Osmotic Stabilisation of Concentrated Emulsions and Foams

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Abstract

In the absence of coalescence, coarsening of emulsions (and foams) is controlled by molecular diffusion of the dispersed phase species from one emulsion droplet (or foam bubble) to another. Previous studies of dilute emulsions have shown how the osmotic pressure of a trapped species within droplets can overcome the Laplace pressure differences that drive coarsening, and “osmotically stabilise” the emulsion. Webster and Cates (Langmuir, 1998, 14, 2068 – 2079) gave rigorous criteria for osmotic stabilisation of mono- and polydisperse emulsions, in the dilute regime. We consider here whether analogous criteria exist for the osmotic stabilisation of mono- and polydisperse concentrated emulsions and foams. We argue that in such systems the pressure differences driving coarsening are small compared to the mean Laplace pressure. This is confirmed for a monodisperse 2D model, for which an exact calculation gives the pressure in bubble $i$ as $P_i = P + \Pi + P_G^i$, with $P$ the atmospheric and $\Pi$ the osmotic pressure, and $P_G^i$ a ‘geometric pressure’ that reduces to the Laplace pressure only for a spherical bubble, and depends much less strongly on bubble deformation than the Laplace pressure itself. In fact, for Princen’s 2D emulsion model, $P_G^i$ is only 5% larger in the dry limit than the dilute limit. We conclude that osmotic stabilisation of dense systems typically requires a pressure of trapped molecules in each droplet that is comparable to the Laplace pressures the same droplets would have if they were spherical, as opposed to the much larger Laplace pressures actually present in the system. We study the coarsening of foams and dense emulsions.
when there is insufficient of the trapped species present. Various rate-limiting mechanisms are considered, and their domain of applicability and associated droplet growth rates discussed. In a concentrated foam or emulsion, a finite yield threshold for droplet rearrangement among stable droplets may be enough to prevent coarsening of the remainder.

1 Introduction

Previous work [1–9] on dilute emulsions has shown that, when coarsening is solely caused by a diffusive flux of dissolved dispersed-phase molecules between droplets (Ostwald ripening [10]), coarsening may be prevented by the addition of a sufficient number of molecules that are insoluble in the continuous phase and hence trapped within droplets. The trapped molecules provide an osmotic pressure which counteracts the Laplace pressure due to surface tension [9] (which drives coarsening); resulting in ‘osmotic stabilisation’. A quantitative criterion for stability, valid even for emulsions with polydispersity in both the droplets’ sizes and number of trapped molecules they contain, was given in [9]. It was also found in [9] that for an ‘insufficiently stabilised’ emulsion (without enough trapped species to obey the required criterion), the subsequent coarsening was qualitatively unaltered from that without any of the trapped species [1,2]. The only effect was is to reduce the effective volume fraction of the coarsening droplets by an amount corresponding to the final volume of a population of small droplets that attain coexistence with the coarsened bulk phase. The latter are prevented from entirely dissolving by the trapped molecules they contain. When the effective volume fraction is reduced to zero, full stability is achieved.

In the present paper we discuss whether analogous conditions exist for the osmotic stabilisation of concentrated emulsions and foams containing trapped insoluble molecules in the dispersed phase; we again consider both the monodisperse and the polydisperse case. Previously the use of Nitrogen as a trapped species to stabilise foams has been investigated with theory [14,15], experiment [14–17], and computer simulations [18], but theoretical conditions for stability of foams with nonspherical bubbles were not found. The use of other trapped gases to inhibit dissolution (as opposed to coarsening) of spherical bubbles is addressed in [19] where the effect of condensation of the included gases is also addressed; we do not consider this here. In our work, we treat the idealised case of a fully insoluble trapped species (perfect trapping) whereas in many cases the results will be modified by residual solubility effects (considered for the dilute case in [9]). Some gases are, however, practically insoluble in water, for example C$_2$F$_6$ [20]; and in the case of emulsions, the insoluble limit is easily achieved (by using oligomeric species). For simplicity we do not consider the effects of residual solubility in the present work.
From now on we use mainly the language of foams, in which the trapped and soluble gas are treated as ideal, but the work is also applicable to dense emulsions whose droplets contain an ideal mixture of soluble and trapped molecules. The only distinction between these cases is that foams are compressible, but in fact much of the paper concerns effectively incompressible foams, in which pressure differences between bubbles are negligible compared with their mean pressures, and the total bubble volume is conserved.

The osmotic stabilisation of foams is a far more complex proposition than for dilute emulsions. In a dilute emulsion, each droplet is spherical with an internal pressure that is increased by the droplets Laplace pressure, which is directly related to the bubble’s volume through its spherical geometry, and equals $2\sigma/R_i$ for a droplet of radius $R_i$ and surface tension $\sigma$. Since nonspherical foam bubbles in contact have no simple relationship between their volume and surface area, there is no direct relationship, in a concentrated foam, between a bubble’s pressure and its volume.

A bubble $i$ with a radius of curvature $r_i$ at its Plateau borders has a Laplace pressure of $2\sigma/r_i$, and an internal pressure of $P_i = P + 2\sigma/r_i$. Given a connected domain of the liquid phase, the atmospheric pressure $P$ equals the pressure in the Plateau borders (we ignore the effects of gravity throughout). The drier the foam, the smaller the borders and the larger the Laplace pressure, so that if osmotic stabilisation of a foam or emulsion required the pressure of trapped molecules to balance the Laplace pressure (as it does in the dilute case) osmotic stabilisation would be hard to achieve. However, another relevant length scale is $R_i \equiv (3V_i/4\pi)^{1/3}$, where $V_i$ is the volume of bubble $i$. Since the curvature of adjacent bubble-bubble faces are of order $1/R_i$, the pressure differences between adjacent bubbles (which are responsible for coarsening), are of order $\sigma/R_i \ll \sigma/r_i$.

So if the osmotic stabilisation of a foam merely requires the partial pressure of trapped molecules to balance $\sigma/R_i$, then osmotic stabilisation is a reasonable proposition. We shall confirm below that this is so. The reduction in the driving force for coarsening from the level suggested by the Laplace pressure has long been recognised (see e.g., [18]) but the implications of this for stabilisation by trapped species has not previously been addressed in detail.

In what follows we first give in Section 2 some results for the dilute case (based on [9]), and then investigate what factors determine the pressure within concentrated foam bubbles. We follow the approach of Princen [21–23], and study the osmotic compression (at atmospheric pressure $P$) of previously spherical foam bubbles by an osmotic pressure $\Pi$. Section 3 discusses the disjoining pressures between bubbles, the uniformity or otherwise of the osmotic pressure $\Pi$, and the condition for mechanical equilibrium with an excess bulk gas phase created by coarsening. The increase in a bubble’s pressure above that of a bulk gas is defined by $P_i^G \equiv P_i - P - \Pi$, and we argue that typically $P_i^G \sim \sigma/R_i$. This is explicitly
confirmed in Section 4 for Princen’s monodisperse 2D model. We call $P^G_i$ the geometric pressure and identify it (rather than Laplace pressure) as the driving force for coarsening, in general. A formal condition for osmotic stabilisation is derived in Section 5 and examined for various limiting geometries. We discuss $P^G_i$ for polydisperse foams in Section 6, and consider exceptions to our estimate that $P^G_i \sim \sigma/R_i$ which might arise under certain conditions (which we argue to be uncommon). We then use the geometric pressure to further investigate the stability requirements of polydisperse foams.

The coarsening of insufficiently stabilised foams is studied in Sections 7-11, starting with a simple mean-field model in Section 8. By considering dissipation rates for the diffusive flux of gas between bubbles and for the viscous rearrangement of bubbles, we are able to predict (as a function of various parameters) the rate-limiting mechanism and the associated growth rate (Section 9). Section 10 shows that when bubble rearrangements are sufficiently rare, elastic stresses may arrest coarsening. Section 11 extends this to the case of a finite yield strain beyond which bubble rearrangements will cause the foam to flow, finding that a foam’s initial state then determines whether coarsening will still occur. We conclude in Section 12 with a brief summary and discussion of our results.

2 Dilute Foams (Spherical Bubbles)

A “dilute foam” comprises of spherical gas bubbles floating freely in a solvent. Following [9], we treat the bubbles as macroscopic objects and neglect their entropy of translation.

Firstly we consider the size (and hence composition) at which spherical bubbles, containing both soluble and trapped gas molecules, may coexist with a bulk gas phase (for example, formed by one bubble in the foam becoming macroscopic). The gas pressure $P_i$ within a spherical bubble labelled $i$ is increased above the atmospheric pressure by its Laplace pressure $2\sigma/R_i$:

$$P_i = P + \frac{2\sigma}{R_i}$$

(1)

We consider bubbles with $N^s_i$ soluble gas molecules and $N^T_i$ trapped gas molecules, and treat the gases as ideal. Then $P_i = P^s_i + P^T_i$, where $P^s_i, P^T_i$ are the partial pressures of the soluble and trapped gas molecules respectively, and for the soluble gas molecules

$$\mu^s_i = \mu^s_b + kT \ln \left( \frac{P^s_i}{P} \right)$$

(2)

where $\mu^s_b$ is the chemical potential of a bulk gas phase of soluble molecules at atmospheric pressure $P$. Using Eqs.1,2 and $P^s_i = P_i - P^T_i$, we may write $\Delta \mu_i \equiv$
\[ \mu_i - \mu_b = kT \ln \left( 1 + \frac{2\sigma / R_i - P_i^T}{P} \right) \] (3)

So that when \( P_i^T = 2\sigma / R_i \), \( \mu_i = \mu_b \) and bubbles may coexist with a bulk gas phase (at pressure \( P \)). Using the ideal gas law for the trapped species \( P_i^T V_i = N_i^T kT \), such coexistence requires

\[ \frac{2\sigma}{R_i} = \frac{N_i^T kT}{(4\pi/3)R_i^3} \] (4)

where \( V_i = (4\pi/3)R_i^3 \). This expression determines a ‘coexistence volume’, \( V_i^B \), at which the Laplace pressure and the partial pressure of trapped gas balance. Solving for \( V_i^B \) we have

\[ V_i^B = \sqrt{\frac{3}{4\pi}} \left( \frac{N_i^T kT}{2\sigma} \right)^{3/2} \] (5)

This is identical to the coexistence volume for a dilute incompressible emulsion droplet, of interfacial tension \( \sigma \), containing \( N_i^T \) molecules of a trapped species \( \mu_i = \mu_b \).

