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Dynamics of spontaneous emulsification

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Abstract. — We present a model for spontaneous emulsification resulting from a transiently negative interfacial tension between water and oil regions, which may be achieved under conditions of strong adsorption of surfactant molecules to the interface. While our approach builds on a linear stability analysis, it addresses the essential non-linear coupling of surface growth to the diffusion flux of surfactants to the interface. We consider a large drop of oil of radius R embedded in a dilute surfactant solution and predict that undulations develop with a characteristic wavelength λ^* , which at long times t obeys $\lambda^* \sim t^{1/3}$. This suggests that the size of the droplets created spontaneously at the interface scales as $\xi_o^{1/3}$, where ξ_o is a diffusion length which is comparable to R under steady state diffusion conditions. We discuss the regimes of applicability of our results to various experimental systems.

1. Introduction.

In recent years there has been considerable progress in understanding the phase diagram of oil-water-surfactant systems [1,2]. It is well known that by lowering the interfacial tension between the oil and water regions to a very low value, one can obtain a microemulsion phase stabilized by entropy of mixing and spontaneous curvature. Since surfactant molecules adsorb to the oil-water interface, they lower its surface tension [2,3]. But large coverages and low values of surface tension are generally limited by the onset of micelles. As concentration is increased above the Critical Micelle Concentration (CMC), the surfactant chemical potential saturates resulting in no further increase in coverage. Very low tension can nonetheless be obtained by either choosing a special surfactant (e.g., AOT) or adding a cosurfactant (which is a short chain molecule, normally alcohol) to the mixture, which – while lowering the CMC – lowers the interfacial tension more markedly [2]. An explanation for the effect of cosurfactant on interfacial tension and CMC values should be on a molecular level, and a theory in this direction has been advanced by Szleifer *et al.* [4].

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Despite the enormous progress on equilibrium microemulsions, there is very little published experimental and theoretical work on the *dynamics* of spontaneous emulsification. By "spontaneous" emulsification we mean that by starting with oil and water as separate phases in contact, with surfactant molecules dissolved in (say) the water, the interface will corrugate and small droplets of (say) oil will break off into the water phase spontaneously, without for example, any stirring of the system. Such processes can provide the initial step of forming a microemulsion from a phase-separated state (far from equilibrium). There appears to be experimental evidence that something like this happens when a solution of water/*n*-dodecyl pentaoxyethylene monoether ($C_{12}E_5$) in the L_1 (micellar) phase is put in contact with *n*-tetradecane (C_{14}) and *n*-hexadecane (C_{16}) [5]. A similar situation exists in a number of systems [5-7]. In fact, spontaneous emulsification has been known to experimentalists for a long time [8,9], but its understanding has remained essentially on the empirical level. While closely related theoretical studies have been described [10], these do not include bending elasticity which is of particular importance for stabilizing the film, as described below.

In this paper we describe a scenario in which, under conditions of large surfactant/cosurfactant adsorption, the oil-water interfacial tension becomes *transiently slightly negative*. The conditions to achieve this situation should be similar to those under which an equilibrium microemulsion is formed; in particular we require that the bulk surfactant concentration corresponding to zero interfacial tension of a hypothetical interface should be below the CMC. Indeed it has been previously suggested that such a *transient* situation can be achieved experimentally [2], and that this may cause spontaneous emulsification [9,11]. We note however that not all systems that would form a microemulsion phase can be described in this way. The initial state of some systems may involve only very low positive values of interfacial tension, and spontaneous emulsification may not occur.

It was also suggested that a negative surface tension can develop in a Langmuir monolayer under sudden compression, which should lead to buckling of the monolayer, similar to the scenario presented below. The statics of this buckling transition was studied by Milner *et al.* [12] and include gravity effects, which can be shown to be negligible in our study. Hence their results are not directly related to ours.

We consider in section 2 a drop of (say) oil, of macroscopic size, embedded in such a water-surfactant solution. When the surface tension becomes negative, the surface becomes unstable so that it wants to expand its area. Since the volume of the drop has to be conserved, only deformations are allowed. Hence the local radii of curvature are decreased in most parts of the surface, which results in a bending energy penalty. However, a band of long wavelength deformations remains unstable and any initial small deformation at such wavelengths will grow exponentially (Sect. 3). A fastest growing wavelength can be defined. We argue that this wavelength determines the size of the droplets detached from the interface when the amplitude of the deformation reaches the size of the wavelength.

When the area increases the surface coverage decreases, which in turn leads to an increase of the surface tension coefficient. Without surfactant transport to the surface the growth is bound to stop at some point, when the tension vanishes. But with continuous transport the area can continue to grow and the deformation amplitudes can become sufficiently large for breakup to occur. In fact, we show that diffusion of surfactant to the interface is the rate limiting process which finally determines the fastest growing wavelength and thereby the droplet size (Sects. 4 and 5). This is the main message of this work.

In section 6 we discuss the complete evaporation process of a single droplet, using the results obtained in section 4 for a single evaporation step. Section 7 is devoted to a discussion of the generality of our results and conclusions.

2. Definition of the problem and free energy model.

Let us assume that we have a spherical macroscopic drop of oil of radius R suspended in an appropriate water/surfactant/cosurfactant solution. Given a certain concentration c_s of surfactant molecules on the surface, we define the surface coverage as $\phi_s = c_s a^2$ where a is the close packing distance (about the diameter of the hydrophilic head of the surfactant).

While we prefer in this work *not to rely* on any specific free-energy model of *adsorption*, it may be helpful to recall the simple Langmuir adsorption isotherm. (A more detailed model is describe in Ref. [4].) In this model the surface free-energy takes the form

$$F = \int ds \gamma[\phi_s(s)] = \int ds \left\{ \gamma_o - \epsilon \frac{\phi_s}{a^2} + \frac{k_B T}{a^2} [\phi_s \log \phi_s + (1 - \phi_s) \log (1 - \phi_s)] \right\}. \quad (1)$$

Here γ_o is the bare oil-water interfacial tension and ϵ is an adsorption energy which is taken independent of coverage in the original Langmuir model; it may be also taken as a mean-field parameter that includes surfactant-surfactant interactions (which are also responsible for bending elasticity, see below), in which case it should depend on ϕ_s linearly. The last term in (1) results from the entropy of mixing within the surface. If the surface is in thermodynamic equilibrium with the bulk, we have $\delta F / \delta \phi_s = \mu_b / a^2$ where μ_b is the surfactant chemical potential. Below the CMC one can use $\mu_b = k_B T \log \Phi_o$ where Φ_o is the surfactant molar fraction in the solution. One therefore obtains the Langmuir isotherm result (for constant ϵ)

$$\phi_s^{\text{eq}} = \frac{\alpha \Phi_o}{1 + \alpha \Phi_o} \quad (2)$$

where $\alpha = \exp[\epsilon/k_B T]$. In the following we will not use the Langmuir adsorption isotherm in any explicit way.

We assume that the surface tension coefficient vanishes at some coverage (e.g., if $\epsilon/a^2 > \gamma_o$ in the Langmuir adsorption) and we denote it as ϕ_c . For $\phi_s > \phi_c$ the surface tension coefficient is negative and is denoted as $-g$. (It should be possible to achieve this situation in systems where $\phi_s^{\text{eq}} > \phi_c$.) In most systems ϕ_c is of order (but not too close to) unity. This is because the bare oil-water interfacial tension (γ_o) is comparable to the adsorption energy per unit area (ϵ/a^2) [13].

