

# The Effect of Oil Solubility on the Oil Drop Entry at Water–Air Interface<sup>†</sup>

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Instability driven by diffusion flux across an asymmetric liquid film is theoretically investigated. To specify the system, we consider an oil–water–air film; the transported species are oil molecules. The latter are dissolved (solubilized) at the oil–water interface, then they are transferred by diffusion across the aqueous film to the water–air interface, where they penetrate between the tails of adsorbed surfactant molecules. Fluctuational capillary waves at the two film surfaces are considered. The set of theoretical equations is solved to derive a dispersion relation between the wavenumber and the exponent of wave growth. The results reveal that if a local decrease in the film thickness appears, the water–air interface enters a zone enriched in dissolved oil. The newly adsorbed oil creates a surface tension gradient, which carries water away and causes a further decrease of the local film thickness in the concave zone, until eventually the film ruptures. The numerical results show that the film becomes less stable when its thickness decreases, its radius increases, and the diffusion flux across it is more intensive. Even very small decrements of the water–air surface tension, caused by the adsorbed oil, are sufficient to trigger the instability. Its appearance is not so sensitive to the degree of mobility of the oil–water interface. If the water–air surface is preequilibrated with the transported component (there is prespread oil), then the surface tension decrement and the instability disappear. The rupture of an asymmetric oil–water–air film is a precondition for entry of an oil drop at the water–air interface and effectuation of its foam-destructive action. Our results about a specific source of film instability could be helpful for a deeper understanding of the mechanisms of antifoaming.

## 1. Introduction

In some cases the formation of foams is desirable (under a certain control); such are the applications in personal-care and house-hold detergency, in fire-fighting, ore flotation, etc. On the other hand, in many cases the spontaneous formation of foams is not wanted insofar as it hampers the efficient operation of industrial processes.<sup>1–3</sup> It has been established that microscopic oil droplets, solid particles, and their combination, may exhibit a foam-destructive effect.<sup>1–13</sup> For example, small oil droplets

dispersed in shampoos provide hair conditioning; special surfactant compositions have been invented to protect the foams from the destructive action of the droplets.<sup>14</sup> In other cases, very active antifoams are intentionally added to suppress the development of unwanted foamability during industrial processes.<sup>11,13</sup> In both cases one could achieve the desired effect utilizing the knowledge about the foam-breaking action of microscopic oil drops and particulates.

Three different mechanisms of antifoaming action have been established: oil-spreading mechanism,<sup>2,3,15–18</sup> bridging-dewetting mechanism,<sup>19–23</sup> and bridging-stretching mechanism.<sup>11–13</sup> All of them involve as a necessary step the entering of an antifoam droplet (or particle) at the

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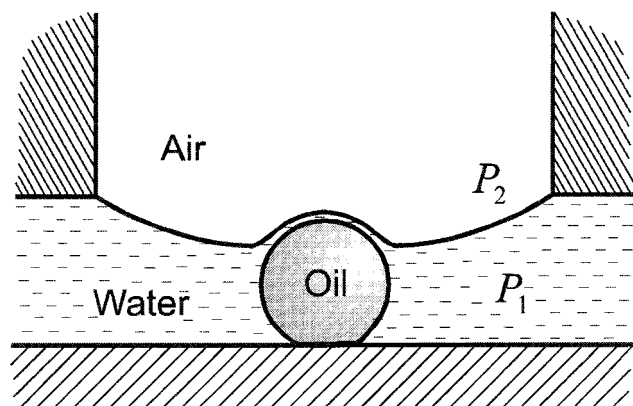
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**Figure 1.** Sketch of a  $\mu\text{m}$ -sized oil drop pressed against a solid substrate by an air bubble blown out of a capillary. When the pressure difference between the air and water phases,  $\Delta P = P_2 - P_1$ , is increased, the asymmetric oil-water-air film breaks at a certain critical value,  $\Delta P_{\text{cr}}$ .

air-water interface, which is equivalent to rupture of the asymmetric droplet-water-air film.

To study the entering of oil drops at the water-air interface, the film-trapping technique<sup>24,25</sup> was recently applied.<sup>26</sup> In these experiments oil drops were trapped in an aqueous film, which was formed between a solid substrate and an air bubble blown out of a capillary, see Figure 1. The aqueous phase always contained dissolved surfactant of concentrations around or beyond the cmc (critical micellization concentration). The pressure difference

$$\Delta P = P_2 - P_1 \quad (1.1)$$

could be controlled and directly measured. It was established that, upon a gradual increasing of  $\Delta P$ , the asymmetric oil-water-air film did break at a certain critical pressure difference,  $\Delta P_{\text{cr}}$ , whose value is rather reproducible.<sup>14,26</sup> Moreover, the measured values of  $\Delta P_{\text{cr}}$  turned out to be systematically lower for oils that exhibit some solubility in water, in comparison with oils that are completely water-insoluble. For example, for hexane  $\Delta P_{\text{cr}} = 42$  Pa, whereas for triolein (water-insoluble triglyceride)  $\Delta P_{\text{cr}} = 350$  Pa.<sup>26</sup> In addition, if a drop of a given oil is placed on the water-air interface, it produces a quick decrease in the surface tension, which could be attributed to a molecular spreading of oil molecules among the tails of the adsorbed surfactant molecules.<sup>27</sup>

Our purpose here is to investigate theoretically whether the diffusion transport of oil (from the oil drop, across the water film, to the water-air interface) could produce instability and film rupture.

The mass and/or heat transfer across a liquid interface, coupled with gradients of surface tension (the Marangoni effect), is known to produce hydrodynamic instability even for a single phase boundary; this phenomenon has been studied by Sternling and Scriven<sup>28</sup> in relation to the spontaneous emulsification. Lin and Brenner,<sup>29</sup> and

Castilo and Velarde<sup>30</sup> investigated the instabilities in wetting films with one deformable open surface, such as the tear films in human eyes. The mechanism of rupture of a liquid film formed between two fluid phases was examined experimentally and theoretically by Ivanov et al.<sup>31-33</sup> for emulsion systems: transfer of alcohols, acetic acid, and acetone across liquid films. The diffusion transport of some solute across the film has been found to lead to the development of Marangoni instability (unstable vortices), which manifests itself as a forced growth of capillary waves at the film surfaces, and eventual film rupture. Destabilizing mass transfer is present also in evaporating (mono- or two-layered) liquid films; the resulting instability has been investigated by Danov et al.<sup>34-37</sup> by means of linear and nonlinear stability analysis.

The subject of the present theoretical study is closer to that of ref 33, where film of infinite area and stationary vortices have been considered. In contrast, here we consider films of finite area (like the one at the top of the oil drop in Figure 1), as well as growing and decaying perturbations (positive and negative values of the wave-growth exponent). In this aspect we will apply the formalism developed in the theory of the critical thickness of liquid films.<sup>38-43</sup>

The paper is organized as follows. In section 2 we consider the diffusion of oil molecules across the film and their adsorption at the water-air interface. In section 3 we describe theoretically the fluctuational capillary waves on the film surfaces and in section 4, the resulting perturbations in the concentration and adsorption of oil. The dispersion relation between the wavenumber and frequency is derived and discussed, and the source of instability is identified. Finally, in section 6 we present numerical data, which demonstrate the effects of the film thickness, area, and the diffusion intensity on the film stability.

## 2. Diffusion of Oil Molecules across the Film

Let us consider a thin aqueous film formed between an oil drop and the water-air interface (Figure 2). The aqueous phase is a surfactant solution. The surfactant is assumed to be insoluble in oil, and its concentration in the water phase is presumably high enough (around or beyond the cmc) to have dense surfactant monolayers formed at the oil-water and water-air interfaces. The magnitude of the film radius  $R$  depends (i) on the size of

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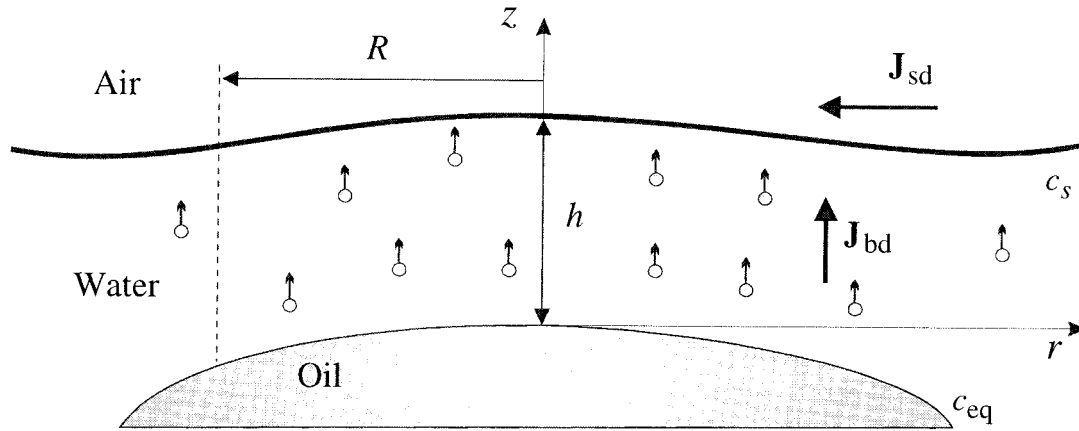
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**Figure 2.** Scheme of the diffusion transport of oil molecules from an oil drop (below) toward the water–air interface;  $c_{eq}$  and  $c_s$  are the subsurface concentrations of dissolved oil at the oil–water and water–air interfaces, respectively;  $J_{bd}$  and  $J_{sd}$  symbolize the fluxes of bulk and surface diffusion of oil;  $h$  and  $R$  are the film thickness and radius.

the oil drop, (ii) on the force pressing the drop against the water–air interface, and (iii) on the specific configuration of interfaces; say, if a drop is captured in a Plateau border within a foam, three asymmetric oil–water–air films will be formed. Below  $R$  is treated as a parameter of the model, whose influence on the stability of the film is investigated. For a specific system  $R$  can be determined from the conditions for mechanical equilibrium.

