Self-Similar Collapse of Stationary Bulk Foams

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In bulk foams, the dependence of bubble size on time can be deduced from a hypothesis of statistical self-similarity and the scaling characteristic of the volume change rate of a foam bubble. If this rate, $\dot{v}$, scales as the mean bubble volume $\bar{v}$ to the power α, the total surface area of the foam decreases as an inverse of time to the power $1/[3(1-\alpha)]$. Coarsening of polyhedral foam scales with $\alpha = 5/6$, when molecular diffusion limits gas transport across lamellae and liquid drainage through Plateau borders limits lamella thinning. Excess liquid is released by disappearing small bubbles and flows into the lamellae and Plateau borders of growing large bubbles. If none of this liquid accumulates in the foam, coarsening is exponential and $\alpha = 1$. When resistance to mass transfer at the lamella surfaces is the rate-limiting step, polyhedral foam coarsens with $\alpha = 1/3$. Coarsening of slowly draining, spherical-bubble foam scales with $\alpha = 0$. The theory is compared with nine measurements of the total surface area of polyhedral and spherical-bubble foams pregenerated from aqueous solutions of sodium lauryl sulfate, hexadecyltrimethylammonium bromide, alpha-olefin sulfonate with alkyl chain lengths from C_{14} to C_{16}, and two shaving creams. The theory also proves that the collapse of a two-dimensional, polygonal foam is self-similar and scales with $\alpha = 1$. In all cases, our theory agrees well with experiment and numerical calculations.

Introduction

Foams are thermodynamically unstable dispersions of gas bubbles in a continuous liquid phase. The coarsening and eventual collapse of foams are a result of gas diffusion between bubbles of different sizes and are similar to the formation and growth of grains in supersaturated solid solutions. Several models have been proposed to describe the rate of foam coarsening (De Vries, 1958; Barber and Hartland, 1975; Lemlich, 1978; Nishioka et al., 1983; Monsalve and Schechter, 1984; Markworth, 1985; Mullins 1986; Marsh and Glicksman, 1988; Ronteltap et al., 1990) as well as Ostwald ripening (Lifshitz and Slyozov, 1961; Wagner, 1961; Psarev, 1968; Markworth, 1972; Hunderi et al., 1979; Voorhees and Glicksman, 1984; Mullins, 1986).

The rate of foam collapse is important, for example, in fire fighting (Ratzer, 1956; Peterson et al., 1956), oil well drilling and workovers (Hutchinson and Anderson, 1972; Rand and Kraynik, 1983), and froth flotation (Sutherland and Clark, 1955). Foam barriers might also be used to control gas migration and water coning in aquifer gas storage projects (Witherspoon et al., 1987; Persoff et al., 1990). The lifetime of a fire fighting foam must be long enough to put the fire out and prevent it from breaking out again. Preformed drilling foams are used to lift crushed rock, sand or mud, and their lifetimes are measured in hours or days. In froth flotation, the foam should be stable enough to float the desired component, but must then release it at a reasonable rate. Foam-protected gas storage would rely on emplacing a foam barrier to confine the stored gas around the injection wells. Water coning in gas-producing wells, in turn, could be decreased by placing a foam lens at the water-gas contact and decreasing the formation permeability. The latter two applications would require foams with lifetimes measured in months or more.

A full review of the extensive literature on foam stability and Ostwald ripening is impossible here; therefore, only the publications that are pertinent to this article will be summarized.

De Vries (1958) showed that (1) the total number of bubbles per unit volume of foam decreases with time as a result of gas diffusion from the smaller to the larger bubbles and (2) the bubble size distribution observed in many bulk foams can be described by an empirical *universal* function containing one adjustable parameter and proportional to average bubble surface area at the time of measurement. De Vries discovered that, when scaled by average bubble radius that itself is a function of time, the radii of foam bubbles are distributed according to a *self-similar* function which is *time-invariant*. He published this result three years before the landmark articles by Lifshitz and Slyozov (1961) and Wagner (1961). Regretably, instead of using the self-similar distribution function, De Vries used the original time-dependent bubble size distribution to show that the volume of the average foam bubble grows as the cube of time divided by the bubble surface area and average thickness of the liquid films separating the foam bubbles. Because both these parameters are unknown functions of time, De Vries's equation lacks predictive capability.

Barber and Hartland (1975) derived an expression for the collapse time of foams preformed during the initial steady-state countercurrent flow of gas and aqueous surfactant solution.

Lemlich (1978) considered the diffusion of gas between bubbles with radii $r(t)$ distributed according to an unknown function $f(r, t)$ and a bubble with average radius $\bar{r}(t)$ that neither grows nor shrinks at time t:

$$\frac{dr}{dt} = \text{const}\left[\frac{\int_0^\infty uf(u,t)du}{\int_0^\infty u^2 f(u,t)du} - \frac{1}{r}\right]. \tag{1}$$

He then numerically solved this integrodifferential equation and plotted $f(r, t)$ vs. $r/\bar{r}(0)$ for various times. Although Lemlich's approach is similar to that of Lifshitz and Slyozov (1961), he did not recognize the *self-similar* nature of the problem.

Nishioka and Ross (1981) proposed and tested a versatile, fundamental and experimentally convenient method of measuring foam stability. Their method is based on an equation of state for foam (Ross, 1969) that relates the total interfacial area of the foam to pressure, temperature and quantity of gas. Nishioka et al. (1983) then tried to fit Lemlich's model (1978) to the experimental data. They realized that the assumption of constant thickness of foam lamellae prevents a good fit of the data and devised an *ad hoc* remedy, as will be discussed later.

Monsalve and Schechter (1984) used Nishioka and Ross's (1981) experimental procedure. They also developed a full bubble population balance:

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial r}(\dot{r}f) = 0, \tag{2}$$

analogous to our Eq. 11 and considered a *special* case of:

$$\dot{r} = \psi(r), \tag{3}$$

that is, the rate of change of bubble radius, $\dot{r}$, depends on r, but not on time. As others before, Monsalve and Schechter did not recognize the self-similar nature of foam decay and resorted to an empirical fit of the experimental data:

$$\frac{A(t)}{A(0)} = k_1 \exp\left(-\frac{t}{\tau_1}\right) + k_2 \exp\left(-\frac{t}{\tau_2}\right), \tag{4}$$

where $A(t)$ is the total interfacial area of foam bubbles, and k_1, k_2, τ_1, and τ_2 are the fit parameters.

Markworth (1985) is the first author who related the self-similar solutions of Ostwald ripening *to* foam stability. [There were many others before who did the *opposite*, such as Hunderi et al. (1979), and used the collapse of foams to describe Ostwald ripening.] Unfortunately, Markworth only developed two limiting solutions: (1) evolution of a narrow size distribution of foam bubbles valid for:

$$\frac{A(0) - A(t)}{A(0)} \ll 1, \tag{5}$$

and (2) an asymptotic size distribution of foam bubbles for large times.

Marsh and Glicksman (1988) presented a statistical description of the global behavior of such geometrically complex systems as bubble flows and droplet mists that are affected strongly by interfacial phenomena. The interfaces are treated as a distribution of differential surface patches, each having two local independent principal curvatures. Statistically-averaged (mean-field) physics of the appropriate phenomena (such as diffusion-controlled bubble growth) are then formulated for the individual patches. The resulting local patch dynamics is used to predict the ensemble behavior and evolution of the dispersed system.