The bending free energy associated with deformations of the drop can be described by the Helfrich Hamiltonian [14,1]. Neglecting the Gaussian curvature this is

$$H_{\text{bend}} = \int ds \left\{ \frac{1}{2} \kappa \left(\frac{1}{R_1} + \frac{1}{R_2} - 2C_o \right)^2 - \frac{1}{2} \kappa \left(\frac{2}{R} - 2C_o \right)^2 \right\} \quad (3)$$

where R_1 and R_2 are local radii of curvature, C_o is the spontaneous curvature, and κ is the bending modulus. In equation (3) we have subtracted from H_{bend} the bending energy of a spherical drop of radius R . This is because this bending energy contribution to the surface tension is already accounted for in $-g$ (by definition). The total free energy of the surface is therefore written as

$$F = H_{\text{bend}} - \int ds g. \quad (4)$$

For simplicity we consider small deformations of the drop from the spherical shape. We therefore assume that we can describe the deviation from a spherical shape by a single-valued

function $u(\theta, \phi)$ [15-17]. But as will be shown below, the wavelengths of deformations that will be of interest to us obey $\lambda \ll R$. Therefore the reference surface can be considered as flat and the deformations will be described by $U(x, y)$ where $x = \theta R$ and $y = \phi R$ [18]. For small deformations where $\nabla U(x, y) \ll 1$, the difference ΔF between the free energy of a spherical (or a planar) sheet and a deformed one, to order U^2 , is given by

$$\Delta F = \int d^2x \left\{ -\frac{1}{2}g(\nabla U)^2 + \frac{1}{2}\kappa (\nabla^2 U)^2 \right\}. \quad (5)$$

In the Fourier space, this difference is given by

$$\Delta F = \frac{1}{2} \sum_q (-gq^2 + \kappa q^4) U_q U_{-q}. \quad (6)$$

The free-energy (6) implies that long wavelength fluctuations are unstable. More precisely, small perturbations of wavenumber $q < q_c$ where

$$q_c = \sqrt{\frac{g}{\kappa}}. \quad (7)$$

will grow rather than decay. This time dependent growth is discussed in the following sections. We note that the dynamic instability we describe is similar to other types of instability of fluid surfaces [19,10,20], e.g., the Rayleigh-Taylor instability that occurs when a heavy fluid lies on the top of a lighter fluid [19].

3. Dynamics – a wrong but instructive model.

While not physical, it is instructive to consider a model where surfactant transport to the surface is *infinitely fast*. Hence, during the process of surface growth the surface coverage does not change so that g and κ are independent of time. The results of such a model will serve to emphasize the importance of surfactant transport.

To analyze the dynamics of the film, let us first discuss the evolution in time of fluctuations by hydrodynamic modes, which can be obtained from textbooks [19]. In the linear regime we generally have

$$U_q \simeq U_q^o \exp[\omega(q)t] \quad (8)$$

and we need an expression for $\omega(q)$. Neglecting inertia [21,22] and gravity it is given by [19,15,17,18]

$$\omega(q) = \frac{1}{4\eta} (gq - \kappa q^3) \quad (9)$$

where η is an effective viscosity which depends on the oil and water densities and viscosities [23]. For example, if the oil and water have equal densities but different viscosities η_o and η_w respectively, we can obtain [23] from reference [19], $\eta = (\eta_o + \eta_w)/2$.

We see that $\omega(q)$ is positive for wavenumbers smaller than q_c defined in equation (7), which means that long wavelength fluctuations are unstable. The most unstable wavenumber q^* , as determined from $\partial\omega/\partial q = 0$, is

$$q^* = \sqrt{\frac{g}{3\kappa}} = \frac{q_c}{\sqrt{3}}. \quad (10)$$

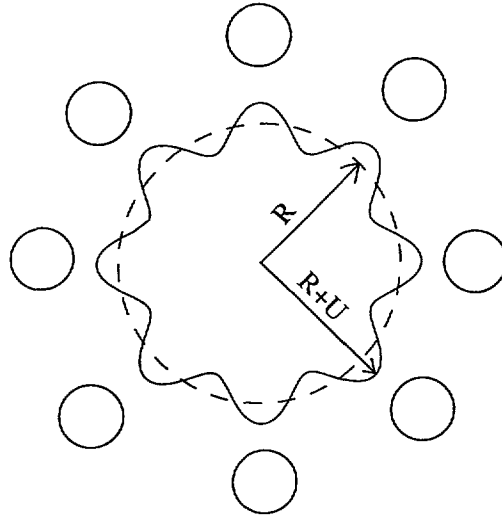


Fig. 1. — Schematic picture of a deformed droplet. The droplets formed at the interface when the amplitude reaches the wavelength size are also shown. The scales are exaggerated.

When the amplitude of fluctuations of the wavelength $\lambda^* = 2\pi/q^*$ becomes equal to λ^* , the surface will be highly corrugated and the linearization inherent in our analysis will become invalid. Nonetheless, it seems reasonable to expect that droplets of size λ^* will tend to form, as depicted schematically in figure 1. A roughly equivalent condition for identifying the onset of non-linearity is to set $\langle (\nabla U)^2 \rangle \simeq 1$. The latter can be expressed as

$$\langle (\nabla U(t))^2 \rangle = \frac{1}{(2\pi)^2} \int d^2q \, q^2 \langle U_q^\circ U_{-q}^\circ \rangle \exp[2\omega(q)t] \tag{11}$$

where $\langle \dots \rangle$ in $\langle U_q^\circ U_{-q}^\circ \rangle$ means average over the initial values, as those may have some statistical distribution. We can evaluate the integral in (11) using the steepest descents method, for $\omega(q)t \gg 1$ (in the unstable region). This leads to

$$\langle (\nabla U(t))^2 \rangle \simeq \frac{1}{\sqrt{6\pi}} \langle U_{q^*}^\circ U_{-q^*}^\circ \rangle \left(\frac{\eta q^{*5}}{\kappa t} \right)^{1/2} \exp [2\omega(q^*)t] \tag{12}$$

and using equation (10) for q^* we have

$$\langle (\nabla U(t))^2 \rangle \simeq \frac{\Delta}{t^{1/2}} \exp \left[\frac{g^{3/2}}{3\sqrt{3}\eta\kappa^{1/2}} t \right] \tag{13}$$

where

$$\Delta = \frac{1}{3^{1/4}\sqrt{54\pi}} \langle U_{q^*}^\circ U_{-q^*}^\circ \rangle \frac{\eta^{1/2} g^{5/4}}{\kappa^{7/4}} \tag{14}$$

Therefore the typical time τ for droplet formation or other non-linear effects, obtained from the condition $\langle (\nabla U)^2 \rangle = 1$, obeys

$$\tau \simeq \frac{3\sqrt{3}\eta\kappa^{1/2}}{g^{3/2}} \log \left(\frac{\tau^{1/2}}{\Delta} \right). \tag{15}$$

We can roughly estimate the coefficients as $\kappa \sim k_B T$ and $g \sim (k_B T/a^2)(\phi_s - \phi_c)$; hence [24] $\tau \sim (\phi_s - \phi_c)^{-3/2} \tau_0$, where $\tau_0 = \eta a^3/(k_B T)$ is a molecular diffusion time, and $\lambda^* \sim (\phi_s - \phi_c)^{-1} a$. In this model the results are independent of the droplet size R . This contrasts with our results of a more realistic approach considered next, which show a strong dependence on R for a wide range of parameter values.

4. Dynamics – including surfactant transport.

Because ϕ_s is inversely proportional to the surface area, surfactant transport cannot be neglected. To visualize this, assume that (by some means) the interface is disconnected from the bulk, and that a given amount of surfactant with $\phi_s > \phi_c$ is adsorbed on it. The surface area would then increase, but only up to the point where $\phi_s = \phi_c$ at which point g vanishes. (This is closely related to the “Gibbs-Marangoni” effect [11] that prevents the rupture of surfactant films.) Clearly, if we start with $\phi_s - \phi_c \ll \phi_c$, the total increase in area would correspond to $(\nabla U)^2 \ll 1$, which is not sufficient to create droplets at the interface.

Before considering in detail the surfactant transport, we note that if $\phi_s(t)$ is time dependent, so is the interfacial tension coefficient $g(t)$ [25]. In this case equation (8) has to be changed to describe correctly the evolution in time of U_q . We can attempt a solution where the time dependence in $U_q(t)$ is given by

$$U_q(t) = U_q^0 \exp \left[\int_0^t dt' \omega(q, t') \right] \quad (16)$$

(and the velocity field follows [19]). Resolving the hydrodynamic equations for this case [19] we find that, in general, this leads to a characteristic equation for $\omega(q, t)$ which is not algebraic any more but rather a (complicated) first order differential equation in time for $\omega(q, t)$. However, neglecting again inertial terms [26] we find that the characteristic equation reduces to the same algebraic equation as before, so that $\omega(q, t)$ is given by (9) with $g(t)$ replacing the constant g . This leads to a great simplification of the problem.

