Phi} - \beta_{\text{osm}} \Phi^2 \quad (4.29)$$

The term $\Phi/[v(1 - \Phi)]$ is nothing else but the slightly modified familiar term in the equation of van der Waals without attraction: $p/(k_B T) = N/(V - vN)$. The last term, included in Eq. (4.29), accounts for the long-range interactions. The corresponding expression for the interaction parameter, β_{osm} , can be found in [35]. This suggests that more precise expressions for the osmotic pressure can be obtained by using more realistic equations of state for the solute molecules. A good candidate for this is the well-

known equation of state of Carnahan–Starling [36,37] (see also Refs. [38–41]), which will lead to:

$$\frac{\Pi_{\text{osm}}}{k_{\text{B}}T} = -\frac{1}{v_{\text{W}}} \ln(1-\Phi) - \frac{\Phi}{v_{\text{W}}} + \frac{\Phi}{v} \frac{1+\Phi+\Phi^2-\Phi^3}{(1-\Phi)^3} - \beta_{\text{osm}} \Phi^2. \quad (4.30)$$

The good validity of Eq. (4.26) raises the question whether it is the result of a “smart guess” or has deeper physical background. We will present some qualitative considerations indicating that the partition function, Q_{W} , can have the form (4.20), but with special meaning of the function, q_{W} . Let us introduce in the exact form of the configurational integral for the water, Z_{W} [see Eqs. (3.1) and (3.2)], the dimensionless variables $\tilde{V}_k \equiv V_k/V$. Then it becomes $Z_{\text{W}} = V^N \tilde{Z}_{\text{W}}$, where \tilde{Z}_{W} has the same form as Eq. (3.2) but with the new variables, \tilde{V}_k . By inserting this expression for Z_{W} in Eq. (3.1) and using Eqs. (4.1) and (4.2), one obtains for the free energy of the water:

$$\frac{F_{\text{W}}}{k_{\text{B}}T} = -N_{\text{W}} \ln \left(\frac{q_0 e}{\Lambda^3} \right) - N_{\text{W}} \ln \left(\frac{V}{N_{\text{W}}} \right) - \ln \tilde{Z}_{\text{W}}. \quad (4.31)$$

The first two terms on the right hand side of Eq. (4.31) give the expression for the free energy of an ideal gas [27,29], so that all the interaction and structural information is contained in \tilde{Z}_{W} . On the other hand, since F_{W} is an extensive function, it is always possible to introduce a free energy per molecule, $f_{\text{W}} \equiv F_{\text{W}}/N_{\text{W}}$. The comparison of f_{W} and Eq. (4.31) suggests, that to satisfy the above condition \tilde{Z}_{W} must have the power form, i.e. $\tilde{Z}_{\text{W}} = \tilde{Z}_1^N$, where \tilde{Z}_1 can be called configurational integral per molecule. Then, by introducing a new partition function, $q_{\text{W}} \equiv q_0 \tilde{Z}_1$, from Eq. (4.31) one recovers Eq. (4.20) for Q_{W} . Therefore, instead of being partition function of a single molecule (as q_0), q_{W} is rather an average partition function per molecule in a large ensemble of interacting molecules. This means that in spite of the formal resemblance, Q_{W} , defined by Eq. (4.20) is not a partition function of an ideal gas, but accounts implicitly (through q_{W}) for all interactions in the bulk water. This conclusion will be valid only if the water in the pure solvent and in the solution has the same structure. It will fail for example if the solvation of the solute molecules is so strong, that in the solution there is virtually no free water — then the structure of the water in the solution and in the pure solvent will be very different.

A different insight on the meaning of f_{W} can be gained from the general thermodynamic expression $F_{\text{W}} = -pV_{\text{W}} + \mu_{\text{W}}N_{\text{W}}$, valid for a homogeneous one component phase. For the free energy per molecule it gives: $f_{\text{W}} = F_{\text{W}}/N_{\text{W}} = -pv_{\text{W}} + \mu_{\text{W}}$. This shows that at constant chemical potential μ_{W} (which is assumed throughout the present paper) the free energy per water molecule in a condensed water phase, f_{W} (i.e. at constant v_{W}), will depend only on the pressure, p (which is different in the solution and the pure solvent). The total free energy of the water, F_{W} , will depend only on the pressure, p , and on the number of molecules, N_{W} . The overall conclusion we reach is that the approach of Hildebrand and Scatchard correctly accounts for the contribution of the water to the free energy of a solution of molecules of finite size.

As shown above, the neglect of the water contribution to the free energy is possible only for point size molecules, more precisely for molecules with zero volume — such is the case when the adsorbed molecules are modeled as discs with zero thickness, but finite area. Since we are looking for a more realistic model with adsorbed molecules of finite size, for the purpose of our calculations in the present paper, we will be calculating Q_{W} as described above, but for Q we will be using Eq. (4.4) with Z_{2N} given either by Eqs. (4.18) or (4.19) depending on the model under consideration. In the next section we will derive the respective thermodynamic functions of a thin liquid film.

5. Thermodynamic functions of a thin liquid film

At constant temperature, T , the total free energy, F_{tot} , of a thin liquid film with a single surfactant will depend on the film variables (the film thickness, h , and the film area, A) and on the total number of molecules of water and surfactant, N_{W} and $2N$, respectively. To simplify the equations we will assume that the area, A , is constant, which unifies the variables h and A into a single variable — the film volume $V^f = Ah$. The reason for such restriction is that the dependence of F_{tot} on A is necessary only for the calculation of the film tension γ^f [42,43], while for us in this work the disjoining pressure, $\Pi(h)$, is of primary interest.

The major difference of the present system with a solution in osmotic equilibrium with pure solvent, considered in Section 4.2, is that now N is not a constant, but an independent variable. It must be determined a posteriori from the condition for chemical equilibrium (i.e. for constant chemical potential) of the surfactant in the film and the one adsorbed at the surfaces of the drops or bubbles, between which the film is formed. If the surfactant is soluble, the condition for equilibrium between the film and the bulk solution can play the same role.

Therefore, in principle the fundamental equation of the film must be written in terms of V^f , N_{W} and N as independent variables [35], similarly to Eq. (4.22). However, the number of water molecules is again subjected to a restriction, analogous to Eq. (4.21), which for a symmetric thin film with N adsorbed molecules at each surface is:

$$V^f = Ah = v_{\text{W}}N_{\text{W}} + 2vN \quad (5.1)$$

By using this restriction to eliminate the variable N_{W} , the fundamental equation of a thin film [42,43] acquires the following form:

$$dF_{\text{tot}} = \left(\frac{\mu_{\text{W}}}{v_{\text{W}}} - p^f \right) dV^f + 2 \left(\mu - v \frac{\mu_{\text{W}}}{v_{\text{W}}} \right) dN \quad (5.2)$$

where p^f is the pressure inside the film.

According to Eqs. (4.1) and (4.2), the total free energy, F_{tot} , is a sum of the contributions of the water, F_{W} , and the surfactant, F . The later is calculated from the respective partition function, Q , given by Eq. (4.4), where the configurational integral, Z_{2N} , is a function only of N and V^f . The concrete form of the expressions for Z_{2N} depends on the model adopted for the surfactant adsorption, i.e. Eqs. (4.18) or (4.19). For F_{W}

and Q_W again Eqs. (4.20) or (4.28) are used. The statistical calculation of the film free energy will lead to the following general form of the fundamental equation:

$$dF_{\text{tot}} = - \left[\left(\frac{\partial \ln Q_W}{\partial V^f} \right)_N + k_B T \left(\frac{\partial \ln Q}{\partial V^f} \right)_N \right] dV^f - \left[\left(\frac{\partial \ln Q_W}{\partial N} \right)_{V^f} + k_B T \left(\frac{\partial \ln Q}{\partial N} \right)_{V^f} \right] dN. \quad (5.3)$$

By comparing this expression with Eq. (5.2), one obtains the following important relationships between the thermodynamic quantities, p^f , μ_W and μ , and the partition functions of water and surfactant:

$$\frac{1}{k_B T} \left(\frac{\mu_W}{v_W} - p^f \right) = - \left(\frac{\partial \ln Q_W}{\partial V^f} \right)_N - \left(\frac{\partial \ln Q}{\partial V^f} \right)_N \quad (5.4)$$

$$\frac{2}{k_B T} \left(\mu - v \frac{\mu_W}{v_W} \right) = - \left(\frac{\partial \ln Q_W}{\partial N} \right)_{V^f} - \left(\frac{\partial \ln Q}{\partial N} \right)_{V^f}. \quad (5.5)$$

First the contributions of the water will be calculated, since they are the same for all adsorption models. We will use Q_W from Eq. (4.20), but will eliminate from it N_W by means of Eq. (5.1). Differentiating the result for F_W so obtained with respect to V^f at a fixed N , one finds:

$$\left(\frac{\partial F_W}{\partial V^f} \right)_N = \frac{k_B T}{v_W} \left[- \ln \left(\frac{q_W v_W e}{A^3} \right) + \ln(1 - \Phi) + \Phi \right] \quad (5.6)$$

where Φ is the volume fraction of the surfactant defined as:

$$\Phi \equiv \frac{2vN}{V^f} \quad (5.7)$$

The contribution of the water to the chemical potential, μ , is found in a similar way:

$$\left(\frac{\partial F_W}{\partial N} \right)_{V^f} = 2k_B T \frac{v}{v_W} \left[\ln \left(\frac{q_W v_W e}{A^3} \right) - \ln(1 - \Phi) - 1 \right]. \quad (5.8)$$

The role of the model used on the partition function of the solute is contained in the configurational integral, Z . Having in mind the obtained results for Z_{2N} , see Eqs. (4.18) and (4.19), it is convenient to rewrite Eq. (4.4) as:

$$Q = \left(\frac{q e \delta_f A}{A^3 N} \right)^{2N} Z_{\text{int}} \quad \text{and} \quad Z_{\text{int}} \equiv Z_{2N} / (\delta_f A)^{2N} \quad (5.9)$$

where Z_{int} is this part of the configurational integral, which accounts only for the interactions between the surfactant molecules. Then, by means of Eqs. (5.1) and (5.9), one easily finds the respective derivatives of Q :

$$\left(\frac{\partial \ln Q}{\partial V^f} \right)_N = \frac{2N}{A} \frac{d \ln \delta_f}{dh} + \frac{1}{A} \left(\frac{\partial \ln Z_{\text{int}}}{\partial h} \right)_N \quad (5.10)$$

$$\left(\frac{\partial \ln Q}{\partial N} \right)_{V^f} = 2 \ln \left(\frac{q \delta_f A}{A^3 N} \right) + \left(\frac{\partial \ln Z_{\text{int}}}{\partial N} \right)_h. \quad (5.11)$$

The disjoining pressure, Π , is defined as excess pressure in the film with respect to the pressure in the continuous bulk phase p_0 [42,43], i.e.

$$\Pi \equiv p^f - p_0 \quad (5.12)$$

An expression for p^f can be obtained from Eqs. (5.4), (5.6) and (5.10):

$$\frac{1}{k_B T} \left(p^f - \frac{\mu_W}{v_W} \right) = \frac{1}{v_W} \left[\ln \left(\frac{q_W v_W e}{A^3} \right) - \ln(1 - \Phi) - \Phi \right] + \frac{2N}{A} \frac{d \ln \delta_f}{dh} + \frac{1}{A} \left(\frac{\partial \ln Z_{\text{int}}}{\partial h} \right)_N \quad (5.13)$$

In the bulk phase the pressure is p_0 , so that by setting in Eq. (5.13) $N=0$ (at that $Z_{\text{int}}=1$) one obtains:

$$\frac{1}{k_B T} \left(p_0 - \frac{\mu_W}{v_W} \right) = \frac{1}{v_W} \ln \left(\frac{q_W v_W e}{A^3} \right) \quad (5.14)$$

The chemical potentials of water, μ_W , appearing in Eqs. (5.13) and (5.14), are the same. By subtracting Eq. (5.14) from Eq. (5.13) and using the definitions (4.13) and (5.12) one finds the final expression for the disjoining pressure, Π :

$$\frac{\Pi}{k_B T} = \frac{1}{v_W} [\ln(1 - \Phi) + \Phi] + \frac{2N}{A} \frac{d \ln \Psi}{dh} + \frac{1}{A} \left(\frac{\partial \ln Z_{\text{int}}}{\partial h} \right)_N \quad (5.15)$$

The first two terms on the right hand side of Eq. (5.15) are the water contribution.

This procedure is not entirely general, since for a soluble surfactants in the bulk of the solution N is not zero, but has some finite, although small value, N_b . We neglected this effect in order to obtain simpler and more transparent equations. If we had accounted for it, our equations would contain terms, stemming from the bulk osmotic pressure, which is usually negligible, compared to the disjoining pressure, Π .

The expression for the chemical potential of the surfactant, μ , is derived by using the relationships (5.4), (5.8) and (5.11). The final result can be presented in the following form:

$$\frac{\mu}{k_B T} = \frac{\mu_0^f}{k_B T} + \ln \left(\frac{\alpha N}{A} \right) - \frac{v}{v_W} \ln(1 - \Phi) - \frac{1}{2} \left(\frac{\partial \ln Z_{\text{int}}}{\partial N} \right)_h \quad (5.16)$$

where μ_0^f , defined as [cf. also Eq. (4.13)]

$$\begin{aligned} \frac{\mu_0^f}{k_B T} &= \frac{v}{v_W} \left[\frac{\mu_W}{k_B T} + \ln \left(\frac{q_W v_W}{A^3} \right) \right] - \ln \left(\frac{q \delta_f \alpha}{A^3} \right) \\ &= \mu_0^s - \ln \Psi \end{aligned} \quad (5.17)$$

has the meaning of standard chemical potential of the surfactant in the film and μ_0^s is the standard chemical potential in a single adsorbed layer.

The final form of the expressions for the disjoining pressure, Π , and the chemical potential, μ , can be obtained by substituting in Eqs. (5.15)–(5.17) the respective expressions

for Z_{int} for the HFL model and the van der Waals model, Eqs. (4.18) and (4.19).

For HFL model this yields:

$$\frac{\Pi^{\text{HFL}}}{k_B T} = \frac{2\theta}{\alpha} \frac{d \ln \Psi}{dh} - \frac{1}{v_W} [\ln(1-\Phi) + \Phi] + \frac{\theta^2}{\alpha} \frac{d\beta_f}{dh} - \frac{2\theta^2}{\alpha} \frac{2-f\theta}{(1-f\theta)^2} \frac{df}{dh} \quad (5.18)$$

$$\frac{\mu^{\text{HFL}}}{k_B T} = \frac{\mu_0^f}{k_B T} + \ln \theta - \frac{v}{v_W} \ln(1-\Phi) - \ln(1-f\theta) + f\theta \frac{3-2f\theta}{(1-f\theta)^2} - \theta\beta_f \quad (5.19)$$

where the degree of surface coverage, θ , is defined as $\theta \equiv \alpha N/A$. We presented the osmotic term in Π through the volume fraction Φ as it is customary. Since the other terms are presented through the surface coverage, θ , sometimes it may be pertinent to express Φ through θ . If only the surfactant hydrophilic head is accounted for in Φ , from Eq. (5.7) one finds:

$$\Phi = \frac{4d}{3h} \theta \quad (5.20)$$

The term with $d \ln \Psi / dh$ in Eq. (5.18) accounts only for the interaction of the surfactant molecules with the bare film surfaces, i.e. it refers to ideal layers. If one ignores the possible dependence of β_f on h (which we will do in Section 6) one comes to the conclusion that the interaction between the two adsorbed layers is accounted only by the last term in Eq. (5.19).

When the thickness of the film becomes equal to $h_s = 2(L+d)$ there is no more interaction between the film surfaces and the film is transformed into two independent adsorbed layers. Hence, the corresponding chemical potential, μ^s , can be found by setting in Eq. (5.19) $h = h_s$. From the condition for chemical equilibrium $\mu(N, h) = \mu^s(N_s)$ one can find then the relation between N and the number of molecules at a single interface N_s :

$$\frac{v}{v_W} \ln \left(\frac{1-\Phi}{1-\Phi_s} \right) + \ln \left[\frac{\Psi \theta_s (1-f\theta)}{\theta (1-\theta_s)} \right] + \theta\beta_f - \theta_s\beta_s = f\theta \frac{3-2f\theta}{(1-f\theta)^2} - \theta_s \frac{3-2\theta_s}{(1-\theta_s)^2} \quad (5.21)$$

where Φ_s , θ_s and β_s are again volume fraction, surface coverage and interaction constant but for a single monolayer of thickness $h_s/2$. Here we have disregarded small terms of the order of $\exp(-L/\delta_s)$ and have used $f(h_s) = 1$. The set of Eqs. (5.18) and (5.21) defines completely the disjoining pressure, $\Pi(h, N_s)$. In the case of soluble surfactants, instead of $\mu^s(N_s)$ one can use the bulk chemical potential

$$\mu_b = \mu_b^0(T) + k_B T \ln c_b \quad (5.22)$$

where c_b is the bulk solute concentration and μ_b^0 — the respective standard chemical potential.