Ronteltap et al. (1990) introduced a model of gas diffusion in beer foams that (1) uses a power law for the dependence of the surface viscosity on the rate of change of the bubble surface area and (2) allows for multicomponent gas mixtures in the bubbles. They show that the rate of foam collapse depends on the partial pressure differences of the gases present. However, when gas composition throughout the foam is uniform, the rheological behavior of the bubble surfaces determines the collapse rate.

In his outstanding article, Mullins (1986) showed that the time dependence of particle size in normal grain growth, bubble growth, and late-stage particle coarsening can be rigorously deduced from a hypothesis of *statistical self-similarity* (SSS) and from the *scaling characteristic* of the volumetric rate of growth or dissolution of an individual grain or particle. Mullins' approach evolved from the pioneering work by Lifshitz and Slyozov (1961) and Wagner (1961).

Recently, Herdle and Aref (1992) calculated the collapse of a two-dimensional, polygonal foam. (Polyhedra in two-dimensions are polygons.) Liquid drainage and the resulting changes of lamella thickness were neglected. The authors showed several numerical results indicative of the emergence of self-similarity.

Building on Mullins' approach, this article shows that the time dependence of bubble size in bulk foam that coarsens at constant volume can be deduced from (1) the hypothesis of SSS and (2) the scaling characteristics of the rate of volume change of individual foam bubbles. The bubble population balance and its self-similar solutions are discussed in the following section. Subsequently, the scaling characteristics of bubble growth or collapse in polyhedral and spherical-bubble (*kugelschaum*) foams are determined. The present theory is then compared with experiments by Nishioka et al. (1981, 1983), Monsalve and Schechter (1984), and Durian et al.

(1991a,b). The numerical results of Herdtle and Aref (1992) are evaluated in the context of our theory.

Mean-Field Theory of Bulk Foam Decay

Manegold (1953) divided foams into two morphological classes: (1) *kugelschaum* (sphere-foam) that consists of spherical bubbles widely separated from each other; (2) *polyederschaum* (polyhedron-foam) that consists of mostly dodecahedral bubbles, separated by almost flat lamellae—thin films of surfactant solution. This is a convenient classification, because distinctly different spontaneous changes take place in each type of foam.

In *kugelschaum* there is a macroscopic outflow of liquid from the foam caused by the buoyancy of the bubbles. Initially, all of the bubbles expand as the hydrostatic pressure drops across the foam. The total interfacial area of the foam first grows with time because of the expansion, but then it declines because of gas diffusion from the smaller bubbles to the bigger ones. Often *kugelschaum* is no more than a merely initial, rapidly-passed stage in the life of *polyederschaum*; however, it can be made to persist for an appreciable time before the polyhedral foam structure emerges (cf. De Vries, 1958; Nishioka and Ross, 1981; Epstein et al., 1954).

In polyhedral foams, the macroscopic liquid outflow stops; the bubbles are in contact, changing size because of gas diffusion from the smaller to the larger ones. The total interfacial area of the foam decreases monotonically with time.

Let us assume that a closed container with volume V above the liquid level contains a large number of foam bubbles, N, with an aggregate volume V_g; the bubbles near the container surface can be neglected and the mean bubble volume is:

$$\bar{v}=\frac{V_g}{N}. \tag{6}$$

Furthermore, we assume that (a) the foam bubbles fill the entire container at all times (as the foam decays, the top portion of the container fills with a slowly growing gigantic bubble) and (b) the volume of liquid in the foam can be neglected ($V_l \ll V_g$):

$$V_g \approx V=\text{const.} \tag{7}$$

With this assumption, differentiation of Eq. 6 yields:

$$\frac{d\bar{v}}{dt}=-\bar{v}\frac{1}{N}\frac{dN}{dt}. \tag{8}$$

To obtain a formal expression for dN/dt, we specify the state of each bubble in the container by the values of two coordinates, the volume v, and the rate of volume change, $\dot{v}=dv/dt$. We may think of v and $\dot{v}$ as rectangular coordinates in a two-dimensional phase space, which is a half-plane $v \geq 0$ and $\dot{v}=(-\infty, +\infty)$ (Figure 1). A point plotted in this half-plane represents the instantaneous state of a foam bubble. We define the number density of bubbles in this phase space as:

$F(v,\dot{v},t)dvd\dot{v}$ = No. of bubbles with volumes between v and $v+dv$ and the rates of volume change between $\dot{v}$ and $\dot{v}+d\dot{v}$, present at time t (9)

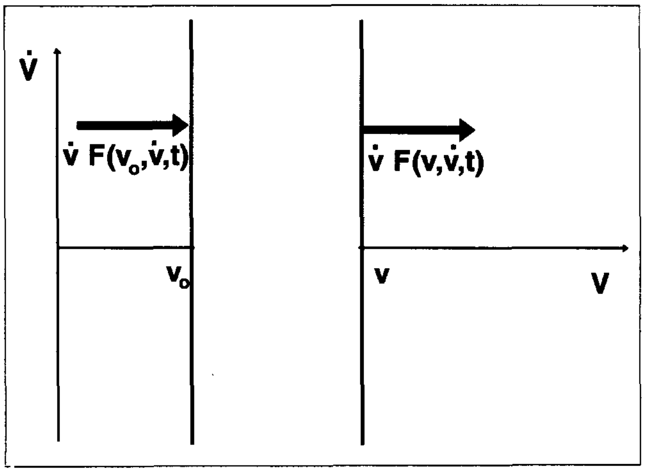

Figure 1. Two-dimensional phase-space in the collapse of bulk foam at constant volume.

The total number of foam bubbles in the container is obtained by integrating $F(v, \dot{v}, t)$ over the entire space:

$$N(t)=\int_0^{+\infty}\int_{-\infty}^{+\infty}F(v,\dot{v},t)d\dot{v}dv. \tag{10}$$

For a sufficiently large number of bubbles in the container, $F(v, \dot{v}, t)$ satisfies a mean-field continuum conservation equation (for example, Hulburt and Katz, 1964; Mullins, 1986; Patzek, 1988):

$$\frac{\partial F}{\partial t}+\frac{\partial}{\partial v}(\dot{v}F)=0, \tag{11}$$

that governs the "fluid" dynamics in the phase space. Equation 11 is a simple population balance of foam bubbles with the nucleation (bubble "birth" rate) set to zero.

The population balance equation (Eq. 11) can be integrated for bubbles with volumes between v_0 and v, and arbitrary rates of volume change (Mullins, 1986):

$$\begin{aligned}\frac{d\bar{v}}{dt}&=-\bar{v}\lim_{v_0\to 0}\int_{-\infty}^{0}\dot{v}\,\frac{F(v_0,\dot{v},t)}{N(t)}\,d\dot{v}\\&=-\bar{v}\lim_{v_0\to 0}\int_{-\infty}^{0}\dot{v}f(v_0,\dot{v},t)d\dot{v},\end{aligned} \tag{12}$$

where

$$f(v,\dot{v},t)\equiv\frac{F(v,\dot{v},t)}{N(t)}, \tag{13}$$

is the normalized probability function for v and $\dot{v}$ at time t.

