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Linear Shear Rheology of Incompressible Foams

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Abstract. — We discuss various mechanisms for viscous dissipation in the linear response to oscillatory shear of incompressible foams (such as biliquid foams or dense emulsions). These include viscous flow of liquid in films and plateau borders; intrinsic viscosity of the surfactant layers; and diffusion resistance. Marangoni-type and marginal regeneration mechanisms are considered for the transport of surfactant. We predict (on the basis of typical parameters for biliquid foams) that the zero shear viscosity is usually dominated by the intrinsic dilational viscosity of the surfactant monolayers, though other forms of dissipation may be important in certain systems. We give a preliminary analysis of the frequency dependent rheology arising from an interplay between these dissipation processes and elastic storage mechanisms.

1. Introduction

Foams and dense emulsions have nontrivial flow properties. They are viscoelastic solids, characterized in linear shear response by a complex modulus $G^*(\omega)$ whose real part, $G'(\omega)$ approaches a limiting value at low frequencies [1-3]. There are several theoretical models for calculating this elastic modulus $G \equiv G'(0)$, which is generally governed by the surface tension of films σ and droplet size R , scaling as $G \sim \sigma/R$ for high volume fractions of the included phase [4, 5]. At the same time, a nontrivial loss modulus, $G''(\omega) = \omega\eta(\omega)$ is observed in experiment; this is a weak function of frequency ω , and often about 10% of G' over a wide frequency band [1-3]. This suggests the presence of a spectrum of viscoelastic relaxation modes extending to very low frequencies (sometimes far below 1 Hz [3]). At even lower frequencies we expect (on general grounds) that $\eta(\omega)$ should approach a constant value $\eta(0)$, the zero shear viscosity.

Previous theoretical studies of foam rheology have mainly focussed on rigorous solution of fluid mechanical equations in several asymptotic (often nonlinear) flow regimes [5-9]. These calculations, though valuable, do not provide a clear overview of the various sources of dissipation in linear response to infinitesimal deformations. A more phenomenological approach has sometimes been taken [10, 11], in which the film is a structureless two-dimensional viscoelastic continuum.

In this work we take a microscopic approach and try to examine qualitatively various mechanisms for dissipation in foams, without exact calculation. The discussion is nonetheless quite delicate and a careful comparison is made of the different mechanisms in both dry and wet

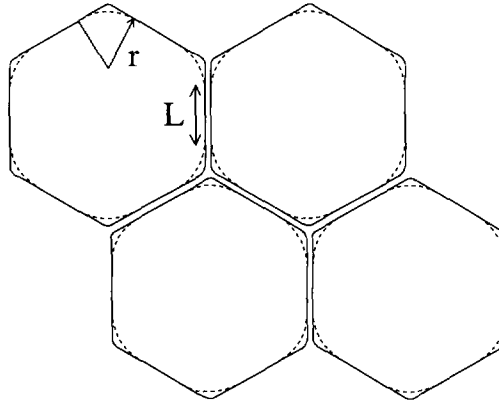


Fig 1. — Dry foam (solid line) and wet foam (dashed line).

foams. As well as estimating the resulting contributions to the viscosity $\eta = \eta(0)$, this allows us to make some qualitative remarks about frequency-dependent effects. Since we are not attempting exact solutions of specific models but use a more qualitative approach, most of our discussion will be applicable to both ordered and disordered foams. An additional mechanism which only appears in a disordered foam in the linear response regime will be discussed explicitly at the end of Section 3.2.

For simplicity we consider only incompressible foams so that we can neglect any bulk dilation effects and the rheology is primarily due to interfacial phenomena. Dense emulsions are always virtually incompressible in this sense. Gas/liquid foams can probably also be considered incompressible under shear if the Laplace pressure (i.e. difference in pressure between the two phases) is much smaller than the pressure of the included phase. We also assume the surfactant is soluble only in the continuous phase, which we will refer to for simplicity as water (and the included phase as oil). Further we assume the volume fraction of the oil phase is close to unity. We neglect fluid inertia throughout, and assume that in the linear response regime, the deformation is small enough to leave the topology of the foam unchanged. (For disordered foams, this may be dangerous; we return to this point at the end of the paper.) When numerical values are needed, we will mainly use those for small-cell biliquid foams [12-14] which have droplet radii R and film lengths L in the range $0.1\text{-}10\ \mu\text{m}$, with film thicknesses d of order $5\text{-}20\ \text{nm}$ and plateau border radii r of order $100\ \text{nm}$. The surface tension is about $10^{-2}\ \text{N m}^{-1}$ and the viscosity $10^{-3}\ \text{kg m}^{-1}\ \text{s}^{-1}$. These foams (in common with most others) are wet, but the dry foam limit ($r \simeq d$) is still of interest as a limiting case (Fig. 1).

For the wet case, more conventional foam size parameters (which we take as $R \simeq 100\ \mu\text{m}$, $r \simeq 10\ \mu\text{m}$, $d \simeq 50\ \text{nm}$) are also discussed. (For even larger cell foams inertial effects may become important.) In discussing wet foams, we assume that there is enough surfactant in the plateau borders for the system to effectively be held at constant chemical potential. The breakdown of this assumption signifies an intermediate regime between wet and dry cases.

In Section 2 we list various sources of dissipation and elasticity, defining the parameters which control their magnitudes. Some of these mechanisms also arise in problems of foam drainage, as discussed in the review of Ivanov and Dimitrov [15]. In Section 3, we consider dissipation in dry foams in which the plateau borders occupy negligible volume; in Section 4, wet foams are considered. Section 5 contains a discussion of relaxation modes and their corresponding frequencies; Section 6 is a summary of our conclusions.