At coexistence with a bulk gas phase, \( \Delta \mu_i = 0 \) and \( P_i^s = P_b^s = P \), so from the ideal gas law the number of soluble gas molecules in bubbles is

\[ N_i^{sB} = \frac{P}{kT} V_i^B = \frac{P}{kT} \sqrt{\frac{3}{4\pi}} \left( \frac{N_i^T kT}{2\sigma} \right)^{3/2} \] (6)

Similarly in two dimensions, dilute (circular) bubbles will coexist with a bulk gas phase only if their areas \( A_i = A_i^B \), with

\[ A_i^B = \frac{1}{\pi} \left( \frac{N_i^T kT}{\sigma} \right)^2 \] (7)

They then contain \( N_i^{sB} \) soluble gas molecules with

\[ N_i^{sB} = \frac{P}{kT} \left( \frac{1}{\pi} \right) \left( \frac{N_i^T kT}{\sigma} \right)^2 \] (8)

### 3 Nondilute Foams

Now we consider “nondilute foams” in which bubbles press on one another and are distorted into nonspherical shapes [25]. Following Princen [21, 23], we consider the compression of a previously dilute foam under an osmotic pressure \( \Pi \).

In a nondilute foam a typical bubble’s interface consists of gently curved faces which contact adjacent bubbles, and highly curved regions at the Plateau borders. Although bubble faces press on one another with a disjoining pressure, this
typically results in a negligible direct contribution to the free energy \[26\]; we may assume that the disjoining forces only indirectly affects a bubble’s free energy, by distorting its shape and increasing surface area. Put differently, throughout the foam the surface tension \(\sigma\) is taken constant, independent of the volume fraction of gas present.

Following Equation \[2\] (the ideal gas law) we obtain \(\Delta \mu_i \equiv \mu^s_i - \mu^s_b\) for nondilute bubbles as \(\Delta \mu_i = kT \ln \left(\frac{P^s_i}{P^s_b}\right)\), where \(\mu^s_b\) is the chemical potential of a bulk gas of soluble molecules subject to pressure \(P^s_b\). Were such a bulk gas to arise by coarsening, \(P^s_b\) would balance both the atmospheric pressure \(P\) and the osmotic pressure \(\Pi\); defining \(\tilde{P} \equiv P + \Pi\) we require \(P^s_b = \tilde{P}\) (see figure \[1\]) \[27\]. So for nondilute foam bubbles we have

\[
\Delta \mu_i = kT \ln \left(\frac{P^s_i}{\tilde{P}}\right) \tag{9}
\]

As we compress the system with a semipermeable membrane, the previously spherical bubbles will distort in shape and the continuous phase will flow \[28\] so that the additional pressure is evenly distributed amongst bubbles. (This contrasts with granular materials for example \[29,30\].) In the simplest scenario of 2D, monodisperse foams, the bubbles are compressed into monodisperse hexagons with ‘rounded’ corners, and equal internal pressures. However, compression of a general polydisperse foam will result in bubbles deforming into various shapes; a given bubble will have a pressure which depends not only on its volume (as for spherical bubbles), but on the arrangement and pressures of all of its neighbours.

The above discussion may be clarified by noting that bubble interfaces which press on one another, do so with a radius of curvature at most of order \(1/R_i\) (where \(R_i\) is the radius of a bubble with the same volume in an uncompressed state). Hence pressure differences between bubbles are of order \(\sigma/R_i\). So if \(\Pi\) exceeds \(\sigma/R_i\) then the increase in bubbles’ pressures will (to within terms of order \(\sigma/R_i\)), be homogeneous throughout the foam \[31\]. So we define the increase in a bubble’s pressure above that of bulk gas \((P^s_b = \tilde{P} = P + \Pi)\), by

\[
P^G_i \equiv P_i - P - \Pi \tag{10}
\]

and expect \(P^G_i\) to be of order \(\sigma/R_i\). Here \(P^G_i\) reduces to the Laplace pressure of the \(i\)th dilute, uncompressed \((\Pi = 0)\), spherical 3D bubble, for which the increase in pressure above a coexisting bulk gas is \(P^G_i = P_i - P = 2\sigma/R_i\). But in a compressed state \(P^G_i\) is no longer the Laplace pressure, for the latter is \(\sigma/r_i\), with \(r_i\) the radius of curvature at a Plateau border of droplet \(i\).

Since we consider an ideal mixture of soluble and trapped gases, then Eq. \[10\] requires \(P^s_i = P + \Pi + P^G_i - P^T_i\), which substituting into Eq. \[9\] gives

\[
\Delta \mu_i = kT \ln \left(1 + \frac{P^G_i - P^T_i}{P}\right) \tag{11}
\]
Coexisting Bubbles

Figure 1: The pressure of a bulk gas $P_b^s$ is negligibly increased by interfacial tension, so $P_b^s$ will balance (and hence equal) $P + \Pi$. If the bulk gas arises by coarsening, so that one bubble grows to macroscopic size, its own trapped species contribute negligibly to the pressure.

So since a bulk gas formed by coarsening has $\Delta \mu_i = 0$, a bubble can coexist with a coarsened bulk gas phase when $P_i^G = P_i^T$.

We note $P_i^G$ as defined by Eq. [10] is generally not easy to calculate from geometric considerations. Nonetheless the origin of $P_i^G$ for a spherical bubble is geometrical, and $P_i^G$ of a nondilute foam bubble is determined by packing geometry, so we refer to $P_i^G$ as a bubble’s “geometric pressure”. To confirm the reasonableness of our arguments for the magnitude of $P_i^G$, the following section considers a 2D model for which $P_i$, $\Pi$, and $P_i^G$ are exactly calculable.

We first clarify what it means for a foam to be “incompressible”. If $P_i^G \ll P + \Pi$ then variations in a bubble’s pressure are negligible compared with its actual internal pressure. So a bubble’s gas density is approximately unaffected by its geometric pressure, and hence we may treat such bubbles as effectively incompressible. We emphasise that bubbles with $P_i^G \ll P + \Pi$ may only be treated as incompressible with respect to coarsening (which changes their geometric pressures); such systems are not incompressible under changes in $P$ or $\Pi$ (which changes their Laplace pressures as well).
4 A Simple 2D Model

We now study a monodisperse, incompressible 2-dimensional foam, at osmotic pressure $\Pi$. (In Appendix A an alternative argument confirms the results for an equivalent, but compressible model.) For $\Pi \neq 0$ monodisperse bubbles will form a hexagonal array, with bubbles distorted into approximately hexagonal shapes but with rounded corners (see figure 2). For simplicity the film thickness between adjacent bubbles is taken to be negligible. We note that an equivalent system of osmotically compressed, monodisperse cylindrical emulsion droplets was considered by Princen [21–23]. Princen’s calculation for the osmotic pressure is used later.

Since the bubbles are taken to be incompressible, the osmotic pressure $\Pi$ does work by removal of the continuous liquid phase from bubbles’ Plateau borders. Writing the area of liquid associated with each bubble as $A_{li}$ (with $A_{li}$ given as the sum of one third of the volume of liquid at each of its Plateau borders), then since we consider a monodisperse system with bubbles of area $A_i$, the osmotic pressure is given by [13, 21–23]

$$\Pi = -\sigma \left( \frac{\partial L_i}{\partial A_{li}} \right) A_i$$

(12)
where \( \mathcal{L}_i \) is the interfacial length of bubble \( i \). (We keep a separate label \( i \) for each bubble, although they are identical, for clarity later on.)

In Eq. [10] we defined \( P^G_i \equiv P_i - P - \Pi \). Since the monodisperse system considered here has hexagonal symmetry, by analogy with the Laplace pressure of a circular bubble we propose that \( P^G_i \) may be calculated by considering the increase in a bubble’s interfacial length with an isotropic expansion at fixed liquid area \( \mathcal{A}_{li} \). So for this system we postulate that

\[
P^G_i = \sigma \left( \frac{\partial \mathcal{L}_i}{\partial \mathcal{A}_i} \right)_{\mathcal{A}_{ni}}
\]  

(13)

with \( \frac{\partial \mathcal{L}_i}{\partial \mathcal{A}_i} \) calculated for an isotropic expansion, and with \( P^G_i \) the same for all bubbles (since the system is monodisperse). \( P^G_i \) will be different for different lattice arrangements, and also varies (along with bubble shape), with liquid content. Only in the absence of bubble-bubble contacts will \( P^G_i \) equal the Laplace pressure, with \( P^G_i = \sigma/R_i = \sigma/\rho_i \).

Since \( P^G_i \) is calculated at a fixed volume of liquid per gas bubble, we have fixed radius of curvature at the Plateau borders. Hence Eq. [13] gives

\[
P^G_i = \sigma \left( \frac{\partial \mathcal{L}_i}{\partial l} \right)_r \left( \frac{\partial l}{\partial \mathcal{A}_i} \right)_r
\]  

(14)

where \( l \) is the length of the flat bubble-bubble faces (all equal).

In Appendix B we obtain the exact expressions for the interfacial length, and area of a nearly hexagonal bubble as

\[
\mathcal{L}_i = 6l + 2\pi r
\]  

(15)

\[
\mathcal{A}_i = \pi r^2 + 6lr + \frac{3\sqrt{3}}{2}l^2
\]  

(16)

After differentiation and some algebra, Eqs [14], [15], and [16] give

\[
P^G_i = \frac{6\sigma}{\sqrt{36r^2 + 6\sqrt{3}(\mathcal{A}_i - \pi r^2)}}
\]  

(17)

We note that \( P^G_i \) may also be written as

\[
P^G_i = \frac{\sqrt{2\sqrt{3}\sigma}}{\sqrt{\mathcal{A}_i + \mathcal{A}_{ni}}}
\]  

(18)

where \( \mathcal{A}_{ni} = \left(2\sqrt{3} - \pi \right) r^2 \) is the area of liquid in Plateau borders, per bubble.
Princen [21, 22] calculated the osmotic pressure of monodisperse, cylindrical emulsion droplets by equating the work done by the osmotic pressure $\Pi$ with the increase in interfacial energy as droplets distort (at fixed droplet volume). For this quasi-2D geometry he obtained

$$\Pi = \frac{\sigma}{R_i} \left( \frac{\phi}{\phi_0} \right)^{1/2} \left[ \left( \frac{1 - \phi_0}{1 - \phi} \right)^{1/2} - 1 \right]$$

(19)

with $\phi$ the volume fraction of emulsion droplets, $\phi_0$ their volume fraction at first contact, and $R_i$ the corresponding radius. Princen’s [21, 22] calculation applies equally to our incompressible, monodisperse 2D foam: the area $A_i$ and volume $V_i$ of monodisperse cylindrical drops of length $\Lambda$ obey

$$A_i = L_i \Lambda, \quad V_i = A_i \Lambda.$$

Therefore $\phi_0 = (\pi R_i^2 / 2\sqrt{3} R_i^2)$ and $\phi = A_i / (A_i + A_{li})$. In the variables used in this paper we have

$$\left( \frac{\phi}{\phi_0} \right)^{1/2} = \left( \frac{2\sqrt{3}}{\pi} \right)^{1/2} \left( \frac{A_i}{A_i + A_{li}} \right)^{1/2} = \frac{\sqrt{2\sqrt{3}}}{\sqrt{A_i + A_{li}}} R_i$$

(20)

and

$$\left( \frac{\phi}{\phi_0} \right)^{1/2} \left( \frac{1 - \phi_0}{1 - \phi} \right)^{1/2} = \left( \frac{2\sqrt{3}}{A_i + A_{li}} \right)^{1/2} R_i \left( \frac{2\sqrt{3} - \pi}{2\sqrt{3}} \right)^{1/2} \left( \frac{A_i + A_{li}}{A_i} \right)^{1/2} = \frac{R_i}{r}$$

(21)

where comparison of Eq. 20 with Eq. 18 shows that $(\phi/\phi_0)^{1/2} = P_i^G R_i$. So using Eqs. 20 and 21, Eq. 19 becomes

$$\Pi = \frac{\sigma}{r} - P_i^G$$

(22)

So since $P_i = P + \sigma/r$, we have the exact result that $P_i = P + \Pi + P_i^G$, which for the system studied confirms both our physical argument for the pressure in an osmotically compressed bubble, and our hypothesis for this 2D monodisperse system that the geometric pressure should be calculated for an isotropic expansion at fixed Plateau border radius $r$ (Eq. 13).