The evolution of $\langle (\nabla U)^2 \rangle$ can again be evaluated in the steepest descents approximation. This involves a time-dependent $q^*(t)$, which is determined from the requirement $\partial[\int_0^t dt' \omega(q, t')]/\partial q = 0$. This procedure yields

$$q^* = \left(\frac{G(t)}{3\kappa t} \right)^{1/2} \quad (17)$$

where

$$G(t) = \int_0^t g(t') dt' \quad (18)$$

so that [27]

$$\langle (\nabla U(t))^2 \rangle \simeq \Delta^* \frac{G(t)^{5/4}}{t^{7/4}} \exp \left[\frac{G(t)^{3/2}}{3\sqrt{3}\eta\kappa^{1/2}t^{1/2}} \right] \quad (19)$$

where

$$\Delta^* = \frac{1}{3^{1/4}\sqrt{54}\pi} \langle U_{q^*}^0 U_{-q^*}^0 \rangle \frac{\eta^{1/2}}{\kappa^{7/4}}. \quad (20)$$

We now turn to discuss the surfactant transport between the surface and the bulk beside it. Let assume that at $t = 0$ the drop is suspended in a well-mixed surfactant solution with

surfactant molar fraction $\Phi_o > \Phi^{\text{crit}}$. Here Φ^{crit} is the value of Φ_o at which a surface coverage of $\phi_s = \phi_c$ (and vanishing interfacial tension) is obtained *at equilibrium*. For simplicity we also require that the bulk consists of free surfactant molecules only, and no micelles are present. The latter requirement limits the concentration regime we consider to $\Phi^{\text{crit}} < \Phi_o < \Phi^{\text{CMC}}$. Nonetheless, some of our results will be valid also for $\Phi_o > \Phi^{\text{CMC}} > \Phi^{\text{crit}}$ (see Sect. 7). In Appendix A.1 we argue that for large droplets ($R \gg a$) the transport from the bulk to the surface is well within the diffusion controlled regime. Consequently (Appendix A.1), the interface coverage and the bulk concentration *near* it are related by an equilibrium relation (e.g., a Langmuir isotherm), so that a given bulk molar fraction Φ (near the surface) corresponds to a unique surface coverage ϕ_s , and vice versa.

We denote by J the diffusion flux of free surfactant molecules to the interface. This flux can be described by an effective diffusion length $\xi(t)$ which enters as $J \propto \xi^{-1}$. In general $\xi(t)$ is time-dependent [28] since it increases from zero at $t = 0$ towards a maximum value of R if there is a sufficient time for a steady state to be reached (Appendix A). The question is then: what is the value of ξ at the time the surface has reached a coverage of ϕ_c (and zero surface tension)? We denote this time as T and the corresponding value of ξ as $\xi_o \equiv \xi(T)$. In Appendix A.2 we obtain two main regimes for ξ_o , depending on the value of R compared to the parameter

$$R_c \simeq \frac{\phi_c}{a^2 \rho \Phi_o} \quad (21)$$

where ρ is the water number density. For $R \gg R_c$ the diffusion profile is still far from a steady state profile at $t = T$ and $\xi_o \simeq R_c$. For $R \ll R_c$ the diffusion profile has already reached nearly a steady state when $t = T$ and $\xi_o \simeq R$. (We obtain in the appendix an interpolation formula for ξ_o between these two extreme limits, see equation (A.12).) As seen from equation (21), the value of R_c is sensitive to the value of Φ_o . For SDS near its CMC [2,13] (under the relevant conditions of high added pentanol) this leads to the estimate $R_c \simeq 10^5 A$. For other typical microemulsion-forming solutions R_c is smaller than 1 mm. We note that it might be possible to prepare different initial conditions so that a steady state profile may be reached at $t = T$ resulting with $\xi_o \simeq R$. For generality however we shall use the value of ξ_o below.

We assume that $\phi_s(t) - \phi_c$ remains small compared to ϕ_c during the process of surface corrugation (which will be shown to be self-consistent with our results). Hence, the bulk concentration near the surface remains almost constant during this process, and we can take it as Φ^{crit} . For example, if we adopt the Langmuir isotherm result we have

$$\Phi^{\text{crit}} = \exp[-\epsilon/k_B T] \phi_c / (1 - \phi_c)$$

where ϵ is the (positive) adsorption energy. We shall also assume that the typical diffusion length $\xi(t)$ remains constant during the process of surface corrugation, even when $R \gg R_c$. This latter assumption is made mainly for clarity and simplicity and we shall discuss later on the conditions under which it is likely to break down. From these assumptions it follows that the surfactant flux to the interface takes the form

$$J = \frac{D\rho}{\xi_o} (\Phi_o - \Phi^{\text{crit}}). \quad (22)$$

In order to proceed further, we need a conservation equation for the surfactant molecules on the interface. Our approximate treatment disregards any inhomogeneity in concentration within the film, which corresponds to assuming fast diffusion *along* the interface. We therefore

omit a term corresponding to the latter process, and replace $(\nabla U)^2$ by its average. One can then write the conservation equation as

$$\frac{d}{dt} \left(\phi_s \sqrt{1 + \langle (\nabla U)^2 \rangle} \right) = a^2 J \equiv \nu. \quad (23)$$

Integrating equation (23) we obtain

$$\phi_s(t) = \frac{\nu t + \phi_c}{\sqrt{1 + \langle (\nabla U(t))^2 \rangle}} \quad (24)$$

where we have defined, for convenience, $\phi_s(0) = \phi_c$. (Since we assume $(\nabla U(0))^2 \ll 1$, this term was neglected in equation (24)).

Equations (19) and (24) are coupled *via* the dependence of g on ϕ_s . In accord with the proximity of ϕ_s to ϕ_c we take the lowest order of this dependence

$$g \simeq \frac{E}{a^2} (\phi_s - \phi_c) \quad (25)$$

where E is a (positive) energy parameter.

In Appendix B we present analytical arguments for the solution of these coupled equations in different regimes. Here we summarize our main results. First we note that these equations depend on two distinct molecular times, a hydrodynamic time $\tau_h = 3\sqrt{3}\eta a^3 \kappa^{1/2} / E^{3/2}$ and a diffusion time $\tau_D = (D\rho a)^{-1}$. However, these are expected to have the same order of magnitude [29] (for not too large surfactants and for roughly similar viscosities of the oil and water), so when making rough estimates below we shall use $\tau_h = \tau_D = \tau_o$, with $\tau_o \simeq \eta a^3 / (k_B T)$ a molecular diffusion ("Zimm") time.

In the regime $\langle (\nabla U)^2 \rangle \ll \nu t$ we can use, as a first approximation, $\phi_s(t) - \phi_c \simeq \nu t$. According to equation (19) this leads to an early "super-exponential" growth $\langle (\nabla U)^2 \rangle \propto \nu^{5/4} t^{3/4} \exp[(t/t_c)^{5/2}]$ where

$$t_c = \nu^{-3/5} \tau_h^{2/5} \quad (26)$$

[Very roughly we can estimate t_c as $t_c \sim (\Phi_o - \Phi^{\text{crit}})^{-3/5} (\xi_o/a)^{3/5} \tau_o$]. However, this exponential behaviour proceeds only at very early times up to the crossover time t_c . At these times $\langle (\nabla U)^2 \rangle$ crosses over to a *linear* growth which is limited by the surfactant flux to the interface, $\langle (\nabla U)^2 \rangle \sim \nu t$. At the crossover therefore $\langle (\nabla U)^2 \rangle \simeq \nu t_c$ or (roughly) $\langle (\nabla U)^2 \rangle \sim (\Phi_o - \Phi^{\text{crit}})^{2/5} (a/\xi_o)^{2/5} \ll 1$. At the same time $\phi_s - \phi_c$ shows a maximum and then decreases at later times. For $t \gg t_c$ we find a decay law

$$\phi_s - \phi_c \simeq \left(\frac{t}{\tau_h} \right)^{-2/3} \quad (27)$$

(ignoring logarithmic corrections which are discussed in Appendix B).