Similar procedure, applied to the model of van der Waals, leads to [cf. Eqs. (4.19), (5.15)–(5.17)]:

$$\frac{\Pi^V}{k_B T} = \frac{2\theta}{\alpha_V} \frac{d \ln \Psi}{dh} - \frac{1}{v_W} [\ln(1-\Phi) + \Phi] + \frac{\theta^2}{\alpha_V} \frac{d\beta_f}{dh} - \frac{2\theta^2}{\alpha_V} \frac{1}{1-f\theta} \frac{df}{dh} \quad (5.23)$$

$$\frac{\mu^V}{k_B T} = \frac{\mu_0^f}{k_B T} + \ln \theta - \frac{v}{v_W} \ln(1-\Phi) - \ln(1-f\theta) + \frac{f\theta}{1-f\theta} - \theta\beta_f \quad (5.24)$$

with condition for equilibrium

$$\frac{v}{v_W} \ln \left(\frac{1-\Phi}{1-\Phi_s} \right) + \ln \left[\frac{\Psi \theta_s (1-f\theta)}{\Psi_s \theta (1-\theta_s)} \right] + \theta\beta_f - \theta_s\beta_s = \frac{f\theta}{1-f\theta} - \frac{\theta_s}{1-\theta_s} \quad (5.25)$$

In this case the degree of surface coverage is defined with respect to the area, α_V , i.e. $\theta \equiv \alpha_V N/A$.

In the next section we will perform numerical calculations of Π for typical values of the system parameters and will obtain some simpler asymptotic expressions for $\Pi(h, N_s)$.

6. Numerical calculation and analysis of the interaction functions and the disjoining pressure

In Section 6.1 the exact expressions for the interaction functions, $f_s(h)$ and $f_o(h)$, derived in the Appendix A, are analyzed and simplified assuming an adequate model for the geometry of the surfactant molecule. The role of the interaction functions on the disjoining pressure, Π , is discussed. The disjoining pressure at constant surface coverage and constant chemical potential is calculated numerically and analyzed in Sections 6.2 and 6.3. Some simple analytical expressions for the disjoining pressure are derived in Section 6.4. Comparison of the theoretical results with some experimental data is carried out in Section 6.5.

6.1. Role of the interaction functions, $f_s(h)$ and $f_o(h)$

The interaction between the surfactant molecules is accounted for through the interaction functions, f_s and f_o [for definitions see Eq. (4.15)]. The function f_s accounts for the interaction between molecules adsorbed at the same surface and the function f_o refers to collisions between molecules adsorbed on opposite surfaces. They depend on the film thickness, h , on the nature of the hydrophobic phase (through the parameter δ_s) and on the molecular geometry (through the length of the hydrophobic tail, L , and the diameters of the tail and the head, $2s$ and d , respectively). We have selected three examples of surfactants for our numerical calculations: one with small polar head (with $d \approx 2s$), say dodecanol, and two polyoxyethylene n -dodecanols: B, with 12 EO-groups and C, with 20 EO-groups. The parameters of these systems are given in Table 1. For air

Table 1
Typical parameters for nonionic surfactant systems used in calculations

	Diameter (Å)	Dimensionless diameter, d/δ_s		
		$\delta_s=0.875$ Å (oil)	$\delta_s=1.16$ Å (air)	$\delta_s=2.4$ Å (hyp.)
	Tail	5.4	6.18	4.66
A	Dodecanol	5.4	6.18	4.66
B	12-groups	10.46	11.96	9.02
C	20-groups	11.94	13.64	10.30
				4.98

and oil the values of δ_s are different [26]. The diameters of the polar heads of the polyoxyethylene n -dodecanols are calculated using the formula $\alpha=25n^{1/2}$, which gives rather well the area occupied by the polar groups of polyoxyethylene n -dodecanols [44]. For the chosen surfactants the values of δ_s are of the order of 1 Å, so that always $\delta_s/d \ll 1$. Since δ_s is inversely proportional to the transfer energy w_t , one can expect larger values for δ_s for surfactants having near the polar group double bonds or aromatic rings, which can decrease the transfer energy from water to oil or air almost twice [25] and increase accordingly δ_s . We could not find examples of such surfactants, but nevertheless, in order to illustrate the effect of the ratio δ_s/d on the interaction function f_s , we considered also the hypothetical situation, when the surfactant A, B and C have $\delta_s=2.4$ Å.

The calculations of f_s and f_o can be performed without any additional approximations at the expense of lengthy and tedious calculations. Since only the final results, which are exact, are of physical interest, all the calculations are presented in Appendix A. The analytical expressions may depend on the value of the ratio h/d . That is why we will sometimes distinguish between three cases: thick films, intermediate films and very thin films.

We will begin the discussion by the function f_s . As one can see from Eq. (4.14a), this function accounts for a possible change of the area per molecule, α , due to the fact that the molecules oscillate, so that the lateral collisions between them can occur not only when the centers of the hydrophilic heads lie in the same plane. We obtained two asymptotic results for f_s . For large film thickness, more precisely, for $(h-d)/\delta_s \gg 1$, we found [see Eq. (A.12)]:

$$f_s = 1 - 2 \frac{\delta_s^2}{d^2} + 2 \frac{\delta_s(b + \delta_s)}{d^2} \exp\left(-\frac{b}{\delta_s}\right) \quad (6.1)$$

where $b^2 \equiv d^2 - (R+s)^2$. For very thin films ($h \rightarrow d$) the result is [see Eq. (A.19)]:

$$f_s = 1 - \frac{(h-d)^2}{6d^2} \quad (6.2)$$

For the surfactant A, the dimensions R and s are equal, $b=0$ and Eq. (6.1) leads to $f_s=1$. For the surfactants B and C, $b \leq d$, and since $\delta_s/d \ll 1$ again $f_s=1$. For all surfactants Eq. (6.2) yields $f_s=1$ for $h \rightarrow d$. Therefore, the conclusion is that the oscillations do not affect the collisions between the molecules in the same adsorbed layer, so that with good precision $\alpha = \pi R^2$. The reason is that the average immersion depth of the molecules, δ_s , is very small, so that the collisions occur always very close to the

equator of the polar head. Hence, we will use in the future for f_s the value 1, so that the total interaction function $f(h)$ will be:

$$f = f_s + f_o = 1 + f_o. \quad (6.3)$$

The situation can be different for the hypothetical surfactant with larger δ_s (see Fig. 3). For the molecule A, the function, f_s , is again unity but for B and C at larger thickness it is slightly lower. The reason is obviously that due to the larger immersion depth at higher thicknesses the deviations from equatorial collisions are more frequent. In this case the area per molecule will be no longer constant, but one must use instead $\alpha = \pi R^2 f_s(h)$. This result will be valid also for a single adsorption layer.

The interaction function, f , enters the expressions for the disjoining pressure, Eqs. (5.18) and (5.23), in two ways: (i) as two additive terms $f\theta$ and (ii) as a derivative df/dh , multiplying the whole interaction term. The first contribution is important only at large surface coverage, since the terms $f\theta$ appear both in the nominator and denominator of the interaction term in Eqs. (5.18) and (5.23). The derivative df/dh is much more important and plays a decisive role for the interaction between the molecules. We have derived in Appendix A analytical expressions for $f(h)$, but since they are rather cumbersome, we will quote here only simplified asymptotic expressions, which are however sufficient to describe correctly the physical effects. They are valid under the following very reasonable conditions: $\delta_s/d \ll 1$ and $(h-d)/\delta_s \gg 1$. The first condition is always valid (see Table 1). The situation with the second one is more complicated — it is in fact a condition, which must be fulfilled in order to avoid a non-physical divergence of some of our results at $h=d$ (for discussion see Section 6.2). We neglected the radius of the hydrophobic tail, s , since we proved numerically that it does not play a considerable role for the value of f_o . We neglected also the terms, proportional to $\exp(-d/\delta_s)$, which are very small.

The asymptotic result for f_o has different forms depending on the film thickness:

(i) For large film thickness Eq. (A.28) leads to:

$$f_o = \frac{2}{d^2} [(h-2d + 2\delta_s)(d-\delta_s) - \delta_s^2] \exp\left(\frac{2d-h}{\delta_s}\right) \quad \text{at } h \geq 2d \quad (6.4a)$$

(ii) In the case $h \leq 2d$ Eq. (A.37) gives:

$$f_o = 1 - 2 \left(\frac{\delta_s}{d}\right)^2 - \left(\frac{h-d-2\delta_s}{d}\right)^2 \quad \text{at } h \leq 2d \quad (6.4b)$$

The respective derivatives are:

$$\frac{df_o}{dh} = -\frac{2}{d^2 \delta_s} [(h-d + 2\delta_s)(d-\delta_s) - d^2] \exp\left(\frac{2d-h}{\delta_s}\right) \quad \text{at } h \geq 2d \quad (6.5a)$$

$$\frac{df_o}{dh} = -2 \frac{h-d-2\delta_s}{d^2} \quad \text{at } h \leq 2d \quad (6.5b)$$

Both functions (6.4a) and (6.4b) and their first derivatives at $h=2d$ are continuous. That is why Eqs. (6.4a), (6.4b) and (6.5a), (6.5b) lead to identical results at $h=2d$:

$$f_O = \frac{4\delta_s}{d} \left(1 - \frac{3\delta_s}{2d}\right) \quad \text{and} \quad \frac{df_O}{dh} = -\frac{2}{d} \left(1 - \frac{2\delta_s}{d}\right) \quad \text{at } h = 2d. \quad (6.6)$$

The exact numerical results for $f(h)=1+f_O(h)$ for the systems A, B and C from Table 1 are plotted in Fig. 4. Since the minimum value of the film thickness is assumed to be $h=d$ and the three molecules have different diameters, the curves start from different points, indicated on the figure. At $h/\delta_s \gg 1$ the function f is unity, which means no interaction. It is still larger than unity at film thicknesses well above $2d$, because due to the oscillation the molecules can collide even when the two adsorbed layers are not yet in direct contact. No qualitative difference between emulsion (Fig. 4a) and foam (Fig. 4b) films is observed. The dashed lines in Fig. 4a are calculated using the asymptotic expression (6.4a), (6.4b). The excellent validity of the simple asymptotic form for $f_O(h)$ is obvious — only some small deviations for very thin films, at $h \approx d$, are visible. The behavior of the curves for the interaction function, f , calculated from the asymptotic expression (6.4a), (6.4b) for foam films is not shown in Fig. 4b, because it is very similar to that for emulsion films (see Fig. 4a).

To demonstrate the role of the interaction function, f_O , on the disjoining pressure, Π , we calculated numerically the derivatives, df_O/dh , appearing in Eqs. (5.18) and (5.23). Fig. 5 shows the dependence of the dimensionless functions, $\delta_s df_O/dh$, on the dimensionless film thickness, h/δ_s , for typical emulsion and foam systems (Table 1). The interaction function has a minimum at a film thickness very close to $h=2d$. The depth of the minimum is different for different types of hydrophilic heads (see Fig. 5), which follows also from Eqs. (6.5a), (6.5b). The dashed lines in Fig. 5a are calculated using the asymptotic expression (6.5a), (6.5b), which has again good validity. The

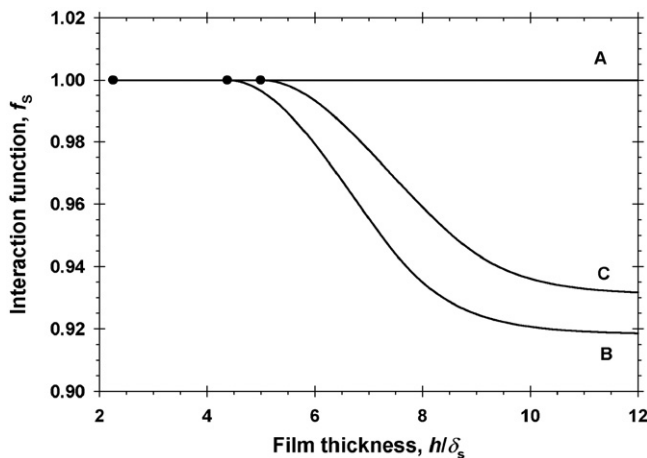


Fig. 3. Interaction function, f_s , vs. dimensionless film thickness, h/δ_s , for a hypothetical surfactant with $\delta_s=2.4$ Å. The parameters of the systems A, B and C are given in Table 1.

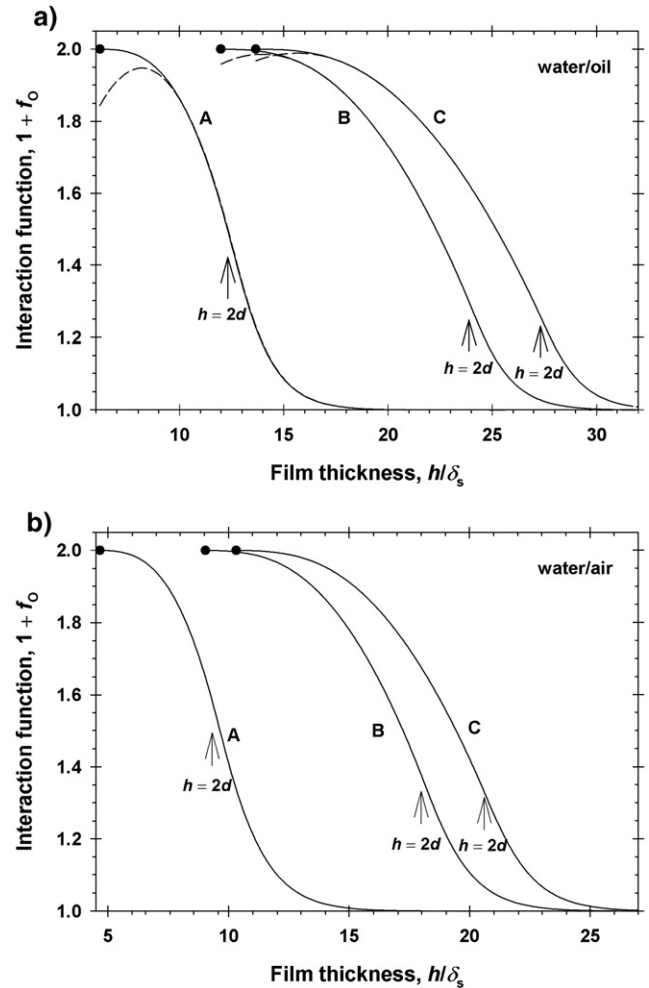


Fig. 4. Interaction function, $1+f_O$, vs. dimensionless film thickness, h/δ_s , for emulsion films (a) and foam films (b). The dashed lines represent the values of the interaction function calculated using the asymptotic expression (6.4).

two branches of the curves for df/dh have different physical meaning, which is discussed in Section 6.2.

6.2. Disjoining pressure and chemical potential at fixed values of the surface coverage

Although the surfactant molecules in the film are always in equilibrium with those on the surfaces of the meniscus encircling the film (and with the bulk solution in the case of soluble surfactant), it is instructive to analyze briefly the case when the film is assumed “closed”, i.e. the adsorption, Γ , and respectively the surface coverage are assumed constant. The dimensionless disjoining pressure, $v_W \Pi / k_B T$, and the chemical potential, μ , in this case are described by Eqs. (5.18) and (5.19) for the HFL model and by Eqs. (5.23) and (5.24) for the van der Waals model. For simplicity we will be assuming here that $\beta_F=0$.

The expressions for Π and μ contain three types of terms with clear physical origin. The first term in Π and the first two terms in μ do not involve interaction between the molecules, i.e. they correspond to ideal adsorbed layers and we will call them

for short “ideal terms”. The next terms, containing the volume fraction Φ , stem from the fact that part of the water molecules in the adsorbed layers are displaced by the surfactant molecules [see Eq. (4.21) and Section 4.2] — hence, we call them “water terms”. The remaining terms, containing the interaction function f are the result of direct interaction between the surfactant molecules — hence, they are called “interaction terms”.