Further, we assume that (i) the oil has some solubility (molecular or micellar) in the aqueous phase and (ii) the oil is able to spread over the surfactant adsorption monolayer and thus to decrease the surface tension of the water–air interface,  $\sigma_{WA}$ . Moreover, in this article we consider the case of nonpreequilibrated aqueous and oil phases. In such a case, oil molecules will be dissolved at the oil–water interface (Figure 2), then they will cross the water film by diffusion, and finally they will adsorb at the water–air interface causing a progressive decrease in  $\sigma_{WA}$ , which is due to the penetration of oil among the hydrocarbon tails of the surfactant molecules.

The concentration of dissolved oil molecules in water is assumed to be much smaller than the surfactant concentration, which is a typical situation for a foam-making system. Consequently, we can accept that the system is (almost instantaneously) equilibrated with respect to the distribution of the *surfactant* and then we can examine only the slow transport of *oil* molecules. This considerably simplifies the diffusion problem considered in the present section, as well as the hydrodynamic problem (see sections 3 and 4).

Since in reality the thickness of the asymmetric oil–water–air film is much smaller than its curvature radius, we can neglect the curvature of the film. Therefore, we will consider a plane-parallel film of constant thickness  $h$ . Our first task is to determine the concentration of the dissolved oil  $c_0(z,t)$ ;  $t$  is time, the  $z$ -axis is perpendicular to the film, and the plane  $xy$  coincides with the oil–water interface. The function  $c_0(z,t)$  obeys the equation of diffusion:

$$\frac{\partial c_0}{\partial t} = D \frac{\partial^2 c_0}{\partial z^2} \quad (0 < z < h) \quad (2.1)$$

where  $D$  is the diffusivity of the oil molecules in water. To specify the initial condition, we assume that there is no dissolved oil at the initial moment  $t = 0$ :

$$c_0(z,0) = 0 \quad (0 < z \leq h) \quad (2.2)$$

The boundary condition at the oil–water interface could be imposed in various ways. Here we will assume that the subsurface layer of the water phase is equilibrated with the oil phase, that is

$$c_0(0,t) = c_{eq} \quad (t > 0) \quad (2.3)$$

where  $c_{eq}$  is the equilibrium concentration of dissolved oil in the water. Equation 2.3 implies that the transport of oil across the water film is limited by the diffusion. The boundary condition at the water–air interface  $z = h$  is

$$\frac{d\Gamma_0}{dt} = -D \frac{\partial c_0}{\partial z} \Big|_{z=h} \quad (2.4)$$

i.e. the adsorption of oil at the water–air interface  $\Gamma_0$  increases due to the supply of oil molecules by diffusion. To complete the set of equations we need an adsorption isotherm. For the sake of simplicity we will use the Henry isotherm (see, e.g., Table 1 in ref 44):

$$\Gamma_0(t) = H_a c_{0s}(t), \quad c_{0s}(t) \equiv c_0(z = h, t) \quad (2.5)$$

$$\sigma_{WA}(t) = \sigma_{WA}^{(0)} - kT\Gamma_0(t) \quad (2.6)$$

Here  $c_{0s}$  is the subsurface concentration of dissolved oil molecules and  $H_a$  is the slope of the Henry adsorption isotherm;  $\sigma_{WA}^{(0)}$  is the surface tension of the water–air interface in the absence of any adsorbed oil molecules (surfactant molecules are presumed to be present).

The linear boundary problem, based on eqs 2.1–2.5, can be solved by means of Laplace transformation. Unfortunately, the inverse Laplace transform of the solution cannot be obtained in analytical form. However, the asymptotic form of the solution for long times can be expressed analytically (see Appendix A):

$$c_0(z,t) = c_{eq} \left[ 1 - \frac{z}{h} \exp\left(-\frac{Dt}{H_a h}\right) \right] \quad (t \gg h^2/D) \quad (2.7)$$

Setting  $z = h$  in eq 2.7 we obtain an expression for the subsurface concentration of oil molecules:

$$c_{0s}(t) = c_{eq} \left[ 1 - \exp\left(-\frac{Dt}{H_a h}\right) \right] \quad (t \gg h^2/D) \quad (2.8)$$

Finally, eliminating the exponential function between eqs 2.7 and 2.8 one obtains

$$c_0(z,t) = c_{\text{eq}} - [c_{\text{eq}} - c_{\text{os}}(t)]z/h \quad (t \gg h^2/D) \quad (2.9)$$

If the time derivative in eq 2.1 is neglected, the linear dependence of  $c_0$  on  $z$  in eq 2.9 can be directly deduced. For typical parameter values,  $D = 5 \times 10^{-6} \text{ cm}^2/\text{s}$  and  $h = 100 \text{ nm}$ , one obtains  $h^2/D = 2 \times 10^{-5} \text{ s}$ , which means that eqs 2.7–2.9 are valid for all values of  $t$ , except for a very short nonstationary initial stage of diffusion.

As already mentioned, the boundary conditions, eqs 2.3 and 2.5, correspond to the assumption that the subsurface layer of the aqueous phase and the adsorption layer are equilibrated with respect to the exchange of oil molecules. Such an equilibration exists if the following criterion is satisfied:

$$\frac{lk_{\text{des}}}{\Gamma_{\text{eq}}D} \frac{\partial \Gamma_0}{\partial c_0} \gg 1 \quad (2.10)$$

where  $l$  is a characteristic thickness of the diffusion layer and  $k_{\text{des}}$  is the rate constant of desorption of oil in the water;  $\Gamma_{\text{eq}}$  is the saturation adsorption of oil. From the Henry isotherm (see eq 2.5), we obtain  $\partial \Gamma_0 / \partial c_0 = H_a$ ; in addition, for our system  $l$  can be identified with the film thickness  $h$ ; then the criterion 2.10 acquires the form

$$h \gg \Gamma_{\text{eq}}D / (k_{\text{des}}H_a) \quad (2.11)$$

For an estimate one can take  $D = 5 \times 10^{-6} \text{ cm}^2/\text{s}$ ,  $H_a = 2.4 \times 10^{-2} \text{ cm}$ , and  $1/\Gamma_{\text{eq}} = 68 \text{ \AA}^2$  per molecule (see section 6.1 below); because of the lack of data for  $k_{\text{des}}$  for oil, we took the value  $k_{\text{des}} = 6.7 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1} = 4.0 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$  for pentanol from Table 9.1 in ref 45. With these parameter values the criterion 2.11 gives  $h \gg 7.6 \text{ nm}$  as a necessary condition for equilibration of surface and subsurface.

In some cases the surfactant micelles serve as carriers of oil in the aqueous phase.<sup>46–49</sup> If such is the case, in the above equations  $D$  should have the meaning of micelle diffusivity.

In other cases, the oil can be completely insoluble in water (like the triglycerides), but it can contain some admixture (say alcohol), which has some solubility in water and can adsorb at the water–air interface. In such a case this admixture can play the same role as the soluble oil considered in this paper.

### 3. Fluctuational Capillary Waves on the Film Surfaces

As already mentioned, the transport of oil molecules to the water–air interface decreases the interfacial tension  $\sigma_{\text{WA}}$  and perturbs the film surfaces. Thus, the inevitable fluctuation capillary waves could be enhanced and the film could rupture.<sup>33</sup> To investigate this problem theoretically, below we apply a linear instability analysis.