To illustrate these results we have solved numerically equations (19), (24) and (25). For simplicity we choose the two molecular times defined above to be equal, namely $\tau_h = \tau_D = \tau_o$ with τ_o a molecular diffusion time. The dimensionless diffusion rate $\tilde{\nu} = \nu \tau_o$ becomes $\tilde{\nu} =$

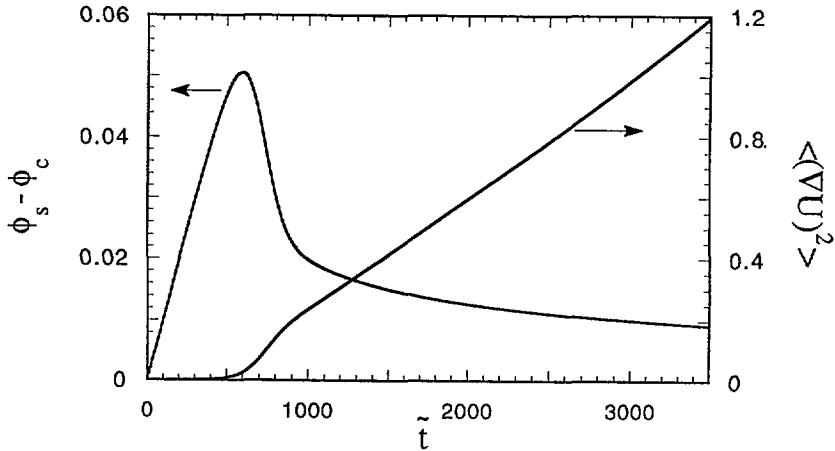


Fig. 2. — Plots of $\phi_s - \phi_c$ and $\langle (\nabla U)^2 \rangle$ against the reduced time $\tilde{t} = t/\tau_0$ for a dimensionless diffusion rate $\tilde{\nu} = \nu\tau_0 = 10^{-4}$. Other parameters used are $\tilde{\Delta} = 3$ and $\phi_c = 0.7$.

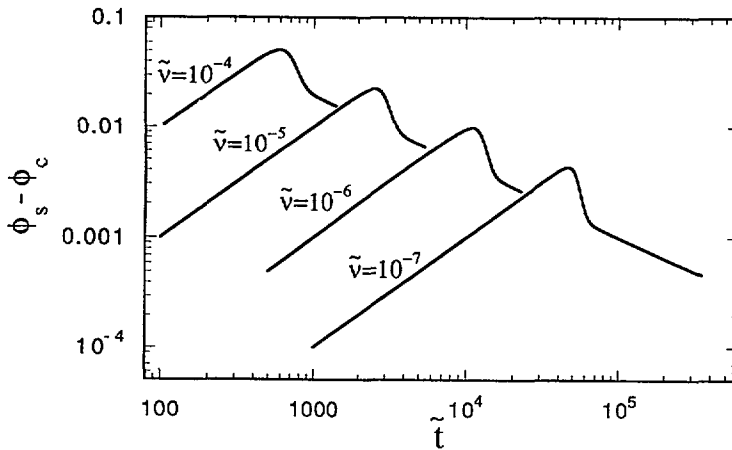


Fig. 3. — $\phi_s - \phi_c$ against the reduced time \tilde{t} for different values of $\tilde{\nu}$.

$(\Phi_0 - \Phi^{\text{crit}})(a/\xi_0)$, so that physical values correspond to $\tilde{\nu} \ll 1$. Another (rather unimportant) dimensionless parameter is $\tilde{\Delta} = \Delta^*(E/a^2)^{5/4}/\tau_0^{1/2}$ which parameterizes the initial value of $\langle (\nabla U)^2 \rangle$, and we have used $\tilde{\Delta} = 3$. In figures 2-4 we plot our results for $\phi_s - \phi_c$ and $\langle (\nabla U)^2 \rangle$ as a function of the dimensionless time $\tilde{t} = t/\tau_0$ for various values of $\tilde{\nu}$. The numerical results indeed show that $\phi_s - \phi_c$ achieves its maximum value much before the time when $\langle (\nabla U)^2 \rangle \sim 1$. At the same time $\langle (\nabla U)^2 \rangle$ shows a crossover from an “exponential” to a linear behaviour. By the time $\langle (\nabla U)^2 \rangle \simeq 1$, $\phi_s - \phi_c$ is already far below its overshoot and is indeed decaying in time as $t^{-2/3}$. The main result to note is that when $\langle (\nabla U)^2 \rangle$ is still very small its growth is

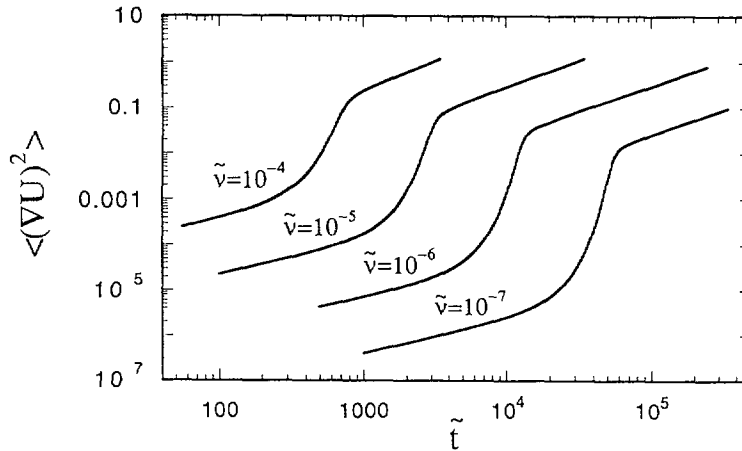


Fig. 4. — $\langle (\nabla U)^2 \rangle$ against the reduced time \tilde{t} for different values of $\tilde{\nu}$.

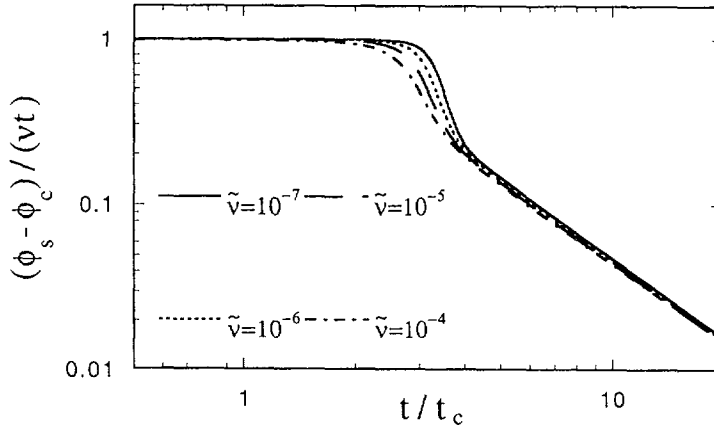


Fig. 5. — $(\phi_s - \phi_c) / (\nu t)$ against t / t_c for different values of $\tilde{\nu}$ (the same values as in Fig. 3).

already controlled *entirely* by the surfactant flux rate to the interface.

We can cast our results for the asymptotic behaviour of $\phi_s - \phi_c$ in a scaling law. This has the form

$$\phi_s - \phi_c = \nu t f(t/t_c) \tag{28}$$

with t_c given by (26) and where f is a scaling function that has the following asymptotes

$$f(x) \sim \begin{cases} 1 & \text{for } x \ll 1, \\ x^{-5/3} & \text{for } x \gg 1. \end{cases} \tag{29}$$

The validity of this scaling assumption is checked numerically in figure 5. We plot $(\phi_s - \phi_c) / (\nu t)$ against t/t_c for different values of $\tilde{\nu}$. We find a weak breakdown of the scaling hypothesis in the crossover regime $t \sim t_c$ possibly due to the logarithmic corrections (discussed in Appendix B), but otherwise it works well.