Since the qualitative behavior is the same for all systems and models, we will analyze now only the HFL model for a film water in oil for the surfactant C (see Table 1) and with $\theta=0.1$. The respective contributions to the disjoining pressure, Π , are shown in Fig. 6. The ideal term (curve 1) is due only to collision of the oscillating molecules with the opposite bare film surface. That is why it starts playing a role at very small thickness. Its very high values at $h \rightarrow d$ are not realistic and are due to a drawback of our model, namely to the assumption that the hydrophilic heads cannot penetrate beyond the planar film surfaces, i.e. that the surfaces are assumed non-deformable. In reality when $h \rightarrow d$ the film surfaces in proximity to the hydrophilic heads most probably deform and form menisci around them as suggested in [45]. This gives rise to a local

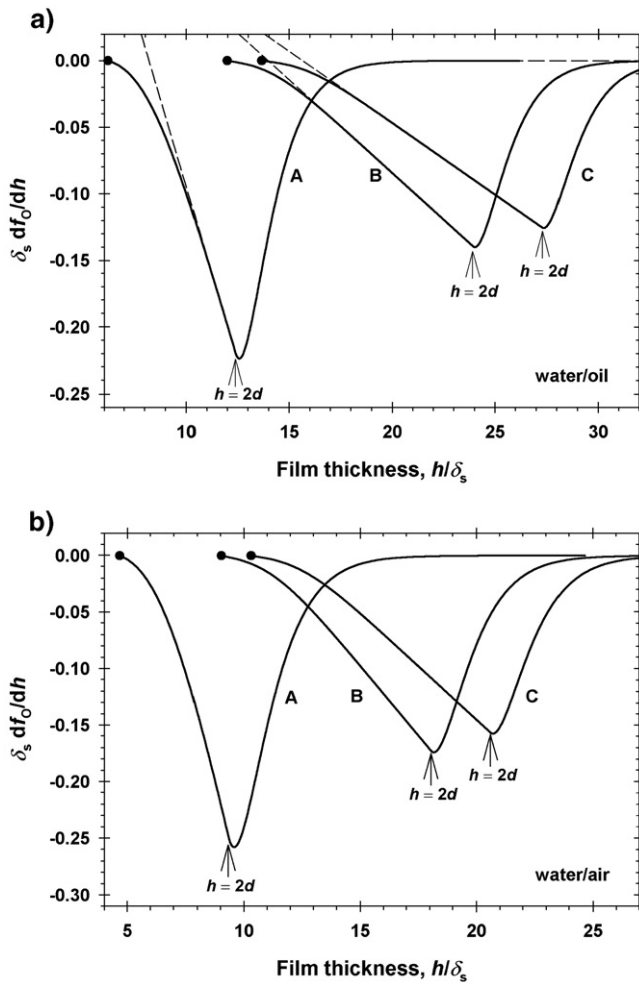


Fig. 5. Dependence of $\delta_s df_O/dh$ on the film thickness for typical emulsion films (a) and foam films (b). The parameters of the surfactants A, B and C are given in Table 1. The dashed lines represent the values of $\delta_s df_O/dh$ calculated using the asymptotic expressions (6.5a), (6.5b).

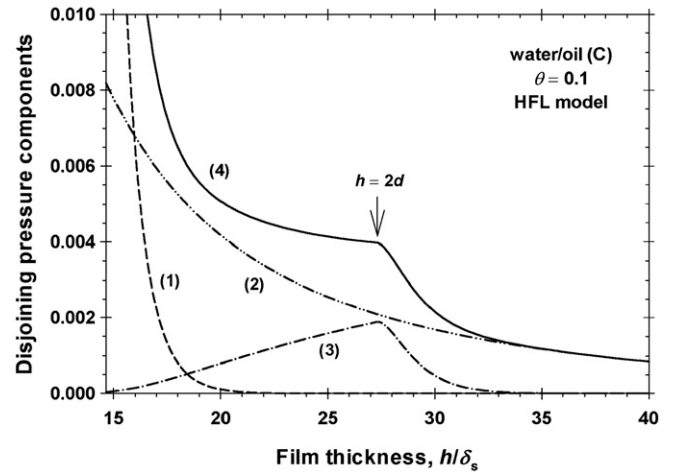


Fig. 6. Fixed surface coverage: (1) ideal term; (2) water contribution; (3) interaction term; (4) total disjoining pressure. The plotted disjoining pressure components are dimensionless, $v_w \Pi / (k_B T)$.

capillary pressure, which then becomes probably the most important stabilizing factor. Since this is a completely different model we will not try to develop it and will avoid the problems stemming from the failure of our model at $h \rightarrow d$ by simply stopping the calculations at $h = d + \delta_s$. Another effect, which was disregarded, because of the assumption for non-deformability of the film interfaces, is the possibility for formation of menisci around the hydrophobic tails due to their wetting by the solvent.

The water contribution (curve 2) smoothly decreases as h increases and it is very long range. With the exception of the region around $h = 2d$ (where it is comparable with the interaction term) it is the major contribution to the disjoining pressure.

The interaction contribution (curve 3) reaches a maximum at $h = 2d$ and steeply decreases at larger values of h . This decrease is due to the fact that the penetration depth δ_s is small, so that the thickness increase above $2d$ makes the collision between molecules adsorbed at opposite layers less and less probable. At thickness smaller than $2d$ the interaction contribution almost linearly decreases to zero at $h = d$. To show the reason for this rather surprising and counterintuitive behavior of the interaction term, we will present a simplified derivation of $f_O(h)$ for $h < 2d$, by assuming $\delta_s = 0$.

In Fig. 7 two colliding molecules are depicted at $h < 2d$. The horizontal distance between their centers, d_{ex} , is in fact the radius of the excluded area for collision in horizontal direction. The excluded area, α_{ex} , where the molecule 3 cannot penetrate, is:

$$\alpha_{ex} = \pi d^2 f_O(h), \quad f_O(h) = \frac{h}{d} \left(2 - \frac{h}{d} \right) \quad (6.7a)$$

$$\frac{df_O}{dh} = -\frac{2(h-d)}{d^2} \quad (6.7b)$$

The expressions for $f_O(h)$ and df_O/dh exactly coincide with Eqs. (6.4b) and (6.5b) if one sets in the latter $\delta_s = 0$. Therefore, the molecule 3 can perform vertical collisions with the molecule 1

only if the radial distance between them, r_{13} , is in the range $d_{\text{ex}} < r_{13} < d$, i.e. if the center of the molecule 3 is in the “collision area” $\alpha_{\text{coll}} = \pi d^2 - \alpha_{\text{ex}}$. Since $f_0(d) = 1$, $\alpha_{\text{coll}} = 0$ at $h = d$. Indeed, at this thickness the centers of all molecules lie in the same plane and no vertical collisions are possible. In the other extreme case, $h = 2d$, the collision area has its maximum, $\alpha_{\text{coll}} = \pi d^2$ since $f_0(2d) = 0$. Then the number of vertical collisions is the largest, which explains the maximum of curve 3 at $h = 2d$. The derivative, df_0/dh , is negative for $d < h < 2d$, which explains the positive contribution of the interaction term to the disjoining pressure, see Eqs. (5.18) and (5.23). Since the terms $f\theta$ in Eqs. (5.18) and (5.23) are small when $\theta = 0.1$, the interaction term is dominated by df_0/dh , which is linear function of h . That is why curve 3 in Fig. 6 is almost linear at $d < h < 2d$.

The total disjoining pressure (with and without water contribution) for the surfactants A and C is shown in Fig. 8. The shape of the disjoining pressure isotherm for the molecule with the smaller hydrophilic head A (see Table 1) is similar to that for the surfactant C, but because of the smaller volume v of the head the water contribution is very small and as a result the disjoining pressure is dominated by the interaction term and has much shorter range.

The highest possible value of θ for the HFL model is $\theta = 0.5$ since the expressions for Π and μ , Eqs. (5.18) and (5.19), contain both terms $1 - f\theta$, which leads to singularities at $h = d$ where $f(h) = 2$. So, we chose as example of high degree of surface coverage, $\theta = 0.4$ (see Fig. 9). Then the behavior of Π vs. h is similar but since in Eq. (5.18) the factors $f\theta$ are larger, they also affect the interaction contribution and its shape is slightly different from that for $\theta = 0.1$ (see Fig. 8). The value of Π for given h is of course larger for $\theta = 0.4$ than it is for $\theta = 0.1$.

The chemical potential, $\Delta\mu = \mu - \mu_0^s$, where μ_0^s is the value of the standard chemical potential at a single interface, also increases with θ for a given value of the film thickness. In Fig. 10 $\Delta\mu$ is plotted as a function of θ for $h = 2d$. The curves correspond to the HFL model, see Eq. (5.19), and emulsion film. The dependence of $\Delta\mu$ on the degree of surface coverage for the van der Waals model, see Eq. (5.24), is similar. It is important to note that for a given film thickness $\Delta\mu$ is a monotonous function of θ , which

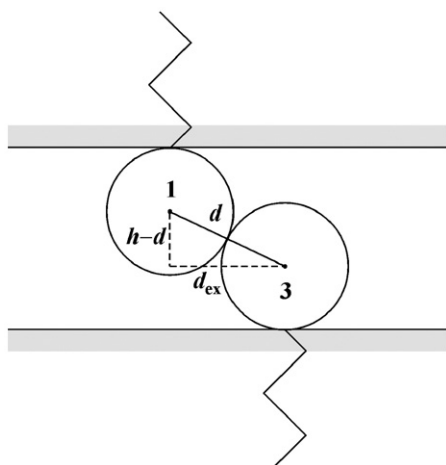


Fig. 7. Sketch of two colliding molecules belonging to the opposite film surfaces at $h < 2d$.

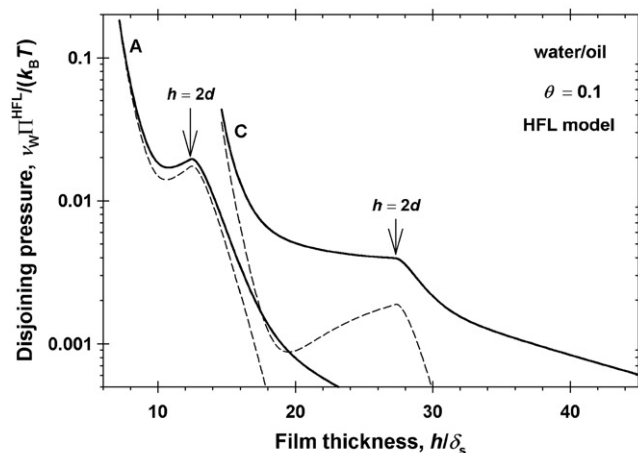


Fig. 8. Dependence of the dimensionless disjoining pressure on the film thickness for emulsion films at fixed values of the surface coverage, $\theta = 0.1$. The dashed lines correspond to the model without water contribution. The parameters for the systems A and C are taken from Table 1.

means that the condition for equilibrium with the meniscus, $\mu(h, \theta) = \mu^s(\theta_s)$ [see Eqs. (5.21) and (5.25)], will lead to a single value $\theta = \theta(h, \theta_s)$ (see Section 6.3).

6.3. Disjoining pressure and surface coverage at fixed values of the chemical potential

When the film thickness h is larger than $h_s = 2(L + d)$, where L is the length of the hydrophobic tails, there is no interaction between the adsorbed layers. At smaller thicknesses the two adsorbed layers can interpenetrate and their molecules start colliding with the molecules adsorbed on the opposite film surface and with the surface itself. This leads to increased chemical potential of the adsorbed molecules. The system can counteract this either by introducing more solvent molecules inside the film region or by pushing some of the adsorbed molecules outside of the film toward the meniscus encircling the film (or toward the bulk solution if the surfactant is soluble). The second process is controlled by the requirement for equilibrium of the adsorbed layers on the film surfaces and on the meniscus, i.e. the surfactant chemical potential in the film, μ , must be equal to that at the meniscus surfaces, μ^s . If the film thins at constant surfactant concentration, both the bulk, μ^b , and the surface, μ^s , chemical potentials will remain constant. That is why the decrease of the film thickness always leads to smaller surface coverage in the film, θ , in comparison with its value at the meniscus surface, θ_s .

The dependence $\theta = \theta(\theta_s, h)$ is described by Eqs. (5.21) and (5.25) for the HFL model and the van der Waals model, respectively. We will again present mainly the results for the system oil/water, since the case air/water differs only quantitatively. The results for the molecules A and C at $\theta_s = 0.1$ for the HFL model are presented in Fig. 11. For the larger molecule C the decrease of θ without the water contribution (the dashed line in Fig. 11a) is considerable, but starts at thickness close to $2d$. The overall decrease of θ (the full line), which includes also the water contribution, starts at much larger thickness and the decrease of the surface coverage θ is also larger. In both cases,

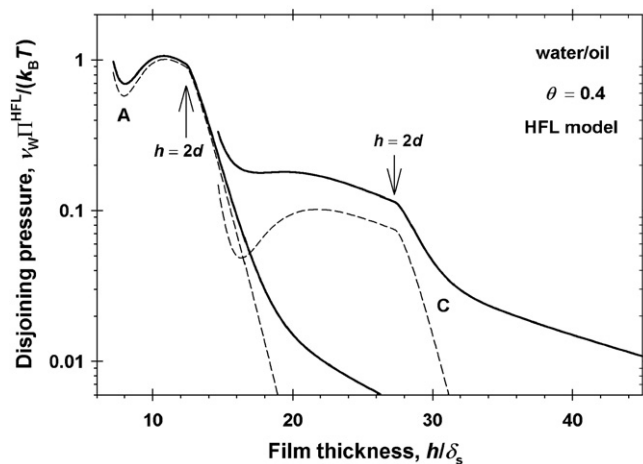


Fig. 9. Dependence of the dimensionless disjoining pressure on the film thickness for emulsion films (surfactants A and C from Table 1) at fixed values of the surface coverage, $\theta = 0.4$. The dashed lines correspond to the model without the water contribution.

with and without the water contribution, θ steeply goes toward zero at $h = d$. The disjoining pressure, Π , exhibits a maximum at $h = 2d$, which is due to the interaction contribution (see Fig. 11b). It has also a very long tail at $h > 2d$, which is obviously due to the water contribution. Similar effects, but much less pronounced, are observed for the smaller molecule A.

It is not surprising that the disjoining pressure, Π , is much smaller for constant chemical potential (about an order of magnitude) than it is for the “closed” system (Section 6.2). Indeed, although the initial coverage in both cases is the same, 0.1, in the open system it drastically decreases with h (see Fig. 11a). Otherwise the relative contribution of the ideal, water and interaction terms is qualitatively the same (compare Figs. 6 and 12), with the exception of the smaller variation with h of the water contribution.

The results for large adsorption, $\theta_s = 0.8$, are presented in Fig. 13. In this case the interaction term is much larger, than it is at smaller θ_s , so that the relative value of the water contribution is

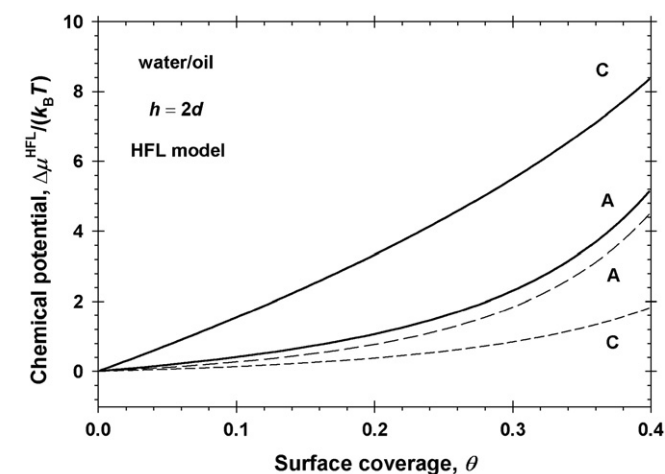


Fig. 10. Dependence of the chemical potential on the degree of surface coverage at a fixed film thickness, $h = 2d$, for emulsion films (surfactants A and C from Table 1). The dashed lines correspond to the model without water contribution.