From Eq. [17], in the dilute limit of circular bubbles ($r^2 = A_i / \pi$) $P_i^G \rightarrow \sigma \sqrt{\pi / \sqrt{A_i}}$, and in the dry limit of hexagonal bubbles $P_i^G \rightarrow \sigma \sqrt{2\sqrt{3} / \sqrt{A_i}}$. So since $\sqrt{2\sqrt{3} / \sqrt{\pi}} \approx 1.05$, we find the surprising result that $P_i^G$ (and hence $P_i$), is only weakly affected by $\Pi$. We return to this in Section 6.1.

The area $A_i^B$ at which bubbles in a hexagonal packing may coexist with a bulk gas (so that $P_i^* = P + \Pi$), obeys $P_i^G(A_i^B) = P_i^T(A_i^B)$. So using Eq. 18 and $P_i^T = N^T kT / A_i$ we obtain

$$A_i^B = A_{Hi}^B \left( 1 + \frac{\sqrt{1 + 4A_{li}/A_{Hi}^B}}{2} + \frac{\sqrt{1 + 4A_{li}/A_{Hi}^B}}{2} \right)$$

(23)
where $A_{hit}^B = (1/4\sqrt{3})(N^T kT/\sigma)^2$, is the area with which an entirely dry foam with hexagonal bubbles ($A_{hit} = 0$) may coexist with a bulk gas. We then obtain the number of soluble species at coexistence from $N^s_i = (\bar{P}/kT)A_i^B$.

5 A Condition for Stability

Having established a general definition of geometric pressure (Eq. [10]), and shown that it corresponds (in at least one special case) to an isotropic expansion at fixed liquid content, we now use conservation of the total number of gas molecules and total number of bubbles to derive a criterion to ensure the formation of a stable distribution of foam bubbles. We take the bubble size distribution to be composed of two parts, a ‘coarsening’ part of the distribution, and a ‘stable’ part consisting of bubbles which have shrunk to a stable size at which they coexist with the coarsening bubbles. For a sufficient quantity of trapped species the assumption of the bubble distribution having a coarsening part is found to be inconsistent, enabling us to derive a stability criterion for foams. These arguments have strong similarities to those in [9], but are considerably generalised.

We take $n^0_b$, $n^S_b$, and $n^C_b$ as the number densities of bubbles overall, in the stable part of the distribution, and in the coarsening part of the distribution respectively. Conservation of bubble number (no coalescence) gives

$$n^0_b = n^S_b + n^C_b \tag{24}$$

where we note that $n^S_b$ and $n^C_b$ may be time-dependent. $N^sB_i$, the number of soluble species present in bubble $i$ when coexisting with a bulk gas phase, is determined by $P^G_i = P^T_i$. However since relations between $P^G_i$ and $V_i$ may vary during coarsening (due to changes in the bubble’s environment), we take $N^sB_i$ as time-dependent. We define the following

- $\bar{N}^{s0} \equiv \langle N^s_i(t) \rangle_i$: The average number of soluble molecules per bubble. This is time independent.
- $\bar{N}^{sB}(t)$: The average number of soluble molecules per bubble in the stable distribution. As coarsening proceeds, $n^C_b/n^0_b \rightarrow 0$ and the bubbles in the stable distribution have $N^s_i \rightarrow N^sB_i$. Then $\bar{N}^{sB}(t)$ tends toward the average number of soluble molecules per bubble at coexistence with a bulk gas phase.
- $\bar{N}^{sC}(t)$: The average number of soluble molecules per bubble, within the coarsening distribution, at time $t$. 


As a coarsening foam tends towards an equilibrium state, conservation of the number of soluble molecules requires

\[ n_b^0 \tilde{N}^s = n_b^s \tilde{N}^s_b(t) + n_b^C \tilde{N}^s_C(t) \]  

(25)

Combining Eqs. 24 and 25, gives

\[ n_b^0 (\tilde{N}^s - \tilde{N}^s_b(t)) = n_b^C (\tilde{N}^s_C(t) - \tilde{N}^s_b(t)) \]  

(26)

So if

\[ \tilde{N}^s_b(t) \geq \tilde{N}^s \]  

(27)

then Eq. 26 requires \( 0 \geq n_b^C (\tilde{N}^s_C(t) - \tilde{N}^s_b(t)) \). But since the larger, coarsening bubbles have \( \tilde{N}^s_C(t) > \tilde{N}^s_b(t) \), then \( n_b^C = 0 \), and the foam must be stable against coarsening. Since \( \tilde{N}^s_b(t) \) depends on \( P_i^G(t) \), whose relation to \( V_i \) is not known, the derivation of a stability condition in closed form is not always possible, unlike the dilute case [9]. However, the above condition enables us to investigate the requirements for stability. This is done in Sections 5.1 and 5.2 below.

### 5.1 Exact Stability Conditions

For both dilute foams and the model of a monodisperse 2D foam, the geometric pressures are calculable exactly, giving exact expressions for \( N_i^s \). These are: Eq. 6; Eq. 8; and \( N_i^s_b = (\tilde{P}/kT)A_i^B \) with \( A_i^B \) given by Eq. 23 for dilute 3D foams, dilute 2D foams, and the monodisperse 2D model respectively. Stability conditions are calculated by averaging over the relevant equation for \( N_i^s \) (where appropriate), and ensuring that Eq. 27 is satisfied.

For dilute 3D foams the requirement is \( \tilde{N}^s \leq \tilde{N}^s_b \), with Eq. 3 giving

\[ \tilde{N}^s_b = \frac{P}{kT} \sqrt{\frac{3}{4\pi}} \left( \frac{kT}{2\sigma} \right)^{3/2} \langle N_i^{T^{3/2}} \rangle_i \]  

(28)

which resembles, but generalises a result in [9]. Similarly for dilute 2D foams we require \( \tilde{N}^s \leq \tilde{N}^s_b \), but with Eq. 8 giving

\[ \tilde{N}^s_b = \frac{P}{kT} \left( \frac{1}{\pi} \right) \left( \frac{kT}{\sigma} \right)^2 \langle N_i^{T^2} \rangle_i \]  

(29)

Finally, since the model of 2D foams considers monodisperse bubbles we merely require that \( N_i^s \leq N_i^s_b \), with Eq. 23 giving

\[ N_i^s_b = \frac{\tilde{P}}{kT} A_i^B = \frac{\tilde{P}}{kT} A_{Hi}^B \left( 1 + \sqrt{1 + 4A_{ii}/A_{Hi}} \right) \]  

(30)
Recall that $\mathcal{A}_B^H = (1/4\sqrt{3})(N^T kT/\sigma)^2$ so that $N_{iB}$ depends on $\sigma$ as expected. The area of liquid associated with each bubble becomes negligible compared to $\mathcal{A}_B^H$ as the foam becomes increasingly dry. Note also that the dry monodisperse hexagonal foam is, even without trapped species, already dynamically stable with respect to infinitesimal volume changes of a single cell but not with respect to geometric reorganisation so as to create five-sided and seven-sided cells. Such a foam is, however, unstable with respect to homogenous cell shrinkage throughout the system (with the excess gas forming a bulk coexisiting phase), whereas sufficient trapped species, as calculated above, will restore full thermodynamic stability in this sense. We accept that the distinction between stability and metastability becomes blurred, especially as the geometry of the foam becomes more complex.

6 Polydisperse Foams

The edges of bubbles in a reasonably dry 2D foam ($\Pi \gg \sigma/R_i$), meet with an angle approximately equal to $2\pi/3$. If the edges met with an angle of exactly $2\pi/3$, then bubbles would need to have exactly equal radii of curvature at their Plateau borders, and hence equal bubble pressures $P_i = P + \sigma/r_i$. Since the curvatures between adjacent bubbles remain of order $1/R_i \ll 1/r_i$, then as a foam becomes increasingly dry, bubbles’ pressure differences become increasingly small compared with the mean bubble pressure ($P_i \gg P_i^G \sim \sigma/R_i$). So provided a polydisperse foam is sufficiently dry, then $P_i^G \sim \sigma/R_i$ and $P_i^G \ll \Pi$.

In a sufficiently wet and polydisperse foam, very small bubbles might reside within the Plateau borders of larger bubbles without mechanically experiencing an osmotic pressure $\Pi$. Such a bubble in a 3D foam will be spherical with $P_i = P + 2\sigma/R_i$ and hence $P_i^G = 2\sigma/R_i - \Pi$. For such bubbles $P_i^G$ need not necessarily be of order $\sigma/R_i$. In fact even for the same bubble size distribution and the same osmotic pressure $\Pi$, a foam’s volume can depend on the arrangement of bubbles it contains (see figure 3). However, given a reasonable osmotic compression $\Pi$, then a reasonably narrow distribution of $N_i^T$ will be sufficient to ensure that such bubbles occupy a negligible volume fraction, and hence may be neglected when calculating the stability condition Eq. 27. This is shown in Appendix C.

6.1 Stability Requirements

To address the stability condition Eq. 27 we need to know the size at which shrunken bubbles in the stable distribution will coexist with a bulk phase of soluble gas. We will assume that for a given $\Pi$ the distribution of $N_i^T$ is sufficiently narrow that we may neglect any tiny bubbles residing wholly within Plateau
Figure 3: At a given osmotic pressure Π, the volume occupied by a weakly compressed polydisperse foam can depend on the way in which bubbles are arranged. The two foams shown both contain the same bubbles but the different bubble arrangements result in their occupying different volumes.