We now return to the calculation of $q^*(t)$. For $t \gg t_c$ we find in Appendix B (still ignoring the logarithmic corrections)

$$G(t) = \int_0^t g(t') dt' = \left(3\sqrt{3}\eta\kappa^{1/2}\right)^{2/3} t^{1/3} \tag{30}$$

and an area growth described by

$$\langle(\nabla U)^2\rangle \simeq \frac{2\nu t}{\phi_c} \tag{31}$$

The maximally growing wavenumber can be computed from equation (17) as

$$q^*(t) = \left(\frac{\eta}{\kappa t}\right)^{1/3} \tag{32}$$

which shows an interesting time dependence $\lambda^* \sim t^{1/3}$. From equations (31) and (32) we find the mean square amplitude, which is dominated by the amplitude at wavelengths near λ^* , to follow

$$\langle U^2 \rangle \simeq \frac{2\nu}{\phi_c} \left(\frac{\kappa}{\eta}\right)^{2/3} t^{5/3} \tag{33}$$

It should be possible to check equations (32) and (33) directly by light scattering experiments.

Let us now examine the assumption of constant ξ_o . The trivial case is when $R \ll R_c$ so that $\xi_o \simeq R$ and this assumption is clearly valid. The regime $R \gg R_c$ is characterized by $\xi(t) \sim \sqrt{t}$, which might change the linear behaviour of $\langle(\nabla U)^2\rangle$ at long times to $\sim \sqrt{t}$. The effect of this property of $\xi(t)$ on our results can be discussed in terms of the parameter

$$x = (\Phi_o - \Phi^{\text{crit}})/\Phi_o \tag{34}$$

which describes the distance from the critical concentration Φ^{crit} . Recall that the time $t = \tau$ is defined as the time for which $\langle(\nabla U)^2\rangle = 1$. If $x \sim 1$, the crossover to \sqrt{t} behaviour of $\langle(\nabla U)^2\rangle$ occurs when $t \simeq \tau$, so that this behaviour is never dominant in the regime $\langle(\nabla U)^2\rangle \leq 1$. In other words, the ratio of $\xi(\tau)$ to ξ_o is of order unity (about two) resulting in marginal effect on $\langle(\nabla U)^2\rangle$ and no effect on $\phi_s - \phi_c$. For other regimes of x we obtain the following results:

(i) if $\max[\Phi_o^{4/3}, R_c/R] \ll x \ll 1$ we find a negligible change to the result for $\langle(\nabla U)^2\rangle$ up to the time $t_{c1} \simeq R_c^2/D$. Since in this regime $t_{c1} \gg t_c$, the initial and the crossover behaviours depicted in figures 2-5 remain unchanged. For $t \gg t_{c1}$ we find $\langle(\nabla U)^2\rangle \sim \sqrt{t}$ (rather than the linear behaviour in Eq. (31)) which proceeds through the time $t \simeq \tau$. Nevertheless, equation (27) for $\phi_s - \phi_c$ remains *unchanged* since any changes occur in the logarithmic corrections (Appendix B). This implies that equation (32) for $q^*(t)$ remains unchanged, while $U^2 \sim t^{7/6}$ in this regime instead of equation (33).

(ii) if $\Phi_o^{4/3} \ll x \ll R_c/R$ there is another crossover time $t_{c1} \ll t_{c2} \ll \tau$ in addition to the crossover time t_{c1} . This time is $t_{c2} \simeq R^2/D$. At $t \sim t_{c2}$ the diffusion profile reaches a steady state (while the surface continues to corrugate) so at later times $\langle(\nabla U)^2\rangle \simeq \nu(R)t$ with R replacing ξ_o in equation (22). Again, no changes are found to equations (27) and (32).

The regime $x \ll \Phi_o^{4/3}$ which is (say for SDS) $x \ll 10^{-6}$ can hardly be obtained in experiment and is therefore disregarded. We note that these additional crossovers are entirely due to the

the time-dependence of the diffusion flux *via* $\xi(t)$. Our conclusion that at times $t \gg t_c$ the area growth is diffusion controlled remains valid.

In this section, we analyzed the dynamics of surface corrugation in conjunction with the coupling to the diffusion flux. The implications of these results on the formation of droplets at the interface are discussed next. For simplicity we shall continue to use mainly the results (31)-(32), keeping in mind however that they may break down for $x \ll 1$ as described above.

5. Formation of droplets.

We now return to our assumption that when the amplitude of the maximum growing wavelength becomes equal to the wavelength itself (i.e., $\langle (\nabla U)^2 \rangle \simeq 1$), the interface will break up leading to a spontaneous creation of small droplets, as depicted schematically in figure 1. We assume that the rate limiting step is the formation of the crumpled interface rather than any local activation barrier associated with topological change. (In the presence of such a barrier, a dendritic structure could form which lies beyond our present scope.)

We can obtain from equation (31) the time τ for droplet formation as

$$\tau \simeq \phi_c / \nu \quad (35)$$

or

$$\tau \sim (\Phi_o - \Phi^{\text{crit}})^{-1} \frac{\xi_o}{a} \tau_o \quad (36)$$

in a rough estimate [29]. This implies $\tau \sim R$ in the regime $R \ll R_c$. Emulsification will take more time in a larger droplet. Using the result (35) for τ in equation (32) we find that the characteristic wavelength $\lambda_m = \lambda^*(\tau)$, which suggests the characteristic droplet size, obeys

$$\lambda_m \simeq \left(\frac{\kappa \phi_c}{\eta \nu} \right)^{1/3} \quad (37)$$

which means $\lambda_m \sim \xi_o^{1/3}$. Note that there is no dependence at all on the parameter E of equation (25) at this level of the calculation. Very roughly [29] λ_m can be estimated as

$$\lambda_m \sim (\Phi_o - \Phi^{\text{crit}})^{-1/3} \left(\frac{\xi_o}{a} \right)^{1/3} a. \quad (38)$$

For the SDS/pentanol system [2,13] (mentioned earlier) near its CMC where $\Phi_o - \Phi^{\text{crit}} \sim 10^{-5}$, and for droplet size of $R \geq R_c \sim 10^5 \text{ \AA}$, these estimates yield (taking $\tau_o \sim 10^{-9} \text{ s}$) $\tau \sim 1 - 10 \text{ s}$ and $\lambda_m \sim 10^3 - 10^4 \text{ \AA}$. (For more accurate estimates one should use Eqs. (35) and (37)). We note that the assumption $\lambda_m \ll R$ (made in the expansion (5)) limits the minimum size of the initial droplet to $R \gg (\Phi_o - \Phi^{\text{crit}})^{-1/2} a$, and for the above (SDS) example this implies $R \gg 10^3 \text{ \AA}$. (For a smaller droplet one needs a calculation [18] that uses a spherical harmonics expansion [15-17].)

As discussed at the end of section 4, these results should change if $R \gg R_c$ ($\xi_o \sim R_c$) and the parameter $x = (\Phi_o - \Phi^{\text{crit}}) / \Phi_o$ is much smaller the unity. Instead of equations (36) and (38) we find the following results: (i) for $R_c/R \ll x \ll 1$ we have $\tau \sim (\Phi_o - \Phi^{\text{crit}})^{-2} \tau_o$ and $\lambda_m \sim (\Phi_o - \Phi^{\text{crit}})^{-2/3} a$. (ii) For $x \ll R_c/R$ we should replace ξ_o by R in these equations so that $\tau \sim (\Phi_o - \Phi^{\text{crit}})^{-1} (R/a) \tau_o$ and $\lambda_m \sim (\Phi_o - \Phi^{\text{crit}})^{-1/3} (R/a)^{1/3} a$.

Finally, let us include the logarithmic corrections from Appendix B. Assuming that $\langle U_q^\circ U_{-q}^\circ \rangle$ is independent of q (so that Δ^* in equation (20) is independent of t) we obtain

$$q_m \sim \left(\frac{\eta\nu}{\kappa\phi_c} \right)^{1/3} \left\{ \log \left[\frac{\phi_c^{4/3}}{3^{5/4}\Delta^*\eta^{5/6}\kappa^{5/12}\nu^{4/3}} \right] \right\}^{1/3} \quad (39)$$

In terms of the dependence on ξ_o , this means the scaling form

$$q_m \sim \xi_o^{-1/3} \left[\log \left(\frac{\xi_o}{\xi^*} \right) \right]^{1/3} \quad (40)$$

where ξ^* is a function of the previous coefficients (and obeys the scaling $\xi^* \sim \Phi_o - \Phi^{\text{crit}}$).