2. Loss and Storage Mechanisms

2.1. FLUID VISCOSITY. — The deformation of a foam sets up flows in the fluid contained in the oil droplets, the plateau borders, and the thin films. For a bulk shear rate $\dot{\gamma}$, the oil phase of viscosity η_o will contribute a dissipation per unit volume of the foam of order

$$T\dot{s} \simeq \eta_o \dot{\gamma}^2 \quad (1)$$

since the local shear rate within a droplet is similar to that of the foam itself. (We assume the viscosity η_o does not greatly exceed that of the water phase, η_w ; recall that the droplet volume fraction is close to unity). In the borders and thin films, where the fluid has viscosity η_w , there is a local dissipation

$$T\dot{s} \simeq \eta_w (\nabla u)^2 \quad (2)$$

which must be integrated over the water region within a unit volume (large enough to contain many droplets). Here ∇u stands for the local shear gradient (recall that the fluid is incompressible), this is often much larger than the bulk average value, $\dot{\gamma}$, since the local flow tends to be amplified by geometrical factors (see Sects. 3 and 4).

2.2. DIFFUSION RESISTANCE. — An applied deformation may set up gradients in the surfactant concentration c , for example by stretching one film and compressing another. The resulting differences in chemical potential can drive a diffusive flux j which, like the flow of charge carriers through a resistor, generates dissipation. The entropy production then obeys [16]

$$T\dot{s} \simeq \frac{T}{Dc} j^2 \quad (3)$$

which must be integrated over the water volume; for an ideal solution c and D are the (monomer) concentration and diffusion constant. (For charged surfactant without salt, D should be the appropriate collective diffusivity.) In an aggregated micellar system, if the micellization/demicellization is fast to reach local equilibrium, we may identify as usual an effective diffusion constant $D = \sum_n n^2 D(n)c(n) / \sum_n n^2 c(n)$ [17, 18] where n is the aggregation number, $c(n)$ the corresponding number density, and $D(n)$ the diffusion constant of an aggregate. The diffusion of large aggregates, although slower, is less dissipative than the molecular diffusion of surfactants and this means the effective diffusion constant cannot be used directly in (3). The correct entropy production is found instead by replacing Dc in the denominator of (3) by the expression $\sum_n n^2 D(n)c(n)$. For simplicity we will normally assume parameters close to or below the critical micelle concentration so that this complication does not arise. However, even a modest micellization (say half the total material in micelles) can lead to a much decreased diffusion resistance.

Diffusive transport could cause a nontrivial relaxation spectrum at frequencies above the inverse diffusion time, $\omega_D \simeq D/\rho^2$, where ρ is the distance over which surfactant must be moved. In principle this could be as large as the droplet size R , giving (for 10 μm droplets) a relaxation frequency in the 1-10 Hz range. This would be a good candidate for the slow relaxations observed in experiment. However, we shall see in Sections 3 and 4 that this very slow process can be bypassed by a Marangoni-type effect.

2.3. INTRINSIC FILM VISCOSITIES. — A surfactant monolayer is characterized by intrinsic surface shear and dilational viscosities μ and κ ; the dissipation is (ignoring prefactors)

$$T\dot{s} \simeq \int \mu(\dot{\gamma}_s)^2 + \kappa(\nabla \cdot u)^2 \quad (4)$$

where the integral is over the monolayer surface in a unit volume, $\dot{\gamma}_s$ is the 2-D shear rate in the layer and $\nabla \cdot u$ a 2-D dilation rate (which need not vanish even if the bulk fluids are incompressible) (see for example p. 33 of [19]). There is little ambiguity about the definition of μ and experimental estimates of it ($\simeq 10^{-7}$ - 10^{-6} kg s $^{-1}$ for SDS under various conditions [20]) are presumably reliable [20-22]. The intrinsic dilational viscosity κ is harder to measure, however, and literature values are somewhat scattered ($\simeq 10^{-6}$ - 10^{-4} kg s $^{-1}$) [22, 23]. This may be because the process of dilating the film interacts nontrivially with the surfactant in the adjacent solution; for example the measured dissipation then includes part of the diffusion resistance considered separately above.

It is convenient to define an intrinsic dilational viscosity κ_N as that relating to dilation with *no exchange of surfactant* to the adjacent solution (i.e., at fixed total number N of molecules adsorbed). However, it will also prove useful to consider two further dilational viscosities. The first is κ_Σ , defined at fixed chemical potential of surfactant (i.e., fixed area per adsorbed molecule Σ), and relevant to situations of fast exchange with a bulk solvent. Any diffusion resistance is excluded, but dissipation associated with the adsorption/desorption process for surfactant in the immediate neighbourhood of the surfactant layer (presumed fast) is included in this definition.

The second, κ_B , is the dilational viscosity of a surface comprising one half of a thin bilayer. Here neither N nor Σ is fixed; instead one has a fixed composition of the bilayer as a whole, which determines a certain adsorption isotherm for the dependence of the local chemical potential on the dilation. (For very thin bilayers, κ_B should approach κ_N .) An experimental measurement of the dilational viscosity $2\kappa_B$ for a bilayer will generally include some diffusion resistance (due to transport of surfactant from the centre of the bilayer to the two surfaces); however, unless the surfactant is very insoluble this is likely to be a small contribution, since the distance involved is so short. In what follows we assume that this diffusion *across* a bilayer is rapid, and the associated dissipation negligible.