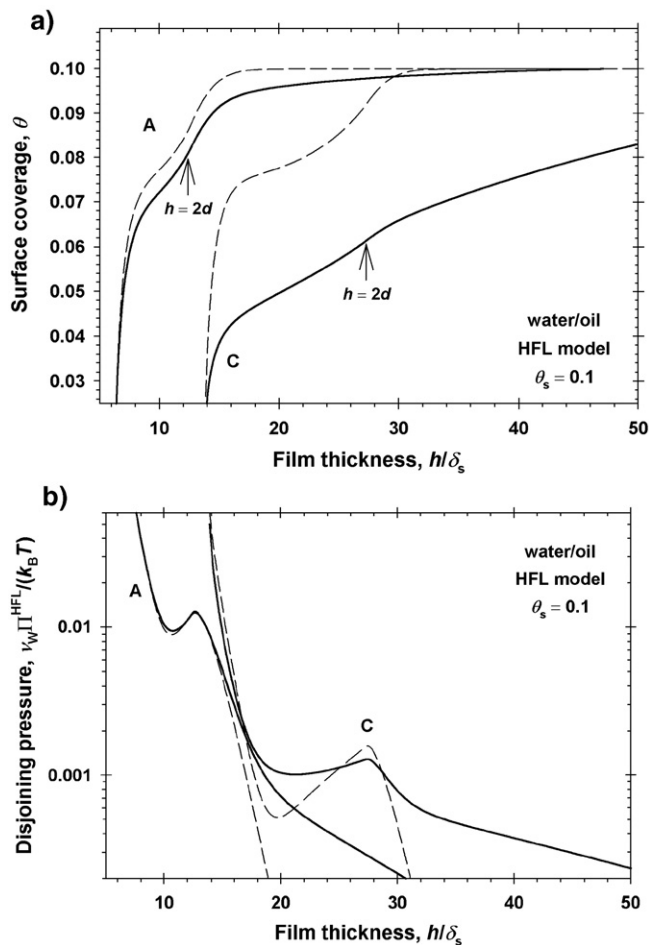


Fig. 11. Dependence of the surface coverage (a) and the disjoining pressure (b) on the film thickness for the HFL model of adsorption and $\theta_s = 0.1$. The curves represent the numerical solution of Eqs. (5.18) and (5.21). The dashed lines correspond to the model, in which the water contribution is neglected.

smaller. This is obvious from the fact that the full line in Fig. 13a, presenting the overall effect, is only slightly shifted with respect to the dashed line, corresponding to the case without water

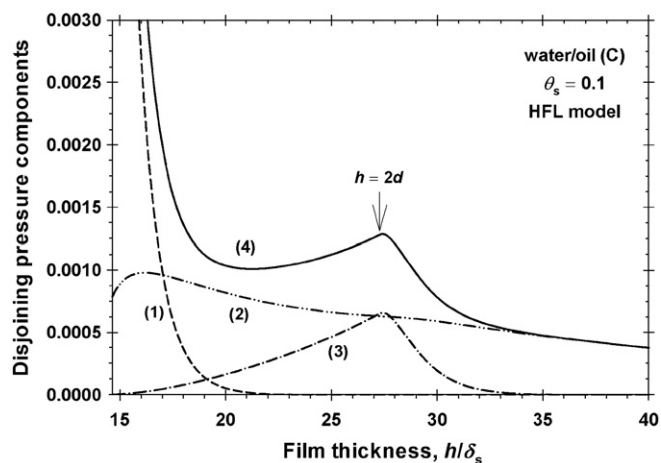


Fig. 12. Disjoining pressure components at fixed chemical potential and $\theta_s = 0.1$: (1) ideal term; (2) water contribution; (3) interaction term; (4) total disjoining pressure. The plotted disjoining pressure components are dimensionless, $\nu_w \Pi / (k_B T)$.

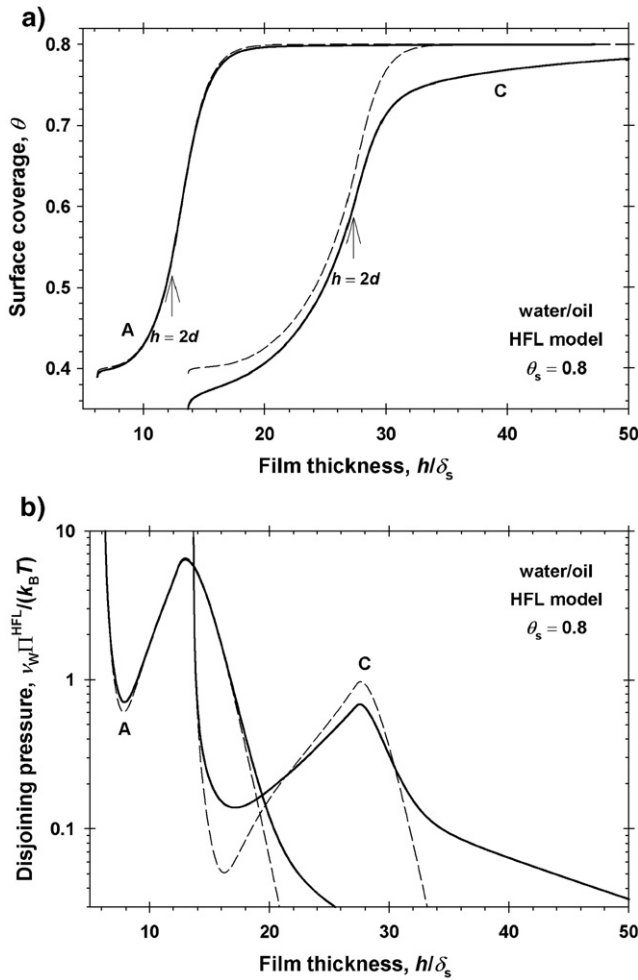


Fig. 13. Dependence of the surface coverage (a) and the disjoining pressure (b) on the film thickness for the HFL model of adsorption and $\theta_s = 0.8$. The curves represent the numerical solution of Eqs. (5.18) and (5.21). The dashed lines correspond to the model, in which the water contribution is neglected.

contribution. Both curves again lead to $\theta \rightarrow 0$ at $h \rightarrow d$. It is also visible that unlike the case of small θ_s (Fig. 11), the significant decrease of θ starts at thicknesses only slightly larger than $2d$. The disjoining pressure (see Fig. 13b) is of course much larger than it is at $\theta_s = 0.1$ (see Fig. 11b) and the maximum is much more pronounced. Due to the water contribution the disjoining pressure again exhibits a long tail at large thickness. The water contribution is almost negligible for the smaller molecule A.

The two cases, (i) fixed surface coverage, $\theta = \theta_s$, and (ii) fixed chemical potential, $\mu = \mu^s$, are compared in Fig. 14. The curves have similar trend, but the “open” film (with constant chemical potential) has much smaller disjoining pressure. The reason is that the open film can fight back the increased chemical potential due to the decreased thickness, by decreasing the surfactant adsorption.

6.4. Simple analytical expressions for the disjoining pressure and the surface coverage

The expressions for the disjoining pressure, Π , and the surface coverage, θ , obtained in Section 5 are analytical, but

transcendental, which makes the numerical calculations a difficult task. It is possible to simplify them by using some reasonable assumptions. The best assumption is that the degree of surface coverage is smaller than 0.2, which allows using the virial expansion of the obtained equations. One advantage of such an approach is that it avoids the assumption that the interaction function $f(h)$, derived only for binary collisions (see Section 4), is valid also for high degrees of surface coverage. Another advantage is that the virial expansions are not based on any specific adsorption model, say the HFL or the van der Waals models. Finally, as we will demonstrate in Section 6.5, such small degrees of surface coverage are most likely to be of importance for real foams and emulsions.

The desired virial expansions of the disjoining pressure, Π , for small degrees of surface coverage, $\theta \ll 1$, can be obtained by expanding the Eqs. (5.18) or (5.23) in series with respect to θ by keeping the terms up to θ^2 . The result is:

$$\frac{\Pi}{k_B T} = 2 \frac{N}{A} \frac{d \ln \Psi}{dh} + \frac{\Phi^2}{2\nu_w} - 4 \frac{\alpha N^2}{A^2} \frac{df}{dh} + \frac{\alpha N^2}{A^2} \frac{d\beta_f}{dh} \quad (6.8)$$

The main problem, which we face now, is how to expand in series the expressions for the chemical potential, see Eqs. (5.19) and (5.24), and the conditions for equilibrium, see Eqs. (5.21) and (5.25), so that the obtained result be consistent with the virial expansion of the disjoining pressure. The answer follows from the fundamental Eq. (5.2) of the system [42,43]. The respective Euler equation, which follows from Eq. (5.2), is $A(\partial \Pi / \partial N)_h = 2(\partial \mu / \partial h)_N$. It suggests that because of the differentiation of Π on N , the virial expansion of μ , consistent with the expansion of Π up to θ^2 , must contain terms only up to N (or θ). This conclusion is valid of course also for Eqs. (5.21) and (5.25). We confirmed the validity of such procedure by analyzing the original virial expansion of the configurational integral (4.16) and the exact expression for the water contribution, F_w , to the free energy.

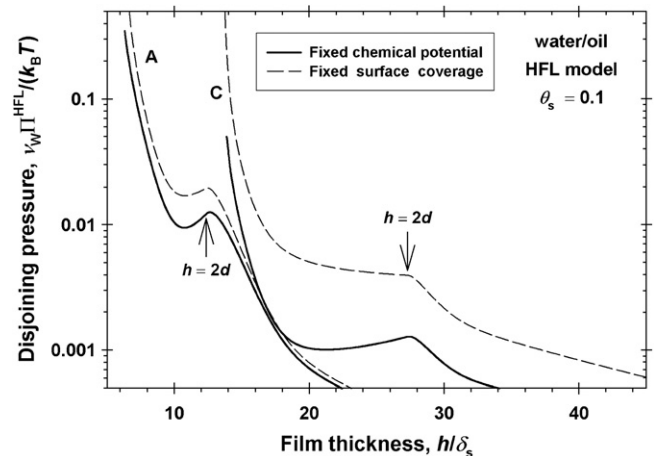


Fig. 14. Comparison of the disjoining pressure calculated at fixed surface coverage, $\theta = 0.1$, and at fixed chemical potential for $\theta_s = 0.1$ using the HFL model.

Then the respective asymptotic form of the transcendental Eqs. (5.21) and (5.25) is:

$$\ln\left(\frac{N}{N_s\Psi}\right) = \beta_s \frac{\alpha}{A}(N-N_s) - 4 \frac{\alpha}{A}(fN-N_s) - \frac{v}{v_W}(\Phi-\Phi_s) \quad (6.9)$$

For simplicity in Eq. (6.9) we assumed that the interaction parameter β_f is a constant, β_s , neglected all small terms proportional to $\exp(-L/\delta_s)$ and since h_s is always larger than h we used $f(h_s)=1$. The last expression gives the explicit dependence $\theta=\theta(h_s, h)$, which must be substituted in Eq. (6.8) to obtain the explicit function $\Pi(h, \theta_s)$. The result can be further simplified by writing Eq. (6.9) in exponential form and keeping again only the linear terms. Then one obtains:

$$\frac{N}{N_s\Psi} = 1 + \beta_s \frac{\alpha}{A}(N-N_s) - 4 \frac{\alpha}{A}(fN-N_s) - \frac{v}{v_W}(\Phi-\Phi_s) \quad (6.10)$$

In terms of degree of surface coverage, $\theta=\alpha N/A$, and volume fraction, Φ , given by Eq. (5.20), Eq. (6.10) can be rewritten as:

$$\begin{aligned} \theta \left[1 + \left(4f - \beta_s + \frac{4dv}{3hv_W} \right) \theta_s \Psi \right] \\ = \theta_s \Psi \left[1 + \left(4 - \beta_s + \frac{4dv}{3hsv_W} \right) \theta_s \right] \end{aligned} \quad (6.11)$$

which represents the final solution for the degree of surface coverage.

If one expresses Φ through θ by means of Eq. (5.20) and if one assumes that the interaction parameter β_f does not depend on h , Eq. (6.8) becomes:

$$\frac{\Pi}{k_B T} = \frac{2}{\alpha\Psi} \frac{d\Psi}{dh} \theta + \frac{8d^2}{9h^2 v_W} \theta^2 - \frac{4}{\alpha} \frac{df}{dh} \theta^2 \quad (6.12)$$

Eqs. (6.11) and (6.12) give explicit simple expressions for the calculation of the degree of surface coverage and the disjoining pressure. One can use here also the asymptotic expressions (6.4a), (6.4b) and (6.5a), (6.5b) for $f_O(h)$ and df/dh , respectively. When the film thickness is large, i.e. when $h \gg 2d$, we have $\theta \approx \theta_s$ and $d\Psi/dh = df/dh = 0$, so that at long distance Π decays as h^{-2} . This is the reason for the tails of Π at large thicknesses due to the water contribution.

For many purposes the whole isotherm $\Pi(h)$ is not needed and only the barrier against coalescence, i.e. the maximum at $h=2d$ is of interest. The respective degree of surface coverage can be found from Eq. (6.11) by simply setting in it $h=2d$. The disjoining pressure is calculated from Eq. (6.12) by substituting in it Ψ from Eq. (4.13) and df/dh from Eq. (6.6):

$$\begin{aligned} \frac{\Pi_{\max}}{k_B T} = \frac{2\theta}{\alpha\delta_s} \exp\left(-\frac{d}{\delta_s}\right) \\ + \frac{2\theta^2}{9v_W} + \left(1 - 2\frac{\delta_s}{d}\right) \frac{8\theta^2}{\alpha d} \quad \text{at } h = 2d. \end{aligned} \quad (6.13)$$

Even simpler equations are obtained if the water contribution [given by the terms proportional to $1/v_W$ in Eqs. (6.11)–(6.13)] is disregarded. Neglecting them, the following simple solutions

for θ and Π are obtained:

$$\begin{aligned} \theta = \theta_s \Psi \frac{1 + (4 - \beta_s)\theta_s}{1 + (4f - \beta_s)\theta_s \Psi} \quad \text{and} \\ \frac{\Pi}{k_B T} = \frac{2}{\alpha\Psi} \frac{d\Psi}{dh} \theta - \frac{4}{\alpha} \frac{df}{dh} \theta^2 \end{aligned} \quad (6.14)$$

The respective value of the disjoining pressure in the maximum, at $h=2d$, is:

$$\begin{aligned} \frac{\Pi_{\max}}{k_B T} = \frac{2\theta}{\alpha\delta_s} \exp\left(-\frac{d}{\delta_s}\right) + \left(1 - 2\frac{\delta_s}{d}\right) \frac{8\theta^2}{\alpha d} \\ \text{at } h = 2d \end{aligned} \quad (6.15)$$

If the case of constant surface coverage is considered, θ in Eqs. (6.13) and (6.15) must be replaced by θ_s .

The good precision of the asymptotic Eqs. (6.11) and (6.12) is visible from Fig. 15 for emulsion films and $\theta_s=0.1$. The deviations of the asymptotic expressions (dashed lines) from the exact numerical calculations (solid lines) are smaller for the surfactant A than for the surfactant C because of the smaller role of the water contribution [recall that when simplifying Eq. (6.9)

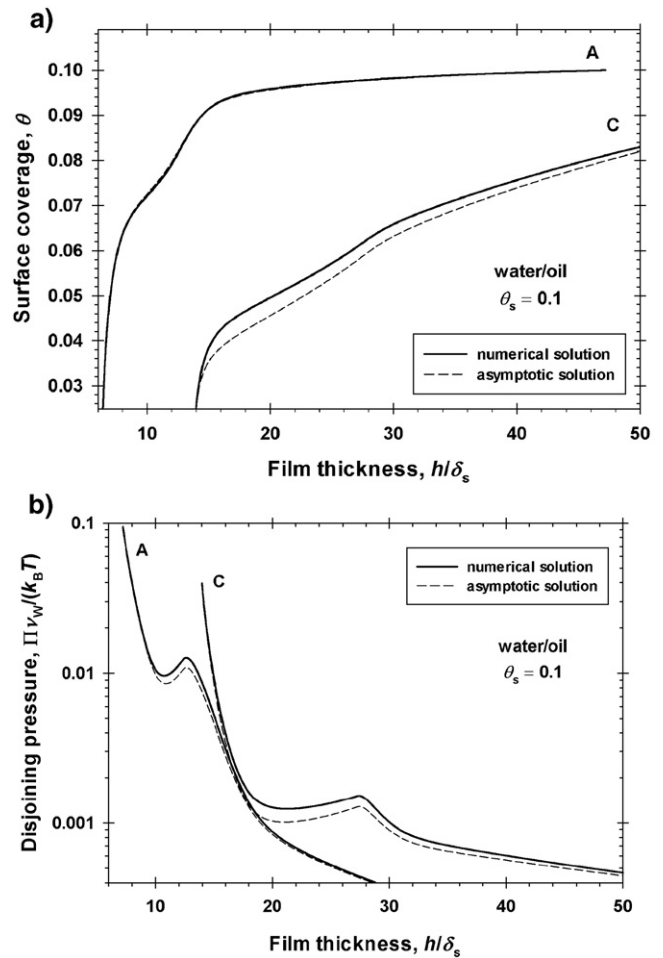


Fig. 15. Comparison between numerical solution (solid lines) and analytical expressions (6.11) and (6.12) (dashed lines) for emulsion films at small degree of surface coverage, $\theta_s=0.1$: a) surface coverage; b) disjoining pressure. The parameters of the surfactants A and C are taken from Table 1.

in order to derive Eq. (6.10) we assumed that $v(\Phi - \Phi_s)/v_W$ is small]. Indeed, for the substance A the ratio v/v_W is 2.75 but for the substance C it is 29.7, which is much larger (see Table 1). One may expect good validity of asymptotic expressions (6.11) and (6.12) up to $\theta_s = 0.2$ and better validity for systems in which the ratio v/v_W is smaller.