Interestingly, it is possible to obtain the correct scaling of q_m by disregarding the dependence of ϕ_s and thus q^* on time (i.e., a steady state assumption) and equating $\omega(q^*)$ with ν . Since $\omega(q^*) \sim g^{3/2}$ we have $g \sim \nu^{2/3}$ and from $q^* \sim g^{1/2}$ we obtain $q^* \sim \nu^{1/3}$ (which is also q_m in this approach). As shown above, this is rather a naive approach, though it seems to have the right ingredients.

6. Evaporation of a droplet.

The above discussion describes a single "evaporation" step, where a small shell of thickness λ_m is removed from a macroscopic droplet of radius R . It is interesting to see how the complete evaporation of a droplet of initial radius R_o proceeds in time. After the first "shell" has been removed a "corona" of small droplets surrounds the macroscopic one (Fig. 1), so that the diffusion field and therefore the expression for J might change. But this would probably lead to only a modest reduction of J , resulting from the partial obstruction by the small droplets of the free surfactant coming to the interface. For simplicity we neglect this effect. Then, since $\lambda_m \ll R$ we can write a simple differential equation for the time-dependence of $R(t)$ of the form (ignoring logarithmic corrections)

$$\frac{dR}{dt} = -\frac{\lambda_m(\xi_o)}{\tau(\xi_o)} \simeq -\frac{C}{\xi_o^{2/3}} \quad (41)$$

where C is a combination of the previous coefficients.

If $R < R_c$, or for the combination of $R > R_c$ and $x \ll R_c/R$, we should use in (41) $\xi_o \simeq R$ and the solution is immediately obtained as

$$R(t) = \left(R_o^{5/3} - \frac{5}{3}Ct \right)^{3/5} \quad (42)$$

where R_o the initial radius. equation (42) shows a very interesting time behaviour demonstrating how the evaporation becomes faster as the droplet size decreases. From this equation we also obtain (very roughly) $t_{\text{evap}} \sim (\Phi_o - \Phi^{\text{crit}})^{-2/3} (R_o/a)^{5/3} \tau_o$. Taking $\tau_o \sim 10^{-9}$ s and (for the SDS system [2,13] mentioned earlier) $\Phi_o - \Phi^{\text{crit}} \sim 10^{-5}$ we obtain, for $R_o \sim R_c \sim 10^5$ A, an evaporation time of the order of $10 - 10^3$ seconds. Interestingly, our results show an anomalous slowing down of the evaporation depending on the proximity of the surfactant bulk concentration Φ_o to Φ^{crit} . Every evaporation step is slowed down according to $\tau \sim (\Phi_o - \Phi^{\text{crit}})^{-1}$

Since $\lambda_m \sim (\Phi_o - \Phi^{\text{crit}})^{-1/3}$ we have $C \sim (\Phi_o - \Phi^{\text{crit}})^{2/3}$ so that the overall evaporation time is slowed down as $t_{\text{evap}} \sim (\Phi_o - \Phi^{\text{crit}})^{-2/3}$. Note that in obtaining equation (42) we have assumed that the diffusion length follows the droplet size as the droplet shrinks. Indeed, comparing t_{evap} to the diffusion time over a distance R_o , $\tau_d = R_o^2/D$, we see that $t_{\text{evap}}/\tau_d \sim (\Phi_o - \Phi^{\text{crit}})^{-2/3} R_o^{-1/3}$; because $R_o \leq R_c \sim \Phi_o^{-1}$ this ratio is always much larger than unity. (For the above example it is ~ 100).

If $R > R_c$ and $x \sim 1$ then $\xi_o \simeq R_c$ and the initial evaporation ($R(t) > R_c$) follows simply

$$R(t) = R_o - \frac{C}{R_c^{2/3}} t. \quad (43)$$

When $R(t)$ becomes of the order of R_c we should have a crossover to equation (42) (with R_c replacing R_o and the time measured from the moment of crossover). To obtain a more precise description in this crossover regime equation (41) can be solved with the expression (A.12) for $\xi_o(R)$. When $R_c/R \ll x \ll 1$ equation (43) does not describe correctly the slowing down and $C/R_c^{2/3}$ should be replaced by $\sim (\Phi_o - \Phi^{\text{crit}})^{4/3} \tau_o^{-1}$.

The slowing down in these equations can also be time-dependent. To get equations (42) and (43) we have assumed that Φ_o is independent of time. That is true if there are enough surfactant molecules in the bulk. Otherwise, Φ_o is time-dependent (although roughly constant during each evaporation step). As the emulsification proceeds we can have a slowing down due to the disappearance of surfactant molecules from the bulk. At this level of approximation, when spontaneous emulsification stops all interfaces have zero surface tension and $\Phi_o = \Phi^{\text{crit}}$. This scenario includes the possibility for (spontaneous) emulsification failure, where only a limited number of "shells" are being removed due to insufficient amount of surfactant in the bulk. The estimates for SDS provided above indeed use very low surfactant concentrations (in order to be able to use equation (22) for the diffusion flux), and emulsification failure is likely to occur for oil and water volumes of comparable order of magnitude. (If the volume of the initial drop is sufficiently small, the evaporation can always be completed.) This is consistent with realistic equilibrium microemulsion systems [1], in which the surfactant volume fraction required for full emulsification is of order 1 % or more. Emulsification failure in equilibrium means that a phase of (say) oil coexists with a microemulsion phase, which is similar to the above picture.

In general, however, since the mechanism we have described is kinetically controlled, the droplets formed by spontaneous emulsification are not in thermodynamic equilibrium with one another. So a second stage of emulsification is needed; this will involve some rearrangement, where droplets will break up and coalesce to form new droplets of different sizes. In addition, a convection process that will move the small daughter droplets far away from their mother drop may be needed. We do not address these issues here.

7. Discussion.

A few remarks on the generality of our results should be made at this stage. The diffusion length ξ_o which controls the approach of surfactants to the interface might be significantly smaller than the macroscopic radius R , as described in section 4. This can be true even in a steady state diffusion profile, for example if the system is subject to a continuous stirring. Another example is when $\Phi_o > \Phi^{\text{CMC}}$, so that the initial increase of surface coverage (before ϕ_c is reached) involves also "evaporation" of micelles resulting in a slower increase of $\xi(t)$. (This latter situation is particularly important for avoiding emulsification failure, as explained

at the end of the previous section.) Our results should still apply if the appropriate ξ_o is used (and possibly, in the case of micelles, an effective diffusion coefficient) and provided that ξ_o is large enough to keep our assumptions valid [18,30,31].

Though our suggestion that λ_m is essentially the droplets size formed at the interface is very appealing, we know in fact very little of how the mechanism of droplet formation proceeds. It is quite possible that long "fingers" (corresponding to $\langle (\nabla U)^2 \rangle \gg 1$) will develop [20] before breakup of the surface occurs. However, this will depend on the details of local energy barriers (for example involving the Gaussian rigidity $\bar{\kappa}$) and so this question should be deferred primarily to experiment. We have also not resolved whether droplets (or fingers) of oil into water are preferred or vice versa; this might be answered by a treatment sufficiently more non-linear [32] to give the spontaneous curvature a quantitative role in the process.

Finally, we want to mention the possible applicability of our results to various diblock copolymer/ homopolymer mixtures. In some systems a small interfacial tension between the homopolymer regions (and thus a microemulsion phase) can be achieved by using a copolymer with a strong amphiphilic character [33]. This suggests that spontaneous emulsification driven by negative interfacial tension might occur in these systems, in which there is a strong dependence of the diffusion coefficient of the copolymer on its molecular weight. Since our results are sensitive to this diffusion coefficient (see, e.g., Eqs. (22), (23),(35) and (37)), these systems could provide an important check on our approach. We hope that studies on these and similar systems will be forthcoming in the near future.

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Appendix A.

A.1. FROM REACTION-CONTROLLED TO DIFFUSION-CONTROLLED ADSORPTION KINETICS. — Here we argue that the surfactant transport to the surface is diffusion controlled. For simplicity we employ a steady-state argument, though our conclusions are valid at all times except at very early times of the order of τ_o .