Borders of larger ones (see above, and Appendix 3). Then for a shrunken bubble in D dimensions of volume \( V_i \), we define a quantity \( \Gamma_i \) such that

\[
P^G_i = \Gamma_i \frac{\sigma}{V_i^{1/D}}
\]  

(31)

and expect \( \Gamma_i \sim 1 \). (Any coarsening or rearrangements will make \( \Gamma_i \) time dependent.) For example, our model 2D foam has (from Eq. 18)

\[
\Gamma_i = \sqrt{2\sqrt{3}} \sqrt{1 - \frac{A_{ii}}{A_i + A_{ii}}}
\]  

(32)

which is graphed in figure 4. In this example \( \Gamma_i \) varies monotonically between \( \sqrt{\pi} \) for an entirely dilute foam (circular bubbles), and \( 2\sqrt{3} \) for an entirely dry foam (hexagonal bubbles), but always remains of order 1.

We may calculate an approximate value for the volumes of shrunken bubbles by taking \( \Gamma_i \) as independent of \( V_i \) (although changes in a bubble’s environment mean that \( \Gamma_i \) may change with time). Using \( N_i^{sB} = (\bar{P}/kT)V_i^B \), and obtaining \( V_i^B \) by equating \( P^G_i = \Gamma_i \sigma V_i^{1/D} \) with \( P^T_i = N_i^T kT/V_i \), gives

\[
N_i^{sB} = \frac{\bar{P}}{kT} \left( \frac{N_i^T kT}{\sigma \Gamma_i} \right)^{D/(D-1)}
\]  

(33)
In Appendix D we use Eq. 33 to investigate the stability requirement Eq. 27 in more detail. By assuming that $\Gamma_i$ and $N_i^T$ are uncorrelated, it is shown that unless the average value $\bar{\Gamma}$ may increase without bound, then a stability threshold does exist. (That is, there will always be some number of trapped molecules per bubble beyond which coarsening will be prevented.) Equation 32 shows that, for a monodisperse 2D foam, $\Gamma$ is bounded above even in the dry limit (in contrast to the Laplace pressure). Also since $\langle P_i^G \rangle \sim \sigma/\bar{R}$ (see appendix A), then for $\bar{\Gamma}$ to increase without bound, $\Gamma_i$ and $R_i$ will need to be correlated in a very specific way. On balance, all these arguments suggest that $\bar{\Gamma}$ remains bounded as a polydisperse foam evolves. Hence our results suggest it should always be possible to osmotically stabilise a polydisperse foam by adding enough trapped species. As a rough estimate, stability requires a sufficient pressure of trapped gas that $\bar{P}_T \gtrsim \sigma/\bar{R}$, which for $\sigma \sim 10^{-1}$Nm$^{-1}$, and $\bar{R} \sim 10^{-5}$m requires $\bar{P}_T \sim 10^{-4}$Nm$^{-2}$, ie of order 0.1 of atmospheric pressure.

Figure 4: Variation of $\Gamma_i$ (vertical axis), from $\sqrt{\pi}$ to $\sqrt{2}\sqrt{3}$, with $X \equiv l/r$. Increasing $X$ corresponds to the bubble becoming increasingly dry, and $X \to 0$ corresponds to the bubble becoming circular in shape.
7 Coarsening of Foams: Qualitative Behaviour

Now we consider the coarsening of incompletely stabilised, non-dilute foams. Previous work on coarsening of dilute emulsions in [9] also applies to dilute foams *mutatis mutandis*. Here we concentrate on non-dilute foams in which bubbles impinge on one another and are distorted from their otherwise spherical shape.

As with dilute emulsions [9], the trapped molecules prevent bubbles from entirely disappearing. The resulting foam morphology and coarsening kinetics will be determined by two main factors. The first is the ‘excess volume fraction’ of dispersed phase, defined as the total volume fraction of gas which ultimately will coexist with a stable ensemble of shrunken bubbles, in osmotic and mechanical equilibrium with it: this is the amount of gas actually available for coarsening. The second factor is the ease with which shrunken bubbles may rearrange to allow larger bubbles to coarsen.

The excess volume fraction of disperse phase, determines a foam’s expected late-stage morphology (see figure [5]):

1. **No excess volume fraction**: The foam is stable.
2. **Very low excess volume fractions**: Larger bubbles are surrounded by a ‘sea’ of shrunken bubbles. Competitive coarsening between larger bubbles requires a gas flux *through* the sea of smaller bubbles.
3. **Very high excess volume fraction**: Larger bubbles are *decorated* by collections of smaller bubbles at their *vertices*, with their *faces* impinging on other large bubbles.
4. **Intermediate volume fractions**: Structures between the previous two extremes.

In what follows, we focus on the case of low but nonzero excess volume fraction. Here coarsening of larger bubbles will require rearrangements of the shrunken bubbles to prevent the build up of excess elastic strains (which will otherwise halt coarsening, as shown below). We envisage four scenarios:

1. **Inviscid rearrangements**: Bubble rearrangements occur easily, and with negligible dissipation of energy.
2. **Viscous rearrangements**: Bubbles can rearrange, but resist doing so and hence slow the rate of coarsening.
3. **Negligible rearrangements (elastic medium)**: Bubbles grow within an effectively elastic medium, which may eventually arrest coarsening.
4. Elasto–plastic rearrangements: There is a maximum yield strain beyond which rearrangements allow flow of the shrunken–bubble sea, but below which it behaves as an elastic medium.

We expect rearrangements to occur easily in a sufficiently wet foam, but rearrangements in a very dry foam to occur rarely or not at all. So we expect the scenarios from 1 $\rightarrow$ 3, to become more applicable as foams become increasingly dry. Since both rearrangements and diffusion of disperse phase are required for coarsening to occur, coarsening will proceed with a rate determined by the slowest process. This contrasts, for example, with phase separation in a binary fluid, where the coarsening rate is governed by the fastest process (with diffusive coarsening at early times, viscous hydrodynamic coarsening at intermediate times, and inertial hydrodynamic coarsening at late times [34]). In the present case rapid coarsening may initially be limited by viscous forces, then later as coarsening slows, viscous forces will become negligible and coarsening diffusion-limited.

Note that a similar classification of kinetic regimes may in part be applicable to the coarsening dynamics of foams containing no trapped species. It would be appealing, perhaps, to study this case in detail first, before addressing the situation where trapped species are present. However, the latter case is actually a lot simpler, at least in the case of low excess volume fractions (figure 5, left) considered here. This is because the actively coarsening bubbles are effectively decoupled by a sea of passive shrunken bubbles; this simplification is absent at excess volume fractions approaching unity (which recovers the unstabilised case).
8 Mean-Field Model: Inviscid Rearrangement

We consider a mean-field model for the coarsening of a small excess volume fraction, in which grown bubbles are already sufficiently large that they contain a negligible quantity of trapped molecules, and have an approximately spherical shape (figure 7). Hence large bubbles have $P^G_i \simeq 2\sigma/R_i$ and $P^S_i \simeq \tilde{P} + 2\sigma/R_i$. We restrict ourselves to incompressible foams (in the sense described in Section 3), and take shrunken bubbles to have an approximately constant size $V_B \equiv 4\pi R_B^3 / 3$, with $R_B \ll R_i$. An average pressure $P^s(r, t)$ of soluble gas in shrunken bubbles at distance $r$ from a grown bubble’s centre is obtained by coarse-graining over bubbles at $r$, and we assume $P^s(\infty, t)$ is the same for all grown bubbles. We at first take rearrangements to be inviscid, so that bubble growth is determined by the rate at which soluble gas diffuses through bubble-bubble interfaces in the shrunken bubble ‘sea’; this assumption is relaxed in Section 4.

Figure 6: We consider a grown bubble with $R \gg R_B$, and shrunken bubbles at a distance $r$ from its centre to have an average pressure of soluble gas $P^s(r, t)$.

Consider the flux of gas from shrunken bubbles at radius $r$ to adjacent bubbles at radius $(r + R_B)$, see figure 6. Following the approach of Von Neumann (see [35]), we take the flux of gas between two bubbles as proportional to both the pressure difference of their soluble gas, and the surface area through which the gas may pass. Defining a flux velocity per unit pressure $K$, we obtain an average volume
flux of gas from bubbles at $r$ to bubbles at $(r + R_B)$ of

$$J_V(r, t) = K 4\pi r^2 \left( P^s(r, t) - P^s(r + R_B, t) \right) \hat{r} \quad (34)$$

Since $R \gg R_B$ then $(P^s(r, t) - P^s(r + R_B, t))/R_B \simeq \partial P^s(r, t)/\partial r$, so solving for a steady state gas flux with $\nabla \cdot J = 0$, we obtain a radial flux

$$J_V(R, t) = K 4\pi R^2 R_B \frac{P^s(R) - P^s(\infty, t)}{R} \quad (35)$$

and a droplet growth rate

$$\frac{dR}{dt} = \frac{KR^2}{R} \left( \Delta P^s(\infty, t) - \frac{2\sigma}{R} \right) \quad (36)$$

where we used $P^s(R) = \tilde{P} + 2\sigma/R$, and wrote $\Delta P^s(\infty, t) = P^s(\infty, t) - \tilde{P}$. For an incompressible system all bubbles have a volume per gas molecule equal to that of a bulk gas, $v_g \equiv kT/\tilde{P}$. So with a little algebra we get

$$\frac{dR}{dt} = \frac{KR^2}{R} \left( \epsilon - \frac{2\sigma v_g}{kT R} \right) \quad (37)$$

where $\epsilon \equiv (P^s(\infty, t) - \tilde{P})/\tilde{P}$.

Previously the thickness of liquid films between bubble faces was taken as zero. Now we take such films to have a small but finite thickness $d$. Then assuming the rate of flux through liquid films to be diffusion limited, we may calculate $K$ in terms of the diffusion constant for dissolved gas molecules $D$, the volume per gas molecule $v_g$, $\tilde{P} = P + \Pi$, and $d$. This gives

$$K = \frac{Dv_g C(\infty)}{\tilde{P}d} \quad (38)$$

So the growth rate may then be written as

$$\frac{dR}{dt} = \left( \frac{R_B}{d} \right) \left( \frac{Dv_g C(\infty)}{R} \right) \left( \epsilon - \frac{2\sigma v_g}{kT R} \right) \quad (39)$$

Note that for a dilute foam the factor $R_B/d$ is absent from Eq. 39. The increase in growth rate is due to the reduced volume fraction of liquid through which gas molecules actually need diffuse, a reduction of order $d/R_B$.