If the hypothesis of SSS holds, then a distribution of relative bubble volumes scaled by $\bar{v}(t)$ is time-invariant. In other words, the evolution of bubble volumes with time is geometrically equivalent to a uniform magnification, provided that $\bar{v}$ increases by the same factor in both cases. With this hypothesis, $f(v, \dot{v}, t)$ may be written in a form that does not depend explicitly on the time, provided that both v and $\dot{v}$ are normalized with respect to scale under uniform magnification.

For a given bubble, its volume v scales as the average volume $\bar{v}$, whereas $\dot{v}$ may scale as $\bar{v}^{\alpha}$, with the constant α determined from the scaling characteristic of the rate of volume change of the bubble:

$$\dot{v} = -\int_{\partial v} \underline{j} \cdot \underline{n} dA. \tag{14}$$

Here, $\underline{j}$ is the volumetric flux of gas across surface element dA of the bubble, with the outward unit normal $\underline{n}$.

We conclude that if SSS holds for a given α, then (Mullins, 1986):

$$f(v,\dot{v},t) = f\left\{\frac{\bar{v}(t_0)}{\bar{v}(t)} v, \left[\frac{\bar{v}(t_0)}{\bar{v}(t)}\right]^{\alpha} \dot{v}, t_0\right\}$$

$$= \tilde{f}(x,y)[\bar{v}(t)]^{-(1+\alpha)}, \tag{15}$$

where

$$x \equiv \frac{v}{\bar{v}(t)} \quad \text{and} \quad y \equiv \frac{\dot{v}}{\bar{v}^{\alpha}(t)}, \tag{16}$$

and the factor $[\bar{v}(t)]^{-(1+\alpha)}$ is necessary to normalize the time-invariant bubble number density function, $\tilde{f}$, so that:

$$\int_0^{+\infty}\int_{-\infty}^{+\infty} f d\dot{v} dv = \int_0^{+\infty}\int_{-\infty}^{+\infty} \tilde{f} dy dx = 1. \tag{17}$$

The meaning of Eq. 15 may become clearer when we note that $\bar{v}(t_0 = 0)$ always can be set to 1. Then, the lapse of time from 0 to t has exactly the same effect on the distribution of bubble sizes as the rescaling of v and $\dot{v}$ by $\bar{v}(t)$ and $\bar{v}^{\alpha}(t)$, respectively.

Substituting Eqs. 15-16 into Eq. 12, we obtain:

$$\frac{d\bar{v}}{dt} = C\bar{v}^{\alpha}, \tag{18}$$

where

$$C \equiv -\lim_{x \to 0} \int_{-\infty}^{0} \tilde{f}(x,y) y dy \geq 0, \quad \text{since } \tilde{f}(x,y) \geq 0, \tag{19}$$

is the cumulative collapse rate of vanishingly small bubbles that in turn determines the rate of growth of an average foam bubble: (i) it is a constant because at all times the distribution of bubble sizes remains self-similar and (ii) for long-lasting foams the distribution of $f\dot{v}$ or $\tilde{f}y$ shifts toward zero and so does the magnitude of C. The inverse C is, therefore, an *intrinsic measure of foam durability* that uniquely characterizes a given gas-surfactant solution system: it tends to zero for fast-collapsing foams and to infinity for long-lasting ones.

Integration of Eq. 18 yields the equation of bubble growth:

$$[\bar{v}(t)]^{1-\alpha} - [\bar{v}(0)]^{1-\alpha} = (1-\alpha)Ct, \quad \alpha \neq 1,$$

$$\bar{v}(t) = \bar{v}(0)e^{Ct}, \quad \alpha = 1. \tag{20}$$

Now, let us introduce a linear measure, $\bar{r}$, proportional to $\bar{v}^{1/3}$, and hence to the bubble radius. If SSS holds, then $b = \bar{r}/\bar{v}^{1/3}$ is also independent of time and Eq. 20 may be transformed into:

$$[\bar{r}(t)]^{3(1-\alpha)} - [\bar{r}(0)]^{3(1-\alpha)} = (1-\alpha)Cb^{3(1-\alpha)}t, \quad \alpha \neq 1,$$

$$\bar{r}(t) = \bar{r}(0)e^{Ct/3}, \quad \alpha = 1. \tag{21}$$

The relative interfacial area of foam is:

$$\frac{A(t)}{A(0)} = \frac{N(t)\bar{r}^2(t)}{N(0)\bar{r}^2(0)}. \tag{22}$$

From Eqs. 7 and 22 it follows that:

$$N(t) = \frac{V}{\bar{v}} \propto \frac{V}{\bar{r}^3(t)}, \tag{23}$$

and

$$\frac{A(t)}{A(0)} = \frac{\bar{r}(0)}{\bar{r}(t)} = \frac{1}{(1+Dt)^{1/3(1-\alpha)}},$$

$$D \equiv (1-\alpha)C\left[\frac{1}{\bar{v}(0)}\right]^{1-\alpha}, \quad \alpha \neq 1,$$

$$\frac{A(t)}{A(0)} = e^{-Ct/3}, \quad \alpha = 1. \tag{24}$$

We will use Eqs. 24 to interpret the experimental collapse rates of bulk foams. Note that the characteristic time scale $1/D$ in the first Eq. 24 depends not only on the intrinsic foam-surfactant solution time scale $1/C$, cf. Eq. 19, but also on the initial average bubble size, $\bar{v}(0)$. The latter dependence makes it impossible to separate the initial experimental conditions from the intrinsic properties of the foam. This difficulty was first recognized by Monsalve and Schechter (1984) and further discussed by Markworth (1985). By contrast, the second Eq. 24 depends only on the intrinsic foam time scale $1/C$.

Scaling of Bubble Growth Rate

The scaling characteristics of bubble growth or collapse in polyhedral foams are derived in this section and those of spherical-bubble (*kugelschaum*) foams in the following one.

Polyhedral foam

To scale the decay of the polyhedral foam, Eq. 24, one only needs to consider (cf. Mullins, 1986) the rate of growth or collapse of an individual bubble, that is, the volumetric flux $j_n = \underline{j} \cdot \underline{n}$ across the bubble surface in Eq. 14. In the transport

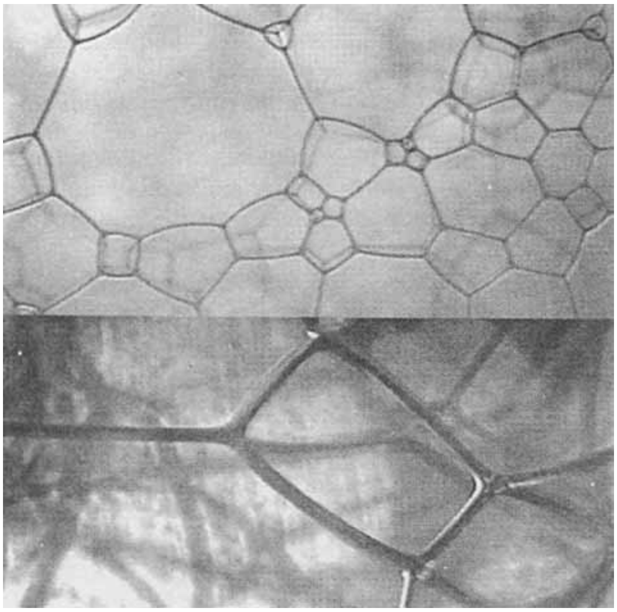

Figure 2. Polyhedral bulk foam (top); plateau borders of dodecahydral bubbles which form a three-dimensional network thus draining liquid due to gravity (bottom).