Some experimental systems, such as lipid bilayers [4,5], revealed a very strong repulsion between the film surfaces at large degree of surface coverage and relatively large distances. Therefore, it is interesting to find asymptotic form of the Eq. (5.18) for the disjoining pressure for film thickness, h , larger than $2d$. The following reasonable approximations can be made in Eq. (5.18) at large h even when θ is close to unity. According to Eq. (5.20) the volume fraction Φ will be always smaller than $2/3$, so that $\ln(1 - \Phi)$ can be expanded in series by keeping only the square term. For large film thickness df/dh can be calculated from Eq. (6.5a) by neglecting of term of the order of $(\delta_s/d)^2$ and Ψ can be replaced by unity. Finally, for simplicity we will assume that β_f can be replaced by the interaction parameter β_s at a single interface. In this way Eq. (5.18) is reduced to:

$$\frac{\Pi^{\text{HFL}}}{k_B T} = \frac{2\theta}{\alpha \delta_s} \exp\left(\frac{d-h}{\delta_s}\right) + \frac{8d^2 \theta^2}{9v_W h^2} + \frac{4\theta^2}{\alpha \delta_s} \frac{2-f\theta}{(1-f\theta)^2} \frac{h-2d+\delta_s}{d} \exp\left(\frac{2d-h}{\delta_s}\right) \quad (6.16)$$

where $f=1+f_0$ and $f_0(h)$ is calculated from Eq. (6.4a).

This is the equation for Π at fixed surface coverage for the HFL model. However, for constant chemical potential the value of θ in Eq. (6.16) must be calculated from the condition (5.21). The same approximations can be used again. In addition, since at $h > 2d$ and at large θ the difference $(\theta - \theta_s)/\theta_s$ is small (see Fig. 13a) we will use also expansion in series with respect to this difference (note that at $h > 2d$, according to Fig. 4 $f_0 \ll 1$). Then Eq. (5.21) for $h > 2d$ and $\delta_s \ll d$ simplifies to:

$$\left[\frac{4vd}{3v_W h} - \beta_s + \frac{1+\theta_s}{\theta_s(1-\theta_s)^2} \right] (\theta_s - \theta) = \frac{4vd(h_s - h)}{3v_W h_s h} \theta_s + \left[\frac{1+\theta_s}{(1-\theta_s)^3} - 1 \right] f_0 + \exp\left(\frac{d-h}{\delta_s}\right) \quad (6.17)$$

which shows again that $\theta_s - \theta > 0$. The solution of Eq. (6.17) has to be substituted in Eq. (6.16) to calculate the disjoining pressure for fixed chemical potential.

Similar calculations for the van der Waals model, see Eq. (5.23), lead to:

$$\frac{\Pi^V}{k_B T} = \frac{2\theta}{\alpha_v \delta_s} \exp\left(\frac{d-h}{\delta_s}\right) + \frac{8\theta^2 \alpha^2 d^2}{9v_W \alpha_v^2 h^2} + \frac{4\theta^2}{\alpha_v \delta_s} \frac{1}{1-f\theta} \frac{h-2d+\delta_s}{d} \exp\left(\frac{2d-h}{\delta_s}\right) \quad (6.18)$$

where the degree of surface coverage is defined with respect to the area α_v , i.e. $\theta \equiv \alpha_v N/A$. The asymptotic form of the

condition for fixed value of the chemical potential, see Eq. (5.25), gives for $h > 2d$ and $\delta_s \ll d$:

$$\left[\frac{4v\alpha d}{3v_W \alpha_v h} + \frac{1}{\theta_s(1-\theta_s)^2} - \beta_s \right] (\theta_s - \theta) = \frac{4v\alpha \theta_s d(h_s - h)}{3v_W \alpha_v h_s h} + \frac{\theta_s(2-\theta_s)}{(1-\theta_s)^2} f_0 + \exp\left(\frac{d-h}{\delta_s}\right). \quad (6.19)$$

The validity of the asymptotic expressions (6.16)–(6.19) is illustrated in Fig. 16 for an emulsion film with $\theta_s = 0.8$ for the HFL model. They describe very well the exact solution at $h > 2d$. The advantages of Eqs. (6.16)–(6.19) with respect to Eqs. (6.11) and (6.12) are that at $h > 2d$ and $\delta_s \ll d$ they are valid for all values of θ . For the surfactant A the ratio d/δ_s is considerably smaller than the respective ratio for the surfactant C (see Table 1) — for that reason the deviations between the asymptotic and numerical solutions are more pronounced for the substance A at $h \approx 2d$ (see Fig. 16).

Another analytical expression for the disjoining pressure of nonionic surfactants was derived by Israelashvili and Wennerström [7]. The model they used can be summarized as follows [see Fig. 17, case (1)]: (i) The surfactant molecules are considered as infinitely thin rods, oscillating normally to the interface; (ii) The energy of a molecule depends on the depth ζ of its immersion, more precisely $u(\zeta)/(k_B T) = \zeta/\delta_s$; (iii) The molecules form couples so that always a molecule on one of the surfaces faces another molecule on the other surface; (iv) Only the molecules in a couple interact with each other with infinite repulsive potential when they collide. By assuming that the motion of the molecules in every couple is correlated, the authors derived a configurational integral, which corresponds to the following partition sum Q :

$$Q = \left(\frac{q e A \delta_s}{A^3 N} \right)^{2N} \left[1 - \left(1 + \frac{h}{\delta_s} \right) \exp\left(-\frac{h}{\delta_s}\right) \right]^N. \quad (6.20)$$

In order to compare more easily this theory with ours, we will present a slightly different derivation of Eq. (6.20) based on

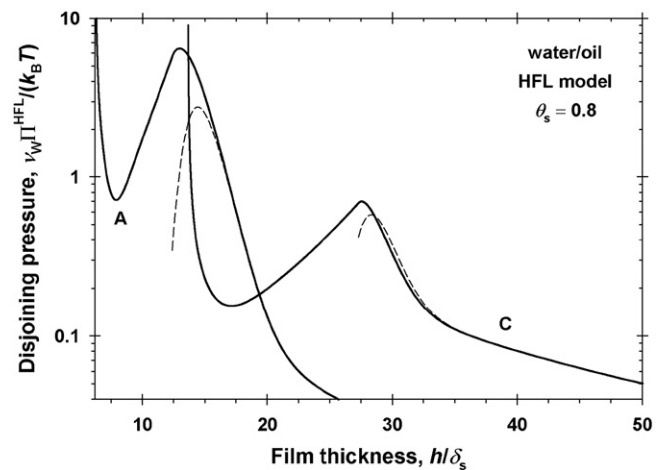


Fig. 16. Comparison between numerical solution (solid lines) and analytical expressions (6.16) and (6.17) (dashed lines) for emulsion films at large degree of surface coverage, $\theta_s = 0.8$. The parameters of the surfactants A and C are taken from Table 1.

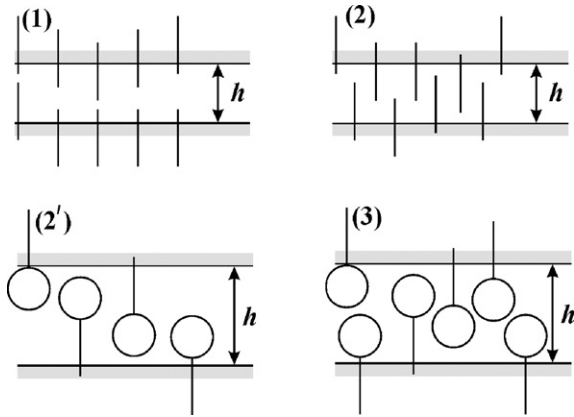


Fig. 17. Model (1) corresponds to adsorbed molecules colliding only with the molecules on the opposite surface but not with the bare surface Ref. [7]; model (2) corresponds to an ideal layer without hydrophilic heads; model (2') to an ideal layer as in case (2) but the hydrophilic heads prevent the hydrophobic tails from reaching the opposite interface; case (3) is the model used throughout this paper.

the concepts used in the present paper. When calculating the configurational integral (3.2) we will assume that the energy U in Eq. (3.2) does not depend on the radial coordinate, since the molecules of different couples do not interact, i. e. in Eq. (4.3) we will assume that $u_{ij}=u_{ij}(z_i, z_j)$ for all molecules. Since the interactions is by couples, only the energies u_{ij} between the molecules facing each other will remain in U , say $u_{1,N+1}$, $u_{2,N+2}$ etc. Then the integration over the area can be performed and leads to a factor A^{2N} . The configurational integral becomes:

$$Z_{2N} = A^{2N} \left[\int_0^h \int_0^h \exp\left(-\frac{\zeta_1 + \zeta_{N+1}}{\delta_s}\right) \exp\left(-\frac{u_{1,N+1}}{k_B T}\right) d\zeta_{N+1} d\zeta_1 \right]^N \quad (6.21)$$

Because of the infinite energy of repulsion, $u_{1,N+1}$, between the overlapping molecules in a couple, the molecule $N+1$, facing the molecule 1, which is in position ζ_1 , can move only from $\zeta_{N+1}=0$ to $\zeta_{N+1}=h-\zeta_1$. Therefore the configurational integral can be written as:

$$Z_{2N} = A^{2N} \left[\int_0^h \exp\left(-\frac{\zeta_1}{\delta_s}\right) \int_0^{h-\zeta_1} \exp\left(-\frac{\zeta_{N+1}}{\delta_s}\right) d\zeta_{N+1} d\zeta_1 \right]^N \quad (6.22)$$

Upon performing the integration in Eq. (6.22) and by using Eq. (4.4) one obtains the expression for the disjoining pressure:

$$\frac{\Pi}{k_B T} = \frac{N}{A \delta_s} \frac{h}{\delta_s} \exp\left(-\frac{h}{\delta_s}\right) \left[1 - \left(1 + \frac{h}{\delta_s}\right) \exp\left(-\frac{h}{\delta_s}\right) \right]^{-1} \quad (6.23)$$

The asymptotic form of Eq. (6.23) for $h/\delta_s \rightarrow 0$ and constant value of the number of molecules, N_s , is:

$$\Pi = \frac{2k_B T}{Ah} N_s \quad (6.24)$$

Eqs. (6.23) and (6.24) are identical to Eqs. (16) and (17) from Ref. [7].

The authors of Ref. [7] considered only a “closed” film, i.e. they did not account for the equilibrium between the film and

the meniscus. We will extend their theory by releasing this limitation. The expression for the chemical potential μ can be easily derived from Eq. (6.20):

$$\begin{aligned} \frac{2\mu}{k_B T} &= - \left(\frac{\partial \ln Q}{\partial N} \right)_h \\ &= 2 \ln \left(\frac{A^3 N}{q A \delta_s} \right) - \ln \left[1 - \left(1 + \frac{h}{\delta_s} \right) \exp\left(-\frac{h}{\delta_s}\right) \right] \end{aligned} \quad (6.25)$$

By setting in Eq. (6.25) h equal to infinity one obtains the chemical potential μ^s of the surfactant on the meniscus surfaces. The condition for equilibrium between the film and the meniscus, $\mu = \mu^s$, yields the connection between the number of molecules at a single interface, N_s , and the number of molecules at one surface of the film, N :

$$N^2 = N_s^2 \left[1 - \left(1 + \frac{h}{\delta_s} \right) \exp\left(-\frac{h}{\delta_s}\right) \right] \quad (6.26)$$

Substituting N from Eq. (6.26) into Eq. (6.23) one obtains the expression for disjoining pressure under constant chemical potential for this model:

$$\frac{\Pi}{k_B T} = \frac{N_s}{A \delta_s} \frac{h}{\delta_s} \exp\left(-\frac{h}{\delta_s}\right) \left[1 - \left(1 + \frac{h}{\delta_s} \right) \exp\left(-\frac{h}{\delta_s}\right) \right]^{-1/2} \quad (6.27)$$

The asymptotic form of Eq. (6.27) for small film thickness is:

$$\Pi = 2^{1/2} \frac{k_B T}{A \delta_s} N_s \left(1 - \frac{2h}{3\delta_s} + \dots \right) \quad (6.28)$$

In this case the disjoining pressure, Π , has a finite value at $h \rightarrow 0$, see Eq. (6.28), and the surface coverage decreases to zero at $h \rightarrow 0$, see Eq. (6.26).

Since the main goal of the authors of Ref. [7] was to emphasize the role of the “protrusion forces”, they did not dwell much on the details of their model. This makes the comparison with our model difficult, since the two models differ in several respects, although they share also some similarities. On the one side the authors of Ref. [7] considered the surface layers as ideal, since they did not account for the lateral interactions. In this respect the model is akin to our ideal case when the water and the interaction contribution are neglected. On the other side, the fact that all adsorbed molecules have molecules facing them suggests that one assumes that the surface is completely covered, which is not the ideal model, of course. If it is so, by thickness of the film one must consider the gap between the adsorbed layers, i.e. in Eqs. (6.20)–(6.28) h must be replaced by $h - 2d$. If the molecular packing is square (as the authors hinted) complete coverage in our notation corresponds to $\theta = \pi/4$. The two models differ even in the ideal case. In the model of Ref. [7] the molecules cannot collide with the opposite surface, whereas in our model it is exactly the opposite — these are the only possible collisions in the ideal case (compare models 1 and 2 in Fig. 17). Besides, in our model the molecules have hydrophilic heads of diameter d , so that the tails of the molecules cannot approach the opposite interface at a distance smaller than d (this is model 2' in Fig. 17).

We will try to compare also numerically the theory of Israelachvili and Wennerström with ours in the two extreme cases discussed above — ideal surface layers and complete coverage. For the “ideal model” one must set in Eq. (4.28) $Z_{\text{int}}=1$ and neglect the contribution of the water molecules. Then, by using also Eqs. (4.13) and (5.15) one finds for our model 2':

$$\frac{\Pi}{k_B T} = \frac{2N}{A\delta_s} \exp\left(\frac{d-h}{\delta_s}\right) \left[1 - \exp\left(\frac{d-h}{\delta_s}\right)\right]^{-1} \quad (6.29)$$

For our model 2 one must set $d=0$ in Eq. (6.29). Eq. (6.29) predicts infinite value of the disjoining pressure when the number of surfactant molecules, N , is fixed and $h \rightarrow d$. If the chemical potential for a dilute layer is constant, see Eqs. (5.16) and (5.17), then $\Psi N_s = N$, where N_s is the number of molecules in a single monolayer. Therefore, the disjoining pressure from Eq. (6.29) for constant chemical potential is in fact:

$$\frac{\Pi}{k_B T} = \frac{2N_s}{A\delta_s} \exp\left(\frac{d-h}{\delta_s}\right) \quad (6.30)$$

Eq. (6.30) shows that for this system the disjoining pressure has finite value for $h \rightarrow d$.

The result of the comparison of models 1 and 2 is shown in Fig. 18 for constant surface coverage. At $h \rightarrow 0$ both models diverge [see Eqs. (6.24) and (6.29), in which d must be disregarded]. As h increases both curves decrease exponentially, but the difference between them increases. We compared also the ideal approximation of our theory for constant chemical potential with our extension of the theory of Israelachvili and Wennerström for such system [see Eqs. (6.30) and (6.27) and Fig. 19]. For models 1 and 2, where the hydrophilic heads are disregarded, the curves for $\Pi(h)$ are rather close. The difference between them is however enormous if the hydrophilic heads are taken into account (curve 2' in Fig. 19; note that the abscissa axis has been interrupted).

The results for the other extreme case, complete coverage at $h > 2d$, are shown in Fig. 20 for $\theta_s = 0.7$. The lines for fixed coverage $\theta = \theta_s = 0.7$ and fixed chemical potential for model 1

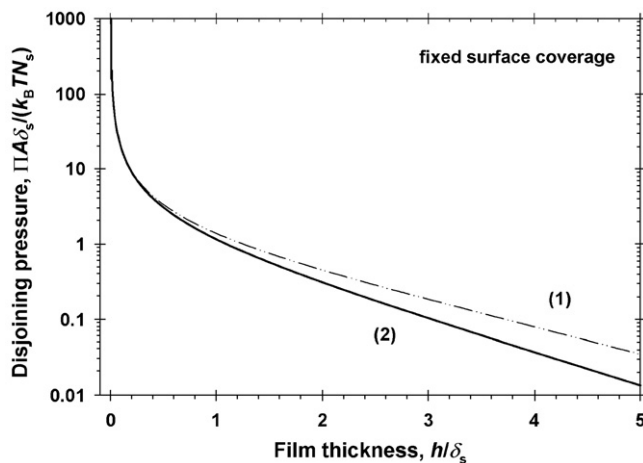


Fig. 18. Comparison of models (1) and (2) from Fig. 17 at fixed values of the surface coverage.

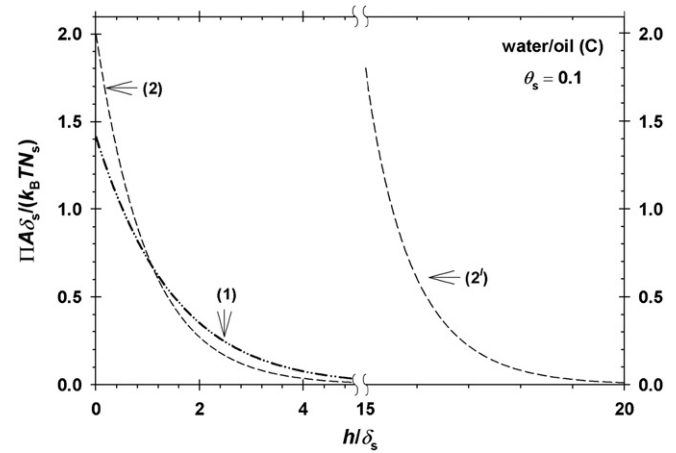


Fig. 19. Components of the disjoining pressure for emulsion film with constant chemical potential and $\theta_s = 0.1$ calculated for models 1, 2 and 2' sketched in Fig. 17.

are calculated again from Eqs. (6.23) and (6.27), respectively, but now with h replaced by $h - 2d$. As one might expect Π decreases exponentially with slope close to unity, i.e. the decay length is δ_s (note that the horizontal coordinate is h/δ_s).