9 Rate-Limiting Mechanisms

We continue to study the mean-field model of Section 8, but no longer require inviscid rearrangements. When bubble rearrangements are inviscid there is dissipation from the diffusion resistance of dissolved-molecules diffusing through liquid
films between bubbles, and if bubble rearrangements are viscous there is also dissipation as bubbles rearrange. By equating the rate of dissipation with the rate of decrease in free energy, in Sections 9.1, 9.2, and 9.3 we obtain the order of magnitude for a droplet’s growth rate. The greatest source of dissipation limits the coarsening rate, so by comparing the dissipation rates we can estimate (Section 9.3) when each type of coarsening will occur. A similar approach applied to emulsion rheology (not coarsening), is found in [26].

As an example, we firstly consider coarsening in the traditional LSW [11, 12] scenario of a vanishingly small volume fraction of bubbles in a liquid (without trapped molecules). Here dissipation is from the diffusion resistance of diffusing, dissolved gas molecules.

9.1 LSW Coarsening of Bubbles

In a steady state the radial flux of dissolved gas molecules, at a distance $r$ from the centre of a bubble of radius $R$ is

$$J(r) = \frac{4\pi R^2 \dot{R}}{r^2} \tag{40}$$

We write $J(r) = c(r)u(r)$, with $c(r)$ and $u(r)$, the concentration and average radial velocity of dissolved gas molecules at $r$ respectively. Since $c(r) \sim C(\infty)$, where $C(\infty)$ is the concentration of dissolved gas molecules adjacent to a bulk gas phase, then

$$u(r) \sim \frac{R^2 \dot{R}}{v_g C(\infty)} \frac{1}{r^2} \tag{41}$$

The number of dissolved gas molecules within spheres of radii $r$ and $r + dr$ is of order $r^2 dr c(r) \sim r^2 dr C(\infty)$. The average dissipation rate per molecule at $r$ is $\zeta u(r)^2$, where $\zeta$ is the viscous drag coefficient on a molecule of disperse phase moving through the liquid. Hence the total dissipation arising from diffusion to a drop is of order $\int_0^\infty r^2 dr C(\infty) \zeta u(r)^2$. Using the Einstein relation $\zeta = \frac{kT}{D}$, Eq. [36], $\zeta = kT/D$, and integrating, we obtain the rate of dissipation due to dissolved molecules diffusing between bubbles $T \dot{S}_D$, as

$$T \dot{S}_D \sim \frac{kT}{DC(\infty)v_g^2} \dot{R}^2 R^3 \tag{42}$$

Coarsening occurs to reduce interfacial energy, with a rate of reduction in energy of order $\sigma R \dot{R}$. So equating $\sigma R \dot{R}$ with Eq. [42] and rearranging, we get

$$\frac{dR}{dt} \sim \frac{Dv_g^2 C(\infty)\sigma}{kTR^2} \tag{43}$$
in agreement with the traditional analysis of LSW \[11,12\] for coarsening of dilute emulsion droplets (as opposed to foam bubbles as studied here).

### 9.2 Inviscid Rearrangements Revisited

We now apply the method to the mean-field model of Section 8, where inviscid rearrangements were assumed. The argument in Section 9.1 gives the average velocity with which dissolved gas molecules will diffuse through liquid films, in Eq. 39, and the dissipation per molecule in liquid films remains $\zeta u(r)^2$. But now dissipation only occurs in the liquid films between bubble faces. To integrate only over the volume of such films, the spatial volume element $r^2 dr$ is reduced by a factor of $d/R_B$. So the dissipation due to diffusion resistance $T\dot{S}_D$ is

$$T\dot{S}_D \sim \frac{d}{R_B} \frac{kT}{DC(\infty)v_g^2} \dot{R}^2 R^3$$

(44)

and we obtain

$$\frac{dR}{dt} \sim \left(\frac{R_B}{d}\right) \left(\frac{Dv_g C(\infty)}{R}\right) \left(\frac{\sigma v_g}{kT R}\right)$$

(45)

in agreement with the mean-field calculation (Eq. 39). This gives a growth law for the mean droplet size, $\bar{R} \sim t^{1/3}$.

### 9.3 Viscous Rearrangements

We now consider the rate of dissipation due to viscous stresses in the thin liquid films, as shrunken bubbles rearrange. Adjacent bubble faces are again taken to be separated by a distance $d$, determined by the disjoining pressure between bubble membranes. Since the excess volume fraction is small, we assume that bubble growth results in fluid flow that is approximately radial. Taking $v(r)$ as the velocity of the shrunken-bubble fluid, then incompressibility of that fluid requires $\nabla \cdot v = 0$, so that in the spherically symmetric case there is a radial velocity

$$v(r) = \frac{R^2 \dot{R}}{r^2}$$

(46)

at distance $r$ from the centre of a bubble of radius $R$, growing with velocity $\dot{R}$.

Consider now two adjacent shrunken bubbles at distances $r$ and $r + R_B$ respectively from the centre of the growing bubble. The differing velocities at $r$ and $r + R_B$ will mean that bubbles must rearrange, and slide past one another. For $r \gg R_B$ the relative velocity of the bubbles is of order $(\partial v(r)/\partial r) R_B$. The shear
rate of the liquid between bubbles is of the order of this relative velocity divided by the film thickness \( d \). Within the film the viscous stress is therefore

\[
\eta \dot{\gamma}(r) \sim \frac{\eta R_B \partial v(r)}{d} \partial r \quad (47)
\]

where \( \eta \) is the viscosity of the continuous liquid phase, and \( \dot{\gamma}(r) \) is the shear rate in a liquid film at \( r \).

The volume-averaged viscous dissipation is dominated by the contribution from within the films [20] and, per unit volume, is of order \( d/R_B \) times the dissipation rate (of order \( \eta \dot{\gamma}(r)^2 \)) within each film. So we obtain the total dissipation rate due to viscous bubble rearrangements, \( T \dot{S}_V \), as

\[
T \dot{S}_V \sim \int_r^\infty r^2 dr \frac{d}{R_B} \eta \left( \frac{R_B}{d} \frac{\partial v(r)}{\partial r} \right)^2 \quad (48)
\]

Using Eq. 46 and integrating, this gives

\[
T \dot{S}_V \sim \frac{R_B d \eta R}{d} \dot{R} \hat{R}^2 \quad (49)
\]

As in the previous calculations (Sections 9.1 and 9.2), the rate of decrease in the surface free energy of the growing bubble is of order \( \sigma R \dot{R} \). Equating \( \sigma R \dot{R} \) with Eq. 49, and rearranging gives

\[
\dot{R} \sim \frac{\sigma}{\eta} \frac{d}{R_B} \quad (50)
\]

and hence a linear growth law, \( \dot{R} \sim t^1 \).

It is interesting to ask why the above argument and the resulting linear growth law does not apply to the conventional LSW coarsening of dilute emulsion droplets in a structureless fluid continuum. In emulsions the volume of a molecule in a droplet is similar to that in the continuous phase, so when a dissolved molecule is incorporated into a drop, the increase in the droplet’s volume equals the volume of liquid previously displaced by the molecule. Hence the only displacement of liquid is that already accounted for by the Stokes-Einstein drag on the molecule as it diffuses through the continuous liquid phase. On the other hand, since the volume per gas molecule in a bubble is much larger than its volume when dissolved in solution, the viscous dissipation may be relevant for coarsening of dilute foam bubbles in a structureless fluid. (In this case, arrival of gas molecules at the surface of a growing bubble causes a net fluid flow radially outward.) A simple order of magnitude estimate gives

\[
T \dot{S}_V \sim \eta R \dot{R} \hat{R}^2 \quad (51)
\]

and \( \dot{R} \sim \sigma/\eta \). This differs from the case where the surrounding medium is a ‘shrunken bubble’ fluid by the absence of the enhancement factor \( R_B/d \).
9.4 Viscous or Diffusion Limited Growth?

In a coarsening dense foam, both rearrangements and diffusion are necessary for bubble growth, so the growth rate will be limited by the greatest source of dissipation. So when $T\dot{S}_D / T\dot{S}_V \gg 1$ coarsening is diffusion limited, and when $T\dot{S}_D / T\dot{S}_V \ll 1$ coarsening is limited by viscous dissipation. Here we estimate the ratio for plausible foam parameters.

Comparing Eqs. 44 and 49, we see that

$$\frac{T\dot{S}_D}{T\dot{S}_V} \sim \left(\frac{d}{R_B}\right)^2 \frac{kT}{DC(\infty)v_M^2\eta} R^2$$

(52)

In terms of a molar concentration $C_M$, the molar volume $v_Mg$ of gas in bubbles at pressure $\tilde{P}$, and the gas constant $R_G$, we have

$$\frac{T\dot{S}_D}{T\dot{S}_V} \sim \left(\frac{d}{R_B}\right)^2 \frac{R_G T}{DC_M(\infty)v_M^2\eta} R^2$$

(53)

At room temperature and atmospheric pressure we take typical values of $R_G T \sim 10^3$J, $D \sim 10^{-9}$m$^2$s$^{-1}$, $C_M(\infty) \sim 10^2$m$^{-3}$, $v_Mg \sim 10^{-2}$m$^3$, and $\eta \sim 10^{-3}$Nm$^{-2}$s$^{-1}$, (eg. for CO$_2$ gas bubbles in water [38]). Taking $R \sim 10^{-6}$m, gives

$$\frac{T\dot{S}_D}{T\dot{S}_V} \sim 10^5 \left(\frac{d}{R_B}\right)^2$$

(54)

So that for micron-sized foam bubbles, viscous dissipation will be observed for $d/R_B$ smaller than $10^{-2.5}$. Thus for sufficiently small bubbles, thin liquid films, and high liquid viscosity, viscous limited growth may be observed (giving $\tilde{R} \sim t$). However at room temperature and pressure we expect diffusion limited coarsening to be more common, and moreover this will always dominate once the radius $R$ of the coarsening droplets becomes sufficiently large. Note that for foams $v_Mg = R_G T / \tilde{P}$, so $T\dot{S}_D / T\dot{S}_V$ is proportional to $\tilde{P}^2 / kT$: at low pressures and high temperatures the prospect of observing viscous limited coarsening is increased. For example if $\tilde{P} \sim 10^3$Nm$^{-2}$ (10$^{-2}$ atmosphere) then $T\dot{S}_D / T\dot{S}_V \sim 10(d/R_B)^2$, which for $d/R_B \sim 10^{-1}$ predicts viscous limited growth.