Let us consider fluctuations of the film thickness  $h$ , of the pressure inside the film  $p$ , and of the concentration of oil molecules in water  $c$ . Each of these variables can be

presented as a sum of its equilibrium value, denoted with a subscript “0”, and of a small perturbation, denoted with tilde, “~”:

$$h = h_0 + \tilde{h}, \quad p = p_0 + \tilde{p}, \quad c = c_0 + \tilde{c} \quad (3.1)$$

It has been established<sup>38–43</sup> that the short capillary waves decay much faster than the long ones due to a higher dissipation of kinetic energy. For that reason, in the present analysis we consider only the long waves, whose length is of the order of the film radius  $R$  (Figure 2), insofar as they are expected to be responsible for the film rupture. The film radius is much greater than the film thickness; that is,  $h/R \ll 1$ . Therefore, to solve the hydrodynamic problem, we can use the Navier–Stokes equation in lubrication approximation,<sup>50</sup> viz.,

$$\frac{\partial^2 v_r}{\partial z^2} = \frac{1}{\eta} \frac{\partial \tilde{p}}{\partial r}, \quad \tilde{p} = \tilde{p}(r,t) \quad (3.2)$$

We use cylindrical coordinates  $(r, \varphi, z)$ , the  $z$ -axis is the axis of rotational symmetry of the system (Figure 2), and  $\eta$  is viscosity of the aqueous phase. The fluid flow is due to the fluctuations; the velocity of the flow is expressed in the form  $\mathbf{v} = v_r \mathbf{e}_r + v_z \mathbf{e}_z$ , where  $\mathbf{e}_r$  and  $\mathbf{e}_z$  are unit vectors of the local basis; the two velocity components  $v_r$  and  $v_z$  are related by the continuity equation<sup>50</sup>

$$\frac{1}{r} \frac{\partial}{\partial r}(rv_r) + \frac{\partial v_z}{\partial z} = 0 \quad (3.3)$$

Integrating eq 3.2 twice with respect to  $z$ , one obtains<sup>51</sup>

$$v_r = \frac{z(z-h)}{2\eta} \frac{\partial \tilde{p}}{\partial r} + \frac{z}{h} \frac{\partial u_2}{\partial r} + \frac{h-z}{h} \frac{\partial u_1}{\partial r} \quad (3.4)$$

where we have introduced the notation

$$\frac{\partial u_1}{\partial r} \equiv v_r|_{z=0}, \quad \frac{\partial u_2}{\partial r} \equiv v_r|_{z=h} \quad (3.5)$$

The functions, describing the shape of the perturbed lower and upper film surfaces, will be denoted by

$$z = \tilde{h}_1(r,t) \quad \text{and} \quad z = h + \tilde{h}_2(r,t) \quad (3.6)$$

Then the perturbation of the film thickness is

$$\tilde{h}(r,t) = \tilde{h}_2(r,t) - \tilde{h}_1(r,t) \quad (3.7)$$

Gumerman and Homsy<sup>52</sup> have found that the results of the instability analysis are not so sensitive to the type of the boundary condition imposed at the periphery of a liquid film. To specify this boundary condition, in our case we will require the perturbations to vanish at the film periphery; that is,  $\tilde{h}_1 = \tilde{h}_2 = 0$  for  $r = R$ . The physical motivation of the latter boundary condition, which is currently used to solve film-instability problems, is that the factors promoting the *growth* of the capillary waves are expected to be operative only inside the liquid film.<sup>53</sup>

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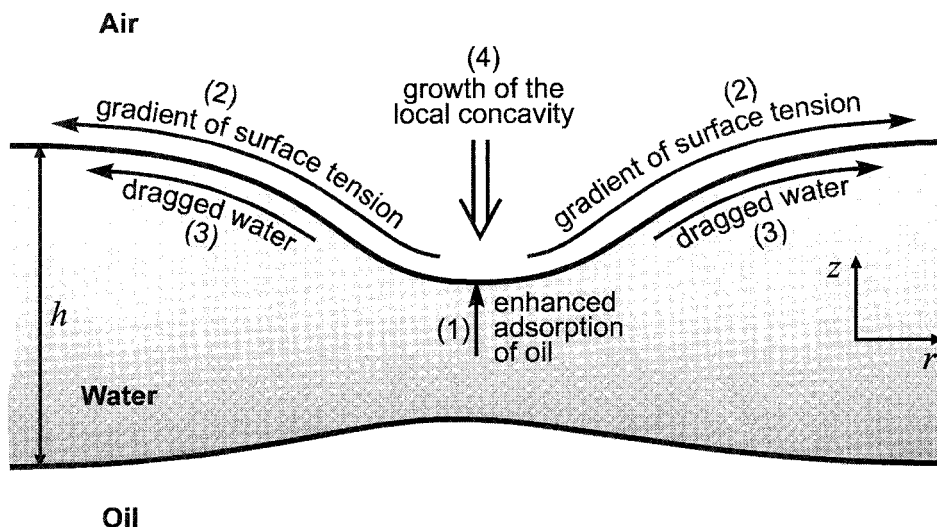
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**Figure 3.** The mechanism of wave growth: (1) In the region of smaller thickness the water–air interface enters a zone enriched in dissolved oil, which leads to enhanced adsorption of oil. (2) The latter gives rise to gradients of surface tension, directed from the zone of smaller thickness outward, which (3) drag away water and thus (4) produce a further growth of the concavity.

Because of the cylindrical symmetry, setting the perturbations zero at the film periphery implies that the fluctuations in the film thickness, velocity, pressure, and oil concentration can be presented as superpositions of terms proportional to the Bessel function  $J_0(\alpha r/R)$ ,

$$(\tilde{h}, \tilde{h}_1, \tilde{h}_2, u_1, u_2, \tilde{p}, \tilde{c}, \tilde{\Gamma}) \propto J_0(\alpha r/R) \quad (3.8)$$

where  $\alpha$  can be any of the zeros of the equation  $J_0(\alpha) = 0$ ;  $\tilde{\Gamma}$  is the fluctuation of the adsorption of oil at the water–air interface. In addition, the boundary conditions for  $v_z$  at the film surfaces are

$$v_z|_{z=0} = \frac{\partial \tilde{h}_1}{\partial t}, \quad v_z|_{z=h} = \frac{\partial \tilde{h}_2}{\partial t} \quad (3.9)$$

Having in mind eqs 3.8 and 3.9 we integrate the continuity eq 3.3 and use eq 3.4 to derive

$$v_z = \frac{\partial \tilde{h}_1}{\partial t} + \frac{\alpha^2}{R^2} \left[ \left( \frac{z^3}{3} - \frac{hz^2}{2} \right) \frac{\tilde{p}}{2\eta} + \frac{z^2}{2h} u_2 + \frac{z(2h-z)}{2h} u_1 \right] \quad (3.10)$$

We have used the fact that  $\nabla^2 J_0(\alpha r/R) = -(\alpha/R)^2 J_0(\alpha r/R)$ , where  $\nabla^2$  is Laplacian. The substitution  $z = h$  in eq 3.10, along with eqs 3.7 and 3.9, yields

$$\frac{\partial \tilde{h}}{\partial t} = \frac{\alpha^2}{R^2} \left[ \frac{h}{2} (u_1 + u_2) - \frac{h^3 \tilde{p}}{12\eta} \right] \quad (3.11)$$

The Laplace equation of capillarity for the two perturbed film surfaces has the form<sup>50,54</sup>

$$\sigma_{OW} \nabla^2 h_1 = p + \Pi(h) - p_{oil} \quad (3.12a)$$

$$\sigma_{WA} \nabla^2 h_2 = p_{air} - p - \Pi(h) \quad (3.12b)$$

where  $\sigma_{OW}$  is the oil–water interfacial tension;  $p_{oil}$  and  $p_{air}$  denote the pressure in the respective phase, and  $\Pi(h)$  is the disjoining pressure, which accounts for the molecular

interactions across the film.<sup>55,56</sup> In view of eq 3.1, for the nonperturbed film surfaces, one can write

$$2\sigma_{OW}/R_f = p_{oil} - p_0 - \Pi(h_0) \quad (3.13a)$$

$$2\sigma_{WA}/R_f = p_0 + \Pi(h_0) - p_{air} \quad (3.13b)$$

where  $R_f$  is the radius of curvature of the film. For small perturbations the disjoining pressure can be expanded in series for small perturbations  $\tilde{h}$ :

$$\Pi(h) = \Pi(h_0) + \Pi' \tilde{h} + \dots; \quad \Pi' \equiv \left. \frac{d\Pi}{dh} \right|_{\tilde{h}=0} \quad (3.14)$$

Having in mind eqs 3.1, 3.8, 3.13a,b, 3.14, and the relationship  $\nabla^2 h_i = -2/R_f + \nabla^2 \tilde{h}_i$ ,  $i = 1, 2$ , from eqs 3.12a,b one can deduce

$$\sigma_{OW} (\alpha/R)^2 \tilde{h}_1 + \tilde{p} + \Pi' \tilde{h} = 0 \quad (3.15)$$

$$\sigma_{WA} (\alpha/R)^2 \tilde{h}_2 - \tilde{p} - \Pi' \tilde{h} = 0 \quad (3.16)$$

In view of eq 3.7, by summation and subtraction of eqs 3.15 and 3.16, one derives the following useful relationships:

$$\tilde{h}_1 = - \frac{\sigma_{WA}}{\sigma_{OW} + \sigma_{WA}} \tilde{h} \quad (3.17)$$

$$\tilde{p} = \left( \frac{\alpha^2}{R^2} \frac{\sigma_{OW} \sigma_{WA}}{\sigma_{OW} + \sigma_{WA}} - \Pi' \right) \tilde{h} \quad (3.18)$$

#### 4. Fluctuations in the Concentration and Adsorption of Oil

To calculate the fluctuations in the concentration of oil dissolved in water, we have to solve the respective linearized diffusion problem. The starting point is the standard equation of convective diffusion:<sup>50</sup>

(55) Derjaguin, B. V. *Theory of Stability of Colloids and Thin Liquid Films*; Plenum Press, Consultants Bureau: New York, 1989.

