

# Phase Transitions in Foams

Nicholas Guttenberg

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## **Abstract**

The properties of coarsening foams of different types are examined: wet foams with drainage, foams with and without rupture, and foams with different liquid fraction all coarsen in qualitatively different ways. These foams can be investigated by a number of numerical techniques such as percolation models, molecular dynamics, and models which use vertex rearrangement to arrive at minimal bubble surfaces. The behavior of foams also provides insight into other systems such as granular fluids and crystal grain growth.

Foams consist of a lattice of bubbles of one phase separated by thin layers of a second phase. They show up in many systems in which there is some form of agitation or phase mixing, for instance in the foam produced by ocean waves breaking on the shore or due to the expansion of inclusions of the one phase within the other until the inclusions make contact as in styrofoam or metal foams. The bubble films in foams are usually stabilized by the presence of surfactants which collect at the phase boundaries, just as micelles are formed by lipid bilayers in biological systems. They may also be stabilized by electrostatic repulsion should the film surfaces become charged. Foams show up in chemical processings, where they can impede the progress of reactions, and in the annealing of metals, where they can cause significant changes to the resultant material properties. Metal foams are often desirable as they are far lighter than the pure metal, but remain stronger than other materials of the same lightness. As a consequence, being able to predict the dynamical properties of foams is important for both chemical and material engineering, as it permits one to design ways of encouraging or discouraging the formation of a foam.

Foams also relate to other physical systems of interest. The topology of a dry foam is visually similar to the arrangement of magnetic domains or the pattern of crystal grains in a material. These other systems may very well share the properties that can be observed in certain foams. The major difference is that grain boundaries are topological defects while bubble films can rupture, but many foam models study foams in which rupture does not play a significant role. Knowledge gained by studying the behavior of foams can be applied to these other systems.

As there are many types of foams - dry foams, wet foams, cellular foams with polyhedral bubbles, foams with spherical bubbles - it is important to be aware of what makes such foams qualitatively different and what rules govern each class of foams. There are geometrical constraints on the meeting of bubbles in cellular foams which can help with the classification of dynamical processes in such foams. But those constraints do not apply to foams in which the bubbles are spherical rather than polyhedral. The specific properties of each type of foam can be used to build models that are ideally suited for one or other type of foam and which can capture the relevant dynamics with minimal models.

Most foams are unstable toward coarsening dynamics - a bubble wall may be ruptured, but new walls do not form without the repetition of the process which originally created the foam. Gas can diffuse between bubbles, causing small bubbles to shrink and large bubbles to grow. However, one question is whether the distribution of bubble sizes remains of the same shape even as the average length scale changes. Is the coarsening self-similar? It is also meaningful to ask how the dynamics of coarsening change qualitatively between different kinds of foams. Drainage, rupture mechanisms, and gas diffusion all contribute certain means for the foam to evolve - a foam dominated by rupture will coarsen differently than a foam dominated by gas diffusion or drainage. Different scaling laws are observed for qualitatively different foams. From these dynamics one can make predictions about how the properties of the foam, such as the mean bubble diameter, vary with time.

One may also look at how the mechanical properties of a specific foam change as a function of parameters such as the surface tension and liquid fraction. It turns out that foams share a certain behavior with granular materials - as the density of the bubbles in the foam increases, the foam stops behaving as a liquid and begins to behave as a solid; this is a jamming transition. This transition also turns out to play a role in the equilibrium state of foams which drain into a bulk liquid phase.

## Types of Foams

Foams can be divided into two classes based on the relative amount of the bubble material and the solvent material. The extreme limit of a bubble-dense foam is a network of long, thin walls with large bubbles that are all in contact with each other along a wall. These are polyhedral, or cellular foams. The walls may be curved due to pressure differences between bubbles, and meet sharply at points.