Most bubbles must either disappear or rearrange their positions, because their shapes are not dodecahydral. Lamellae curve toward bigger bubbles, indicating pressure-driven gas diffusion.

of gas across a flat lamella of uniform thickness, we assume that:

$$j_n = \lambda \Delta p, \qquad (25)$$

where λ is the gas mobility and Δp is the thermodynamic driving force, here a difference of gas pressure across the lamella (Figure 2).

Mass transport across the flat, thin and uniform lamellae can be rate-limited by either of the two processes: (1) *gas diffusion* across the lamella or (2) *mass transfer* (dissolution and evaporation) at the lamella surfaces.

Rate-Limiting Diffusion. In diffusion-limited case, the molar flux of gas across the lamella is:

$$j_n^* = -\mathfrak{D}\frac{\partial c}{\partial x} = \mathfrak{D}\frac{c_2^{eq} - c_1^{eq}}{h} = \mathfrak{D}\frac{(p_2 - p_1)/H}{h} = \frac{\mathfrak{D}}{Hh}\Delta p. \qquad (26)$$

Here, $\mathfrak{D}$ is diffusivity and c concentration of the gas in the surfactant solution; $c_i^{eq} = p_i/H$ is the dissolved gas concentration in equilibrium with the gas pressure in the bubble i; H is Henry's constant; x is distance normal to the lamella surface; and h is the lamella thickness. Now

$$j_n = j_n^* \frac{M_g}{\rho_g} = \left(\frac{\mathfrak{D}M_g}{H\rho_g h}\right)\Delta p, \qquad (27)$$

where M_g is the molecular weight and ρ_g the density of the gas. From Eqs. 25 and 27 it follows that:

$$\lambda = \left(\frac{\mathfrak{D}M_g}{H\rho_g}\right)\frac{1}{h}, \qquad (28)$$

with $h(t)$, the average thickness of foam lamellae, as the only variable.

If the foam decay is self-similar, h too is a function of the average bubble volume, say $\bar{v}^{\beta}$. Let's assume that the rate of lamella thinning is limited by the gravity-driven liquid drainage through a three-dimensional network of connected Plateau borders (Figure 2). The scaling exponent β can be deduced from an overall mass balance of liquid in a stationary foam in the container:

$$\frac{d}{dt}\{n(t)[n_l A_l(t)h(t) + n_{pb}A_{pb}(t)l_{pb}(t)]\}$$
$$= -\frac{1}{L}n_a(t)n_{pb}'A_{pb}(t)u'(t), \qquad (29)$$

where $n = N/V = \bar{v}^{-1}$ is the number of bubbles per unit volume of the container; n_l is the average number of lamellae per bubble (equal to 6 in the dodecahedron geometry); $A_l \propto \bar{v}^{2/3}$ is the average surface area of a lamella; n_{pb} is the average number of Plateau borders per bubble (equal to 10); $A_{pb} \propto \bar{v}^{\gamma}$ is the average cross-sectional area of a Plateau border; $l_{pb} \propto \bar{v}^{1/3}$ is the average length of a Plateau border; L is the container length; $n_a(t) \propto \bar{v}^{-2/3}$ is the average number of bubbles per unit area of the horizontal plane; n_{pb}' is the average number of Plateau borders per bubble on a horizontal cross section (equal to $n_{pb}/5 = 2$); and $u' = 2/3u$ is the average velocity of liquid drainage through randomly oriented Plateau borders, u being the velocity of drainage under the action of gravity. Note that according to Eq. 29, some of the excess liquid released by the disappearing small bubbles accumulates in the existing lamellae and Plateau borders.

If the hypothesis of SSS holds, then both terms on the lefthand side of Eq. 29 must scale identically with $\bar{v}$. Hence,

$$\gamma = \beta + \frac{1}{3}, \qquad (30)$$

and

$$\frac{d(\,)}{dt} = \frac{d(\,)}{d\bar{v}}\frac{d\bar{v}}{dt} \propto \bar{v}^{\beta - 4/3 + \alpha}. \qquad (31)$$

The velocity of liquid drainage through a vertical Plateau border under the action of gravity is:

$$u \propto A_{pb}\frac{\Delta p}{l_{pb}} = A_{pb}\Delta\rho g \propto \bar{v}^{\gamma} = \bar{v}^{\beta + 1/3}, \qquad (32)$$

$\Delta\rho g$ being the hydrostatic pressure gradient.

Equations 29-32 relate β to α as:

$$\beta = \alpha - 4/3, \qquad (33)$$

and we are now ready to derive the scaling characteristic of the volumetric rate of bubble growth or collapse. The pressure inside bubble i, p_i, relative to a constant external pressure, p_e, is:

$$p_i - p_e = 4\sigma \overline{C}_{m_i} \equiv \frac{4\sigma}{r_i}, \tag{34}$$

where

$$\overline{C}_{m_i} \equiv \frac{1}{r_i} = -\frac{1}{2A} \int_{\partial v_i} \nabla_s \cdot \underline{n} \, dA. \tag{35}$$

Here, A is the surface area of the bubble; $\nabla_s \cdot \underline{n}$ is the surface divergence of the outward unit normal (Weatherburn, 1927); and the integral is calculated over the entire surface ∂v_i of bubble i. Hence, the pressure difference between two bubbles, say 1 and 2, is:

$$\Delta p = p_2 - p_1 = 4\sigma(\overline{C}_{m_2} - \overline{C}_{m_1}) = 4\sigma\left(\frac{1}{r_2} - \frac{1}{r_1}\right). \tag{36}$$

Without any loss of generality, we can set $r_2 = \bar{r}(t)$ and $r_1 = r$, and combine Eqs. 25, 28 and 36 into

$$\dot{v} \propto \left(\frac{r}{h}\right)\left(\frac{r}{\bar{r}} - 1\right). \tag{37}$$

Thus, at each time there exists a critical radius $\bar{r}(t)$, such that a bubble with the equivalent radius, r, equal to $\bar{r}(t)$, is in equilibrium with all its neighbors: the influx of gas across some lamellae balances the outflux across the remaining ones. If $r > \bar{r}$ the bubble grows and when $r < \bar{r}$, it collapses.

From Eqs. 33 and 37, with $r \propto \bar{v}^{1/3}$ and $\dot{v} \propto \bar{v}^{\alpha}$, it follows that the scaling exponent in Eq. 18 is:

$$\alpha = 5/6, \tag{38}$$

and the average lamella thickness scales as:

$$h(t) \propto \bar{v}^{-1/2}. \tag{39}$$

With $\alpha = 5/6$, Eq. 24 yields:

$$\frac{A(t)}{A(0)} = \frac{1}{(1+Dt)^2}, \quad D \equiv \frac{1}{6} C[\bar{v}(0)]^{-1/6}. \tag{40}$$

When diffusion controls gas transport through the lamellae and gravity drainage of liquid through Plateau borders controls the rate of lamella thinning, the relative interfacial area of a self-similar polyhedral foam decreases with the square of time. This was noted by Nishioka et al. (1983) who conceded that by allowing capillary pressure to increase with the square of time, a much better empirical fit of the experimental data was obtained.