(56) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: London, 1992.

(54) Ivanov, I. B.; Kralchevsky, P. A. In *Thin Liquid Films*, I. B. Ivanov, Ed.; M. Dekker: New York, 1988; p 49.

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = D \nabla^2 c \quad (4.1)$$

As discussed at the end of section 2, for times longer than  $\tau \equiv h^2/D \approx 2 \times 10^{-5}$  s, the derivative  $\partial c/\partial t$  in eq 4.1 can be omitted. The latter approximation is valid also for the perturbations considered by us, insofar as the characteristic time of growth of the capillary waves (see the values of  $\omega^{-1}$  in Figures 4–7 below) is much greater than the above value of  $\tau$ . Having in mind that  $c = c_0 + \tilde{c}$ , we calculate  $\nabla c_0$  from eq 2.9 and bring eq 4.1 into the following linearized form:

$$-v_z \delta c/h = D \frac{\partial^2 \tilde{c}}{\partial z^2}, \quad \delta c \equiv c_{\text{eq}} - c_{0s}(t) \quad (4.2)$$

The boundary conditions at the two perturbed film surfaces are

$$c = c_0(\tilde{h}_1, t) + \tilde{c} = c_{\text{eq}} \quad \text{at } z = 0 \quad (4.3)$$

$$\frac{\partial \Gamma}{\partial t} = -\nabla_s \cdot (\Gamma \mathbf{v}) + D_s \nabla_s^2 \Gamma - D \frac{\partial \tilde{c}}{\partial z} \quad \text{at } z = h \quad (4.4)$$

where  $\nabla_s$  and  $D_s$  are the surface gradient operator and the coefficient of surface diffusion and  $\Gamma$  is the adsorption of oil at the water–air interface. The three terms in the right-hand side of eq 4.4 account, respectively, for the effects of interfacial expansion/compression, surface diffusion of oil molecules and their bulk diffusion. Expanding in series in eq 4.3, and using eqs 2.3 and 2.9, one obtains

$$-(\delta c/h)\tilde{h}_1 + \tilde{c}|_{z=0} = 0 \quad (4.5)$$

Likewise, in eq 4.4 we substitute  $\Gamma = \Gamma_0 + \tilde{\Gamma}$  and obtain the following relationship between the perturbations of the involved variables:

$$\frac{\partial \tilde{\Gamma}}{\partial t} = \frac{\alpha^2}{R^2} (\Gamma_0 u_2 - D_s \tilde{\Gamma}) - D \frac{\partial \tilde{c}}{\partial z} \Big|_{z=h} \quad (4.6)$$

To derive eq 4.6 we have used eqs 3.5 and 3.8. The subsurface concentration of oil at the water–air interface can be expressed in the form  $c_s = c_0(\tilde{h}_2, t) + \tilde{c}_s$ . With the help of eqs 2.5, 2.9, 4.2, and the Henry isotherm,  $\Gamma = H_a c_s$ , we obtain the following relationship between the perturbations:

$$\tilde{\Gamma} = H_a [\tilde{c}_s - (\delta c/h)\tilde{h}_2] \quad (4.7)$$

where  $\tilde{c}_s \equiv \tilde{c}|_{z=h}$ . Next, we integrate eq 4.2 twice with respect to  $z$ , substituting  $v_z$  from eq 3.10. The two constants of integration are determined from eqs 4.5 and 4.7. The resulting expression for  $\tilde{c}$  is differentiated to derive

$$D \frac{\partial \tilde{c}}{\partial z} \Big|_{z=h} = \frac{D}{h} \left( \frac{\tilde{\Gamma}}{H_a} + \frac{\delta c \tilde{h}}{h} \right) - \frac{\delta c}{2} \left[ \frac{\partial \tilde{h}_1}{\partial t} + \frac{\alpha^2 h}{4R^2} \left( u_2 + \frac{5}{3} u_1 - \frac{7h^2}{30\eta} \tilde{p} \right) \right] \quad (4.8)$$

Substituting eq 4.8 into eq 4.6 we obtain

$$\frac{\partial \tilde{\Gamma}}{\partial t} - \frac{\delta c}{2} \frac{\partial \tilde{h}_1}{\partial t} + \frac{D \delta c \tilde{h}}{h^2} + \left( \frac{D}{H_a h} + \frac{\alpha^2 D_s}{R^2} \right) \tilde{\Gamma} = \frac{\alpha^2}{8R^2} \left[ (h \delta c + 8\Gamma_0) u_2 + \frac{5}{3} h \delta c u_1 - \frac{7h^3}{30\eta} \delta c \tilde{p} \right] \quad (4.9)$$

One additional relationship follows from the tangential stress balance at the water–air interface (in lubrication approximation)

$$\eta \frac{\partial v_r}{\partial z} \Big|_{z=h} = \frac{\partial \sigma_{\text{WA}}}{\partial r} \quad (4.10)$$

Since we consider relatively slow surface corrugations (the surfaces are presumed to be equilibrated with the bulk with respect to the surfactant), the variation of  $\sigma_{\text{WA}}$  in eq 4.10 is completely due to the variation of the adsorption of oil at the water–air interface. With the help of eq 3.4 and the Henry isotherm,  $\sigma_{\text{WA}} = \sigma_{\text{WA}}^{(0)} - kT \Gamma$ , eq 4.10 can be represented in the form

$$\frac{1}{2} h \tilde{p} + \eta (u_2 - u_1)/h = -kT \tilde{\Gamma} \quad (4.11)$$

In summary, we have to determine six unknown variables:  $\tilde{h}$ ,  $\tilde{h}_1$ ,  $\tilde{p}$ ,  $u_1$ ,  $u_2$ , and  $\tilde{\Gamma}$ . Up to here, we have a set of five equations relating these variables, viz., eqs 3.11, 3.17, 3.18, 4.9, and 4.11. The necessary sixth equation stems from the tangential stress balance at the oil–water interface; this balance equation, and its consequences, are considered below.

### 5. Tangential Stress Balance at the Oil–Water Interface and Dispersion Relation

Since we consider fluctuational capillary waves, we can seek the perturbation of the film thickness  $\tilde{h}$  in the form<sup>39,50</sup>

$$\tilde{h} = H(r) \exp(\omega t) \quad (5.1)$$

where  $H(r) \propto J_0(\alpha r/R)$  is amplitude and  $\omega$  is the *exponent of growth* of the capillary waves. Indeed, for  $\omega > 0$  the capillary waves grow until break the liquid film, whereas for  $\omega < 0$  the capillary waves decay with time. Therefore, the condition  $\omega = 0$  corresponds to transition from regime of stability to regime of instability. Our aim below is to investigate how this transition depends on the physical parameters of the system.

As mentioned in section 2, in the present study we assume that the surfactant concentration is sufficiently high, viz., around or beyond the cmc; in fact, this is the concentration range in which stable foam films and foams do exist. For such concentrations the surfactant adsorption monolayer on the *water–air* interface certainly behaves as tangentially immobile.<sup>53</sup> (In this study, any motion at the water–air interface is entirely due to molecular spreading of oil, see eq 4.10.) On the other hand, for the same bulk concentrations, the adsorption of surfactant (and the surface elasticity) at the *oil–water* interface could be essentially lower than that at the water–air interface.<sup>57</sup> So, one might expect that the oil–water interface is more fluid than the water–air one.

Below we consider the two limiting cases (i) tangentially *mobile* and (ii) tangentially *immobile* oil–water interface. We will mention in advance, that these two cases give numerically close results about the transition from stable to unstable films. In other words, it turns out that the stability of the asymmetric film is not so sensitive to the degree of tangential mobility of the oil–water interface.