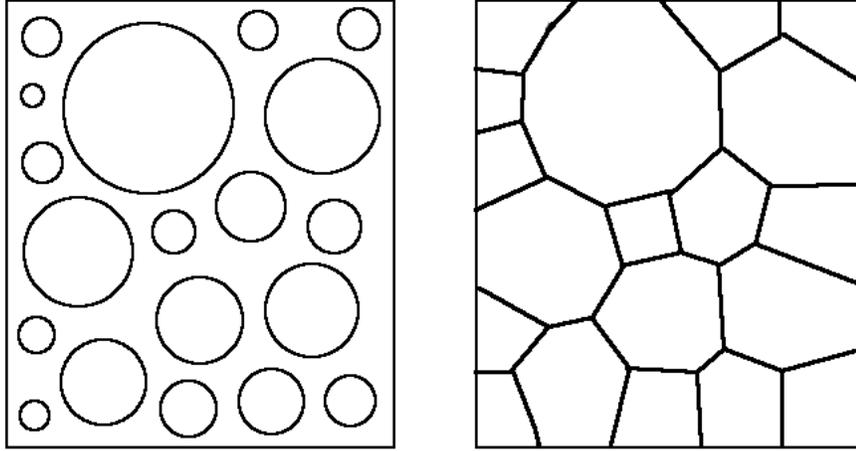


Figure 1: On the left is an example of a foam with a large amount of interfacial material. The bubbles are spherical (circular in two dimensions) and are barely in contact. On the right is an example of a foam with a cellular structure, produced when there is a small amount of interfacial material. The motion of this foam is jammed as the bubbles cannot easily change their relative positions.

The resultant structure is qualitatively the same as the pattern of cells in tissue - that is an example of such a foam.

The limit of a solvent-dense foam is small bubbles that are suspended in the solvent and are not in direct contact. The bubbles in foams of this type are spherical (or circular in two dimensions). Foams of this sort have mechanical properties akin to granular materials. In such a foam the bubbles can deflect each other without merging due to interactions through the intervening fluid. As a result, the bulk motion of the foam is governed by the motion of many small mutually-repelling spheres, and so the same phenomena observed in granular materials (shear hysteresis and jamming for example) are also observed in such foams [8]. The oil-vinegar emulsion in salad dressing is an example of a foam of this type.

It is also relevant in the case of a cellular foam whether gas diffusion or wall rupture is the dominant mechanism for foam decay. Rupture results in qualitatively different bubble distributions. Additionally, one can separate foams into wet foams and dry foams, the difference being that the walls of a wet foam will become thinner with time as the fluid that composes them drains out of the foam. The stability of a wet foam is a balance between gravity and capillary forces. On the other hand, while the bubble walls of a dry foam may still deform and rupture, the volume fraction of bubble wall material will not change and there cannot be a flow of material *along* the bubble wall.

## Properties of Foams

Foams have been studied in the form of individual bubbles and bubble walls for quite some time. There is a set of two geometrical constraints for a foam in equilibrium known as Plateau's laws (published in [15]). They are derived from the condition that a foam in equilibrium minimizes its surface area. Three bubble walls meet to form an edge, and in equilibrium their angles must be  $120^\circ$ . Four edges meet at a point and must have a tetrahedral geometry (all mutual angles the same  $109.5^\circ$ ). When more than three walls meet, or more than four edges meet, the result is unstable [6].

This does not necessarily hold for a foam out of equilibrium (and as most of the foams we are

considering are unstable foams, this brings up the question of whether this applies at all). However, the motion of the bubble surfaces in response to surface tension and pressure is much faster than the process of gas diffusion between bubbles, and so these laws are observed. In a foam with a significant amount of rupture, cascades of rupturing can result from stresses induced as the walls, edges, and vertices reconfigure to try to minimize surface area.