The numerical results from our theory for the HFL model in Fig. 20 also exhibit a portion with exponential decay, which starts almost at $h = 2d$. However, its slope $\delta_s/\lambda = 0.279$ is much smaller than unity. The reason may become clear by inspection of the approximate Eqs. (6.16) and (6.17). One sees that the exponential functions in them are multiplied by polynomials of h , which lead to the change of the slope (the deviation from the straight line at large h/δ_s is due to the water effect). Since the theory, accounting only for the protrusion effects, Eqs. (6.23) and (6.27), leads to slope equal or very close to unity, the observed larger slope is obviously due to the additional effects (besides the protrusion of the molecules), accounted by us. This finding leads us to the following important conclusions: (i) The exponential dependence of Π on h is by no means an indication

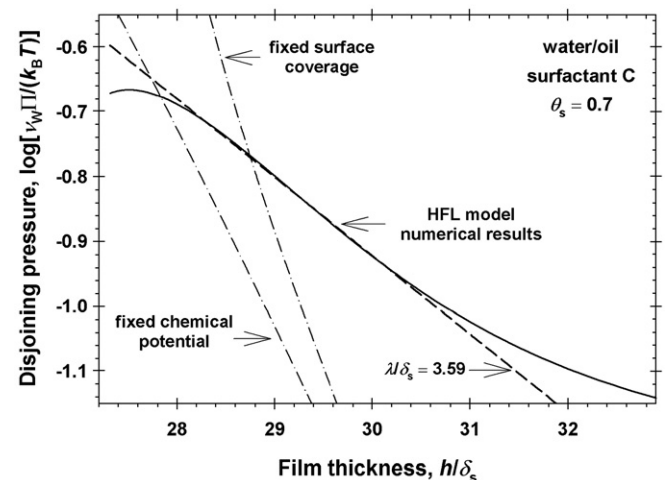


Fig. 20. Dependence of the disjoining pressure, Π , on the film thickness, h , at $\theta_s = 0.7$ for different models: fixed surface coverage, Eq. (6.23); fixed chemical potential, Eq. (6.27); the HFL model.

that only protrusions are important; (ii) The contribution of all effects, playing a role, leads to a decay length λ , which is several times larger than the “theoretical” decay length δ_s (in the case under consideration $\lambda = 3.59\delta_s$), stemming only from the energy, w_t , related to the molecular protrusion [see Eq. (3.3)]. We will return to this problem in Section 6.5.

6.5. Comparison with experimental data

There are only a few experimental data, which can be used to check our theory. Unfortunately, in most cases only some of the needed experimental parameters are known. This forced us to use data from different sources and to make sometimes speculations, but we tried, whenever possible to give arguments in their support.

The systems, closest to our model are the bilayers. The structure and the interaction force between the monolayers have been studied by several methods [4–6]. However, in most cases bilayers of lipids were investigated, which are not suitable for our purposes, since they have two tails. Nevertheless, a few results are in qualitative agreement with our theory. One of them is the fact that the decay length is much larger (2–3 Å) than what it should be, having in mind that because of the two tails the lipids must have theoretical decay length two times smaller than the surfactants with one chain (i.e. it must be of the order of 0.5 Å). As explained in Section 6.4 (see also Fig. 20), the large decay length is due to the fact that the true dependence $\Pi(h)$ is not described by a simple exponential function. A second effect which is consonant with our theory is that for most lipid bilayers the disjoining pressure suddenly drops at constant thickness equal to the double thickness of the extended molecules — according to our model at such thickness (which we denoted by h_s in Section 5) the interaction between the two layers ceases.

The only data about bilayers, which we were able to treat in more details, were those of Lyle and Tiddy [6] with Brij 30 ($C_{12}EO_4$). The points in Fig. 21 are their experimental data for the disjoining pressure, Π , vs. h (the spacing between the hydrophobic parts of the layers) in 10^{-1} N.m^{-2} , for $C_{12}EO_4$ /water L_α phase at 25 °C. The dashed line is the exponential fit, used by the authors $\Pi = 1.64 \times 10^{10} \exp(-h/4.2)$. The solid line is the fit of the same experimental data with our theory, based on the HFL model with fixed chemical potential. We obtained very good fit by using only two adjustable parameters — the hydrophilic head radius, R , and the effective thickness of the adsorption layer, δ_s . From the fit we found $R = 2.66 \text{ Å}$ and $\delta_s = 2.5 \text{ Å}$. These results call for discussion.

We already explained that δ_s can be calculated from the transfer energy per unit length, w_t , of the hydrophobic tail from the water phase to a hydrocarbon phase or to air, see Eq. (3.3) — the respective values we found are 0.875 Å and 1.16 Å. However, the environment of the tail in a monolayer can be rather different from that in oil. Hall and Pethica [46] argued that in micelles it is closer to air, rather than to oil. On the other hand, Aniansson [8] suggested that the free ends of the hydrophobic tails in micelles can be rather disordered, which gives rise to additional entropy and can increase twice δ_s with respect to its value calculated from the transfer energy. Both

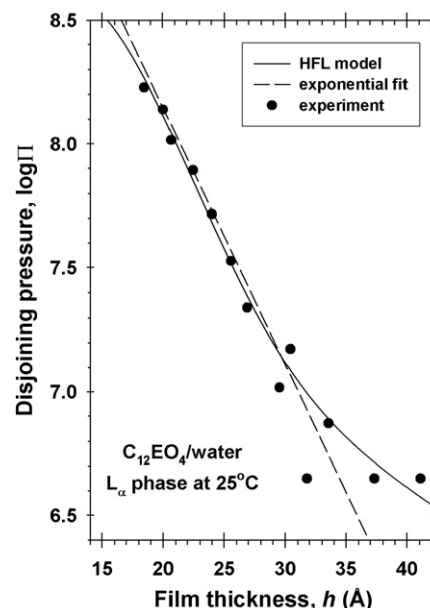


Fig. 21. Disjoining pressure, Π in 10^{-1} N.m^{-2} , of $C_{12}EO_4$ /water L_α phase at 25 °C [6].

arguments are most probably valid also for bilayers. Finally, there might be one more reason for the increase of δ_s . It is well known that the oxygen atoms in the EO-groups are hydrated, but the hydration decreases as the hydrophobic tail is approached [47]. Moreover, there are claims that the EO group linked to the hydrophobic tail is totally dehydrated and is not immersed in the water. This means that this EO group will dominate the transfer energy and since the oxygen is more hydrophilic than the $-\text{CH}_2-$, the transfer energy will be lower and δ_s larger. All these arguments make a value of δ_s more than twice larger than it is for air not unrealistic. However, the even larger value of the decay length found by the authors of [6], $\lambda = 4.2 \text{ Å}$, is actually due to the complicated dependence of Π on h , which is close to exponential only in a narrow thickness interval, but with effective slope larger than δ_s — see Section 6.4 and Fig. 20. There are also arguments that the value of the radius, R , is reasonable. It corresponds to area per molecule $\alpha = \pi R^2 = 22.23 \text{ Å}^2$. Röscher [48] reported for the cross-sectional area in the meander configuration (which is probable for short EO chains) 28 Å^2 . Schick [49] published experimental data for the equilibrium surface tension of $C_{12}EO_4$ solution from which we found that the area of the adsorbed molecule close to the critical micelle concentration (CMC) is $\alpha_{\text{CMC}} = 30.5 \text{ Å}^2$. Both quoted values of α are not so different from the value 22.23 Å^2 , which we found. The molecular diameter $d = 2R = 5.32 \text{ Å}$, found by us, also conforms with the length 1.8 Å of one EO group normally to the interface [48]. Indeed, if one assumes that only three of the EO groups are immersed in the water, this gives $3 \times 1.8 = 5.4$ for d . Lyle and Tiddy [6] reported that the area per chain in the bilayer is 42.6 Å^2 . With $\alpha = 22.23 \text{ Å}^2$ this gives for the degree of surface coverage, $\theta_s = 0.52$. They also found 16 Å for the thickness of the hydrocarbon part of the bilayer, which is approximately the length of a single chain. Hence, the tails of the two layers most probably interpenetrate. Since the radius of

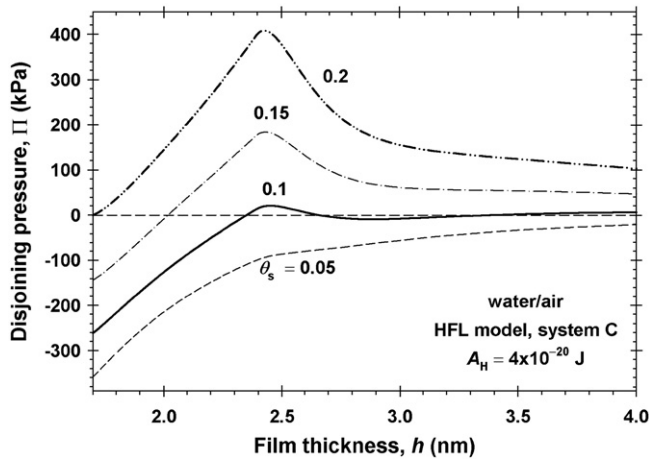


Fig. 22. Total disjoining pressure for foam films and for the surfactant C. The Hamaker constant is $A_H = 4 \times 10^{-20}$ J.

the hydrophobic chain, 2.7 \AA , is almost equal to the value of R found by us, this is possible only if θ_s is around 0.5.

For bubbles and drops stabilized by low molecular nonionic surfactants one must account also for the van der Waals disjoining pressure, which is caused by the molecular attraction: $\Pi_{\text{vdW}} = -A_H / (6\pi h^3)$, where A_H is the Hamaker constant [14]. Fig. 22 shows the total disjoining pressure as a function of the film thickness for different degrees of surface coverage and fixed chemical potential. For small degrees of surface coverage the curve $\Pi(h)$ has no maximum because the attraction prevails. Starting from degree of surface coverage above 0.075 a maximum of the disjoining pressure appears whose height increases with the increase of the degree of surface coverage. At θ_s of the order of 0.1 the film must be almost infinitely stable, since the typical bubbles in foam have size of the order of millimeter. Their capillary pressure is only 200–300 Pa, which is much smaller than the disjoining pressure at $\theta_s = 0.1$ and the barrier cannot be overcome. A legitimate question then is “why foams stabilized by nonionic surfactants are not always stable?” There are many factors determining foam destabilization (see e.g. [50,51]) but we are now interested only in the role of the disjoining pressure. Therefore, it is interesting to find out under what conditions the surface coverage will be very small for nonionic surfactants. For the lack of appropriate experimental data we will propose some speculative considerations. As example we will take Brij 58, which has critical micelle concentration $\text{CMC} = 0.008 \text{ mM}$, $\Gamma_{\text{CMC}} = 3.4 \text{ } \mu\text{mol/m}^2$ and diffusion coefficient $D = 3 \times 10^{-10} \text{ m}^2/\text{s}$ [52,53]. If the time elapsed between the bubble formation and subsequent collision with another bubble is $t_A = 1 \text{ s}$, then the adsorption rate will obey the short time asymptotic [54], so that:

$$\Gamma = c_b(Dt_A)^{1/2} \quad (6.31)$$

where the bulk concentration, c_b , in this case is equal to the CMC. Substituting here the respective values, quoted above, one finds that $\Gamma/\Gamma_{\text{CMC}} = 0.04$. Therefore, even at the CMC the surface coverage will be very low and the bubble will break (see Fig. 22). That is why in order to make the foam stable one must

use concentrations well above the CMC when the diffusivity D and the adsorption rate are larger [55,56]. This situation is typical for nonionic surfactants, which have very low values of the CMC.

Another indirect confirmation can be obtained by the results for emulsification of soybean oil in water with surfactant Brij 58 (with $d = 12 \text{ \AA}$). It was found [57] that the average drop diameter decreases with increasing surfactant concentration (see Fig. 2 in Ref. [57]). This variation of the drop diameter was attributed to coalescence of some drops. The drop diameter stops changing, when the surfactant concentration is 0.1 wt.%, and at higher concentrations remains constant, $5 \text{ } \mu\text{m}$. Since diameter of $5 \text{ } \mu\text{m}$ for the specific experimental conditions corresponds to the minimum radius, which can be achieved according to the Kolmogoroff theory [58] the authors concluded that at 0.1 wt.% concentration the coalescence ceases.

According to the thermodynamic theory of thin films [10] the thin film between the drops will stop thinning and will reach equilibrium when the capillary pressure, P_c , of the drops with interfacial tension σ and diameter d_d , $P_c = 4\sigma/d_d$, becomes equal to the disjoining pressure. If the difference $\Pi - P_c$ is negative, the film cannot reach equilibrium and the drops will coalesce. The authors of Ref. [57] calculated the adsorption time, t_A , which depends on the drop diameter. For concentration 0.1 wt.% they found t_A equal to 10 μs , 5 μs and 2.5 μs for diameters $5 \text{ } \mu\text{m}$, $10 \text{ } \mu\text{m}$ and $20 \text{ } \mu\text{m}$, respectively. For such short times Eq. (6.31) probably gives a fair estimate of the adsorption and the surface coverage, which was found to be 0.039, 0.028 and 0.02 for the respective times quoted above. The respective dependences $\Pi(h)$ for fixed chemical potential were calculated from Eqs. (5.18) and (5.21). The capillary pressure was calculated for the quoted diameters by using the value $\sigma = 30 \text{ mN/m}$, determined in [57]. The results, plotted in Fig. 23, show that for the drops with diameter $5 \text{ } \mu\text{m}$ the difference $\Pi - P_c$ is positive, which means that these drops will be stable, whereas the others with larger diameters will be unstable. This is in agreement with the experimental observation.

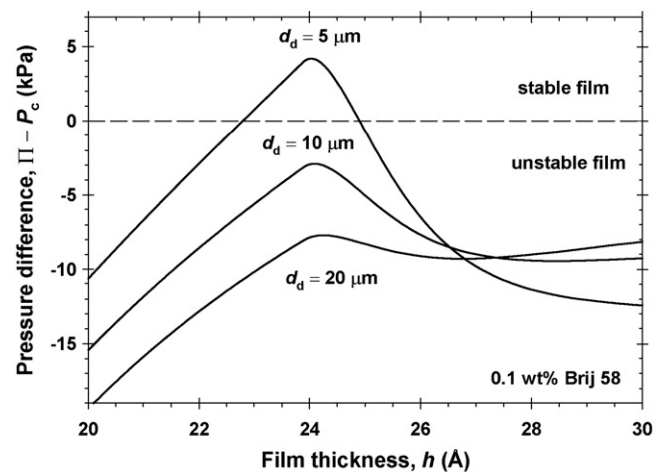


Fig. 23. Pressure difference, $\Pi - P_c$, as a function of the film thickness, h , for Brij 58 emulsion films. The drop diameters are 5, 10 and $20 \text{ } \mu\text{m}$.

7. Concluding remarks

We have tried to develop a theory for the stabilizing effect of nonionic surfactants on interacting fluid surfaces. We assumed that at each interface there is a layer of adsorbed surfactant, whose molecules were modeled as having spherical hydrophilic heads of diameter d attached to linear hydrophobic tails of diameter $2s$ and length L . The adsorption is assumed non-localized, i. e. the surfactant molecules move freely along the surfaces. They can perform however also thermal fluctuations normally to the interface with average immersion depth δ_s , which depends on the transfer energy per unit length from the water to the hydrophobic phase. These fluctuations lead to collisions with the opposite film surface and with the molecules adsorbed on it. The adsorption leads to increase of the solute concentration in the film with respect to the concentration in the continuous bulk phase and this gives rise to a repulsive disjoining pressure. There is also a purely osmotic contribution to the disjoining pressure, due to the water molecules expelled from the film region by the adsorbed molecules. The collisions lead to increase of the chemical potential of the surfactant, which is pushed out by this effect toward the bulk phase or toward the interfaces encircling the film.

In summary, we accounted for the main effects playing a role in this process for the chosen type of surfactants: (i) The thermal fluctuations of the adsorbed surfactant molecules, due to the fact that the energy of adsorption of a $-\text{CH}_2-$ group is approximately equal to the average thermal energy $k_B T$; (ii) The contribution of the collisions between molecules adsorbed on different surfaces; (iii) The restriction imposed on the fluctuation of the molecules by the presence of a second surface situated at a small distance h from the interface where the molecules are adsorbed; (iv) The volume of the hydrophilic heads, which expel part of the water molecules from the film region; (v) The equilibrium between the molecules adsorbed at the film surfaces and the menisci surrounding the film.