**5.1. Tangentially Mobile Oil–Water Interface.** In this limiting case we neglect the effects of surface elasticity and viscosity. Then the tangential stresses in the water and oil phases directly counterbalance each other at the interface:

(57) van Hunsel, J.; Joos, P. *Colloids Surf.* **1987**, *24*, 139.

$$\eta \frac{\partial v_r}{\partial z} = \eta^d \left( \frac{\partial v_r^d}{\partial z} + \frac{\partial v_z^d}{\partial r} \right) \quad \text{at } z = 0 \quad (5.2)$$

The superscript “*d*” denotes quantities which refer to the oil drop; in particular,  $\eta^d$  is the viscosity of the oil. The lubrication approximation is not applicable to describe the hydrodynamic flow inside the drop. For that reason we used the complete Navier–Stokes equation in conjunction with eq 3.3; the solution was sought in the form of capillary waves, which decay exponentially in the depth of the oil phase. As a result we obtained a modified form of eq 5.2:

$$\eta \frac{\partial v_r}{\partial(z/h)} = -2\alpha\eta^d v_r \frac{h}{R} \quad \text{at } z = 0 \quad (5.2a)$$

For real thin films  $h/R \ll 1$ . Consequently, if  $\eta$  and  $\eta^d$  have the same order of magnitude, then the right-hand side of eq 5.2a is much smaller than the left-hand side and it can be neglected. Thus, the tangential stress balance at the oil–water interface reduces to

$$\eta \frac{\partial v_r}{\partial z} \Big|_z = 0 \quad (5.3)$$

The substitution of eq 3.4 into eq 5.3 yields

$$u_2 = u_1 + (h^2/2\eta)\tilde{p} \quad (5.4)$$

The linear set of five equations, 3.11, 3.17, 3.18, 4.11, and 5.4, allows one to express the five variables,  $\tilde{h}_1$ ,  $\tilde{p}$ ,  $u_1$ ,  $u_2$ , and  $\tilde{\Gamma}$  in terms of  $\tilde{h}$  and  $\partial\tilde{h}/\partial t$ . The resulting expressions are then substituted in eq 4.9 to derive a connection between  $\tilde{h}$  and  $\partial\tilde{h}/\partial t$  (see Appendix B for details):

$$A(\partial\tilde{h}/\partial t) = B\tilde{h} \quad (5.5)$$

where

$$A = 1 + \frac{h\delta c}{6\Gamma_0} \frac{2\sigma_{OW} - \sigma_{WA}}{\sigma_{OW} + \sigma_{WA}} + \frac{h^2 f}{E_G} \quad (5.6)$$

$$B = \frac{D\delta c}{h\Gamma_0} - \left( \frac{\delta c}{2} - \frac{\alpha^2 \sigma_{OW} h}{R^2} \frac{kTD\sigma_{OW}}{(\sigma_{OW} + \sigma_{WA})^2 \Gamma_0} \frac{\delta c}{\Gamma_0} - \frac{\alpha^2 h^3 f}{R^2 3\eta} \left( 1 - \frac{h\delta c}{15\Gamma_0} + \frac{R^2 b}{\alpha^2 h^2} + \frac{h_s}{h} \right) \right) \quad (5.7)$$

$$f \equiv \frac{\alpha^2}{R^2} \frac{\sigma_{OW}\sigma_{WA}}{\sigma_{OW} + \sigma_{WA}} - \Pi' \quad (5.8)$$

The quantities

$$b = \frac{3\eta D}{E_G h_a}, \quad h_s = \frac{3\eta D_s}{E_G}, \quad E_G = -\Gamma_0 \frac{\partial\sigma_{WA}}{\partial\Gamma_0} = kT\Gamma_0 \quad (5.9)$$

take into account, respectively, the effects of bulk diffusion, surface diffusion, and surface (Gibbs) elasticity; to obtain the expressions for  $b$  and  $E_G$  we have used the Henry isotherm, see eqs 2.5 and 2.6. The substitution of eq 5.1 into eq 5.5 gives the sought after expression for  $\omega$ :

$$\omega = \frac{B}{A} \quad (5.10)$$

where  $A$  and  $B$  are given by eqs 5.6 and 5.7. In fact, eq 5.10 represents a dispersion relation between the wave-

growth exponent  $\omega$  and the wavenumber  $q \equiv \alpha/R$ . A substitution of experimental values of the physical parameters shows that usually  $A > 0$ . Then, the sufficient condition for instability,  $\omega > 0$ , is transformed to  $B > 0$ . Positive values of  $B$  are possible when the first term in eq 5.7

$$\frac{D\delta c}{h\Gamma_0} = \frac{h}{\Gamma_0} Q, \quad Q \equiv \frac{D\delta c}{h^2} \quad (5.11)$$

is large enough. It turns out that for the considered type of systems this term, proportional to  $Q$ , is the major source of instability. For that reason, the physical meaning of  $Q$  deserves a special discussion.

The term with  $Q$  originates from the mass balance equation at the water–air interface, eq 4.9; the latter can be presented in the form

$$\frac{\partial\tilde{\Gamma}}{\partial t} = -Q\tilde{h} + (\text{other terms}) \quad (5.12)$$

Equation 5.12 shows that for a local fluctuational decrease in the film thickness,  $\tilde{h} < 0$ , the term with  $Q$  contributes to a local increase in the adsorption  $\tilde{\Gamma}$ . The latter increase is due to the fact that in the region of smaller thickness the water–air interface enters a zone enriched in dissolved oil, which is being transferred by diffusion from the lower film surface toward the upper one (Figure 3). The newly adsorbed oil (the local increase of  $\tilde{\Gamma}$ ) creates a surface tension gradient, which in its own turn gives rise to a two-dimensional flow (molecular spreading of oil) in the water–air interface, see eqs 4.10 and 4.11. This surface flow, directed from the zone of smaller thickness outward, carries water away, which causes a *further decrease* of the local film thickness in the concave zone (Figure 3). In other words, there is a positive feedback, which promotes a growth of the fluctuation (deepening of the concavity) until eventually the two film surfaces touch each other and the film ruptures. A feature of this mechanism of film breakage is that the oil diffusion across the film precedes and feeds the molecular spreading of oil.

The formal substitution  $\delta c = 0$  (no diffusion across the film) and  $E_G \rightarrow \infty$  (tangentially immobile surfaces) brings eq 5.10 in the simpler form

$$\omega = \frac{h^3 q^2}{3\eta} \left( \Pi' - q^2 \frac{\sigma_{OW}\sigma_{WA}}{\sigma_{OW} + \sigma_{WA}} \right), \quad q \equiv \frac{\alpha}{R} \quad (5.13)$$

In this limiting case instability ( $\omega > 0$ ) can appear only if  $\Pi' > 0$ , which may happen in the case of predominant van der Waals attraction between the film surfaces.<sup>38–42</sup> Setting  $\omega = 0$  in eq 5.13 we arrive at a known expression for the transitional wavenumber (corresponding to a transition from stability to instability):<sup>33</sup>

$$q^2 = \frac{\sigma_{OW} + \sigma_{WA}}{\sigma_{OW}\sigma_{WA}} \Pi' \quad (5.14)$$

For symmetric films,  $\sigma_{OW} = \sigma_{WA} = \sigma$ , eq 5.14 has been derived long ago;<sup>38,39,41</sup> it corresponds to instability driven only by the disjoining pressure  $\Pi$ . In contrast, eq 5.10 predicts instability even in the case of  $\Pi' < 0$ ; as discussed above, the latter instability is driven by the diffusion transport of a surface-active solute (the oil) across the film (Figure 3). In this aspect eq 5.10 involves a new source of instability, as compared to eq 5.13.

**5.2. Tangentially Immobile Oil–Water Interface.** In this case, the immobilization could be due to high surface

viscosity or high surface elasticity. In such a case the tangential component of surface velocity is equal to zero:  $v_r|_{z=0} = 0$ . Combining the latter equation with eq 3.5, we obtain

$$u_1 \equiv 0 \quad (5.15)$$

where we have taken into account the fact that  $u_1$  is a perturbation. In view of eq 5.15, the linear set of four equations, 3.11, 3.17, 3.18, and 4.11, allows one to express the 4 variables,  $\tilde{h}_1$ ,  $\tilde{p}$ ,  $u_2$ , and  $\tilde{\Gamma}$  in terms of  $\tilde{h}$  and  $\partial\tilde{h}/\partial t$ . The resulting expressions are then substituted in eq 4.9 to derive a connection between  $\tilde{h}$  and its time derivatives (see Appendix C for details):

$$A_1 \frac{\partial^2 \tilde{h}}{\partial t^2} + B_1 \frac{\partial \tilde{h}}{\partial t} = C_1 \quad (5.16)$$

where

$$A_1 = \frac{R^2}{\alpha^2} \frac{\eta}{hE_G} \quad (5.17)$$

$$B_1 = 1 - \frac{h\delta c}{8\Gamma_0} \frac{\sigma_{WA} - \sigma_{OW}}{\sigma_{WA} + \sigma_{OW}} + \frac{h^2 f}{3E_G} + M \quad (5.18)$$