The walls of bubbles in a foam are usually curved, due to pressure variations between chambers. A general formulation based on bubble gas pressure and surface tension can be made, resulting in rules for how the volume and surface area of bubbles in equilibrium change following a rupture of a bubble wall. A consequence of the bubble structure being maintained by surface tension is that the pressure of a bubble above external pressure scales inversely with its radius. This leads to a relation to the change in surface area with the change in volume for free-floating clusters of bubbles[6]:

$$3P\Delta V + 2\sigma\Delta A = 0 \tag{1}$$

Here  $P$  is atmospheric pressure,  $\Delta V$  is the change in bubble volume due to expansion (pressure from surface tension is reduced when bubbles merge),  $\sigma$  is the surface tension, and  $\Delta A$  is the change in net surface area. In a wet foam, an extra term must be added to balance the difference between the force of gravity on the interfacial material and that of the bubbles. This relation allows one to draw a connection between the shrinking of the surface area of small bubbles and the change in the volume of large bubbles, which allows for a prediction of the coarsening dynamics if the rate of bubble mergers is known by considering the rate of gas diffusion across the walls between bubbles [6]. For a confined foam, the external pressure can be arbitrarily large (at least, compared to the pressures the foam is able to exert) to prevent a volume change, and so this relation does not provide useful information for the entire foam in that case ( $P \rightarrow \infty$  and so  $\Delta V = 0$  for any finite  $\Delta A, \sigma$ ). However, for a small subregion of the foam, where the surrounding bubbles exert some known pressure, it can describe how a merger of bubbles in that subregion will change the volume of the subregion.

## Foam Models

Different methods must be used to simulate foams with spherical bubbles and cellular foams, as the constraints which apply to cellular foams do not apply to those with spherical bubbles. As a complete model of the foam physics would need to resolve down to the molecular scale to treat the surfactants, most if not all numerical work on foams takes advantage of the limit of a very dry or very wet foam.

In order to simulate a foam with a large liquid fraction, standard techniques of molecular dynamics used to study granular materials can be applied. In [7], a foam on the interior of a cylindrical tube was simulated by taking the bubbles of a foam to be point particles interacting through a Lennard-Jones potential, which has an equilibrium separation that in a foam can be considered to be the bubble wall thickness. The equilibrium separation between bubbles must be finite in order to satisfy the conservation of the interfacial phase, and so the interaction cannot simply be repulsive (except in the case where there is some externally applied pressure). The foam was taken to be composed of bubbles of equal size, in static equilibrium with the exception of a defect in the regular bubble array. As a hexagonal lattice of bubbles of equal size in two dimensions is in static equilibrium as far as gas diffusion between bubbles, it was not necessary to model the change in radius of the component particles. The motion of defects in that array was compared with experiments in this geometry with good agreement (in terms of the pattern of topological transitions, the same sequence was observed in both experiment and simulation up to thirteen steps).

The dynamics of a cellular foam are usually described in terms of a series of topological transitions which preserve Plateau's laws. For simplicity, these will be described for two dimensional bubble

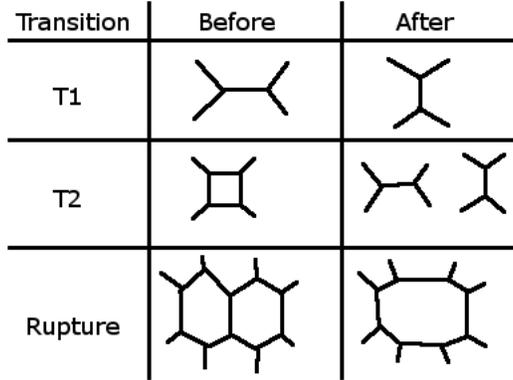


Figure 2: Different transitions in the local topology of a two-dimensional bubble network. T1 transitions preserve the number of bubbles and the number of edges. T2 transitions and rupture do not.

networks (so bubble walls are edges, and the meeting of edges is a vertex). In two dimensions, there are T1 transitions, T2 transitions, and rupture.