For dilute foams $T\dot{S}_D$ and $T\dot{S}_V$ are given by Eqs. 42 and 51 respectively, so that

$$\frac{T\dot{S}_D}{T\dot{S}_V} \sim \frac{R_G T}{DC_M(\infty)v_M^2\eta} R^2$$

(55)

Hence at room temperature and pressure, taking $R_G T$, $D$, $C_M(\infty)$, $\eta$, $v_Mg$, and $R$ as above, $T\dot{S}_D / T\dot{S}_V \sim 10^5$ and coarsening will be diffusion limited [39]. Writing $v_Mg = R_G T / \tilde{P}$ we find that viscous limited growth requires $\tilde{P}^2 / R_G T \lesssim 10^2$Nm which at room temperature requires $\tilde{P} \lesssim 10^{-3}$ atmosphere.
10 Negligible Rearrangements: Elastic Medium

Suppose we no longer allow bubbles to rearrange, so that the sea of shrunken bubbles acts as an elastic medium. By estimating the increase in elastic energy as a growing bubble changes volume, we show that coarsening will halt, with the foam now ‘elastically’ (as opposed to ‘osmotically’) stabilised.

The assumption of negligible rearrangement requires detailed explanation, since in any foam (containing trapped species or otherwise) local rearrangement follows inevitable when certain conditions are reached at the junctions between adjacent cells. However, it is well known that, in the absence of coarsening, a foam can exhibit a finite macroscopic yield strain, below which there may be occasional local rearrangements but these are insufficient to allow plastic deformation of the medium as a whole [18].

Our physical picture is that the shrunken–bubble sea, which is fully stabilised against coarsening by virtue of the trapped species that it contains, can then offer elastic resistance to the growth of an isolated large bubble, even though the latter is at lower chemical potential of gas than other, less large bubbles that have coarsened elsewhere in the system.

The elastic coarsening inhibition mechanism that we advance is thus only possible because of the stability against coarsening of the shrunken–bubble sea. If the bubbles in this sea were themselves members of the coarsening population, then the rearrangement conditions at the junctions between them would be constantly met within it, and there would be an incessant rearrangement of bubbles caused by their local volume changes. Such a medium could not exhibit a yield stress in any conventional sense, and would be unable to elastically stabilise the growth of isolated large bubbles. This remark is consistent with von Neumann’s theorem, which (in two dimensions) establishes that in the absence of trapped species, coarsening can never cease for any structure other than a perfect hexagonal lattice. The theorem does not apply in the presence of trapped species [37], and so the elastic arrest mechanism considered below leads to no contradiction with it.

For definiteness we consider an initial state comprised of spherical ready-grown bubbles in an elastically unstrained sea of shrunken bubbles (see figure 5). Such a system could be formed by osmotically compressing a previously dilute, partially coarsened foam.

Consider a layer of shrunken bubbles initially at distance $r_0$ from the centre of a grown bubble of initial radius $R_0$ (see figure 7). Then growth of the larger bubble from radius $R_0$ to radius $R$ will require the given layer to move so as to leave a volume equal to the change in the larger bubble’s volume, which is $\frac{4\pi}{3}(R^3 - R_0^3)$. 


So a layer with initial inner radius $r_0$ must move so that $r_0$ is increased to $r$, with

$$r^3 - r_0^3 = R^3 - R_0^3 \quad (56)$$

Hence we obtain a bubble layer’s new position $r(r_0)$ as

$$r(r_0) = \left( r_0^3 + R^3 - R_0^3 \right)^{1/3} \quad (57)$$

In the absence of rearrangements, the linear extension $H$ of bubbles in a layer with initial inner radius $r_0$ is

$$H = \Delta u(r_0 + R_B) - \Delta u(r_0) \quad (58)$$

where $\Delta u(r)$ is the distance by which shrunken bubbles at $r$ will move (see figure 7), due to the larger bubbles growth. So using $\Delta u(r_0) = r(r_0) - r_0$, $\Delta u(r_0+R_B) = r(r_0+R_B) - (r_0 + R_B)$, and Eq. 57, we expand in terms of $R_B/r_0$, which to lowest order gives

$$H \simeq R_B \left( \frac{r_0^2}{r^2} - 1 \right) \quad (59)$$

If we again use Eq. 57, then for small strains or large distances $r_0$ from a bubble we may expand in terms of $(R^3 - R_0^3)/r_0^3$, to obtain

$$H \simeq -\frac{2}{3} R_B \left( \frac{R^3 - R_0^3}{r_0^3} \right) + O \left( \frac{R^3 - R_0^3}{r_0^3} \right)^2 \quad (60)$$
Now consider the energy of extending or contracting along one axis of a single shrunken bubble, with its length changed from $R_B$ to $R_B + H$. Restricting ourselves to small strains (or equivalently $r_0 \gg R$), we may expand the associated increase in energy $\Delta E_1(H)$ in terms of a power series in $H$,

$$\Delta E_1 = \sigma \left( \alpha_1 H + \alpha_2 H^2 + O(H^3) \right)$$

(61)

Since we consider an initial state with unstrained bubbles, equilibrium requires that both positive and negative values of $H$ will give positive $\Delta E_1$, requiring $\alpha_1 = 0$. So to lowest order $\Delta E_1 = \sigma (\alpha_2 H^2) \sim \sigma H^2$.

Initially we have of order $r_0^2 dr_0 / R_B^3$ shrunken bubbles between spheres at $r_0$ and $r_0 + dr_0$. So the change in elastic energy due to a large bubble’s growth or shrinking is

$$\Delta E \sim \int_{R_0}^{\infty} \left( \frac{r_0^2 dr_0}{R_B^3} \right) \Delta E_1$$

(62)

which upon substitution of Eq. 60, $\Delta E_1 = \sigma H^2$, and integrating gives

$$\Delta E \sim \sigma \int_{R_0}^{\infty} \frac{r_0^2 dr_0}{R_B^3} H^2 \sim \frac{\sigma}{R_B} \frac{(R^3 - R_0^3)^2}{R_0^3}$$

(63)

The asymptote of $\Delta E \sim R^6$ for $R \gg R_0$ means that in the absence of bubble rearrangements the elastic energy in the surrounding foam will ultimately prevent coarsening, and elastically stabilise the system.

### 11 Finite Yield Strain

The approximation of $\Delta E_1 \sim \sigma H^2$ is strictly only valid for large $r_0$ or sufficiently small strains. For large strains we might expect plastic rearrangements to occur.

Consider the following simple model: the shrunken bubbles may elastically support a maximum (yield) strain $y^*$, beyond which macroscopic rearrangements will occur. Then

$$y^* \sim H^* / R_B$$

(64)

with $H^*$ the plastic threshold for bubble rearrangement. In the absence of rearrangements Eq. 60 gives

$$H \sim R_B \frac{|R^3 - R_0^3|}{r_0^3}$$

(65)

so that $H^*$ implicitly defines a radius $r_0^*$ within which rearrangements occur, but beyond which the medium behaves elastically. So from Eq. 60, we may define $r_0^* \equiv (R_B / H^*) (|R^3 - R_0^3|)$, which since $H^* \sim y^* R_B$ gives

$$r_0^* \sim \frac{|R^3 - R_0^3|}{y^*}$$

(66)
For a plastic region to exist around a bubble, we require \( r_0^* > R \); Eq. 66 then requires \(|R^3 - R_0^3| > y^* R^3\).

Whether sufficient growth is possible for this threshold to be reached depends on the radius \( R' \) at which bubble growth would halt, in a purely elastic system as considered in the previous section. If the inequality \(|R^3 - R_0^3| > y^* R^3\) is not satisfied (as occurs for large enough \( y^* \)) one requires a large fluctuation, either thermally or in the initial condition, to establish a plastic zone around a droplet, allowing it to coarsen further. In that case the foam is at least metastable and in practice this may be sufficient.

To get a stability condition, we consider next the elastic energy stored around a droplet that has grown from size \( R_0 \) to size \( R \). Taking deformations within any plastic region to be of order \( H^* \), we may calculate the elastic energy as

\[
\Delta E \sim \sigma \int_{R_0}^{R} \frac{r^2 dr_0}{R^3_B} H^* + \sigma \int_{R_0}^{\infty} \frac{r^2 dr_0}{R^3_B} H(r_0)^2
\]

(67)

giving

\[
\Delta E \sim y^* \frac{\sigma}{R_B} \left( |R^3 - R_0^3| - y^* R_0^3 \right) + y^* \frac{\sigma}{R_B} \left| R^3 - R_0^3 \right|
\]

(68)

where, since \( y^* < \frac{|R^3 - R_0^3|}{R_0^3} \), both terms on the right are positive.

We now assume that a grown bubble adopts a state of mechanical equilibrium with the surrounding shrunk-bubble sea, on a timescale fast compared to any coarsening process. Then for a reversible fluctuation in bubble volume by \( dV \), the work done by the bubble’s gas equals the work done on the bubbles surrounding environment. Hence

\[
P_i dV \sim \left( P + \Pi + \frac{\partial (\sigma A)}{\partial V} + \frac{\partial (\Delta E)}{\partial V} \right) dV
\]

(69)

So differentiating Eq. 69, with \( \Delta E \) given by Eq. 63 for \(|R^3 - R_0^3| < y^* R^3\) and by Eq. 68 for \(|R^3 - R_0^3| > y^* R^3\), we get

\[
P_i \sim P + \Pi + \frac{\sigma}{R_i} + \left[ \frac{\sigma}{R_B} \left( \frac{R^3 - R_0^3}{R_0^3} \right) \right] \quad |R^3 - R_0^3| < y^* R^3
\]

\[
P_i \sim P + \Pi + \left[ \frac{\sigma}{R_B} \frac{R^3 - R_0^3}{R_0^3} \right] \quad |R^3 - R_0^3| > y^* R^3
\]

(70)

This means that any bubble that has successfully coarsened to become a bulk gas phase (whose pressure clearly cannot be infinite as \( R \to \infty \)) has overcome the plastic threshold and has a pressure \( P_b \) obeying

\[
P_b - P - \Pi \simeq y^* \frac{\sigma}{R_B}
\]

(71)

Now we are able to estimate a stability threshold for a foam that combines a finite amount of trapped species with a finite yield strain (under the simplified initial
condition we chose above, that the initial state has a dilute array of partially grown bubbles in an unstrained, shrunken-bubble sea). In this case the lowest possible free energy obtainable by coarsening is that of a bulk gas at pressure $P_b$. So unless the initial pressure $P_i$ of grown bubbles exceeds $P_b$, then the foam must be stable [10]. An initially unstrained bubble has

$$P_i - P - \Pi \simeq \frac{\sigma}{R_0} \tag{72}$$

so instability requires $P_i > P_b$, and hence

$$\frac{\sigma}{R_0} \gtrsim \frac{y^* \sigma}{R_B} \tag{73}$$

So since $R_B \ll R_0$, such a foam may only be unstable if $y^* \ll 1$. For example, considering foams formed by the osmotic compression of a dilute partially coarsened foam, then if $R_0$ is small enough that $R_0 < R_B/y^*$ then coarsening may occur, but if it has already coarsened sufficiently that $R_0 > R_B/y^*$, then after osmotic compression it will be elastically stabilised.