2.4. FILM ELASTICITY. — The mechanisms considered so far are purely dissipative. Mechanical energy is however stored in the films, and this is the origin of the elastic modulus $G'(\omega)$ of the foam. The free energy change δF of a piece of surface of whose area A is increased by δA obeys

$$\delta F/A = \sigma \delta A/A + \frac{1}{2}E(\delta A/A)^2 \quad (5)$$

where σ is the equilibrium surface tension and E is the Gibbs elasticity. As with κ , we can formally distinguish three values of the Gibbs elasticity. The first,

$$E_N = -\frac{\partial \sigma}{\partial \ln \Gamma} \quad (6)$$

(with $\Gamma = N/A$) is the usual definition at fixed adsorbed number which is of order 10^{-2} Nm $^{-1}$ for SDS [22, 24], whereas E_Σ is that at fixed chemical potential (i.e., for a surface in contact with a large reservoir); this vanishes identically. Finally, E_B can be defined, by analogy with κ_B , as the value pertaining to bilayer conditions; this obeys

$$E_B = -E_N \left(\frac{\partial \ln \Gamma}{\partial \ln A} \right)_B \quad (7)$$

where the subscript denotes that the composition of the bilayer is held fixed. (The result is obtained from the definition, which follows from (5), that $E_B = A(\partial^2 F/\partial A^2)_B$.) Note that E_B vanishes in the limit of a thick bilayer which acts as a perfect reservoir.

At zero frequency, per unit volume one has a stored free energy $F \simeq G\gamma^2$ where γ is the strain and $G \equiv G'(0) \simeq \sigma/R$. This arises purely from the first term in (5); the fractional area change in the system is of order γ^2 since there can be no linear term if the resting state is in equilibrium.

In a high frequency measurement, the dilation of individual regions of surfactant monolayer will vary from place to place, and hence so will the surface area per head Σ . Locally, in a step strain for example, individual films have fractional changes in area of order γ , with a signed coefficient that is orientation dependent and vanishes on average to linear order in γ ; however the modulus could be higher than $G'(0)$ due to the fact that the area increment is not optimized globally. At high frequency, when the value of surface tension varies locally, the Gibbs elasticity term in (5) can also contribute to order γ^2 . Accordingly, the stored elastic energy is higher than in equilibrium, and $G'(\omega)$ will be an increasing function of frequency.

Elastic energy can be stored also by varying the film thickness, so that work is done by or against the disjoining pressure Π between and the hydrostatic pressure within droplets (these balance in equilibrium). The corresponding modulus is of order $(d^2/R)\partial\Pi/\partial d$; it can be estimated using models for the interactions (van der Waals, Coulomb, etc.) in the films. This contribution is generally negligible for a wet foam [25]. However, for a dry foam it can be significant. Indeed, assuming that $d\partial\Pi/\partial d \simeq \Pi$, it is of order $\Pi d/R$, where the Laplace condition applied to the plateau border regions gives $\Pi \simeq \sigma/r$. For a dry foam $r \simeq d$, and so the modulus arising from film compression is of order σ/R , i.e., comparable to that from changes in film area. (It could even be larger in the extreme dry limit of $r \ll d$ which we do not consider further.)

2.5. FURTHER COMMENTS.. — In principle, of course, at very high frequencies the intrinsic film viscosities (Sect. 2.3) and Gibbs elasticity (Sect. 2.4) must merge into a single viscoelastic behaviour. However, we expect this to occur at a frequency associated with molecular relaxation within the film which should be much higher than any connected with the various other processes of interest here. Therefore we treat the Gibbs elasticity E_N , surface shear viscosity μ , and surface dilational viscosities κ_N, κ_Σ as frequency independent. The same can be done in practice for E_B and κ_B , though these involve contributions from diffusive transport between the centre and edges of a bilayer: for bilayers of 10 nm thickness, this would lead to diffusive relaxation frequencies in the high MHz range, far above those of interest in rheological experiments.

3. Dissipation in Dry Foams

If a dry foam is subjected to oscillatory shear (of infinitesimal amplitude), there is at low frequency a certain entropy production which can be calculated by imagining the strain rate to be constant. As the foam is deformed, some films are stretched and others compressed at (fractional) rates of order $\dot{\gamma}$. This process generates an intrinsic entropy production controlled by κ_B , considered in Section 3.3 below. But in addition, to prevent accumulation of the continuous phase fluid (which lies within the films) and of surfactant, there must be fluxes of each species from the regions of compression to those of stretching. The driving force for the surfactant current is differential expansion of the surfactant bilayers; its strength depends on the Gibbs elasticity E_B . The driving force for equilibration of film thickness (fluid transport) gives a comparable modulus contribution, and arises from disjoining pressure changes as discussed above. Each flux generates a certain dissipation, which we now estimate. Since we consider only linear response, when more than one mechanism is able to relax the same quantity, the physical one will be that of least dissipation [26].

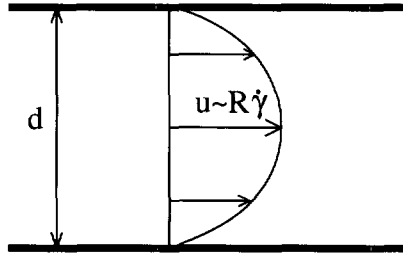


Fig. 2. — Poiseuille flow profile within a stationary bilayer (bold lines) of thickness d

3.1. FLUID TRANSPORT. — Fluid transport within the films requires local velocity gradients of order $\nabla u \sim \dot{\gamma}R/d$. This scaling follows from considering a Poiseuille-type flow within a bilayer whose surfaces are stationary (Fig. 2). In practice, the surfactant monolayers will move also at a rate that depends on the interfacial stresses, but so long as this is significantly different from the flow velocity in the bilayer midplane, the scaling of the dissipation rate per unit volume of foam is unchanged:

$$T\dot{s} \simeq \eta_w \frac{R}{d} \dot{\gamma}^2 \quad (8)$$

This is much larger than that contributed by fluid flow within the oil droplets (we assume, as stated previously, that η_o is not too large compared to η_w).