It is worthwhile to note that average lamella continues to thin down with time as an inverse of the square root of average bubble size, Eq. 39, or as the average bubble area to the power $-3/4$. This is possible even when the disjoining pressure stabilizes foam lamellae against unobstructed drainage caused by capillary suction from their Plateau borders. This suction continues to increase, because the Plateau borders continue to stretch and drain. Now, let's investigate a special case when none of the excess liquid from the disappearing bubbles accumulates in the foam. If this happens, then the liquid losses from the lamellae and Plateau borders of growing bubbles are negligible. In other words, the increasing disjoining pressure in the lamellae balances the increasing suction from the Plateau borders:

$$\frac{d}{dt}\{n(t)[n_l A_l(t) h(t) + n_{pb} A_{pb}(t) l_{pb}(t)]\}$$

$$\approx (n_l A_l h + n_{pb} A_{pb} l_{pb}) \frac{dn}{dt} \propto -Cn. \tag{41}$$

Thus, the rate of liquid drainage from the foam depends only on a *constant* fraction C, Eq. 19, of all bubbles per unit volume that disappear per unit time, and the average lamella thickness scales as an inverse of average bubble area:

$$h(t) \propto \bar{v}^{-2/3}. \tag{42}$$

In this case,

$$\alpha = 1, \tag{43}$$

and exponential foam coarsening results.

Rate-Limiting Mass Transfer. When the interfacial resistance to *mass transfer* across the lamella surfaces is the rate-limiting step of gas transport, Eq. 26 is no longer valid because the concentrations of dissolved gas on both sides of the lamella, c_1 and c_2, are no longer in equilibrium with the gas in the bubbles. In this limit, the transport of gas becomes independent of the diffusion coefficient and lamella thickness:

$$j_n = \left(\frac{k_l}{H}\frac{M_g}{\rho_g}\right)\Delta p = \lambda \Delta p, \tag{44}$$

where k_l is the liquid-phase mass-transfer coefficient,

$$\lambda = \text{const}, \quad j_n \propto \bar{v}^{-1/3}, \quad \alpha = \frac{1}{3}, \tag{45}$$

and Eq. 24 yields:

$$\frac{A(t)}{A(0)} = \frac{1}{\sqrt{1+Dt}}, \quad D \equiv \frac{2}{3} C[\bar{v}(0)]^{-2/3}. \tag{46}$$

The relative interfacial area of a self-similar polyhedral foam decreases with the square root of time when mass transfer is the rate-limiting step. Note that with $\alpha = 1/3$, D becomes the cumulative collapse rate of small bubbles per unit surface area of average bubble.

Sphere foam

In a slowly draining *kugelschaum*, the spherical bubbles can be viewed as "holes" in a continuous liquid "matrix." The collapse of this foam is therefore controlled by slow, quasi-steady-state diffusion of gas dissolved in the liquid:

$$\nabla^2 c = 0 \quad \text{in} \quad V_l = V - V_g, \tag{47}$$

with the boundary conditions that express the conservation of mass of the gas in the bubbles:

$$\dot{v}_i = \frac{\rho_g}{\rho_L c_{g_i}} \int_{\partial v_i} \mathfrak{D} \nabla c \cdot \underline{n} dA,$$

$$i = 1, \ldots, \text{total number of bubbles}, \tag{48}$$

and no flow across the container walls,

$$\nabla c(\underline{x}) \cdot \underline{n} = 0 \quad \text{when} \quad \underline{x} \in \partial V. \tag{49}$$

Here, c_{g_i} is gas concentration in bubble i per unit volume of the gaseous phase. We require that $c_{g_i} \gg c\rho_g/\rho_L$, so that Eq. 47 is a valid approximation.

Equation 48 replaces Eq. 37 for the spherical-bubble foams. We further assume that for a given point P at the interface on the liquid side, the concentration has the local equilibrium value, $c_{eq}(r) = p(r)/H$ and that this value obeys the scaling equation:

$$c_{eq}^{\vartheta} - c_0 = \frac{1}{\vartheta} (c_{eq} - c_0), \tag{50}$$

where $c_{eq}^{\vartheta} \equiv c_{eq}(\vartheta r)$ is the concentration at the point P^{ϑ} into which P is mapped by a uniform magnification; $c_0 \equiv c_{eq}(\infty)$ is the dissolved gas concentration in equilibrium with bulk gas. Equation 50 states that as a gas-liquid interface flattens, $r \to \infty$, the *excess* concentration on the liquid side of this interface, $c_{eq} - c_0$, vanishes.

Equations 48 and 50 are sufficient to determine the scaling exponent α for *kugelschaum*. At the bubble interface on the liquid side:

$$\nabla c_{eq}^{\vartheta}(\underline{x}^{\vartheta}) \equiv \frac{\partial c_{eq}^{\vartheta}}{\partial \underline{x}^{\vartheta}} = \frac{\partial \left(\frac{1}{\vartheta} c_{eq} \right)}{\partial (\vartheta \underline{x})} = \frac{1}{\vartheta^2} \nabla c_{eq}. \tag{51}$$

Because the outward unit normal vector $\underline{n}$ is *invariant* under a uniform magnification, Eq. 51 proves that:

$$\nabla c \cdot \underline{n} \propto \frac{1}{\vartheta^2} \propto \bar{v}^{-2/3}. \tag{52}$$

The use of invariance of $\underline{n}$ makes the superposition Eqs. 33 and 34, and the ensuing scaling arguments in Mullins' article (1986) unnecessary.

Hence, for the diffusion-controlled collapse of separate spherical bubbles in a liquid "matrix" $\alpha = 0$, Eq. 24 yields:

$$\frac{A(t)}{A(0)} = \frac{1}{\sqrt[3]{1 + Dt}}, \quad D \equiv C[\bar{v}(0)]^{-1}. \tag{53}$$

The relative interfacial area of a self-similar *kugelschaum* decreases with the cube root of time. Because our description of *kugelschaum* is essentially equivalent to that of diffusion-controlled Ostwald ripening, it should be no surprise that the scaling exponent $\alpha = 0$ was obtained in other ways by Landau and Slyozov (1961), Wagner (1961), and Mullins (1986), and numerically confirmed by Voorhees and Glicksman (1984). Note that for $\alpha = 0$, D becomes the cumulative collapse rate of small bubbles per unit volume of the average foam bubble.

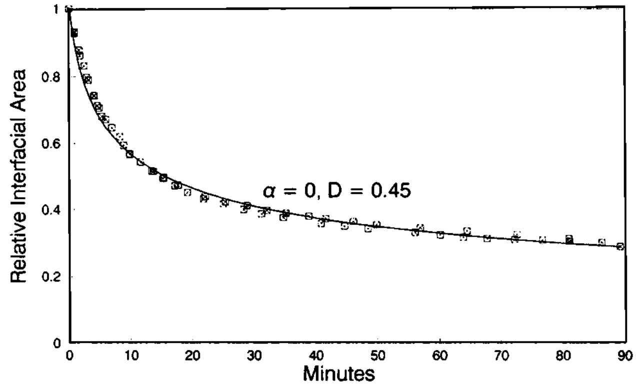

Figure 3. Self-similar collapse of a *kugelschaum* pregenerated from a 0.52 wt. % aqueous solution of unpurified sodium lauryl sulfate scales with $\alpha = 0$ and is a function of the inverse of cube root of time.