In the framework of the formulated model and geometry of the surfactant molecules we derived practically exact equations for the case of low surface coverage, up to 20%. We achieved that by assuming that only binary collisions play a role, an assumption corresponding to the use of a virial expansion of the configurational integral with second virial coefficient only. The most important effect, the collisions between the surfactant molecules, is accounted for by the interaction function f , which was calculated also exactly (see the Appendix A). The contribution of the expelled water to the disjoining pressure and the chemical potential was calculated by a modification of the theory of Hildebrand and Scatchard [11–13] for the osmotic pressure of concentrated solutions. We used a substantial approximation to generalize the theory for higher surface coverage, by assuming that the expressions of the interaction functions, derived for binary collisions remain valid even when collisions between 2, 3, ... molecules play a role. We achieved that by using the partition functions for the adsorption models of Helfand, Frisch and Lebowitz [32,33] and of Volmer [31], in which we introduced an effective molecular area, accounting for the intermolecular collisions. This assumption is akin to the

assumption used to derive the van der Waals surface equation of state and most probably has similar validity — it is certainly not correct quantitatively, but there is hope that it describes correctly the behavior of the system at high concentrations.

The derived equations and the numerical calculations, based on them, revealed that there are three main effects, each of them with different range of validity: the collisions of the surfactant molecules with the bare film surface are important only at small thickness, the collisions between the molecules play substantial role at thickness close to $2d$, where it causes the appearance of a repulsive maximum, and the water contribution to the disjoining pressure depends much more weakly on the thickness and is more uniformly distributed. As expected, it turned out that the condition from constant chemical potential leads to a strong decrease of the surface coverage in the film and to much smaller disjoining pressure. An interesting finding was that the maximum of the disjoining pressure, Π , is followed by a portion, where the decay is almost exponential as a function of the thickness h , but the decay length is several times larger than the immersion depth δ_s .

To make the use of the theory easier we derived simplified asymptotic equations for two cases: (i) low surface coverage for any film thickness; (ii) large surface coverage for thickness $h > 2d$. It turned out that both approximations work very well. We tried also to compare our theory with the theory of the protrusion forces of Israelachvili and Wennerström [7]. The two theories are based on rather different models, so that the results are also very different, although the general trend of the disjoining pressure is similar and under certain conditions the quantitative differences are not too large.

The experimental data, which could be used to verify our theory, are scarce, but we found reasonable agreement with the data of Lyle and Tiddy [6] for bilayers of C_{12}EO_4 . The data of Parsegian et al. [4,5] for lipid bilayers also confirmed qualitatively some of our theoretical conclusions.

Acknowledgement

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Appendix A. Calculation of the interaction function, $f_s(h)$ and $f_o(h)$

To calculate the interaction functions, $f_s(h)$ and $f_o(h)$, the following simplified geometry of the surfactant molecule is formulated (see Fig. A.1a). The hydrophilic head of the molecule is a sphere with radius, R . The hydrophobic tail of the molecule is a cylinder with radius s and length L . The length of the surfactant molecule, L , is assumed to be very large more precisely one assumes $L/\delta_s \gg 1$. Whenever necessary we will discuss the role of the finite value of L . The calculation of $f_s(h)$ (molecules at the same surface) is considerably different from that of $f_o(h)$ (molecules at opposite surfaces) because the orientation of the tail of the molecule $N+1$ is opposite to that of molecule 2, which modifies strongly the hard-core trajectory of molecule 2 (compare Fig. A.1a and b).

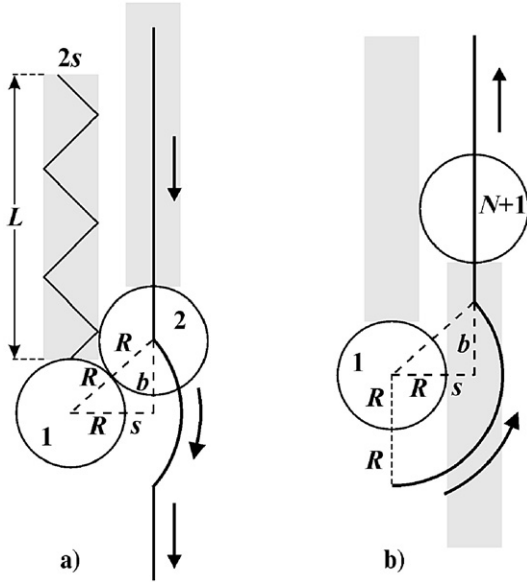


Fig. A.1. Sketch of the possible trajectories of hard-core interactions between two surfactant molecules — molecule 1 stays at a given position. a) Molecule 2 slides along the head or the tail of molecule 1 — the solid line represent the possible position of the center of the head of molecule 2, which give contribution in the calculation of f_s . b) Molecule $N+1$ has an opposite orientation than molecule 2 — the trajectory, for which the hard-core interactions take place, is different.

From physical viewpoint it is obvious that f_s must depend weakly on h , while f_o must decrease strongly when the film thickness, h , increases. Both interaction functions are universal in the sense that they do not depend on the mechanism of adsorption — they depend only on the geometry of the surfactant molecules and of the energy of interaction of the hydrophobic tail, w_l (through δ_s).

Calculation of $f_s(h)$ (molecules in the same adsorption layer). Substituting the definition (4.15) into Eq. (4.14a) the following expression for the interaction function, $f_s(h)$, is obtained:

$$f_s = \frac{\pi}{4\delta_f^2\alpha} \int_R^{h-R} \varphi(\zeta_1) \left[\int_{V_{12}} \varphi(\zeta_2) dr_{12}^2 dz_2 \right] dz_1 \quad (\text{A.1})$$

where $V_{12}(z_1)$ is the contact volume of the molecule 1 and 2, i.e. the volume in which molecule 2 overlap at least in one point the molecule 1, which is supposed to be fixed at position z_1 (see Fig. A.2). Note that the distances from the upper surface are $\zeta_1 = z_1 - R$ and $\zeta_2 = z_2 - R$, respectively. The volume V_{12} is bounded in radial direction by a given value of r_{12} denoted by ρ_{12} . Different values of ρ_{12} correspond to different vertical positions of the molecules and therefore, generally speaking $\rho_{12} = \rho_{12}(z_1, z_2)$. Taking into account the definition (4.5) the integral in Eq. (A.1) is transformed to:

$$f_s = \frac{1}{\delta_f^2 d^2} \int_R^{h-R} \int_{V_{12}} \exp\left(\frac{R-z_1}{\delta_s}\right) \exp\left(\frac{R-z_2}{\delta_s}\right) \rho_{12}^2(z_1, z_2) dz_2 dz_1. \quad (\text{A.2})$$

To obtain an explicit mathematical definition of the volume V_{12} we will use the geometry of the surfactant molecule (see Fig. A.1a). When the hydrophilic heads of the two molecules are in contact, the maximum possible vertical displacement between their centers is b , where

$$b^2 = d^2 - (R + s)^2 \quad (\text{A.3})$$

Depending on the film thickness, h , there are three cases and in each case the integration is carried out differently: (a) $h \geq d + 2b$ (thick film); (b) $d + b \leq h \leq d + 2b$ (intermediate film); (c) $d \leq h \leq d + b$ (very thin film).

a) *Thick film* ($h \geq d + 2b$). In this case depending on the position of molecule 1 we have three possibilities (see Fig. A.2a):

a.1) Molecule 1 is close to the upper film surface, i.e. $R \leq z_1 \leq R + b$. The possible trajectory of molecule 2 is shown in Fig. A.2a (solid line). In this case ρ_{12} is

$$\rho_{12}^2 = d^2 - (z_2 - z_1)^2 \quad \text{for} \quad R \leq z_2 \leq z_1 + b \quad (\text{A.4a})$$

$$\rho_{12}^2 = d^2 - b^2 \quad \text{for} \quad z_1 + b \leq z_2 \leq h - R \quad (\text{A.4b})$$

Therefore, the corresponding part of the integral in Eq. (A.2) becomes

$$J_1 = \int_R^{R+b} \exp\left(\frac{R-z_1}{\delta_s}\right) \left\{ \int_R^{z_1+b} \exp\left(\frac{R-z_2}{\delta_s}\right) [d^2 - (z_2 - z_1)^2] dz_2 + \int_{z_1+b}^{h-R} \exp\left(\frac{R-z_2}{\delta_s}\right) (d^2 - b^2) dz_2 \right\} \quad (\text{A.5})$$

a.2) Molecule 1 is not close to the upper and lower film surfaces, i.e. $R + b \leq z_1 \leq h - (R + b)$. The respective trajectory of molecule 2 is illustrated in Fig. A.2b (solid line). There are two regions in which the hydrophilic head of molecule 2 is sliding along the tail of molecule 1 and an arc trajectory of the sliding of

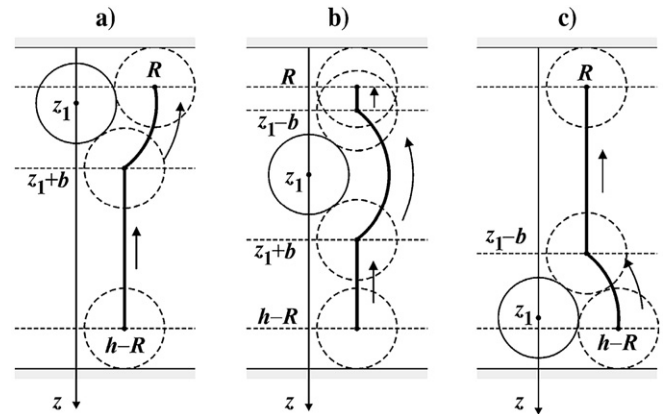


Fig. A.2. Possible trajectories of molecule 2 sliding along molecule 1, which stays at a fixed position z_1 , for large film thickness, h : a) molecule 1 is close to the upper film surface; b) molecule 1 is not close to the film surfaces; c) molecule 1 is close to the lower film surface. The solid lines represent boundaries of integration for the calculation of f_s (these are the contact trajectories of molecule 2).

the head of molecule 2 along the head of molecule 1. In this case ρ_{12} is defined as

$$\rho_{12}^2 = d^2 - (z_2 - z_1)^2 \quad \text{for} \quad z_1 - b \leq z_2 \leq z_1 + b \quad (\text{A.6a})$$

$$\rho_{12}^2 = d^2 - b^2 \quad \text{for} \quad R \leq z_2 \leq z_1 - b \quad \text{and} \quad z_1 + b \leq z_2 \leq h - R \quad (\text{A.6b})$$

The corresponding part of the integral appearing in Eq. (A.2) is reduced to:

$$J_2 = \int_{R+b}^{h-(R+b)} \exp\left(\frac{R-z_1}{\delta_s}\right) \left\{ \int_{z_1-b}^{z_1+b} \exp\left(\frac{R-z_2}{\delta_s}\right) [d^2 - (z_2 - z_1)^2] dz_2 + \int_R^{z_1-b} \exp\left(\frac{R-z_2}{\delta_s}\right) (d^2 - b^2) dz_2 + \int_{z_1+b}^{h-R} \exp\left(\frac{R-z_2}{\delta_s}\right) (d^2 - b^2) dz_2 \right\} dz_1. \quad (\text{A.7})$$

a.3) Molecule 1 is close to the lower film surface, i.e. $h - (R + b) \leq z_1 \leq h - R$. The solid line in Fig. A.2c illustrates the trajectory of the molecule 2 at a fixed position of molecule 1. This case is opposite to a.1 and ρ_{12} becomes

$$\rho_{12}^2 = d^2 - b^2 \quad \text{for} \quad R \leq z_2 \leq z_1 - b \quad (\text{A.8a})$$

$$\rho_{12}^2 = d^2 - (z_2 - z_1)^2 \quad \text{for} \quad z_1 - b \leq z_2 \leq h - R \quad (\text{A.8b})$$

The last part of the integral in Eq. (A.2) is transformed into:

$$J_3 = \int_{h-(R+b)}^{h-R} \exp\left(\frac{R-z_1}{\delta_s}\right) \left\{ \int_{z_1-b}^{h-R} \exp\left(\frac{R-z_2}{\delta_s}\right) [d^2 - (z_2 - z_1)^2] dz_2 + \int_R^{z_1-b} \exp\left(\frac{R-z_2}{\delta_s}\right) (d^2 - b^2) dz_2 \right\} dz_1. \quad (\text{A.9})$$

The integrals, J_1 , J_2 and J_3 , are calculated exactly and the obtained results are added in order to obtain the following relationship:

$$J_1 + J_2 + J_3 = 2\delta_s^2 \left\{ (2R^2 - \delta_s^2) \left[1 + \exp\left(\frac{4R-2h}{\delta_s}\right) \right] - (d^2 - b^2) \exp\left(\frac{2R-h}{\delta_s}\right) + \delta_s(b + \delta_s) \exp\left(-\frac{b}{\delta_s}\right) - \delta_s(b - \delta_s) \exp\left(\frac{4R+b-2h}{\delta_s}\right) \right\} \quad (\text{A.10})$$

By substituting Eq. (A.10) into Eq. (A.2) the expression for f_s is obtained:

$$f_s = \frac{1}{\Psi^2} \left\{ \left(1 - 2\frac{\delta_s^2}{d^2} \right) \left[1 + \exp\left(-\frac{2\tilde{h}}{\delta_s}\right) \right] - 2 \left(1 - \frac{b^2}{d^2} \right) \exp\left(-\frac{\tilde{h}}{\delta_s}\right) + 2 \frac{\delta_s(b + \delta_s)}{d^2} \exp\left(-\frac{b}{\delta_s}\right) - 2 \frac{\delta_s(b - \delta_s)}{d^2} \exp\left(\frac{b-2\tilde{h}}{\delta_s}\right) \right\} \quad (\text{A.11})$$

where the reduced film thickness, \tilde{h} , is defined as $\tilde{h} \equiv h - d$.

It is important to note that in the special case of surfactant molecules, for which the radius of the tail, s , is equal to the radius of the head, R , Eq. (A.3) yields $b = 0$ and from Eq. (A.11)

it follows that $f_s = 1$. Indeed, the overlapping area of two cylinders is exactly 4α .

At large values of the film thickness, i.e. with $\tilde{h}/\delta_s \gg 1$, f_s becomes:

$$f_{s\infty} = 1 - 2\frac{\delta_s^2}{d^2} + 2\frac{\delta_s(b + \delta_s)}{d^2} \exp\left(-\frac{b}{\delta_s}\right) \quad (\text{A.12})$$

Since however $\delta_s/d \ll 1$, the deviations of $f_{s\infty}$ from unity will be small.

b) *Intermediate film* ($d + b \leq h \leq d + 2b$). In this case the trajectories of molecule 2 are similar to those in Fig. A.2. We have three possibilities depending on the position of molecule 1:

b.1) Molecule 1 is close to the upper film surface, i.e. $R \leq z_1 \leq h - (R + b)$. In this case ρ_{12} is defined by Eqs. (A.4a) and (A.4b). Therefore, the corresponding part of the integral in Eq. (A.2) becomes

$$J_1 = \int_R^{h-(R+b)} \exp\left(\frac{R-z_1}{\delta_s}\right) \left\{ \int_R^{z_1+b} \exp\left(\frac{R-z_2}{\delta_s}\right) [d^2 - (z_2 - z_1)^2] dz_2 + \int_{z_1+b}^{h-R} \exp\left(\frac{R-z_2}{\delta_s}\right) (d^2 - b^2) dz_2 \right\} dz_1. \quad (\text{A.13})$$

b.2) Molecule 1 is not close to the lower and upper film surfaces, i.e. $h - (R + b) \leq z_1 \leq R + b$. In this case the regions a.1 and a.2 are overlapping and ρ_{12} is defined as:

$$\rho_{12}^2 = d^2 - (z_2 - z_1)^2 \quad \text{for} \quad R \leq z_2 \leq h - R \quad (\text{A.14})$$

The integral in Eq. (A.2) is simplified to:

$$J_2 = \int_{h-(R+b)}^{R+b} \exp\left(\frac{R-z_1}{\delta_s}\right) \int_R^{h-R} \exp\left(\frac{R-z_2}{\delta_s}\right) [d^2 - (z_2 - z_1)^2] dz_2 dz_1. \quad (\text{A.15})$$

b.3) Molecule 1 is close to the lower film surfaces, i.e. $R + b \leq z_1 \leq h - R$. This case is opposite to b.1 and for ρ_{12} Eqs. (A.8a) and (A.8b) are used. Therefore, the integral in Eq. (A.2) is transformed to:

$$J_3 = \int_{R+b}^{h-R} \exp\left(\frac{R-z_1}{\delta_s}\right) \left\{ \int_{z_1-b}^{h-R} \exp\left(\frac{R-z_2}{\delta_s}\right) [d^2 - (z_2 - z_1)^2] dz_2 + \int_R^{z_1-b} \exp\left(\frac{R-z_2}{\delta_s}\right) (d^2 - b^2) dz_2 \right\} dz_1. \quad (\text{A.16})$$

The sum of integrals, given by Eqs. (A.13), (A.15) and (A.16), is substituted into Eq. (A.2) to obtain again exactly the expression (A.11).

c) *Very thin film* ($d \leq h \leq d + b$). In this case both coordinates, z_1 and z_2 , change from R to $h - R$ and $b_{12}^2 = d^2 - (z_2 - z_1)^2$. The film is so thin that the regions illustrated in Fig. A.2a and c overlap. Therefore, Eq. (A.2) is presented in the following form:

$$f_s = \frac{1}{\delta_s^2 d^2} \int_R^{h-R} \int_R^{h-R} \exp\left(\frac{R-z_1}{\delta_s}\right) \exp\left(\frac{R-z_2}{\delta_s}\right) [d^2 - (z_1 - z_2)^2] dz_2 dz_1 \quad (\text{A.17})$$

Simple calculations give the final result:

$$f_s = 1 - 2 \frac{\delta_s^2}{d^2} + 2 \frac{\tilde{h}^2}{d^2 \Psi^2} \exp\left(-\frac{\tilde{h}}{\delta_s}\right) \quad (\text{A.18})$$

From Eq. (A.18) it is not obvious what will be the value of f_s at $h \rightarrow d$ because Eq. (A.18) contains $\Psi(h)$ in the denominator and $\Psi(d)=0$, see the definition (4.13). The serial expansion of Eq. (A.18) at $(h-d)/d \ll 1$ leads to

$$f_s \approx 1 - \frac{\tilde{h}^2}{6d^2} + \dots \quad (\text{A.19})$$

and therefore, f_s has a limiting value of 1, which could be expected.