It is convenient to construct the surface grand-canonical free-energy

$$\Omega = F - \frac{\mu_b}{a^2} \int_S ds \phi_s \quad (\text{A.1})$$

where F is the Helmholtz free-energy (of the surface) and μ_b is the surfactant chemical potential in the bulk, which can be taken as $\mu_b = k_B T \log \Phi$. Then, if we are in the linear (Onsager) regime, we can write the flux from the bulk to the surface (negative when its going the opposite way) as

$$J = - \frac{\Lambda}{k_B T} \frac{\delta \Omega[\phi_s, \Phi]}{\delta \phi_s} \quad (\text{A.2})$$

Here Λ is an Onsager coefficient which has dimensions of 1/time. When $J = 0$ we recover the equation for equilibrium coverage.

Coupling the surface-bulk transport to the transport in the bulk, equation (A.2) can serve as a boundary condition, and Φ in this equation would correspond to its value near the surface.

In the bulk we should have simple diffusion

$$\frac{\partial \Phi}{\partial t} = D \nabla^2 \Phi \quad (\text{A.3})$$

with the boundary condition (taking the positive axis direction in the water region)

$$D \rho \nabla \Phi|_{\text{surface}} = J. \quad (\text{A.4})$$

The final equation is the conservation law

$$\phi_s = a^2 \int_0^t J(t') dt' \quad (\text{A.5})$$

which implies that the boundary conditions (A.2) and (A.4) are actually time-dependent.

Solving the diffusion equation (A.3) with the boundary conditions (A.2) and (A.4) is a formidable task even for the Langmuir isotherm model. But we can gain some intuition by using a quasi steady-state assumption, where we ignore the time-dependence of ϕ_s . Let us consider a spherical droplet of radius R . Given a (yet unknown) boundary value $\Phi(R)$, we can solve the *steady state* diffusion equation ($\partial \Phi / \partial t = 0$)

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial \Phi}{\partial r} \right) = 0 \quad (\text{A.6})$$

to obtain the relation

$$\frac{\partial \Phi}{\partial r} \Big|_R = \frac{\Phi_o - \Phi(R)}{R} \quad (\text{A.7})$$

where Φ_o is the molar fraction at the bulk far from the surface. Equating the two fluxes leads to an equation for $\Phi(R)$

$$\Phi_o - \Phi(R) = -\zeta^{-1} \frac{a^2}{k_B T} \frac{\delta \Omega[\phi_s, \Phi(R)]}{\delta \phi_s} \quad (\text{A.8})$$

where ζ is a dimensionless parameter given by

$$\zeta = \frac{D \rho a^2}{\Lambda R} \quad (\text{A.9})$$

If $\zeta \gg 1$ we are in the "reaction controlled" regime, and we can neglect transport in the bulk. If $\zeta \ll 1$ this is the "diffusion controlled" regime, and bulk transport is the rate limiting process.

Let us roughly estimate ζ . Since the surface-bulk exchange is also *diffusive* in nature, we may relate D to Λ by

$$\Lambda \simeq D a^{-2} \exp(-E_a / k_B T) \quad (\text{A.10})$$

where the activation energy $E_a \sim k_B T$ accounts for the fact that the surfactant tail has to "push" some oil molecules in the adsorption process. Taking $\rho \sim a^{-3}$ (ignoring the small difference between the water and surfactant sizes) we have

$$\zeta \sim \frac{a}{R} \exp(E_a / k_B T). \quad (\text{A.11})$$

For macroscopic droplets this means $\zeta \ll 1$ which is the diffusion controlled regime. It is unlikely that the process will be in the reaction controlled regime because R is very large while

the activation energy E_a is small. We should bear in mind however that if (say) $E_a \sim 5k_B T$ than for $R \sim 100a$ we have $\zeta \sim 1$.

Consider the diffusion controlled limit $\zeta \rightarrow 0$. Since the LHS in equation (A.8) cannot become infinite, $\delta\Omega/\delta\phi_s$ on the RHS have to be $\sim \zeta$. Therefore the bulk concentration near the surface is in equilibrium with the surface, namely $\Phi(R) \rightarrow \Phi^{\text{eq}}(\phi_s) + O(\zeta)$. In a steady-state diffusion profile we therefore obtain equation (22) with $\xi_o = R$. The result for ξ_o in a non-steady state situation is discussed in the second part of this Appendix.

A.2. ESTIMATE OF ξ_o IN EQUATION (22). — Here we estimate the value of $\xi_o \equiv \xi(T)$. Our result is

$$\frac{1}{\xi_o} = \frac{1}{R} \left(1 + \frac{1}{\left(1 + \frac{2R_c}{R}\right)^{1/2} - 1} \right) \quad (\text{A.12})$$

where

$$R_c = \frac{\pi\phi_c}{2a^2\rho\Phi_o} \quad (\text{A.13})$$

This result was obtained as follows. The time T to reach a coverage of $\phi_s = \phi_c$ is obtained from equation (A.5). In the expression for $J(t)$ in this calculation we can neglect $\Phi(R, t)$ and keep our estimate correct to an order of magnitude (unless Φ_o is extremely close to Φ^{crit}). We therefore use $J(t) = D\rho\Phi_o/\xi(t)$ where [28]

$$\frac{1}{\xi(t)} = \frac{1}{R} \left(1 + \frac{R}{\sqrt{\pi Dt}} \right). \quad (\text{A.14})$$

Note that $\xi(t)$ behaves as $\xi \simeq \sqrt{\pi Dt}$ for $R^2 \ll Dt$ and $\xi \simeq R$ for $R^2 \gg Dt$. Integrating J in (A.5) and solving for T we obtain

$$T = \frac{R^2}{\pi D} \left[\left(1 + \frac{2R_c}{R} \right)^{1/2} - 1 \right]^2 \quad (\text{A.15})$$

where R_c is given by (A.13). Using (A.15) in (A.14) we finally obtain equation (A.12).

Appendix B.

ANALYTICAL TREATMENT OF EQUATIONS (19), (24) AND (25). — For brevity we denote $y = \langle (\nabla U)^2 \rangle$. Let us rewrite equation (24) for the regime $y \ll 1$. To first order in y we obtain

$$\phi_s - \phi_c = \nu t - \phi_c y/2. \quad (\text{B.1})$$

If $y \ll \nu t$ (which is a stronger condition) we can use, as a first approximation, $\phi_s(t) - \phi_c \simeq \nu t$. This leads to an early “super-exponential” growth

$$y \simeq \Delta^* (E\nu/a^2)^{5/4} t^{3/4} \exp(\alpha t^{5/2}) \quad (\text{B.2})$$

where $\alpha \simeq (E\nu)^{3/2}/(\eta a^3 \kappa^{1/2})$. However, we can see from equation (B.1) that when $y \sim \nu t$ there should be a crossover to another behaviour.

We can find this crossover by obtaining a rigorous upper bound for y . From equations (19), (24) and (25) it is clear that $\phi_s - \phi_c$ cannot become negative. This is because of the negative feedback in these equations. Any decrease of this quantity due to the increase of y will lead to a decrease in the growth of y , which subsequently will slow down the decrease of $\phi_s - \phi_c$. From equation (24) (corrected for non-vanishing $y(0)$) we can obtain the bounds for the growth of y using the condition $\phi_s - \phi_c > 0$. We easily get

$$y \leq \left(\frac{\nu t}{\phi_c} + \sqrt{1 + y(0)} \right)^2 - 1. \quad (\text{B.3})$$

Hence, instead of growing *exponentially* with time, y cannot grow faster than a *power law*. At sufficiently long times y should therefore crossover from the early exponential increase and saturate at its upper bound

$$y \simeq \frac{2\nu t}{\phi_c} + \frac{\nu^2 t^2}{\phi_c^2} \quad (\text{B.4})$$

This in turn implies a decay of $\phi_s - \phi_c$ as obtained below.

Let us find this crossover time t_c . Close to the crossover (but for $t > t_c$) we can use $\nu t \ll 1$ so that equation (B.4) is approximated as

$$y \simeq \frac{2\nu t}{\phi_c} \quad (\text{B.5})$$

The crossover time is obtained by equating equation (B.5) with (B.2), which is actually the same condition obtained by looking at equation (B.1). Neglecting logarithmic corrections we then have $t_c \sim \alpha^{-2/5} \sim \nu^{-3/5}$. At the crossover time $y \simeq \nu t_c \sim \nu^{2/5}$ and is therefore still much smaller than unity.