From the experiment by Nishioka and Ross (1981).

The scaling regime in Eq. 53 may not emerge if a spherical foam becomes vertically stratified during drainage. This may be especially true if a particular surfactant does not stabilize lamellae against rupture near the top of the foam column.

Experimental Evidence

Nishioka et al. (1981, 1983), as well as Monsalve and Schechter (1984), had studied the decay of bulk foams in a thermostated closed chamber connected to a pressure transducer. The following procedure was used: (1) foam had been pregenerated by blowing gas through a surfactant solution; (2) as the foam decayed, the concomittant increase in head space pressure over the foam was recorded.

Using an equation of state for bulk foam in a closed system (Ross, 1969), one can show that:

$$\frac{A(t)}{A(0)} = 1 - \frac{\Delta p_h(t)}{\Delta p_{h\infty}}, \tag{54}$$

where $\Delta p_h(t)$ is the increase in head space pressure over a bulk foam at time t, and $\Delta p_{h\infty}$ is the ultimate pressure increase after complete collapse of the foam.

Nishioka and Ross (1981) tested reproducibility of their new method by measuring collapse of foams generated from an aqueous solution containing 0.52 wt. % of unpurified sodium lauryl sulfate (SLS). They reported that in early and intermediate stages of collapse (down to, say, 20% of the initial surface area), these foams were essentially *kugelschaum*. In Figure 3, the measured coarsening rate of two such SLS foams scales with $\alpha = 0$, and agreement is excellent. In addition, Nishioka and Ross tested reproducibility of their method by using

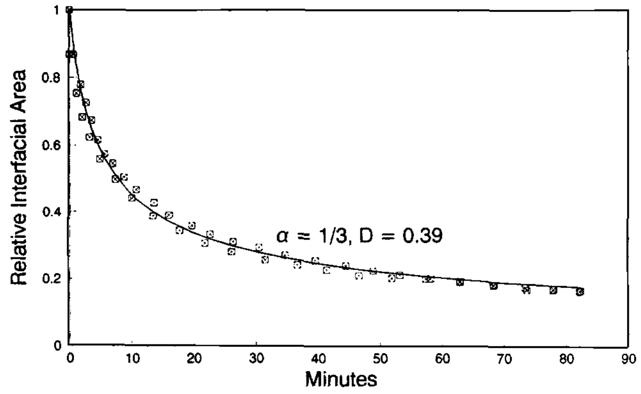

Figure 4. Self-similar collapse of a polyhedral foam pregenerated from a 0.4 wt. % aqueous solution of hexadecyltrimethylammonium bromide (CTAB) scales with $\alpha = 1/3$ and is a function of the inverse of square root of time.

From the experiment by Nishioka and Ross (1981).

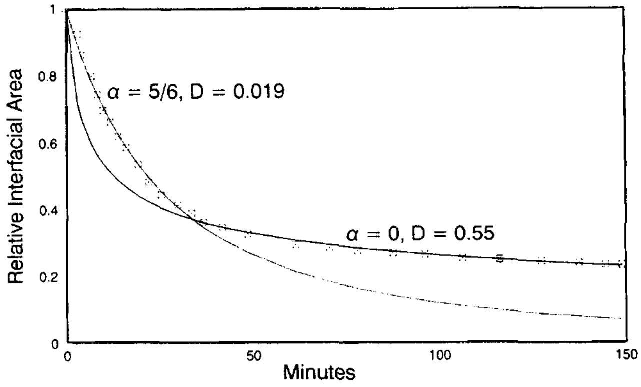

Figure 6. Wet foam pregenerated from a 0.4 wt. % aqueous solution of purified sodium lauryl sulfate mixed with lauryl alcohol collapses with $\alpha = 5/6$ for the first 30 min, and $\alpha = 0$ thereafter.

From the experiment by Nishioka and Ross (1981).

foams generated from a 0.4 wt. % aqueous solution of hexadecyltrimethylammonium bromide (CTAB). It appears that CTAB molecules created resistance to mass transfer at the lamella surfaces. In Figure 4, the coarsening rate that scales with $\alpha = 1/3$ reproduces the experimental data entirely. Monsalve and Schechter (1984) used Nishioka and Ross' (1981) method to measure collapse of foams generated from a 0.5 wt. % aqueous solution of AOS-1416, an alpha-olefin sulfonate with alkyl chains ranging from C_{14} to C_{16}. Figure 5 shows that these foams collapsed at a rate that scales with $\alpha = 5/6$. The data in Figure 5a have been also replotted on a log-log scale to show good agreement with theory for both short and long times.

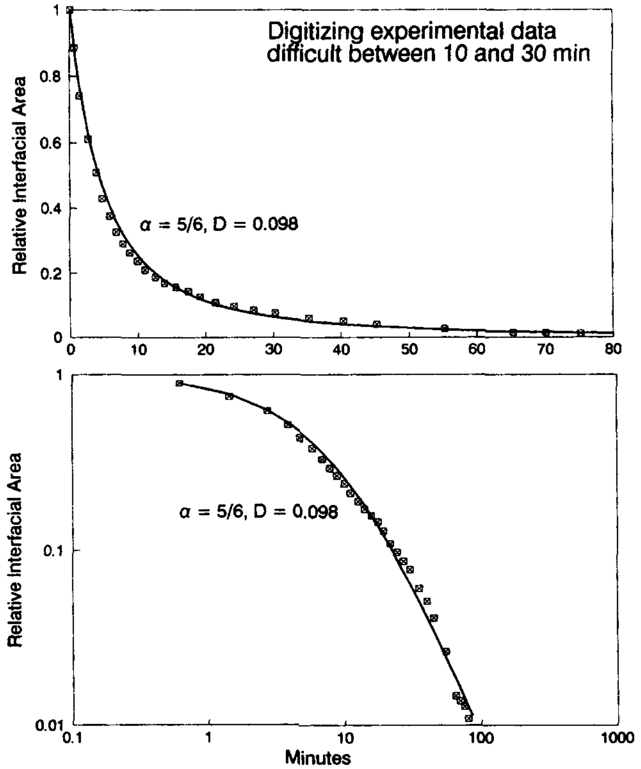

Figure 5. Self-similar collapse of a polyhedral foam pregenerated from a 0.5 wt. % aqueous solution of alfa-olefine sulfonate (AOS-1416) scales with $\alpha = 5/6$ and is a function of the inverse of square of time.

From the experiment by Monsalve and Schechter (1984).