$$C_1 = \frac{D\delta c}{2h\Gamma_0} - \frac{\alpha^2}{R^2} \frac{h^3 f}{12\eta} \left( 1 - \frac{h\delta c}{20\Gamma_0} + 4M \right) - \left( \frac{\delta c}{2} - \frac{\alpha^2}{R^2} \frac{2\sigma_{OW}h}{3kT} \right) \frac{kTD\sigma_{OW}}{(\sigma_{OW} + \sigma_{WA})^2 2\Gamma_0} \frac{\delta c}{2\Gamma_0} \quad (5.19)$$

$$M = \frac{R^2}{\alpha^2} \frac{b}{3h^2} + \frac{h_s}{3h} \quad (5.20)$$

The substitution of eq 5.1 into eq 5.16 yields a quadratic equation for  $\omega$ :

$$A_1 \omega^2 + B_1 \omega - C_1 = 0 \quad (5.21)$$

Equation 5.21 represents the sought for dispersion relation between the frequency  $\omega$  and the wavenumber  $q \equiv \alpha/R$ . The roots of eq 5.21 are

$$\omega_{1,2} = [-B_1 \pm (B_1^2 + 4A_1C_1)^{1/2}]/(2A_1) \quad (5.22)$$

The exponent of wave growth is to be identified with the greater of the *real* parts of the roots  $\omega_1$  and  $\omega_2$ . Substituting typical experimental values of the parameters in eqs 5.17–5.20 (see section 6.1), we obtain that always  $A_1 > 0$ ; excluding some unrealistically large values of  $\delta c$  we also have  $B_1 > 0$ . Then the necessary and sufficient condition for appearance of instability is  $C_1 > 0$ ; in such a case the exponent of wave growth coincides with the larger root, that with sign "+" in eq 5.22. Positive  $C_1$  is ensured when the term  $D\delta c/(2h\Gamma_0)$  in eq 5.19 is large enough. Hence the physical origin of the instability is the same as in section 5.1, i.e. diffusion transport of a surface-active solute (the oil) across the film; see the discussion after eq 5.11 and Figure 3.

Performing the limiting transition  $\delta c \rightarrow 0$  (no diffusion across the film) and  $E_G \rightarrow \infty$  (tangentially immobile surfaces) in eq 5.21, one arrives at a known result, eq 5.14.

## 6. Numerical Results and Discussion

**6.1. Parameter Values.** Our purpose here is to obtain numerical results about the influence of various physical factors (concentration of dissolved oil, film thickness  $h$ , film radius  $R$ , etc.) on the wave-growth exponent  $\omega$ , and especially, on the existence of stability–instability transition at  $\omega = 0$ . To obtain realistic results, we take the following experimental values from ref 26 for aqueous solution of 0.09 wt % (about 10 cmc) of the surfactant dodecyl-benzene-sulfonate with added 12 mM NaCl, viz., oil–water interfacial tension,  $\sigma_{OW} = 2.2$  mN/m; tension of the oil-free water–air interface,  $\sigma_{WA}^{(0)} = 32.4$  mN/m; tension of water–air interface *equilibrated* with a floating oil lens,  $\sigma_{WA}^{(eq)} = 26.4$  mN/m. The equilibrium concentration of oil dissolved in water is taken  $c_{eq} = 10^{-5}$  M, see ref 58. Then from eqs 2.5 and 2.6 we determine  $H_a = (\sigma_{WA}^{(0)} - \sigma_{WA}^{(eq)})/(kTc_{eq}) = 2.43 \times 10^{-2}$  cm. The calculated equilibrium adsorption of oil,  $\Gamma_{eq} = H_a c_{eq}$ , corresponds to 68 Å<sup>2</sup> per oil molecule in the spread oil layer, which means that we deal with *molecular* spreading (incorporation of separate oil molecules among the tails of the surfactant molecules), rather than with spreading of thick (bulk) layer of oil. For the coefficients of bulk and surface diffusion of oil we use the values  $D = D_s = 10^{-10}$  m<sup>2</sup>/s; in addition, the viscosity of the aqueous phase is  $\eta = 0.89 \times 10^{-3}$  Pa/s.

To simplify the calculations we assume that the electrostatic component of disjoining pressure is suppressed by the added salt and that the van der Waals interaction is predominant; then we can use the expression<sup>55,56</sup>

$$\Pi = -\frac{A_H}{6\pi h^3} \quad (6.1)$$

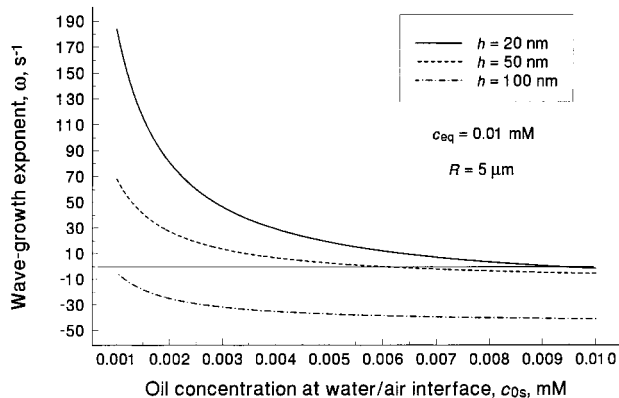
where  $A_H$  is the compound constant of Hamaker. Since the magnitude of the Hamaker constant of water is intermediate between those of the oil and air, we obtain a negative value of the compound constant:  $A_H = -2 \times 10^{-21}$  J. The latter fact implies that the van der Waals interaction is *repulsive*, and consequently, it can ensure the formation of equilibrium oil–water–air films.

When calculating the exponent of wave growth  $\omega$ , we have substituted  $\alpha$  equal to the first zero of the Bessel function  $J_0$ ; that is  $\alpha = 2.4048$ . This means that we calculate  $\omega$  for the longest possible wave, which does usually first become unstable.<sup>59</sup>

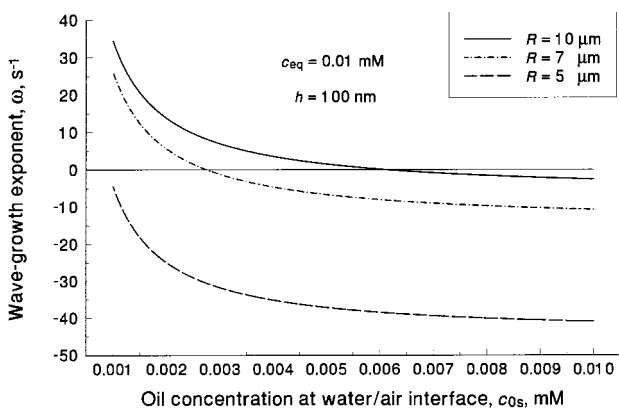
The parameter values given in section 6.1 are used for the calculation of all theoretical curves reported in sections 6.2 and 6.3.

**6.2. Numerical Results for the Wave-Growth Exponent.** In Figure 4 we present plots of  $\omega$  versus the subsurface concentration of dissolved oil  $c_{0s}$ . The theoretical curves are calculated by means of eq 5.10 for three different values of the film thickness  $h$ ; the film radius is the same for the three curves,  $R = 5$  μm. One sees that  $\omega < 0$  for  $c_{0s} = c_{eq}$  ( $= 0.01$  mM); see the right end-points of the curves in Figure 4. This means that the film is stable with respect to capillary waves, if there is no diffusion of oil across it (as it should be expected). The thicker film, the one with  $h = 100$  nm, is stable ( $\omega < 0$ ) in the whole range of variation of  $c_{0s}$  shown in the figure; this film could become unstable ( $\omega > 0$ ) for  $c_{0s} < 0.001$  mM, but such low values of  $c_{0s}$  seem to be unrealistic. Indeed, the real oil–water–air films can reach a given thickness, say  $h = 100$  nm, in a process of thinning; during the thinning not only the diffusion, but also the convection could transport oil molecules to the water–air interface.<sup>53</sup>





**Figure 4.** Plot of the wave-growth exponent  $\omega$  vs the subsurface concentration of oil at the water-air interface,  $c_{0s}$ ; the equilibrium concentration of dissolved oil is  $c_{eq} = 0.01$  mM and the film radius is  $R = 5$   $\mu\text{m}$ . The three curves, calculated from eq 5.10, correspond to three different values of the film thickness:  $h = 20, 50,$  and  $100$  nm.