More relevant to our purpose is the behaviour of $G(t) = \int_0^t g(t') dt'$ for $t \gg t_c$, which is needed in the calculation of $q^*(t)$. To obtain the asymptotic behaviour let us rewrite equation (24) in a different form. We have

$$y = \left[\frac{\nu t - (\phi_s - \phi_c)\sqrt{1+y}}{\phi_c} + 1 \right]^2 - 1, \quad (\text{B.6})$$

hence, from equation (19),

$$G(t)^{3/2} = A t^{1/2} \log \left\{ \frac{\left[\frac{\nu t - (\phi_s - \phi_c)\sqrt{1+y}}{\phi_c} + 1 \right]^2 - 1}{f(t)} \right\} \quad (\text{B.7})$$

where

$$A = 3\sqrt{3}\eta\kappa^{1/2} \quad (\text{B.8})$$

and

$$f(t) = \Delta^* t^{-7/4} G(t)^{5/4} \quad (\text{B.9})$$

Now we may argue that for $t \gg t_c$, $(\phi_s - \phi_c)$ is far beyond its maximum and is therefore decaying. Hence we can use in the logarithm $(\phi_s - \phi_c)\sqrt{1+y} \ll \nu t$ for these times. Solving for $G(t)$ we then obtain

$$G(t) = A^{2/3} t^{1/3} \left[\log \left(\frac{\nu^2 t^2}{f(t)\phi_c^2} + \frac{2\nu t}{f(t)\phi_c} \right) \right]^{2/3} \quad (\text{B.10})$$

It is now worthwhile checking that $g(t) \sim \phi_s(t) - \phi_c$ is indeed decaying in this regime. Differentiating both sides of equation (B.10) we obtain

$$g(t) = A^{2/3} t^{-2/3} \left\{ \frac{1}{3} \left[\log \left(\frac{\nu^2 t^2}{f(t)\phi_c^2} + \frac{2\nu t}{f(t)\phi_c} \right) \right]^{2/3} + \frac{2}{3} \left[\log \left(\frac{\nu^2 t^2}{f(t)\phi_c^2} + \frac{2\nu t}{f(t)\phi_c} \right) \right]^{-1/3} \left[1 - \frac{t\partial f/\partial t}{f(t)} + \frac{1}{1 + 2\phi_c/(\nu t)} \right] \right\} \quad (\text{B.11})$$

(Note that self-consistently $f(t)$ has a power law behaviour $f(t) \sim t^\beta$ so that $t\partial f/\partial t/[f(t)]$ is independent of t .) The dominant part of the dependence is of course $g(t) \sim t^{-2/3}$ (which leads to equation (27)) and is self-consistent with the assumption that $g(t)$ is, at these long times, far beyond its maximum and is therefore decaying. This result allows us to calculate the small corrections to equation (B.4) (valid for $t \gg t_c$). We obtain

$$y \simeq \left(\frac{\nu t + \phi_c}{\phi_c + \text{const.}(t/\tau_h)^{-2/3}} \right)^2 - 1 \quad (\text{B.12})$$

which shows that the upper bound (B.4) is saturated only as $t \rightarrow \infty$, though it is approximately reached for $t \gg t_c$.

We can now find the logarithmic corrections to q_m in equation (39). When $y = 1$ ($t = \tau$) we obtain from equations (B.4) and (B.10)

$$G(\tau) = A^{2/3} \tau^{1/3} \left[\log \left(\frac{1}{f(\tau)} \right) \right]^{2/3} \quad (\text{B.13})$$

Iterating once $G(\tau)$ (which appears in $f(\tau)$, see Eq. (B.9)) in equation (B.13) we find

$$G(\tau) \simeq A^{2/3} \tau^{1/3} \left[\log \left(\frac{\tau^{4/3}}{\Delta^* A^{5/6}} \right) \right]^{2/3} \quad (\text{B.14})$$

Using the expression (35) for τ and equation (B.14) in equation (17) for q^* we arrive at equation (39).

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- [13] ϕ_c can be estimated from measurements of interfacial tension with use of Gibbs isotherm, as done in reference [2]. For example, in a SDS/salty-water/pentanol system of composition [SDS] = 2×10^{-5} g/g, [pentanol] = 20% and [NaCl] = 0.3 M, interfacial tension measurements [2] suggest an area of 90 \AA^2 per SDS molecule so that $\phi_c \simeq 0.3$ ($a = 5 \text{ \AA}$). We can also estimate ϕ_c using the Langmuir adsorption model. Taking (say for water-cyclohexane) $\gamma_o = 0.12 k_B T / A^2$. $\epsilon = 4 - 5 k_B T$ and $a = 5 \text{ \AA}$, we arrive at $\phi_c \simeq 0.4 - 0.6$.
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- [18] When using $u(\theta, \phi)$ rather than $U(x, y)$ the expansion in spherical harmonics Y_{lm} is equivalent to the q expansion described here. The result for ω_{lm} using the Y_{lm} expansion of references [15,16] and [17] reduces to equation (9) for $l \gg 1$ with the definition $q = l/R$ (with the exception of a small difference in surface tension terms). Using this result [15-17] for ω_{lm} we can obtain the first corrections to q_m (c.f., equation (37)), and we find

$$q_m \simeq q_{m0} \left(1 - \frac{1}{2q_{m0}R} + \frac{1}{24q_{m0}^2R^2} \right)$$

where q_{m0} is q_m of section 5, $q_{m0} = [\eta\nu/(\kappa\phi_c)]^{1/3}$.

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- [21] More precisely we use the common assumption [22]

$$\omega \ll \eta_\alpha q^2 / \rho_\alpha$$

and

$$\rho_\alpha \omega^2 \ll q^3 |g - \kappa q^2|$$

where ρ_α and η_α are the oil or water densities and viscosities respectively.

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- [23] More generally we obtain using reference [19]

$$\eta = \frac{(\rho_o + \rho_w)n_o n_w}{n_o + n_w + W(n_o - n_w)} \left\{ \frac{4\rho_o\rho_w}{(\rho_o + \rho_w)^2} + \frac{[n_o - n_w + W(n_o + n_w)]^2}{4n_o n_w} \right\}$$

where

$$W = \frac{\rho_o - \rho_w}{\rho_o + \rho_w}$$

and where ρ_α , η_α and $n_\alpha = \eta_\alpha/\rho_\alpha$ are the densities, viscosities and kinematic viscosities (of the oil or water) respectively.

- [24] Since these results can only be relevant so long as $a \ll \lambda^* \ll R$, ϕ_s cannot be too far from ϕ_c , or too close to it.
- [25] κ also becomes time-dependent since it depends on ϕ_s as well. But to the lowest order in $\phi_s - \phi_c$ we can evaluate κ at ϕ_c to make it independent of time in this approximation.
- [26] This limit now reads

$$\omega + \frac{d\omega/dt}{\omega} \ll \eta_\alpha q^2 / \rho_\alpha$$

and

$$\rho_\alpha \left(\omega^2 + \frac{d\omega}{dt} \right) \ll q^3 |g - \kappa q^2|.$$

Note that if $\omega^2 \gg d\omega/dt$ the generalization (16) always applies, but if the above conditions for neglecting inertia do not hold, $\omega(q, t)$ is not given by (9).

- [27] We note that Δ^* might be time-dependent if the initial value $\langle U_q^0 U_{-q}^0 \rangle$ is q -dependent. We are unable to determine this relation, but since it enters only as a logarithmic correction to our final results, we ignore this possible time dependence.
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- [30] An expansion of J in powers of ζ and thus corrections to the diffusion controlled regime can be obtained using equation (A.8).
- [31] Taking the next order expansion in the small parameter $\phi_s - \phi_c$ in equations (22) and (25) we obtain the correction to equation (35) for τ as $\tau \simeq \frac{\phi_c}{\nu} + (a^2/E)\eta^{2/3}\kappa^{1/3}\phi_c^{1/3}\frac{\delta}{\nu^{4/3}}$ where $\delta \propto Da^2\rho/\xi_0$. No corrections are found to equation (32) for $q^*(t)$ so that the corrections to q_m in equation (37) can be obtained by using this result for τ .
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