3.2. SURFACTANT TRANSPORT. — As mentioned above, Poiseuille-type flow of the fluid entrains motion of the monolayers; it also causes convection of the dissolved surfactant. Both will contribute to the surfactant current; however, this will not in general give the correct surfactant transport to maintain the steady state. Therefore a second process, with a different ratio of surfactant to fluid transport, is also required.

One possibility is the diffusive motion of surfactant through the fluid in the centre of the films. (We assume that the local equilibration between the fluid and its adjacent monolayers is fast.) To maintain a differential dilation rate of order $\dot{\gamma}$ between two neighbouring films, the local surfactant current density j within the fluid of the film (over and above that provided by the Poiseuille-type flow) obeys

$$j \simeq \frac{R}{\Sigma d} \dot{\gamma} \quad (9)$$

This arises as follows: an area A of film expands or contracts at a rate $\dot{A} \simeq \dot{\gamma}A$, resulting in a source or sink of surfactant molecules \dot{A}/Σ . (Σ is the area per molecule.) This must be balanced by a divergence term of order $Ad\nabla \cdot j$. The divergence $\nabla \cdot j$ is essentially the current gradient in the plane of the film, which is everywhere of order j/R . The resulting dissipation (see (3)) obeys

$$T\dot{s} \simeq \frac{d}{R} \frac{T}{Dc} j^2 \simeq \frac{RT}{dDc\Sigma^2} \dot{\gamma}^2 \quad (10)$$

To this must be added the intrinsic contribution from steady dilation of the monolayers comprising the film surfaces; this dilation, of order $\dot{\gamma}$ everywhere, occurs at constant composition of the local bilayer and gives a dissipation $\kappa_B \dot{\gamma}^2$ per unit area [27]. The result can be written

$$T\dot{s} \simeq \frac{R}{d} \frac{\eta_w}{\phi} \dot{\gamma}^2 + \frac{\kappa_B}{R} \quad (11)$$

where $\bar{\phi} = Dc\eta_w\Sigma^2/T$. For aggregated species $\bar{\phi}$ has no particular significance and can be large or small compared to unity. However for nonaggregated species $\bar{\phi}$ is, to within a prefactor, the volume fraction ϕ of surfactant; typically (e.g., for SDS) $\bar{\phi} \simeq 0.1\phi$. The dissipation in (10) can thus be very large at low surfactant concentrations; for example, in SDS close to but below the CMC ($\bar{\phi} \simeq 10^{-4}$) it is of order 10^4 times that from fluid transport (8). This suggests that another, less dissipative, mechanism for surfactant transport will dominate, if it exists.

Such a mechanism is provided by the motion of surfactant molecules in the monolayers themselves (as opposed to those dissolved in the water films) in response to the differences in surface concentration that arise. There are two contributions to this motion: diffusion of molecules within the monolayer, and a Marangoni process [21, 28]. Surface diffusion (with surface diffusion constant D_s as usually defined [28]) occurs without momentum transport in the monolayer; it therefore requires local backflow of fluid, which occurs in small regions (whose size is of order the hydrodynamic radius $a \simeq T/\eta_w D_s$ of a surfactant) around each molecule. This backflow leads to fluid dissipation which can also be viewed as a diffusion resistance; the entropy production is given by an expression similar to equation (3) as

$$T\dot{s} \simeq \left(\frac{E_N}{T\Gamma}\right) \frac{\eta_w a}{\Gamma R} j_s^2 \quad (12)$$

where j_s is the surface current density, and the factor $1/R$ comes from the area to volume ratio. (The factor $E_N/T\Gamma$ arises from the dependence of the chemical potential on surface concentration Γ and is unity in the ideal gas limit, $\Gamma \rightarrow 0$.) In contrast, the Marangoni effect consists of surfactant transport by convection of the adjacent fluid which moves in response to a surface tension gradient. Alternatively one can view it as a coherent motion of the surfactant monolayer in response to a concentration gradient, but now this motion entrains the neighbouring fluid and momentum balance is not local to the monolayer. (In smectic liquid crystals this would be referred to as a collective diffusion which is responsible for the peristaltic mode [29, 30].) As shown below, the corresponding entropy production is of order

$$T\dot{s} \simeq \frac{\eta_w}{\Gamma^2 R d} j_s^2 \quad (13)$$

Comparison with (12) allows us to identify a characteristic length $\lambda \simeq (T\Gamma/E_N)\Sigma/a$. For $d \geq \lambda$, the dissipation from the Marangoni process is lower, and therefore this occurs in preference to the surface diffusion. For typical dense monolayers, λ is a molecular length ($\simeq 1$ nm), so we assume from now on that surface diffusion can be neglected.