T1 transitions occur when due to the relative motion of bubbles in a cluster, two vertices at either side of a bubble edge merge, forming a vertex with four edges. This is unstable, and so the result is that the vertex splits into a pair of vertices which then spread apart, but with a different topology (see figure 2). T1 transitions conserve the number of bubbles but change the topology (one can visualize it as two bubbles coming together to pinch off a previous connected pair of bubbles). The result of a T1 transition is that an edge is transferred between bubbles, so that the total number of edges is conserved but a pair of bubbles with five and seven edges may transition to a pair of bubbles that both have six edges [13].

T2 transitions occur when a bubble shrinks to a point from gas diffusion. A bubble with six sides will become a vertex with a coordination number of six. This state is unstable, and so the vertices then split off until each vertex has a coordination number of three. If the bubble which disappears has more than three sides, there are multiple configurations which can result from its removal. The different possible end states are all connected by sets of T1 transitions. The significance of a T2 transition is that it does not conserve the number of bubbles or the number of edges, and so T2 transitions are essential to the coarsening dynamics of a foam.

One model for the evolution of foams involves a combination of evaluating T1 and T2 transitions to reach a local equilibrium based on Plateau's laws, and then computing the changes of bubble volumes based on gas diffusion across the membranes between bubbles. The diffusion rate is taken to be proportional to the pressure difference and the length of the contact region [13]:

$$\Delta V_{i \rightarrow j} \propto l_{ij}(P_i - P_j) \quad (2)$$

Balancing forces due to surface tension and internal pressure leads to an equation for the pressure difference between two bubbles in terms of the relative geometries.

$$\Delta P_{ij} = \sigma \kappa - \lambda v_{\perp} \quad (3)$$

Here  $\sigma$  is the surface tension,  $\kappa$  the curvature of the interface,  $\lambda$  the viscous drag and  $v_{\perp}$  the velocity of the interface [13]. The rate of change of volume is the integral of the interface velocity around the perimeter of a bubble, and from Plateau's laws, the curvature of the interface is determined by the number of sides of the bubble. If a bubble has fewer than six sides, the net curvature must be positive so that each vertex can have angles of  $120^{\circ}$  between its edges, and if a bubble has more than six sides

the net curvature must be negative. Integrating around the bubble perimeter, one can determine a differential equation for the evolution of bubble area; this is von Neumann's law[14]:

$$\frac{dV}{dt} = \kappa'(n - 6) \quad (4)$$

where  $n$  is the number of sides of a bubble and  $\kappa'$  is a constant related to the surface tension, viscous drag, and diffusivity. The consequence of this is that a bubble network is only in static equilibrium if every bubble has exactly six sides (except in the case of bubbles at a solid boundary, where there can be no transfer of gas, no interface velocity, and no surface tension constraint on the segments of the wall). A consequence of von Neumann's law is that the bubble area in two dimensions scales linearly with time, which implies that the length scale of bubbles scales as  $r \propto t^{1/2}$ [13].

In [12], the coarsening of a cellular foam was modelled analytically by applying von Neumann's law to a distribution of bubbles. When a bubble undergoes a topological transition (T1 or T2), the resulting number of sides is a function of the number of sides of neighbors. In this model, the neighbors were chosen randomly from the distribution of bubbles with size  $n$  and bubbles with size  $m$ . A master equation for the evolution of the distribution function can then be written:

$$\left(\frac{\partial}{\partial t} + v_{\perp} \frac{\partial}{\partial V}\right)p_n(V; t) = \sum_{m=n-1}^{n+1} T_{n,m} p_m(V; t) \quad (5)$$

The transfer function  $T_{n,m}$  is a function of the current average area, rate of change of the area, and the particular combination of  $n$  and  $m$ . The transfer function is itself a function of the probability of finding a bubble with a certain number of sides as a neighbor (this is the contribution of the random-neighbor model, that random configurations obeying the statistics are used rather than the specific topology of the bubble network). The average area and rate of change of area are computed by integrating the distribution function. So consequently, this is a nonlinear partial integro-differential equation. One of the results that follows from this model is that the distribution function of bubble sizes is predicted to be self-similar at long times, so there is a dynamic equilibrium under which these foams can be considered as long as the length scale is adjusted with time. This model is essentially a mean field theory for dry cellular bubble networks without rupture.