### 12 Conclusions

We have considered dilute foams with spherical bubbles, and nondilute foams in which bubbles are compressed by an osmotic pressure $\Pi$ (which distorts bubbles and increases their gas pressure). Prior to osmotic compression, variations in bubble pressures are of order $\sigma/R_i$, so bubbles may only support large osmotic pressures ($\Pi \gg \sigma/R_i$) by deforming and pressing on one another. Pressure differences between such osmotically compressed bubbles generally remain limited to $\sigma/R_i$ (with a possible exception in the case of extreme polydispersity in initial droplet size). If coarsening occurs, a coexisting bulk gas is created that has pressure $P_b = P + \Pi$, with $P$ the ambient atmospheric pressure. We defined the excess in a bubble’s pressure above that of such a bulk gas by $P_i^G \equiv P_i - P - \Pi$, and argued that $P_i^G \sim \sigma/R_i$. This was confirmed quantitatively and explicitly for a monodisperse 2D model of foam in Section 4, $P_i^G$, which we call the geometric pressure, provides the driving force behind coarsening in the case of a compressed foam or emulsion; in general it is very different from the Laplace pressure but reduces to it in the dilute limit. For dilute 2D and 3D systems and also for a concentrated but monodisperse 2D foam, $P_i^G$ can be found explicitly. This allows one to find rigorous conditions (Eqs. 28, 29, and 30) for their stability. More generally we have argued that for a reasonably large $\Pi$ and a reasonably narrow distribution of $N_i^T$, osmotic stabilisation should generally be possible, and typically requires $P_i^T \gtrsim \sigma/R_i$.

The morphology of an insufficiently stabilised foam (containing inadequate levels of a trapped species), is determined by the ‘excess volume fraction’ of dispersed
phase; this will form a bulk gas phase if the system is allowed to reach full equilibrium (i.e., subject only to the constraint that the trapped species stay in their designated droplets and coalescence is absent, which with trapped species present will ensure conservation of droplet number). The kinetics of coarsening will be determined either by the rate of diffusion of gas between bubbles or the rate at which shrunken bubbles rearrange, with the slowest process determining the bubble growth rate. We studied coarsening of a small excess volume fraction, finding diffusion limited growth to result in $\bar{R} \sim t^{1/3}$ (as opposed to $\bar{R} \sim t^{1/2}$ as arises in foams without trapped molecules [35]), and viscous limited growth to give $\bar{R} \sim t$.

For typical parameters we expect diffusion limited growth to be more common, with viscous limited growth more likely to be observed if the liquid viscosity is high, the temperature is high, and the pressure is low [41]. Under conditions of negligible bubble rearrangements, the buildup of elastic stresses among the sea of shrunken, stabilised bubbles will arrest coarsening of well-separated large bubbles and ‘elastically stabilise’ the entire foam. This can sometimes occur when there is a finite yield strain; whether a foam will be elastically stabilised is then determined by the foam’s initial state (and the yield strain $y^*$). Thus osmotic compression of a partially coarsened dilute foam, may halt coarsening and elastically stabilise the foam; the further the foam has coarsened initially, the more likely this is to occur.

Our work applies, substantially unchanged, to concentrated emulsions. As with nondilute foams the disjoining energy between repelling droplets in emulsions may usually be neglected [26], and the osmotic pressure of trapped molecules in droplets equals the partial pressure of trapped gas molecules in bubbles (so long as both are treated as ideal [9, 13]). Hence if we replace the volume per gas molecule $v_g = \tilde{P}/kT$ with the molecular volume of disperse phase in droplets $v_b$, and also replace $N_{iB} = (kT/\tilde{P})V_i^B$ with $N_{iB} = (1/v_b)V_i^B$, then most of the above work applies equally well to concentrated emulsions.

## A Force Balance

We adopt a similar approach to one previously used by Princen [21, 22], which will enable us to determine the order of magnitude of $P^G_i$ when bubble sizes are polydisperse. Unlike the one in the main text, this approach is equally valid for compressible and incompressible bubbles.

Consider a semipermeable membrane with a shape which follows the top surface of a line of hexagonal bubbles (see figure 8), so that bubbles remain hexagonal in shape. Then since the membrane doesn’t move, the total force on the membrane due to $\Pi + P$ must balance the total force on the membrane acting from below. Then we consider a typical bubble adjacent to the membrane (see figure 8). Such
Figure 8: Imagine a flexible semipermeable membrane initially between bubble layers, which subsequently hardens and enables you to remove bubbles above the membrane, while maintaining a pressure $\Pi$ on the bubbles below. At equilibrium the forces above and below the membrane must balance. The same thought experiment may also be applied to polydisperse bubbles.

A bubble will have a geometry as in Figure 9 but with the bubble rotated by $\pi/6$ to leave two flat edges vertical. The force acting from below the membrane is $P_i$ multiplied by the projection onto the horizontal axis of the flat bubble edges ($P_i \times 2(l\sqrt{3}/2)$), plus $P$ multiplied by the projection of the Plateau borders onto the horizontal axis ($P \times 2r$). The force acting from above the membrane is simply $P + \Pi$ multiplied by the bubble’s width $2(l\sqrt{3}/2) + 2r$. Then for the forces above and below to balance we require

$$P_i 2\frac{l\sqrt{3}}{2} + P 2r = (\Pi + P) \left(2\frac{l\sqrt{3}}{2} + 2r\right)$$

(74)

Writing $P_i = P + \sigma/r$ and rearranging, we obtain

$$\Pi = \frac{\sigma}{r} - \frac{6\sigma}{3\sqrt{3}l + 6r}$$

(75)

which writing in terms of $A$ and $A_l$ and comparing with Eq. 18 gives $\Pi = \sigma/r - P_i^G$ as before. Note that since the method may be applied to compressible systems, both $P_i$ and $P_i^G$ for the monodisperse 2D model will remain the same for both compressible and incompressible bubbles.

We now generalise the argument to a polydisperse system. The projections of the bubble faces and plateau borders onto the horizontal axis are written as $l_i^P$. 
and $l_i^P$ respectively. Then considering a suitably shaped membrane, force balance requires
\[ \langle P_i^P \rangle_i + P_i = (\Pi + P) \left( \langle l_i^P \rangle_i + \langle l_i^P \rangle_i \right) \] (76)
So writing $P_i = P + \sigma/r_i$ and restricting ourselves to fairly dry foams with $r_i \approx r_j$, then $\langle l_i^P/r_i \rangle_i \approx \langle l_i^P \rangle_i/r$ where $r \equiv \langle r_i \rangle_i$, and we can obtain
\[ \Pi \approx \frac{\sigma}{r} - \frac{\sigma}{r} \frac{\langle l_i^P \rangle_i}{\langle l_i^P \rangle_i + \langle l_i^P \rangle_i} \] (77)
Now we note that since $l_i^P \sim r$ and $l_i^P \sim R$, where $R \equiv \langle \sqrt{A}/\pi \rangle_i$, then $\Pi \sim \sigma/r - \sigma/R$ so that if $P_i^G \equiv P_i - P - \Pi$ then $\langle P_i^G \rangle \sim \sigma/R$.

In 3D the same argument but with projected areas $\langle A_i^F \rangle \sim R \times r$, and $\langle A_i^P \rangle \sim R^2$ leads to $\Pi \sim \sigma/r - \sigma/R$ which for $P_i^G = P_i - P - \Pi$ gives
\[ \langle P_i^G \rangle \sim \sigma/R \] (78)
Finally we note that in higher dimensions the equivalent argument will continue to give $\langle P_i^G \rangle \sim \sigma/R$.

## B Geometry of Monodisperse, 2D Bubbles

The area of a hexagon of side $l$ is six times the area of the equilateral triangles of which it is composed. The area of each triangle is $(l/2)h$, with $h = l \sin(\pi/3) = l\sqrt{3}/2$. Hence we obtain the area of a hexagon as $A = (3\sqrt{3}/2)l^2$. Its interfacial length is simply given by $L = 6l$.

We now describe a nearly hexagonal bubble in terms of the length of the flattened faces $l$, and the radius of curvature of the plateau border $r$ (see figure 9). Then the area $A$ of a nearly hexagonal bubble is given by the sum of six sections of a circle, each of angle $\pi/3$ and radius $r$, plus six rectangles of length $l$ and height $r$, plus the area of a hexagon of side length $l$. So
\[ A = \pi r^2 + 6lr + \frac{3\sqrt{3}}{2}l^2 \] (79)
and the surface length obeys
\[ L = 6l + 2\pi r \] (80)

## C Bubbles in Plateau Borders

What is required for states such as that in figure 3 to exist? Using $P_i^s = P + 2\sigma/R_i - P_i^F$ and the ideal gas law (for the trapped gas), the pressure of soluble
Figure 9: Nearly hexagonal foam bubble with flat edges of length $l$, and radii of curvature $r$. The perpendicular distance between two flat edges is $l\sqrt{3} + 2r$.

gas in a spherical bubble residing in a Plateau border is $P^s = P + 2\sigma/R_i - N_i^T kT/(4\pi/3)R_i^3$, which has a maximum value of $P + 4(8\pi)^{1/2}\sigma^{3/2}/9(kTN_i^T)^{1/2}$. So in a system which coarsens with $P^s \to P + \Pi$, the existence of spherical bubbles in Plateau borders requires

$$P + 4\sqrt{\frac{8\pi\sigma^3}{kTN_i^T}} \geq P + \Pi$$

(81)

Hence such bubbles will need a sufficiently small quantity of trapped species that

$$N_i^T \leq \left(\frac{8}{9}\right)^{2} \frac{2\sigma^3}{kT} \frac{1}{\Pi^2}$$

(82)

which writing $\Pi$ in terms of the Laplace pressure of a bulk gas, $\Pi = 2\sigma/r_b$, requires

$$N_i^T \leq \left(\frac{8}{9}\right)^{2} \frac{\sigma r_b^2}{2kT} \sim \frac{\sigma r_b^2}{kT}$$

(83)

We may compare $N_i^T$ with that for a typical stable (and compressed) bubble of radius $\bar{R}$, containing $\bar{N}^T$ trapped molecules. Then since $P^T(\bar{N}^T, \bar{R}) = \bar{N}^T kT/(4\pi/3)\bar{R}^3 \sim \sigma/\bar{R}$ one requires

$$\bar{N}^T \sim \frac{\sigma \bar{R}^2}{kT}$$

(84)

A spherical bubble in a Plateau border has

$$N_i^T \sim \bar{N}^T \frac{r_b^2}{\bar{R}^2}$$

(85)