As shown in Figure 3, the Marangoni motion requires adjacent monolayers, separated by a fluid film of thickness d , to be moving in opposite directions with velocities of order $R\dot{\gamma}$. The flow pattern is too complicated to work out in detail, but typically establishes shear gradients of order $\nabla u \simeq \dot{\gamma}R/d$ in the film; the dissipation from this motion is then the same as for fluid transport. (Writing this in terms of the surface current $j_s \simeq \Gamma R\dot{\gamma}$ leads to Eq. (13) above.) There is also a dissipation from the stretching or contraction of the film surfaces as they move through the system. The total dissipation is therefore of order

$$T\dot{s} \simeq \eta_w \frac{R}{d} \dot{\gamma}^2 + \frac{\kappa_B}{R} \dot{\gamma}^2 \quad (14)$$

This mechanism is able to relax the surface coverage within any given droplet. In an ordered foam, all droplets have the same area as each other, both before and after shear, so that complete relaxation is possible. In principle, however, relaxation of a disordered foam may also require transport from one droplet to another. For soluble surfactant, the Marangoni process can combine with diffusion over very short distances (of order the bilayer thickness d) to achieve this effect at a minimal further cost in dissipation.

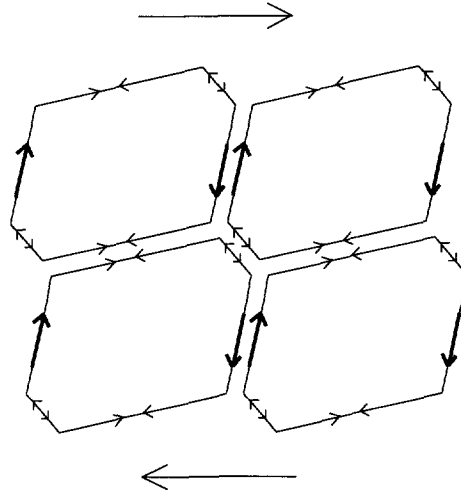


Fig. 3 — Marangoni motion in a foam under shear requires some adjacent monolayers to move in opposite directions (as indicated by the bold arrows).

3.3. VISCOSITY. — The total dissipation rate from the currents of fluid and surfactant, under low frequency shear (of infinitesimal amplitude), will be the sum of two contributions; one scaling as (8) and another which is the lesser of (11) and (14). In either case, the overall contribution to the viscosity of the foam is of order $\eta_w R/d + \kappa_B/R$. Hence for the dry foam we estimate the shear viscosity (ignoring prefactors) as

$$\eta \simeq \frac{R}{d} \eta_w + \frac{\kappa_B}{R} \quad (15)$$

This result is similar to that for the bulk dilational viscosity of a dry foam undergoing a uniform volume expansion as calculated in some detail by Edwards *et al.* (p. 363 of Ref. [19]). However, those authors neglect the second term since it is formally negligible in the limit of small d . Although definitive values of κ_B (defined for a bilayer) are not available, published estimates of dilational viscosities are of order $10^{-5} \text{ kg s}^{-1}$, which means that in practice, for a small-cell biliquid foam, the second term is typically of order $10^3 - 10^4 \eta_w$ and should dominate over the first.

4. Dissipation in Wet Foams

We now turn to the case of wet foams, which differ from the dry case in that plateau borders are present at the edges where thin films meet. These serve as reservoirs for both water and surfactant, thereby altering the dynamics of the foam (Note also that the borders form a connected, three dimensional network of pores which are wider than the thickness of the adjoining films) As mentioned in Section 1, we assume that the reservoirs are large enough for the surfactant monolayers to deform at constant chemical potential. This requires in effect that there is more surfactant dissolved in the water at the borders than is present in the monolayers. Although this will be true for macroscopic borders, there should also be an intermediate regime where $r \gg d$ (so the foam is not dry) and yet the surfactant reservoirs contain only a minority

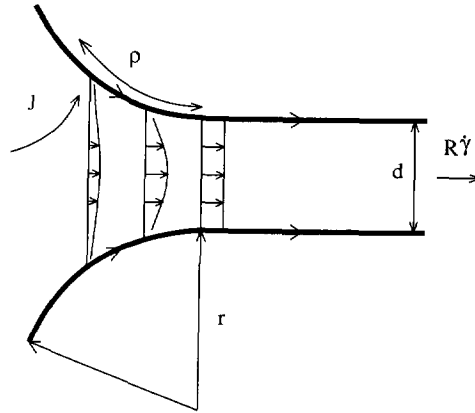


Fig. 4. — Marginal regeneration (MR) process, allowing for finite film thickness d . In this case, the plateau border is stretched. Stretching is concentrated in a region of length ρ and viscous dissipation takes place only in the “mouth” of the film. In MR, the stretched part of the monolayer acts as the sink for the surfactant flux with flux density j

of the total surfactant present. This regime will display behaviour intermediate between the dry limit, considered above, and the wet one considered here.

In principle, all the relaxation mechanisms considered previously for the dry foam are still available for the wet case. However, because of the borders, in the wet foam there are further processes which may alter the dissipation associated with surfactant and water transport. We consider these now.

4.1. MARGINAL REGENERATION. — Marginal regeneration (MR) is a process whereby fully-formed films are drawn out of the plateau border regions [31]. This process concentrates the stretching of the layers into small regions where films meet the borders (giving greater dissipation there) but reduces the viscous losses in the films [32]. In the wet case, there is no flow in the central regions of the film, but surfactant and fluid flows are set up in the connecting regions between films and borders. A detailed study of this process has been made in the case of films of negligible thickness [8], for which the dissipation has a singular dependence on the flow rate (so there is no linear response regime). To find the linear response, we must allow for the finite thickness d of the films. In this case the dissipation takes place within the borders and the “mouths” of the films, that is regions extending distances of order ρ obeying $d < \rho < r$ into the borders (Fig. 4). Films are drawn from the borders at velocities of order $R\dot{\gamma}$, and so in the mouth regions the local velocity gradients of order $R\dot{\gamma}/\rho$. The mouths have specific volumes of order $(\rho/R)^2$ so that the dissipation per unit volume of foam from fluid motion is of order

$$T\dot{s} \simeq \eta_w \gamma^2 \quad (16)$$

Note that the precise value of ρ is unimportant.