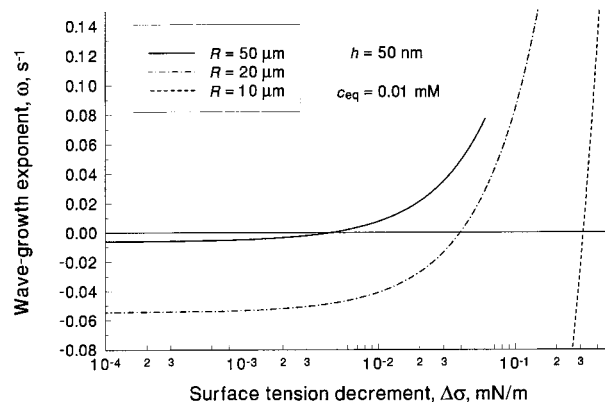


**Figure 5.** Plot of the wave-growth exponent  $\omega$  vs the subsurface concentration of oil at the water-air interface,  $c_{0s}$ ; the equilibrium concentration of dissolved oil is  $c_{eq} = 0.01$  mM and film thickness is  $h = 100$  nm. The three curves, calculated from eq 5.10, correspond to three different values of the film radius:  $R = 5, 7,$  and  $10$   $\mu\text{m}$ .

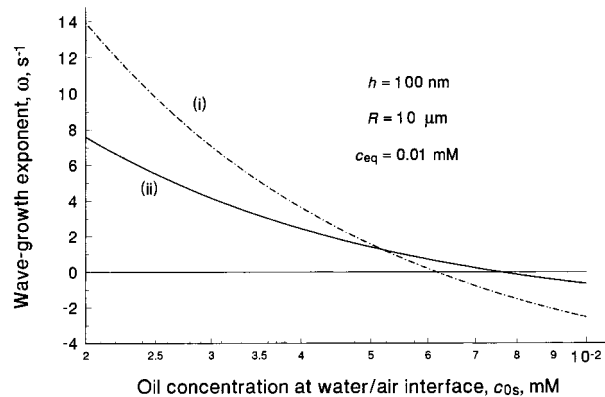
With the decrease of the film thickness the region of instability (the part of the curve with  $\omega > 0$ , Figure 4) increases, and for  $h = 20$  nm almost the whole curve belongs to the region of unstable films. Qualitatively, this transition from stable to unstable films with the decrease of the film thickness  $h$  could be identified with the experimentally observed breakage of the film at a certain  $\Delta P_{cr}$ , when the pressure difference  $\Delta P = P_2 - P_1$  is increased, see Figure 1. (Larger  $\Delta P$  leads to smaller  $h$  because of the squeezing of water from the film.)

Figure 5 demonstrates the strong influence of the film radius,  $R$ , on the film stability at fixed thickness  $h$ . The increase of  $R$  with few  $\mu\text{m}$  leads to a considerable shift of the  $\omega(c_{0s})$ -curve upward, i.e., toward positive  $\omega$  and unstable films. The physical implication of this fact is that the films at the top of larger oil drops (with larger  $R$ ) should be less stable, see Figures 1 and 2. The major conclusion from Figures 4 and 5 is that the transition from stability to instability, at  $\omega = 0$ , does really exist for reasonable values of the system parameters;  $\omega$  increases (the films become less stable) when the thickness  $h$  decreases, the radius  $R$  increases, and  $\delta c = c_{eq} - c_{0s}$  is greater; that is, the diffusion flux of oil across the film is more intensive.

As already mentioned, if a drop (lens) of oil is put at the water-air interface, covered by surfactant adsorption



**Figure 6.** Plot of the wave-growth exponent  $\omega$  vs the decrease of the water-air surface tension,  $\Delta\sigma(c_{0s})$ , due to the adsorption of oil; the equilibrium concentration of dissolved oil is  $c_{eq} = 0.01$  mM and film thickness is  $h = 50$  nm. The three curves, calculated from eq 5.10, correspond to three different values of the film radius:  $R = 10, 20,$  and  $50$   $\mu\text{m}$ .



**Figure 7.** Plot of the wave-growth exponent  $\omega$  vs the subsurface concentration of oil at the water-air interface,  $c_{0s}$ ; the equilibrium concentration of dissolved oil is  $c_{eq} = 0.01$  mM; the film thickness and radius are  $h = 100$  nm and  $R = 10$   $\mu\text{m}$ . Curve (i) is calculated from eq 5.10, and curve (ii) from eq 5.22, for tangentially mobile and immobile oil-water interface, respectively.

monolayer, the interfacial tension  $\sigma_{WA}$  decreases. The equilibrium (maximum) value of the decrement is  $\Delta\sigma^{(0)} \equiv \sigma_{WA}^{(0)} - \sigma_{WA}^{(eq)}$ . The fact that  $\Delta\sigma^{(0)} > 0$  means that the oil exhibits a surface activity (oil molecules spontaneously penetrate among the tails of the adsorbed surfactant molecules), which is a necessary condition for the appearance of surface tension gradients and film instability, as sketched in Figure 3. Under dynamic conditions, the surface tension decrement is  $\Delta\sigma \equiv \sigma_{WA}(c_{0s}) - \sigma_{WA}^{(eq)}$ . In general  $\Delta\sigma \leq \Delta\sigma^{(0)}$  because of the preliminary partial saturation of the water-air interface with oil; if equilibrium is attained ( $c_{0s} = c_{eq}$ ), then  $\Delta\sigma = 0$ . Figure 6 demonstrates that the wave-growth exponent  $\omega$  increases with the rise of  $\Delta\sigma$ . It is interesting to note that even a very small  $\Delta\sigma$  can provoke a stability-instability transition: for  $R = 50$   $\mu\text{m}$  the point  $\omega = 0$  corresponds to  $\Delta\sigma \approx 4 \times 10^{-3}$  mN/m, which is a vanishingly small value compared to the experimental accuracy of the surface tension measurements. For smaller  $R$  the stability of the film increases, and then a larger  $\Delta\sigma$  is necessary to induce instability: for  $R = 10$   $\mu\text{m}$  the point  $\omega = 0$  corresponds to  $\Delta\sigma \approx 0.3$  mN/m, see Figure 6. In conclusion, small values of  $\Delta\sigma$  are sufficient to trigger the instability.

In Figure 7 we compare the dependencies of  $\omega$  on  $c_{0s}$  for the cases of tangentially mobile and immobile interface

oil–water. The respective curves are calculated from eqs 5.10 and 5.22, the latter with “+” before the square root. One sees that the wave-growth exponent  $\omega$  is almost everywhere greater by magnitude for the mobile oil–water interface as compared to the immobile one. On the other hand, the points with  $\omega = 0$  are close for the two curves. Hence, the transition from stability to instability is not so sensitive to the degree of mobility of the oil–water interface.

**6.3. Limits of Action of the Proposed Mechanism and Alternative Sources of Instability.** Finally, let us make a brief recapitulation of the possible sources of instability, which could cause film rupture, and subsequent drop “entry” at the water–air interface (Figure 1).

*A. Instability Driven by Diffusion Flux across the Film.* This is the mechanism investigated in the present paper. The necessary conditions this instability to occur are, first, some component to be transported by diffusion from the oil–water to the water–air interface, and second, this component to be surface-active, i.e., to give rise to a decrement  $\Delta\sigma$  of the water–air surface tension, see Figure 6 and the related text. If the water–air interface is preequilibrated with the transported component, say the interface is covered with prespread oil, then  $\Delta\sigma = 0$  and this type of instability disappears.

*B. Instability Driven by Disjoining Pressure.* This is the classical type of instability in liquid films,<sup>38,39</sup> which appears only for  $\Pi' > 0$ , see eq 5.14. The latter condition can be satisfied if there is negligible double layer (electrostatic) repulsion between the two film surfaces; such is the case of nonaqueous films,<sup>41</sup> or aqueous films with much electrolyte.<sup>60</sup> However, the condition  $\Pi' > 0$  is not satisfied for typical foam systems in the presence of ionic surfactants at not too high salt concentrations ( $< 0.1$  M); in the latter type of systems there could be another source of instability:

*C. Instability Driven by Surface Electric Current.* This mechanism could be operative if the kinetic constant of surfactant desorption is much smaller than the constant of adsorption,  $K_{\text{des}} \ll K_{\text{ads}}$ . In this case the adsorbed surfactant ions are closed in a two-dimensional world, i.e., they could migrate only tangentially to the interface. A local fluctuational decrease in the film thickness induces a local increase in the magnitude of the surface potential, which gives rise to a surface electric current. The latter carries the adsorbed surfactant ions away from the concave zone and drags water outward. Thus, the system promotes the growth of the concavity, i.e., a positive feedback takes place, just as it is in Figure 3. A detailed theoretical description of this mechanism is now under way.<sup>61</sup>

*D. Instability Due to the Piercing Effect of Solid Edge.* This effect is achieved by addition of hydrophobic solid particles (crystallites) to the oil. They usually occupy the oil–water interface and are able to break the oil–water–air film if the protrusion of their sharp edges is comparable or greater than the film thickness. This effect is often used in the formulations of fast antifoams.<sup>3–7,10–13</sup>

It may happen that two (or even more) of the above mechanisms are simultaneously operative. For example, the increasing concentration of oil, spread over the water–air interface, suppresses the action of mechanism “A” due

to a decrease in the chemical-potential gradient of oil across the water film; on the other hand, the spread oil facilitates the effectuation of mechanism “C” owing to a decrease in the surface elasticity. For intermediate surface concentrations of oil both mechanisms could simultaneously operate. In such a case, a careful analysis of the experimental data is needed to reveal the real driving factor(s) of instability.