Using multiple light scattering techniques, Durian et al. (1991a,b) measured the coarsening rate of a Gillette Foamy Regular foam (water, stearic acid, triethanolamine, and hydrocarbon gases) and scaled it with $\alpha = 1/3$ after the first 20 min. They also observed that groups of several bubbles in a coarsening stationary foam rearrange occasionally and abruptly, and change the packing conditions of the foam. Durian et al. found that the frequency of these rearrangements scaled as t^{-2}. The discontinuous rearrangements of foam packing may lead to a change in the scaling coefficient α from one value at early stages of coarsening to another one thereafter. This phenomenon may be observed in the experiments by Nishioka et al. Figure 6 shows that the coarsening rate of a wet foam generated from a mixture of 0.4 wt. % aqueous SLS and lauryl alcohol scales initially with $\alpha = 5/6$, but after 30 min this rate decreases and scales with $\alpha = 0$. It is well known (Epstein et al., 1954) that SLS at concentrations above the CMC and lauryl alcohol form liquid crystals that make the lamellae viscous and liquid drainage very slow. This may explain why this foam behaves like *kugelschaum* at later stages of coarsening, when the individual bubbles act independent of one another. Conversely, the coarsening rate of a shaving cream foam (Figure 7) scales initially with $\alpha = 5/6$, but after 60 min it increases and scales with $\alpha = 1$. Finally, the coarsening rate of a foam generated from a 0.4 wt. % solution of SLS scales with $\alpha = 1/3$ for the first 10 min, but then it increases and scales with $\alpha = 5/6$ (Figure 8). Note that the shaving cream and SLS foam increased their coarsening rates by a fractal exponent $\Delta\alpha = 1/6$ and 1/2, respectively.

Because agreement between the present theory and published experiments is so good, it should be pointed out that it was

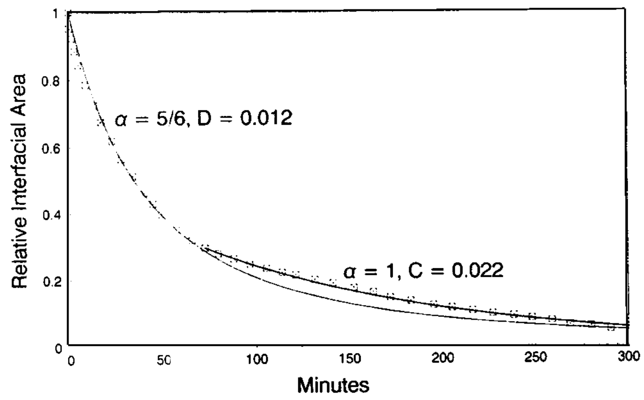

Figure 7. Polyhedral foam pregenerated from a commercial shaving cream collapses with $\alpha = 5/6$ for the first 60 min, and with $\alpha = 1$ thereafter.

From the experiment by Nishioka et al. (1983).

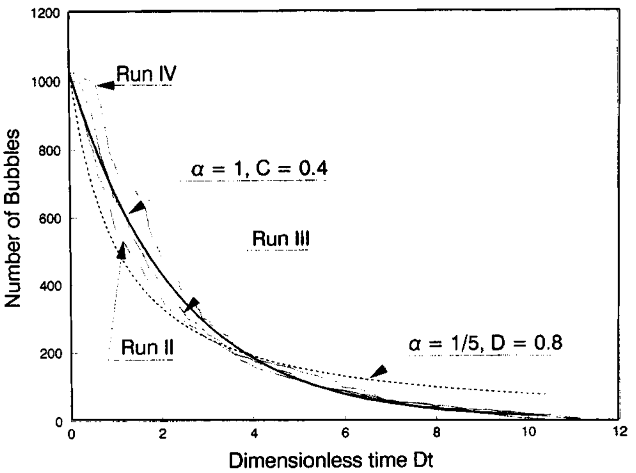

Figure 9. Number of bubbles in a simulated two-dimensional, polygonal foam decreases exponentially with $\alpha = 1$.

Numerical calculations by Herdtle and Aref (1992), Figure 12, runs II-IV.

impossible to match the experimental data with more than one *rational* value of scaling exponent α and it was also impossible to match the data with rational exponents *other than* those derived in this article. The scaling exponent α is a rational number that can have only discrete values dictated by the dimensional analysis of the processes controlling transport of gas and liquid in bulk foam. According to our analysis, $\alpha = 0$, 1/3, 5/6, or 1. Therefore, the total surface area of foam decreases as a function of time to the power of 1/3, 1/2, 2 or exponentially.

Numerical Evidence

Herdtle and Aref (1992) calculated the collapse of a two-dimensional, polygonal foam with a constant permeability λ of the lamellae and no liquid drainage. The largest system followed by these authors started with 1,024 bubbles and the calculation took about 30 CPU h on the Cray YMP supercomputer. Herdtle and Aref mentioned that: "we found that a three-parameter fit

$$N(t) = N_0\left(1 + \frac{t}{t_0}\right)^{-\alpha'}, \tag{55}$$

where N_0, t_0, and α' are all to be determined in a least-square sense using log N vs. $\log(1 + t/t_0)$, gave very satisfactory representations of the data ... Equation 55 incorporates the idea of a 'virtual origin' in time, when the foam was infinite ... The unit of time is taken as the average area per bubble in the initial state, divided by the coefficient in von Neumann's law." The authors reported that values of α' in the range of 1.13–1.21 were obtained, depending on the fitting window, for some unreported values of N_0 and t_0. Figure 9 shows the results of runs II-IV (from Figure 12 in Herdtle and Aref); run I was similar to run II. As N_0 was not reported in the article, $N_0 = N(t = 0) = N(0) = 1{,}024$ was assumed here. From Eqs. 23 and 22, one obtains readily:

$$N(t) = N(0)(1 + Dt)^{-1/(1-\alpha)}, \quad \alpha \neq 1$$
$$N(t) = N(0)e^{-Ct}, \quad \alpha = 1, \tag{56}$$

and by inspection $N_0 = N(0)$, $t_0 = 1/D$, and $\alpha' = 1/(1-\alpha)$, $\alpha \neq 1$. Figure 9 shows that with $N_0 = 1{,}024$, $t_0 = 1.25$, and $\alpha' = 1.17$, that is, $\alpha = 1/5$, Eq. 55 does *not* fit the numerical results of Herdtle and Aref, nor will it fit these results with any other values of t_0 and $\alpha' \approx 1$. Herdtle and Aref were aware of the limitations of their numerical solutions and wrote: "we now turn to issues that indicate ... the limitations of observing the scaling behavior inherent in working with systems as small as 1,000 bubbles." They were also aware of the emergence of self-similarity in the solutions: "clearly, a strong case for a similarity form of this (number-of-the-sides distribution) $\rho(n)$ emerges," and "also, clearly, a power law fit for N vs. t, as in Eq. 55, will not succeed very well." Both of these statements

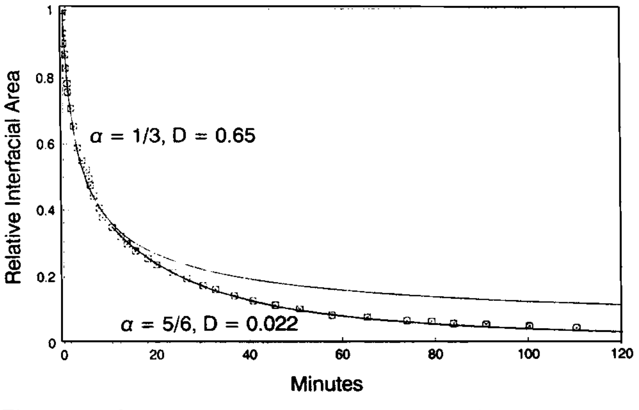

Figure 8. Polyhedral foam pregenerated from a 0.4 wt. % aqueous solution of purified sodium lauryl sulfate collapses with $\alpha = 1/3$ for the first 10 min, and with $\alpha = 5/6$ thereafter.