At the same time, surfactant currents are set up in the plateau borders. The material is transported from near the centre of the border to the surface in a region where a film is being drawn, and in the opposite direction at the edge of a contracting film. The details of the surfactant current density j are not clear, but assuming source and sink regions of order ρ in

size and r in separation, one finds

$$T\dot{s} \simeq \frac{T \ln(\alpha r / \rho)}{Dc\Sigma^2} \dot{\gamma}^2 \quad (17)$$

with $\ln \alpha \simeq 1$. Note that again the value of ρ is only of minor importance, since in practical terms the logarithm is of order unity. This dissipation for the MR process is reduced by a factor d/R compared to that for diffusive transport through the bilayers themselves (see (10)); it can be written to within logarithms as (compare (11))

$$T\dot{s} \simeq \frac{\eta_w}{\phi} \dot{\gamma}^2 \quad (18)$$

For micron scale biliquid foams containing SDS at or below the CMC, this process might give an effective viscosity of order $10^4 \eta_w$.

The MR process of course requires local dilation of monolayer and therefore incurs a dissipative contribution governed by the intrinsic dilational viscosity. At low frequency, the relevant value is κ_Σ , since the monolayer is in contact with a reservoir (the border). Supposing (as previously) the dilation is localized to regions of order ρ in size, the local dilation rate is of order $(R/\rho)\dot{\gamma}$ and the corresponding dissipation

$$T\dot{s} \simeq \frac{\kappa_\Sigma}{\rho} \dot{\gamma}^2 \quad (19)$$

This depends more strongly on the length scale chosen for ρ ; for small-cell biliquid foams the enhancement in dissipation over a uniform dilation process (as arises in the Marangoni mechanism, for example) could be of order 10-1000 (this assumes κ_Σ is comparable to κ_B , which is not certain). The resulting viscosity contributions are very large ($\eta/\eta_w \sim 10^5$ - 10^7).

4.2. COMPETITION WITH MARANGONI PROCESS. — For the MR process the total dissipation (from (16), (18), (19)) is

$$T\dot{s} \simeq \eta_w \dot{\gamma}^2 + \frac{\eta_w}{\phi} \dot{\gamma}^2 + \frac{\kappa_\Sigma}{\rho} \dot{\gamma}^2 \quad (20)$$

where $d \leq \rho \leq r$. Recall from (14) that the Marangoni process has in contrast

$$T\dot{s} \simeq \eta_w \frac{R}{d} \dot{\gamma}^2 + \frac{\kappa_B}{R} \dot{\gamma}^2 \quad (21)$$

[33]. In view of the large intrinsic dissipation represented by the third term in (20), we expect the Marangoni-type process to dominate the transport of surfactant for wet foams, as it did for dry ones. (However, this is subject to our rather inaccurate knowledge of the typical magnitudes of κ_Σ and κ_B .) For MR to dominate over Marangoni, one would require a relatively modest κ_Σ and a relatively high surfactant concentration and/or diffusivity (this last requirement is easily satisfied above the CMC). Also MR will be important under conditions when the sliding of one monolayer over its neighbour in a bilayer is essentially forbidden. (This process is a key component of the Marangoni mechanism.) That could arise if the water films in the bilayers are so thin as to be essentially frozen, giving a very large dissipation for sliding to replace the first term in (21).

4.3 FLUID TRANSPORT. — To maintain a uniform bilayer thickness, Poiseuille-type flow of the kind discussed in Section 3.1 is required, unless the MR mechanism is operative. (In the

case of MR, films of the equilibrium thickness are drawn directly out of the borders). This gives a dissipation, as there, of

$$T\dot{s} \simeq \eta_w \frac{R}{d} \dot{\gamma}^2 \quad (22)$$

However, there is also a need to equilibrate the volumes of the plateau borders themselves. Since the edges in the foam have order γ changes in length when a strain is applied, the border volumes are themselves perturbed linearly in strain (though with a coefficient that vanishes on the average). The resulting water flux from one border to another could flow through the films, but a less dissipative route exists; the borders form a connected network and fluid can flow from one to another directly. This gives a dissipation which can be estimated by imagining the surfactant monolayer at the border surface to have no velocity along the axis of the border, though it will still have a dilational motion as the fluid leaves or enters. This leads to an excess or depletion of surfactant on the surface, so that a diffusive current must be maintained to allow surfactant to equilibrate between the centre of the border and its surface. The result of all these processes including fluid flow, dilational viscosity, and diffusive transport of surfactant is of order

$$T\dot{s} \simeq \left(\eta_w + \frac{\kappa_{\Sigma} r}{R^2} + \frac{\eta_w r^2}{\phi R^2} \right) \dot{\gamma}^2 \quad (23)$$

where the first term is much smaller than (22), though the second could be larger for small droplets. The final term (diffusion resistance) could be large compared to the second for border radii $r \geq 1 \mu\text{m}$ in systems at or below the CMC.