Calculation of $f_O(h)$. This function accounts for the collision of molecules adsorbed on different (opposite) film surfaces. According to Eq. (5.19) and (5.24) it effectively increases the degree of surface coverage, θ . Besides, its derivative with respect to h is a factor, which significantly enhances the role of the interaction terms in Eqs. (5.18) and (5.23).

From the definition (4.15) and Eq. (4.14b) the following expression for the interaction function, $f_O(h)$, is obtained:

$$f_O = \frac{\pi}{4\delta_f^2 \alpha} \int_R^{h-R} \varphi(\zeta_1) \left[\int_{V_{1N+1}} \varphi(\zeta_{N+1}) dr_{1N+1}^2 dz_{N+1} \right] dz_1 \quad (\text{A.20})$$

where $V_{1N+1}(z_1)$ is the contact volume of molecule 1 and $N+1$, i.e. the volume in which molecule $N+1$ overlaps at least in one point with the molecule 1, which is supposed fixed at the position z_1 (see Fig. A.1b). The distance from the lower surface is $\zeta_{N+1} = h - (z_{N+1} + R)$. The volume V_{1N+1} is bounded in radial direction by a given value of r_{1N+1} denoted as ρ_{1N+1} , where generally $\rho_{1N+1} = \rho_{1N+1}(z_1, z_{N+1})$. Taking into account the definition (4.5), the integral in Eq. (A.20) is reduced to:

$$f_O = \frac{1}{\delta_f^2 d^2} \int_R^{h-R} \int_{V_{1N+1}} \exp\left(\frac{R-z_1}{\delta_s}\right) \exp\left(\frac{R-h+z_{N+1}}{\delta_s}\right) \times \rho_{1N+1}^2(z_1, z_{N+1}) dz_{N+1} dz_1. \quad (\text{A.21})$$

The regions of integration, defined by V_{1N+1} , are: (a) $h \geq 2d$ (thick film); (b) $d+b \leq h \leq 2d$ (intermediate film); (c) $d \leq h \leq d+b$ (very thin film).

a) **Thick film** ($h \geq 2d$). In this case we have two different sub-cases, which finally lead to the same mathematical expression for f_O .

The first sub-case is $h \geq 2d+b$. Depending on the position of molecule 1 we have three possibilities (see Fig. A.3a):

a.1) Molecule 1 is close to the upper film surface, i.e. $R \leq z_1 \leq R+b$. Molecule $N+1$ will interact with molecule 1 only for $R \leq z_{N+1} \leq z_1+d$ — for other values of z_{N+1} molecule $N+1$ is below molecule 1 and there is no possibility for overlapping. The possible trajectory of molecule $N+1$ is illustrated in Fig. A.3a. Therefore, ρ_{1N+1} is

$$\rho_{1N+1}^2 = d^2 - (z_{N+1} - z_1)^2 \quad \text{for} \quad R \leq z_{N+1} \leq z_1 + d \quad (\text{A.22})$$

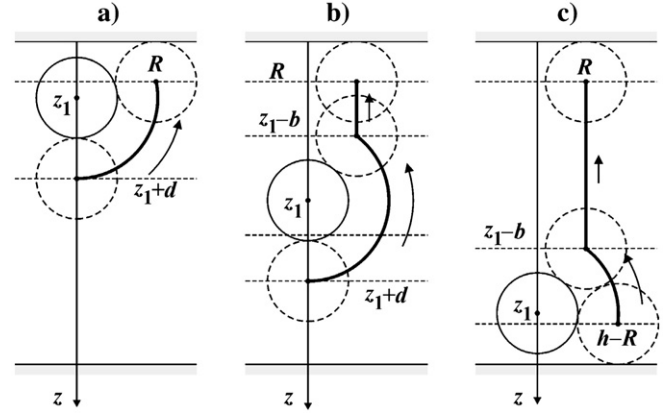


Fig. A.3. Contact trajectories of molecule $N+1$ sliding along molecule 1, which is fixed at a position z_1 , for large film thickness, h : a) molecule 1 is close to the upper film surface; b) molecule 1 is not close to the film surfaces; c) molecule 1 is close to the lower film surface. The solid lines represent boundaries of integration for the calculation of f_O . Because of the different orientation of the tails only part of the contact trajectories of molecule $N+1$ must be accounted for in the integrals.

The corresponding part of the integral in Eq. (A.21) becomes

$$J_1 = \int_R^{R+b} \exp\left(\frac{R-z_1}{\delta_s}\right) \int_R^{z_1+d} \exp\left(\frac{R-h+z_{N+1}}{\delta_s}\right) \times [d^2 - (z_{N+1} - z_1)^2] dz_{N+1} dz_1. \quad (\text{A.23})$$

a.2) Molecule 1 is not close to the upper or the lower film surfaces, i.e. $R+b \leq z_1 \leq h-3R$. Molecule $N+1$ will interact with molecule 1 only when $R \leq z_{N+1} \leq z_1-b$ and when $z_1-b \leq z_{N+1} \leq z_1+d$ — for other values of z_{N+1} the molecule $N+1$ is below the molecule 1 and there is no possibility for overlapping. The boundaries of integration are illustrated in Fig. A.3b (solid line). The expression for ρ_{1N+1} is

$$\rho_{1N+1}^2 = d^2 - (z_{N+1} - z_1)^2 \quad \text{for} \quad z_1 - b \leq z_{N+1} \leq z_1 + d \quad (\text{A.24a})$$

$$\rho_{1N+1}^2 = d^2 - b^2 \quad \text{for} \quad R \leq z_{N+1} \leq z_1 - b \quad (\text{A.24b})$$

The corresponding part of the integral appearing in Eq. (A.21) is reduced to:

$$J_2 = \int_{R+b}^{h-3R} \exp\left(\frac{R-z_1}{\delta_s}\right) \left\{ \int_{z_1-b}^{z_1+d} \exp\left(\frac{R-h+z_{N+1}}{\delta_s}\right) \times [d^2 - (z_{N+1} - z_1)^2] dz_{N+1} + \int_R^{z_1-b} \exp\left(\frac{R-h+z_{N+1}}{\delta_s}\right) \times (d^2 - b^2) dz_{N+1} \right\} dz_1. \quad (\text{A.25})$$

a.3) Molecule 1 is close to the lower film surface, i.e. $h-3R \leq z_1 \leq h-R$. Molecule $N+1$ will interact with molecule 1 for $R \leq z_{N+1} \leq z_1-b$ and for $z_1-b \leq z_{N+1} \leq h-R$. The trajectory of molecule $N+1$ at a fixed position of molecule 1 is plotted in Fig. A.3c. In this case ρ_{1N+1} is defined as

$$\rho_{1N+1}^2 = d^2 - (z_{N+1} - z_1)^2 \quad \text{for} \quad z_1 - b \leq z_{N+1} \leq h - R \quad (\text{A.26a})$$

$$\rho_{1N+1}^2 = d^2 - b^2 \quad \text{for} \quad R \leq z_{N+1} \leq z_1 - b \quad (\text{A.26b})$$

Substituting Eqs. (A.26a) and (A.26b) into Eq. (A.21) leads to the following integral:

$$J_3 = \int_{h-3R}^{h-R} \exp\left(\frac{R-z_1}{\delta_s}\right) \left\{ \int_{z_1-b}^{h-R} \exp\left(\frac{R-h+z_{N+1}}{\delta_s}\right) \times [d^2-(z_{N+1}-z_1)^2] dz_{N+1} + \int_R^{z_1-b} \exp\left(\frac{R-h+z_{N+1}}{\delta_s}\right) \times (d^2-b^2) dz_{N+1} \right\} dz_1. \quad (\text{A.27})$$

The integrals (A.23), (A.25) and (A.27) are calculated exactly, the obtained results are added and substituted into Eq. (A.21) to derive the expression for the interaction function, $f_O(h)$:

$$f_O = \frac{1}{\psi^2} \left[\left(1 - \frac{b^2}{d^2}\right) \exp\left(-\frac{2\tilde{h}}{\delta_s}\right) + 2 \frac{(\tilde{h}-3\delta_s)(b+\delta_s)-b^2}{d^2} \times \exp\left(-\frac{b+\tilde{h}}{\delta_s}\right) + 2 \frac{(\tilde{h}-d+2\delta_s)(d-\delta_s)-\delta_s^2}{d^2} \times \exp\left(-\frac{\tilde{h}-d}{\delta_s}\right) - 2 \left(1 - 6 \frac{\delta_s^2}{d^2}\right) \exp\left(-\frac{\tilde{h}}{\delta_s}\right) \right] \quad (\text{A.28})$$

It is important to note that at large film thickness, h , the interaction function, $f_O(h)$, exponentially decays.

The second sub-case is $2d \leq h \leq 2d+b$. Depending on the position of molecule 1 we have three possibilities slightly different from above (see Fig. A.3):

a.1) Molecule 1 is close to the upper film surface, i.e. $R \leq z_1 \leq h-R$. The molecule $N+1$ will interact with the molecule 1 for $R \leq z_{N+1} \leq z_1+d$ and the expression for ρ_{1N+1} is Eq. (A.22). The analogous integral to Eq. (A.23) is:

$$J_1 = \int_R^{h-3R} \exp\left(\frac{R-z_1}{\delta_s}\right) \int_R^{z_1+d} \exp\left(\frac{R-h+z_{N+1}}{\delta_s}\right) \times [d^2-(z_{N+1}-z_1)^2] dz_{N+1} dz_1. \quad (\text{A.29})$$

a.2) Molecule 1 is not so close to the upper film surface, i.e. $h-3R \leq z_1 \leq R+b$. Molecule $N+1$ will interact with molecule 1 for $R \leq z_{N+1} \leq h-R$ and ρ_{1N+1} is defined as:

$$\rho_{1N+1}^2 = d^2 - (z_{N+1}-z_1)^2 \quad \text{for} \quad R \leq z_{N+1} \leq h-R \quad (\text{A.30})$$

The respective integral appearing in Eq. (A.21) is reduced to:

$$J_2 = \int_{h-3R}^{R+b} \exp\left(\frac{R-z_1}{\delta_s}\right) \int_R^{h-R} \exp\left(\frac{R-h+z_{N+1}}{\delta_s}\right) \times [d^2-(z_{N+1}-z_1)^2] dz_{N+1} dz_1. \quad (\text{A.31})$$

a.3) Molecule 1 is close to the lower film surface, i.e. $R+b \leq z_1 \leq h-R$. Molecule $N+1$ will interact with molecule 1 for $R \leq z_{N+1} \leq z_1-b$ and for $z_1-b \leq z_{N+1} \leq h-R$ and ρ_{1N+1} is given by Eqs. (A.26a) and (A.26b). It leads to:

$$J_3 = \int_{R+b}^{h-R} \exp\left(\frac{R-z_1}{\delta_s}\right) \left\{ \int_{z_1-b}^{h-R} \exp\left(\frac{R-h+z_{N+1}}{\delta_s}\right) \times [d^2-(z_{N+1}-z_1)^2] dz_{N+1} + \int_R^{z_1-b} \exp\left(\frac{R-h+z_{N+1}}{\delta_s}\right) \times (d^2-b^2) dz_{N+1} \right\} dz_1. \quad (\text{A.32})$$

The integrals (A.29), (A.31) and (A.32) are calculated exactly, the obtained results are added and substituted into Eq. (A.21). The final expression for $f_O(h)$, which is obtained is exactly Eq. (A.28). For that reason we will not distinguish between these sub-cases in the future.

b) *Intermediate film* ($d+b \leq h \leq 2d$). In this case we have two possibilities depending on the position of the molecule 1 — a case like a.2 (Fig. A.3b) does not exist. There is a partial overlapping of the regions in Fig. A.3a and c.

b.1) Molecule 1 is close to the upper film surface, i.e. $R \leq z_1 \leq R+b$. Molecule $N+1$ will interact with molecule 1 in the whole interval $R \leq z_{N+1} \leq h-R$. Therefore, ρ_{1N+1} is

$$\rho_{1N+1}^2 = d^2 - (z_{N+1}-z_1)^2 \quad \text{for} \quad R \leq z_{N+1} \leq h-R \quad (\text{A.33})$$

and the contribution to f_O is given by:

$$J_1 = \int_R^{R+b} \exp\left(\frac{R-z_1}{\delta_s}\right) \int_R^{h-R} \exp\left(\frac{R-h+z_{N+1}}{\delta_s}\right) \times [d^2-(z_{N+1}-z_1)^2] dz_{N+1} dz_1. \quad (\text{A.34})$$

b.3) Molecule 1 is close to the lower film surface, i.e. $R+b \leq z_1 \leq h-R$. Molecule $N+1$ will interact with the molecule 1 for $R \leq z_{N+1} \leq z_1-b$ and for $z_1-b \leq z_{N+1} \leq h-R$ and ρ_{1N+1} is given by Eqs. (A.26a) and (A.26b). The resulting integral is that, given by Eq. (A.32).

Adding the results of the calculations for Eqs. (A.32) and (A.34) and substituting into Eq. (A.21) we arrive to:

$$f_O = \frac{1}{\psi^2} \left[\left(1 - \frac{b^2}{d^2}\right) \exp\left(-\frac{2\tilde{h}}{\delta_s}\right) + 2 \frac{(\tilde{h}-3\delta_s)(b+\delta_s)-b^2}{d^2} \times \exp\left(-\frac{b+\tilde{h}}{\delta_s}\right) + 1 - 2 \frac{\delta_s^2}{d^2} - \left(\frac{\tilde{h}-2\delta_s}{d}\right)^2 - 2 \left(1 - 6 \frac{\delta_s^2}{d^2}\right) \exp\left(-\frac{\tilde{h}}{\delta_s}\right) \right]. \quad (\text{A.35})$$

c) *Very thin film* ($d \leq h \leq d+b$). In this case both coordinates, z_1 and z_{N+1} , change from R to $h-R$ and $\rho_{1N+1}^2 = d^2 - (z_{N+1}-z_1)^2$. Full overlapping of the regions, shown in Fig. A.3a and c, occurs. Eq. (A.21) is presented as:

$$f_O = \frac{1}{\delta_s^2 d^2} \int_R^{h-R} \int_R^{h-R} \exp\left(\frac{R-z_1}{\delta_s}\right) \exp\left(\frac{R-h+z_{N+1}}{\delta_s}\right) \times [d^2-(z_1-z_{N+1})^2] dz_{N+1} dz_1 \quad (\text{A.36})$$

Simple calculations give the final result:

$$f_O = \frac{1}{\psi^2} \left\{ 1 - 2 \frac{\delta_s^2}{d^2} - \left(\frac{\tilde{h}-2\delta_s}{d}\right)^2 - 2 \left(1 - 6 \frac{\delta_s^2}{d^2}\right) \exp\left(-\frac{\tilde{h}}{\delta_s}\right) + \left[1 - 2 \frac{\delta_s^2}{d^2} - \left(\frac{\tilde{h}+2\delta_s}{d}\right)^2 \right] \exp\left(-\frac{2\tilde{h}}{\delta_s}\right) \right\} \quad (\text{A.37})$$

It is interesting to note that at $h \rightarrow d$ the limiting value of f_O , predicted from Eq. (A.37), is $f_O=1$, which could be expected.

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