Considering $\Pi$ for which $r_b/\bar{R} \sim 10^{-1}$ or smaller, then we require $N_i^T \lesssim 10^{-2} \bar{N}^T$. So for a reasonable $\Pi$ of order $\sigma/r_b$, and a reasonably narrow distribution for $N_i^T$, then there will be a negligible volume fraction of bubbles residing in Plateau borders.
D Stability Requirements

We examine the form of $\bar{N}_{i}^{sB}(t)$, the number of soluble species per bubble below which a stable foam is ensured. Noting that $\bar{N}_{i}^{sB}(t) = \langle N_{i}^{sB}(t) \rangle_i$, we write it out in full to obtain,

$$\langle N_{i}^{sB}(t) \rangle_i = \frac{\tilde{P}}{kT} \left( \frac{kT}{\sigma} \right)^{D/(D-1)} \left\langle \frac{N_{i}^{T} \Gamma_{i}^{D/(D-1)}}{\Gamma_{i}^{D/(D-1)}} \right\rangle_i$$  \hspace{1cm} (86)

We note that $D \geq 2$ so that

$$\left\langle \frac{1}{\Gamma_{i}^{D/(D-1)}} \right\rangle_i \geq \frac{1}{\langle \Gamma_{i}^{D/(D-1)} \rangle_i}$$  \hspace{1cm} (87)

We assume that $\Gamma_{i}$ and $N_{i}^{T}$ are uncorrelated, that is for a given bubble volume we assume that variations in $P_{i}^{G}$ are independent of $N_{i}^{T}$. Then using Eqs. 86 and 87, we have

$$\langle N_{i}^{sB}(t) \rangle_i \geq \frac{\tilde{P}}{kT} \left( \frac{kT}{\sigma} \right)^{D/(D-1)} \frac{\langle N_{i}^{T} \rangle_{i}^{D/(D-1)}}{\langle \Gamma_{i}^{D/(D-1)} \rangle_i}$$  \hspace{1cm} (88)

In Section A we found that $\langle P_{i}^{G} \rangle \sim \sigma/R$, which suggests $\bar{\Gamma}$ is of order a constant $\bar{\Gamma}_{C}$. Then since

$$\langle N_{i}^{sB}(t) \rangle_i \geq \frac{\tilde{P}}{kT} \left( \frac{kT}{\sigma} \right)^{D/(D-1)} \frac{\langle N_{i}^{T} \rangle_{i}^{D/(D-1)}}{\bar{\Gamma}_{C}^{D/(D-1)}}$$  \hspace{1cm} (89)

a foam formed with an initial number of soluble species $\bar{N}_{s0}$ such that

$$\frac{\tilde{P}}{kT} \left( \frac{kT}{\sigma} \right)^{D/(D-1)} \frac{\langle N_{i}^{T} \rangle_{i}^{D/(D-1)}}{\bar{\Gamma}_{C}^{D/(D-1)}} \geq \bar{N}_{s0}$$  \hspace{1cm} (90)

will be stable. Similarly if $\bar{\Gamma}$ is bounded by $\bar{\Gamma}_{\text{max}}$, then a stability condition is obtained by replacing $\bar{\Gamma}_{C}$ with $\bar{\Gamma}_{\text{max}}$ in Eq. 90. Alternately, if $\bar{\Gamma}$ is a decreasing function of time, then $\bar{\Gamma}(0) \geq \bar{\Gamma}(t)$ and hence $1/\bar{\Gamma}(t)^{D/(D-1)} \geq 1/\bar{\Gamma}(0)^{D/(D-1)}$, so provided

$$\frac{\tilde{P}}{kT} \left( \frac{kT}{\sigma} \right)^{D/(D-1)} \frac{\langle N_{i}^{T} \rangle_{i}^{D/(D-1)}}{\bar{\Gamma}(0)^{D/(D-1)}} \geq \bar{N}_{s0}$$  \hspace{1cm} (91)

then we could again guarantee a stable foam. In contrast to the above cases, if $\bar{\Gamma}$ increases without bound, then $\bar{N}_{sB}(t)$ will decrease without bound, and a stability condition will never strictly exist. The only way a stability condition can fail to exist is if $\bar{\Gamma}$ can increase in time without bound.
E Table of Notation

$A_i, A_{hi}, A^B_i, A^B_{hi}$: area of two-dimensional bubble $i$; area of surrounding liquid (within hexagonal unit cell); area at which such a bubble (containing trapped species) coexists osmotically with a bulk gas phase; the same, but for a completely dry hexagonal foam.

$C(R)$: equilibrium concentration of dissolved gas adjacent to a bubble of radius $R$.

c$(r)$: mean concentration of dissolved gas within the continuous phase at distance $r$ from the centre of a bubble.

$D$: diffusivity of dissolved gas within the continuous phase.

$D$: dimensionality of space.

d: thickness of films of continuous phase separating faces of adjacent bubbles.

$H, H^*$: local extensional or compressive strain of bubbles within a sea of shrunken bubbles; its maximum value before yielding occurs.

$J_V$: volume flux of soluble gas around coarsening bubble.

$K$: flux/pressure coefficient for gas permeation across a fluid film.

$L_i$: the perimeter length of bubble $i$ in a two-dimensional foam.

$l$: length of a flat interface between adjacent bubbles in a two-dimensional hexagonal monodisperse foam.

$N^T_i, N^s_i, N^{sB}_i$: number of trapped molecules in $i$th bubble; number of soluble molecules within $i$th bubble; the number of soluble molecules within $i$th bubble when coexisting with a bulk gas phase.

$\bar{N}^{s0}, \bar{N}^{sB}, \bar{N}^{sC}$: average number of soluble gas molecules per bubble; average number of soluble molecules per bubble within the stable (noncoarsening) population; average number of soluble molecules per bubble within the (unstable) coarsening population.

$n_b^0, n_b^s, n_b^C$: total number density of bubbles in the system; number density of shrunken bubbles; number density of coarsening bubbles.

$P$: ambient pressure at which a foam is maintained.

$\bar{P}$: defined as $\bar{P} \equiv P + \Pi$. 
$P^s_b$: partial pressure of soluble gas in a bulk gas phase created by a coarsening process, and equal to the total gas pressure in this phase.

$P_i, P^s_i, P^T_i$: gas pressure within $i$th bubble; partial pressure of soluble species within it; partial pressure of trapped species within it.

$P^G_i$: geometric pressure of $i$th bubble (see text for definition of geometric pressure).

$P_s(r, t)$: mean partial pressure of soluble gas in shrunken bubbles at radius $r$ from a growing bubble.

$R_i, \bar{R}, R_0, R(t), R', R_B$: radius of $i$th bubble; mean bubble radius; initial radius of a coarsening bubble; its radius at time $t$; radius at which its growth is arrested in absence of rearrangement; radius of a shrunken bubble at or near coexistence with a bulk gas phase.

$R_G$: the gas constant.

$r, r_0, r_0'$: radial distance of a given layer of shrunken bubbles from the centre of a growing bubble; its initial value; the latter quantity for bubbles whose local strain coincides with the yield strain of the shrunken bubble sea.

$r_i$: radius of curvature at Plateau border of $i$th bubble.

$\dot{S}_D, \dot{S}_V$: entropy production due to dissipative and viscous fluxes during coarsening.

$u(r), v(r)$: radial velocity of dissolved gas molecules at distance $r$ from the centre of a coarsening bubble; radial velocity of shrunken-bubble fluid.

$V_i, V^B_i$: volume of bubble $i$; its volume at osmotic coexistence with a bulk gas phase.

$v_g, v_{Mg}$: molecular volume of disperse phase species; its molar volume.

$y^*$: yield strain of the shrunken bubble sea.

$\alpha_1, \alpha_2$: numerical coefficients (dimensionless).

$\Delta E, \Delta E_1(H)$: change in elastic energy of shrunken bubble sea on growth of a coarsening bubble; change in energy of a single shrunken bubble due to deformation $H$.

$\Delta \mu_i$: chemical potential difference, $\mu^s_i - \mu^B_i$.

$\epsilon$: dimensionless supersaturation $(P^s(\infty, t) - \bar{P})/\bar{P}$.
\( \eta \): viscosity of continuous phase.

\( \phi, \phi_0 \): volume fraction of bubbles; its value at first contact.

\( \Gamma_i, \bar{\Gamma} \): for the \( i \)th bubble, the value of \( P_i G V_i^{1/D} \sigma \); its mean value.

\( \dot{\gamma} \): shear rate.

\( \mu_i^s, \mu_b^s \): chemical potential of soluble disperse phase in \( i \)th bubble; chemical potential of a bulk phase of the same species (at pressure \( P \)).

\( \Pi \): osmotic pressure in a foam.

\( \sigma \): surface tension of films in a foam.

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Nondilute foams resemble concentrated emulsions, which consist of incompressible emulsion droplets which are pressed together by the action of a semipermeable membrane (through which only continuous phase may pass).

Since $P_T^b$ is negligible for a bulk gas formed via coarsening, we take $P_T^b = 0$.

Assumed to be much more rapid than diffusion of gas between bubbles.

The present argument ignores highly polydisperse systems in which very small bubbles may be uncompressed ($\Pi = 0$), by residing in bubble’s Plateau borders.
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[37] von Neumann’s law gives in two dimensions the rate of change of area of the $i$th bubble as $dA_i/dt = K\sigma\pi(n_i - 6)/3$ where $n_i$ is its number of edges. With trapped species present, one has $dA_i/dt = K\sigma\pi(n_i - 6)/3 + K \sum_j (P^T_i - P^T_j)l_{ij}$ where $j$ is a neighbouring cell and $l_{ij}$ the length of the common edge. The sign of the extra term depends on the volumes of the neighbouring cells (and the number of trapped species they contain) so that static equilibrium may be reached in a system where not all cells have 6 neighbours. See [33].

[38] CRC Handbook of Chemistry and Physics, 74th edition, 1993 CRC press, inc., Ed. DL Lide.

[39] We note that molecules in dilute emulsion droplets have a much smaller value of $v_{Mg}$ than do molecules in gaseous foam–bubbles. Hence even if there is a significant discrepancy between the molecular volumes of dissolved disperse
phase and disperse phase in droplets, coarsening of dilute emulsions will be
diffusion limited.

[40] We continue to take the pressure of trapped gas in grown bubbles as negli-
gible, so that a grown bubble’s pressure is its soluble gas pressure.

[41] It is interesting that the viscous limited and diffusion limited growth laws
Eqs. [43, 50] may be predicted (up to constant prefactors), by the most naive
order of magnitude arguments for the phase ordering kinetics of binary fluids
(see [34], page 375). However such arguments do not correctly predict when
each regime will apply, this depends on the structure of the shrunken–bubble
fluid.

[42] Where the force acting is pressure multiplied by distance over which it acts,
projected onto the horizontal axis.