4.4. VISCOSITY. — Summarising the above, we expect surfactant and water fluxes to be accommodated by a combination of Poiseuille-type flow (22), the Marangoni process (21), and the border processes (23). (The first two are essentially the same as in the dry foam considered in Sect. 3). Thus we obtain our final estimate

$$\eta \simeq \frac{R}{d} \eta_w + \frac{\kappa_B}{R} + \frac{\eta_w r^2}{\phi R^2} \quad (24)$$

where we have assumed $\kappa_B \gg \kappa_{\Sigma} r/R$. This final result differs from the case of a dry foam only by the last term, which arises from diffusion within the borders. Assuming literature estimates of κ_B [23], the second term typically dominates. The first term assumes that the bilayer films can be sheared with the viscosity of water; for black films, an appropriate sliding friction should be used instead.

The results for wet foams given above assume that MR does not take place; the effective viscosity if it does is of order

$$\eta \simeq \eta_w + \frac{\eta_w}{\phi} + \frac{\kappa_{\Sigma}}{\rho} \quad (25)$$

where the three contributions are from fluid flow, diffusion resistance and intrinsic dilation. (The contribution from the flow of fluid along border channels, discussed above, is negligible.) If this viscosity is lower than the Marangoni one, (24), the MR mechanism will dominate.

5. Mode Structure

By superposing the mechanisms described above, we can construct an informed guess for the mode structure governing the shape of $G^*(\omega)$ at higher frequencies. Formally one should write down and diagonalize a full set of equations of motion for the conserved (hydrodynamic)

variables (see for example Ref [34]); for our problem these can be chosen as the local concentrations (averaged over the film thickness) of surfactant and fluid. (The latter is equivalent to the film thickness itself.) Here we take a more heuristic approach.

5.1. MARANGONI CASE: WET FOAM. — Formally we can separate the driving forces for the surfactant and water fluxes; for a wet foam, these have very different orders of magnitude (they become similar in the dry case as discussed in Sect. 2.4). We study first systems where the Marangoni relaxation mechanism dominates over marginal regeneration.

The dissipation rate $\Delta\eta\dot{\gamma}^2$ for the Marangoni process is given by (14), and the driving force is of order $\Delta G\gamma$, where the modulus contribution $\Delta G \simeq E_B/R$ arises from the local dilation of bilayers). Hence the relaxation frequency is of order

$$\omega_M \simeq \frac{\Delta G}{\Delta\eta} \simeq \frac{E_B}{\eta_w R^2/d + \kappa_B} \quad (26)$$

which is similar to the results of reference [35, 36]. For small-cell biliquid foam parameters in the dry limit (say $d \simeq r \simeq 10$ nm, $R \simeq 10$ μ m) the characteristic frequency ω_M should be around 1 kHz. For conventional droplets ω_M could be of order 50 Hz at low surfactant concentrations (so that $E_B \simeq E_N$) which lies in the rheologically detectable range. At higher surfactant concentrations the frequency is reduced further but the mode amplitude E_B/R , and hence the low frequency loss from this mode, is also reduced to a very small fraction of $G(0)$. This contrasts with usually reported values of 5-20%, and would be swamped by other contributions.

For a wet foam with thin bilayers (so that E_B is not small), the elastic modulus arising from changes in film thickness is much weaker than that governing the Marangoni process, of order $\Delta G \simeq d\sigma/Rr \simeq G(0)d/r$ (see Sect. 2.4). Combining this with the corresponding Poiseuille-type dissipation ($\Delta\eta \simeq \eta_w R/d$) gives a characteristic time scale

$$\omega_\Pi \simeq \frac{\Delta G}{\Delta\eta} \simeq \frac{\sigma d^2}{R^2 r \eta_w} \quad (27)$$

This expression is similar to the results of [37-39] for the overdamped peristaltic mode (or “squeezing mode”) of thin films. For small-cell biliquid foams, the result is of order 100 Hz; for macroscopic foams $R \simeq 10^{-4}$ m, $r \simeq 10$ μ m, $d \simeq 50$ nm, we have instead $\omega_\Pi \simeq 1$ Hz. The slow equilibration of film thicknesses might therefore be a candidate for the low frequency loss phenomena observed in many foam systems [1, 2]. However the associated elastic modulus (mode amplitude) ΔG is typically only a percent or so of the equilibrium elastic modulus $G(0)$. The corresponding $G''(\omega)$, even assuming a single loss peak rather than the disperse band seen experimentally, could not exceed a percent or so of $G(0)$. This mode is again not a good candidate for the low frequency loss seen experimentally.

There is in addition a very weak elastic modulus of order $\Delta G \simeq G(0)r/R$ associated with the changes of volume of the plateau borders. This modulus is found by calculating the change in area of the border surfaces needed to account for the local change in border volume associated with a strain γ . It can drive a fluid flow through the network of pores made up by these borders, with a dissipation given by (23). The resulting relaxation frequency is

$$\omega_B \simeq \frac{\sigma r}{R^2 \eta_w + \kappa_\Sigma r + \eta_w r^2 / \bar{\phi}} \quad (28)$$

This relaxation frequency is likely to be in the kHz range for small cell foams. For large cell foams the frequency can be reduced, but is large compared to ω_Π .

5.2. THE DRY LIMIT. — The dry foam can be studied by taking the limit $r \simeq d$ in the treatment just outlined. In this case the driving forces E_B/R and σ/R for the modes ω_M and ω_Π are similar and the dissipations are also similar whenever $\kappa_B \leq \eta_w R^2/d$ (see (26)). In this regime the two modes may become strongly mixed [39], the relaxation frequencies will remain comparable to the expressions given above.