From the experimental data by Nishioka et al. (1983).

are true, because Figure 9 indicates that $\alpha = 1$ and $C = 0.4$ fit the numerical data perfectly well with $N(0) = 1{,}024$. This fit, however, is *exponential.*

It appears, therefore, that even for relatively few polygons, and different initial distributions of the polygon areas and shapes, the numerical solutions converge to a self-similar form with the power exponent $\alpha = 1$. This self-similar solution is independent of the initial conditions. Because the initial number of bubbles is so small, the rate of convergence to this solution depends somewhat on the initial conditions (compare run IV with run II). This can be explained as follows (Herdtle and Aref used a discrete expression for the rate of polygon growth or collapse):

$$\frac{dA_n}{dt} = 2\pi\lambda\sigma(n/6 - 1), \tag{57}$$

where n is the number of polygon sides. This expression changes sign when the number of polygon sides is less than a *constant* average number of sides, equal to 6. On the other hand, we use a continuous rate expression, Eq. 37, with the average bubble radius $\bar{r}(t)$ that *changes* with time. Therefore, in Eq. 57, the constant average number of polygon sides must be replaced with a function of time $\bar{n}$:

$$\frac{dA}{dt} = \frac{1}{3}\,\pi\lambda\sigma\bar{n}\left(\frac{n}{\bar{n}} - 1\right), \tag{58}$$

where $\bar{n}(t)$ is the average number of polygon sides ($\bar{n} \approx 6.0$). Clearly, Eq. 58 scales with $\bar{n}$ to the first power, and $\alpha = 1$. This proves that *regardless of the initial conditions*, all polygonal foams with $\lambda = \text{constant}$ will decay exponentially, after the early dependence on the initial conditions fades away. Equation 58 proves that the numerical algorithm of Herdtle and Aref is correct, although some of their interpretations of the results, such as the power law (Eq. 55), are not. Finally, Eq. 58 and other results presented here provide convenient tests of accuracy of numerical models of foam collapse in two and three dimensions, and with gravity drainage.

Conclusions

A hypothesis of statistical self-similarity (SSS) and scaling characteristics of the rate of volume change of a foam bubble were used to obtain four different power laws of coarsening of polyhedral and spherical-bubble foams.

It was shown that when the rate of volume change of a foam bubble scales as the mean bubble volume $\bar{v}$ to the power α, then the total surface area of the foam decreases as an inverse of time to the power $1/[3(1-\alpha)]$.

It was also shown that the coarsening rate of polyhedral foam scales with $\alpha = 5/6$, when molecular diffusion limits the transport of gas across lamellae, and liquid drainage through Plateau borders limits the rate of thinning of these lamellae. When none of the excess liquid released by disappearing small bubbles accumulates in the foam, its coarsening becomes exponential, with $\alpha = 1$. When resistance to mass transfer at the lamella surfaces is the rate-limiting step, then foam coarsens with $\alpha = 1/3$. Finally, coarsening of slowly draining, spherical-bubble foam was shown to scale with $\alpha = 0$.

The total surface area of polyhedral foams decreases as: (a) the square root of time when $\alpha = 1/3$; (b) the square of time when $\alpha = 5/6$; and (c) exponentially when $\alpha = 1$. The total surface area of spherical-bubble foams decays as the cube root of time.

With $\alpha \neq 1$, the expressions for foam coarsening depend on the intrinsic time scale of foam collapse $1/C$ and the initial volume of average bubble $\bar{v}(0)$. The latter dependence makes it impossible to separate the initial experimental conditions from the intrinsic properties of the gas-surfactant solution system. For $\alpha = 1$, the dependence on the initial bubble volume disappears.

The present theory has been tested against nine experiments with polyhedral- and spherical-bubble foams generated from aqueous solutions of SLS with or without lauryl alcohol, CTAB, AOS-1416, and two shaving creams. In all cases agreement was excellent, although in some cases foam decay was characterized by two scaling coefficients. This was attributed to often intense rearrangements of foam bubbles within the first $O(10)$ min of foam collapse, followed by a different collapse regime at later times. It is concluded that the SSS hypothesis holds—at least for the relatively small volumes of bulk foam in these experiments. The coarsening of stationary polyhedral foams at constant volume is controlled by either gas diffusion or mass transfer across the ever thinning lamellae between the ever fewer and bigger bubbles. The lamella thinning is controlled by gravity-driven liquid drainage through Plateau borders and scales as an inverse of the mean bubble area to the power of 3/4 or 1.

The present theory also proves that the numerically simulated coarsening of a two-dimensional, polygonal foam scales with $\alpha = 1$, when the lamella permeability is constant and the early dependence on initial conditions vanishes.

The results presented here can be used to test the accuracy of numerical models of foam collapse in two and three dimensions, and with gravity drainage.

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Notation

A = surface area, m^2
b ≡ $[\bar{r}(t)]/[\bar{v}(t)]^{1/3}$ = ratio of the mean bubble radius to the cube root of mean bubble volume
c = concentration, kmol/m^3
C = cumulative rate of collapse of the vanishingly small bubbles, m$^{3(1-\alpha)}$/s
C_m = mean curvature, m^{-1}
D = constant, s^{-1}
$\mathfrak{D}$ = liquid-phase diffusion coefficient m^2/s
f = normalized probability function, s/m^6
F = probability function for bubble volume v and rate of volume change $\dot{v}$, s/m^6
h = lamella thickness, m
H = Henry's constant, Pa·m^3/kmol
j = mass flux, kg/m^2·s
j^* = molar mass flux, kmol/m^2·s
k_l = liquid-phase mass-transfer coefficient, 1/s
L = container length, m
n = bubble density, 1/m^3

n = number of sides in a two-dimensional foam "bubble"
$\underline{n}$ = unit outward normal
$\overline{N}$ = total number of bubbles
p = pressure, Pa
r = radius, m
t = time, s
v = bubble volume, m^3
V = total (container) volume, m^3
$x \equiv v(t)/\overline{v}(t)$ = ratio of bubble volume to the mean bubble volume
$y \equiv \dot{v}(t)/\overline{v}^{\alpha}(t)$ = ratio of the rate of change of bubble volume to the mean bubble volume risen to the scaling power α

Greek letters

α, β, γ = scaling exponents
λ = gas mobility, $kmol/m^2 \cdot s \cdot Pa$
μ = viscosity, cp
Π = disjoining/conjoining pressure, Pa

Subscripts

a = areal, cross section
g = gas
i = bubble i in *kugelschaum*
l = liquid, lamella
n = vector component normal to an interface
n = number of sides in a polygon
pb = Plateau border
s = vector component parallel to an interface

Superscripts

* = molar
$\bar{}$ = mean value
$\dot{}$ = time derivative
$\tilde{}$ = time-invariant

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