When rupture is included, spatial correlations in the arrangement of bubbles become especially important. Cascades occur, in which a single rupture creates an expanding set of ruptures nearby as the foam is rearranged. In [10], numerical simulations of a two dimension foam with and without wall rupture were performed in order to investigate these cascades and the transition between the different forms of coarsening.

The method of simulation was to perform a splitting between two time scales. On short time scales, T1 and T2 rearrangements occur which change the topology of the foam without significantly redistributing gas between the bubbles. On long time scales, diffusion adjusts the bubble areas according to von Neumann's law. The authors compute the forces due to pressure and surface tension acting on each vertex in the bubble network and adjust the vertex positions. This uses the fast time step and is iterated until an equilibrium configuration is obtained. Then, the pressures inside the bubbles are updated using von Neumann's law with the longer time step, and the process is repeated.

Rupture events can be computed simply by merging two bubbles. The difficulty in modelling rupture in this model is determining the probability for a particular bubble wall to break. Chae and Tabor reported the results of three different rupture models: one in which the probability is constant, one in which the probability is proportional to the edge length, and one in which the probability is proportional to the square of the edge length. These models are based on observations that the rate of soap bubble bursting is proportional to its surface area. It is also necessary to select a time scale

on which rupture occurs compared to the diffusion and vertex movement timescales. This timescale determines the relative importance of rupture on the bubble dynamics.

Qualitative differences were observed between the foams that resulted from rupture-less and rupture-dominated evolution. In the absence of rupture, the bubble shape and size distributions were narrow, with roughly symmetrical bubbles. Foams with rupture produced large asymmetrical bubbles with very many small bubbles neighboring them.

## Critical Dynamics

There are different predictions for the scaling of foams depending on the properties of the foam in question.

For foams with spherical bubbles, coarsening is due to diffusion of gas between the isolated bubbles which are not in direct contact. This can be modelled in the same way as Ostwald ripening (the coarsening of domains in binary alloys and formation of crystal grains from solution). In such systems, there is a dissolved material which diffuses between bulk regions of that material. In the case of foams with spherical bubbles this is dissolved gas diffusing between the bubbles[13].

The growth law for systems undergoing Ostwald ripening is derived by considering the velocity of a spherical interface which grows due to diffusive flux. The interface velocity is proportional to the current of dissolved material across the bubble interface. One can find the interface velocity by considering the chemical potential at the bubble interface due to surface tension  $\mu = -\frac{\sigma}{r}$ . The interface grows with a velocity proportional to the gradient of the chemical potential  $\nabla\mu$ , and so the interface velocity is  $\frac{dr}{dt} \propto r^{-2}$ . From this, one can conclude that the bubble radius scales as  $r \propto t^{1/3}$  [16].

For cellular foams in two dimensions without rupture, von Neumann's law predicts that the area of bubbles will scale proportionally to time. As a result, the length scale of bubbles in the system will scale as the square root of the area, and so for cellular foams the predicted scaling is  $r \propto t^{1/2}$ . This exponent has also been observed in three dimensional foams, even though there is no direct analog to von Neumann's law in three dimensions.

The behavior of foams with rupture is less clear, and the dynamical exponent is not independent of the details of the initial conditions and dynamics [9, 10, 11]. Experiments have been performed to measure this scaling exponent, hereby labelled  $z$ , in different foams.