For the “intermediate” regime between wet and dry foams, there can be a further mode of relaxation which arises because of a shift in the concentration of surfactant in the border regions stemming from the deformation. (In intermediate foams, the concentration of surfactant in the border is shifted significantly as the total surface area is increased; see the introduction to Sect. 4). In this case, there can be a significant deficit of surfactant in one border and an excess in another, which does not match the corresponding deficit or excess of water. The driving force cannot be large (at most $E_N r/R^2$) and becomes vanishingly small in the wet limit of large borders. The border surfactant concentration could relax by diffusion (which is highly dissipative) or more efficiently by a “border Marangoni” effect in which the monolayers in the border regions move in response to the chemical potential (and hence surface tension) gradient, entraining the border fluid. This sets up surface shear gradients of order $\dot{\gamma}$ in the adjacent bilayers (giving a dissipation of order $\mu \dot{\gamma}^2/R$) and also flow dissipation in the borders obeying (23). The resulting relaxation mode has frequency typically in the kHz range or less, but with a small amplitude.

5.3. MARGINAL REGENERATION. — We now consider the case where MR dominates the relaxation (which is feasible only for a wet foam). The MR process is subject to a driving force which arises from the fact that, if film regions are held at fixed area (no MR permitted) the monolayer surfaces become nonminimal. As usual, the resulting total extra film area increases quadratically with the strain. The driving force is governed by an area change $\delta A/A \simeq R\gamma^2/r$, and gives a modulus of order σ/r [40]. The corresponding dissipation is given by (20), resulting in a relaxation frequency of order

$$\omega_{MR} \simeq \frac{\sigma/r}{\kappa_\Sigma/\rho + \eta_w/\bar{\phi} + \eta_w} \quad (29)$$

which could be around 1 kHz. In addition, the border mode, governed by (28) is still present and typically also in the kHz range.

Another characteristic relaxation frequency may be important in the MR case. This is associated with the diffusion time to get from the centre of a plateau border to the edge:

$$\omega_D \simeq D/r^2 \quad (30)$$

which is typically in the kHz range for small-cell foams but possibly much lower, of order 10 Hz, for macroscopic foams ($r \simeq 10 \mu\text{m}$). This frequency marks the onset of a spectrum of relaxations associated with diffusion over different length scales within the border, analogous to the behaviour seen in monolayers in diffusive equilibrium [41, 24]. If $\omega_{MR} \geq \omega_D$, there may be modifications to (29) arising from the enhancement of the driving force for area minimization under conditions where the border surfaces cannot maintain constant area per molecule Σ . This also means that the intrinsic dilation viscosity will be different from κ_Σ . The viscosity associated with diffusion resistance should also be reduced since some of the diffusion modes are no longer involved. In principle a similar complication will also occur for other plateau border modes, i.e. the border mode given by equation (28) and the “border Marangoni” effect for foams in the intermediate regime.

6. Discussion

We have calculated viscosities and characteristic frequencies for incompressible foams (e.g., dense emulsions, with the surfactant soluble only in the continuous water phase) for both the wet and dry foam limits. In both cases it seems likely that the zero frequency shear viscosity $\eta = G''/\omega$ is dominated by the intrinsic dilational viscosity of the film. Estimates of this for SDS give viscosities of order 10^3 - $10^4\eta_w$ for small-cell biliquid foams. However, other dissipation processes may play a significant part in determining the zero shear viscosity for systems with different parameter values than those for SDS. Experiments on more conventional (larger cell, wet) foams [1, 2] and on small cell systems [3] show a spectrum of loss modes extending to the lowest measured frequencies; this we have so far been unable to explain. Perhaps the best candidate among the mechanisms we consider is the slow equilibration of film thicknesses for large cells (only); this leads to suitably low characteristic frequencies ω_{Π} but amplitudes of the loss modulus that are too small. Similar remarks apply to the Marangoni relaxation governed by ω_M (26) in systems of small E_B . Long relaxation times and large viscosities are also possible whenever diffusion over long distances is involved. However, for typical emulsion parameters, it appears that diffusive transport over scales larger than the bilayer thickness d is generally bypassed by Marangoni-type transport, driven by surface tension gradients.

Our work complements that of earlier authors who have made asymptotic analyses of various limiting cases [5-9] or studied simplified models involving only the intrinsic rheology of structureless films [10, 11]. The true origin of low frequency loss modes in foams and dense emulsions remains obscure. The observed loss modulus is often almost frequency-independent at low frequencies [1-3]; this is also seen in some other materials such as slurries [42, 43]. According to linear response theory $G''(\omega)$ must be an odd function and therefore $G''(0)$ cannot be finite; hence this behaviour suggests extremely long relaxation times.

One possibility is that the published data is not in the true linear response region, but instead in a "quasilinear" regime (reminiscent of the above-yield response of a Bingham plastic) which might permit a constant part of $G''(\omega)$. A constant G'' means that the energy dissipated per cycle is almost independent of frequency, a phenomenon characteristic of hysteresis. A candidate for this type of response is the topological rearrangement of the foam [11]. For an ordered structure under small strain, there is no rearrangement [4, 5] and therefore this mechanism does not arise. For disordered foams, some rearrangement must occur with each cycle but it is not obvious whether this should lead to a quasilinear response. More careful experiments may be needed on a range of different systems before the situation becomes clear.

Finally, we note that some of the relaxation modes that we have predicted to arise at high frequencies (above those typically encountered in conventional rheological experiments) might be probed by other techniques, such as acoustic attenuation spectroscopy, or the new method of Mason and Weitz [44] based on dynamic light scattering.

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