## 7. Concluding Remarks

In the present article we investigate theoretically an instability, which is driven by diffusion flux across an asymmetric liquid film. For example, such a flux can appear across an asymmetric oil–water–air film, formed between an oil drop pressed against the water–air interface (Figure 1), if the oil is slightly soluble in water.

In our model we assume that the oil molecules, dissolved (solubilized) at the oil–water interface, are transported by diffusion across the aqueous film to the water–air interface, where they penetrate between the tails of the adsorbed surfactant molecules and thus cause a decrease of the water–air surface tension. The concentration profile of the dissolved oil across the film is given by eqs 2.8 and 2.9. Next, we consider fluctuational capillary waves at the two film surfaces. The set of hydrodynamic equations and boundary conditions has been solved to obtain relationships between the fluctuations of film thickness, pressure, velocity potential at the interfaces, and adsorption of oil at the water–air surface, see eqs 3.11, 3.17, 3.18, 4.9, and 5.4. As a result, we derive a dispersion relation between the exponent of wave growth,  $\omega$ , and the wavenumber, see eqs 5.10 and 5.21. For  $\omega > 0$  the amplitude of a perturbation grows until the film ruptures, see eq 5.1. The physical meaning of the term, which leads to  $\omega > 0$  (see eq 5.11), suggests that the instability is engendered in the following way.

If a local fluctuational decrease in the film thickness appears, the water–air interface enters a zone enriched in dissolved oil. The newly adsorbed oil creates a surface tension gradient, which gives rise to a two-dimensional flow (molecular spreading of oil) in the water–air interface. The surface flow carries water away, which causes a further decrease of the local film thickness in the concave zone (Figure 3). So, there is a positive feedback, which promotes a deepening of the concavity until eventually the film ruptures.

The numerical results show that the transition from stability to instability at  $\omega = 0$  does really exist for reasonable values of the parameters of the system; the film becomes less stable when its thickness decreases, its radius increases, and the diffusion of oil across it is more intensive (Figures 4, 5, and 7). Even very small decrements of the water–air surface tension, caused by the adsorbed oil, are sufficient to trigger the instability (Figure 6). It turns out that the transition from stability to instability is not so sensitive to the degree of mobility of the oil–water interface (tangentially mobile or immobile), see Figure 7. If the water–air interface is preequilibrated with the transported component (there is prespread oil), then the surface tension decrement, and the instability, disappears.

The rupture of the asymmetric oil–water–air film is a precondition for entry of an oil drop at the water–air interface and effectuation of its foam-destructive action. Our results about one specific source of film instability could be helpful for a deeper understanding of the mechanisms of antifoaming.

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### Appendix A: Diffusion of Oil Across the Water Film

The linear boundary problem consists of the diffusion eq 2.1, the initial condition, eq 2.2, and two boundary conditions. The first one is eq 2.3; the second boundary condition is obtained by elimination of  $\Gamma_0(t)$  between eqs 2.4 and 2.5:

$$H_a \frac{\partial c_0}{\partial t} = -D \frac{\partial c_0}{\partial z} \quad \text{for } z = h \quad (\text{A.1})$$

We apply a Laplace transformation to eq 2.1:

$$\frac{\partial^2 \hat{c}}{\partial z^2} - \frac{s}{D} \hat{c} = 0 \quad (\text{A.2})$$

where  $\hat{c}(z,s)$  is the Laplace transform of  $c_0(z,t)$ . The solution of the latter equations reads

$$\hat{c}(z,s) = A(s) \sinh(az) + B(s) \cosh(az), \quad a^2 \equiv s/D \quad (\text{A.3})$$

To determine  $A(s)$  and  $B(s)$  we use the two boundary conditions; the Laplace transforms of eqs 2.3 and A.1 are

$$\hat{c}(0,s) = c_{\text{eq}}/s \quad (\text{A.4})$$

$$H_a s \hat{c}(h,s) = -D \left. \frac{\partial \hat{c}}{\partial z} \right|_{z=h} \quad (\text{A.5})$$

In accordance with eq 2.2, at the last step we have set  $c(h,0) = 0$ . Combining eqs A.3–A.5 we obtain

$$\hat{c}(z,s) = \frac{c_{\text{eq}}}{s} \left( \cosh az - \frac{aH_a + \tanh(ah)}{1 + aH_a \tanh(ah)} \sinh(az) \right) \quad (\text{A.6})$$

In the limiting case of long times,  $s \rightarrow 0$ , and thin films,  $h \ll H_a$ , eq A.1 reduces to

$$\hat{c}(z,s) = \frac{c_{\text{eq}}}{s} - \frac{c_{\text{eq}} z}{h} \frac{1}{D/(H_a h) + s} \quad (\text{A.7})$$

The inverse Laplace transform of eq A.7 is eq 2.7.

### Appendix B: Derivation of Equations 5.5–5.7

The linear set of five equations, 3.11, 3.17, 3.18, 4.11, and 5.4, allows one to express the 5 variables,  $\tilde{h}_1$ ,  $\tilde{p}$ ,  $u_1$ ,

$u_2$ , and  $\tilde{\Gamma}$  in terms of  $\tilde{h}$  and  $\partial \tilde{h}/\partial t$ , as follows:

$$\tilde{h}_1 = (\lambda - 1)\tilde{h}, \quad \lambda \equiv \sigma_{\text{OW}}/(\sigma_{\text{OW}} + \sigma_{\text{WA}}) \quad (\text{B.1})$$

$$\tilde{p} = f\tilde{h} \quad (\text{B.2})$$

$$\tilde{\Gamma} = \frac{hf}{kT} \tilde{h} \quad (\text{B.3})$$

$$u_1 = \frac{R^2}{h\alpha^2} \frac{\partial \tilde{h}}{\partial t} - \frac{h^2 f}{6\eta} \tilde{h} \quad (\text{B.4})$$

$$u_2 = \frac{R^2}{h\alpha^2} \frac{\partial \tilde{h}}{\partial t} + \frac{h^2 f}{3\eta} \tilde{h} \quad (\text{B.5})$$

Combining eqs 5.8 and B.1, one obtains

$$f = \frac{\alpha^2}{R^2} \sigma_{\text{OW}} (1 - \lambda) - \Pi' \quad (\text{B.6})$$

Equations B.1–B.5 are substituted in eq 4.9 to derive a connection between  $\tilde{h}$  and  $\partial \tilde{h}/\partial t$ , which is eq 5.5. In the derivation we have taken into account that  $\lambda$  (and, consequently,  $f$ ) are dependent on time  $t$ . With the help of eqs 2.5, 2.6, 2.8, and 4.2 we obtain

$$\frac{\partial \lambda}{\partial t} = -\frac{\lambda^2}{\sigma_{\text{OW}}} \frac{\partial \sigma_{\text{WA}}}{\partial t} = \frac{\lambda^2 k T H_a}{\sigma_{\text{OW}}} \frac{\partial c_{\text{Os}}}{\partial t} = \frac{\sigma_{\text{OW}} k T}{(\sigma_{\text{OW}} + \sigma_{\text{WA}})^2} \frac{D \partial c}{h} \quad (\text{B.7})$$

### Appendix C: Derivation of Equations 5.16–5.19

In view of eq 5.15, the linear set of four equations, 3.11, 3.17, 3.18, and 4.11, allows one to express the 4 variables,  $\tilde{h}_1$ ,  $\tilde{p}$ ,  $u_2$ , and  $\tilde{\Gamma}$  in terms of  $\tilde{h}$  and  $\partial \tilde{h}/\partial t$ . The expressions for  $\tilde{h}_1$  and  $\tilde{p}$  are again eqs B.1 and B.2. The expressions for  $u_2$  and  $\tilde{\Gamma}$  are

$$\tilde{\Gamma} = -\frac{2}{kT} \left( \frac{hf}{3} \tilde{h} + \frac{\eta R^2}{h^2 \alpha^2} \frac{\partial \tilde{h}}{\partial t} \right) \quad (\text{C.1})$$

$$u_2 = \frac{2R^2}{h\alpha^2} \frac{\partial \tilde{h}}{\partial t} + \frac{h^2 f}{6\eta} \tilde{h} \quad (\text{C.2})$$

Next, eqs 5.15, B.1, B.2, C.1, and C.2 are substituted in eq 4.9 to derive a connection between  $\tilde{h}$  and its time derivatives, that is, eq 5.16; in particular, the second derivative  $\partial^2 \tilde{h}/\partial t^2$  in eq 5.16 originates from the differentiation of eq C.1. The time dependence of  $\lambda$  and  $f$  is taken into account with the help of eqs B.6 and B.7.

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