In [1, 2], an experiment was performed in which a transparent glass box was filled with Gillette shaving cream, which has an 8% liquid fraction. Then, a coherent light source was used to provide plane-parallel illumination of one of the sides of the box, and the intensity at the other sides was measured. By measuring the portion of the light which was deflected within the foam, they were able to deduce the mean free path of a photon in the foam, which is proportional to the mean bubble radius (as the light is only scattered at interfaces, the mean free path is the distance between interfaces). The foam was allowed to coarsen for a time on the order of hours, and the time dependence of the mean bubble radius was measured.

These studies make observations of the dynamical critical exponent  $z$ , which they determined to be  $0.47 \pm 0.05$  in [1] and  $0.45 \pm 0.05$  in [2]. Scaling behavior was observed between times twenty minutes after the foam was generated until the end of the measurements at one thousand minutes. The authors point out that as this is not the idealized limit of a cellular foam, one expects there to be some crossover between the  $t^{1/3}$  behavior predicted of isolated bubble foams and the prediction of  $t^{1/2}$  for cellular foams. The predicted scalings for foams without rupture are the equivalent of a mean field theory for foams, and it is not necessarily the case that the scaling exponent will be the same in two or three dimensions, and yet they are within error of the mean field theory prediction for a cellular foam.

One of the results of the study of Chae and Tabor on foams with rupture is that they determined

that for rupturing foams, the remaining number of bubbles provided a better measure of time than time-stepping. When analyzing their results from that perspective, they found that the evolution of bubble radius in a rupturing foam scaled as  $r \propto (1/N)^\beta$  in two dimensions. From dimensional analysis, one would expect that  $\beta = 1/2$ . They observed in their simulations of rupturing foam a value of  $\beta = 0.41$  when the probability of an edge breaking was constant. When the probability was proportional to edge length, they observed smaller values of  $\beta$  between 0.325 and 0.394 depending on the initial bubble structures, and for the  $l^2$  model, they observed values between 0.245 and 0.306, which of the three models are closest to experimental observations of breaking dry foams which had  $\beta$  between 0.25 and 0.32 [9]. Interestingly, in [9] the evolution of bubble area with respect to time was not measured to be exponential, but rather to be a power law in which the exponent depended upon the rate at which breaking of bubbles walls was induced by applying a changing temperature.

The work in [11] follows that of Chae and Tabor by considering a foam with rupture as modelled by percolation theory. They simulated a system on a hexagonal grid with links between the vertices of the hexagons (so each vertex has three possible links). The system was initialized with each of the links being a wall, and the breaking probability used by Chae and Tabor ( $P_{rupture} \propto l$ ) was used to eliminate entire chains of links, the chain being defined as a set of links that are each only connected to two other wall links plus the terminal links at either end. From this simulation, they observed  $\beta = 0.38$ , in close agreement with the results of Chae and Tabor's numerical study. So from this, they concluded that the statistics of rupture were sufficient to generate the observed scaling, and that bubble relaxation did not play a large role in determining the dynamical exponent  $\beta$ . Additionally, they observe a critical time  $t_c$  which is independent of system size at which a bubble spanning the system emerges. Note that time in this case is stepped per rupture by an amount  $\Delta t = 1/l_{total}$  (from  $P_{rupture} \propto l$ ), so that it is not the variable  $1/N$  used for time by Chae and Tabor. The analysis of fluctuation scaling in the simulation results led the authors to the conclusion that the connectedness transition at  $t_c$  is a first order phase transition.

The variation in exponents observed for rupture-based foam coarsening, in addition to the observation by Hasmy, et al. that there is a first order transition at a critical time for rupture-based coarsening suggests that there is a critical point in foam coarsening at infinitely slow rupture rate, around which the coarsening dynamics become universal, similar to the zero-field limit of an Ising model or zero-roughness limit for turbulent flow through a pipe. A qualitative picture of the phase diagram of the coarsening dynamics is shown in figure 3.

## Structural Phase Transitions

The different scaling between the polyhedral/cellular and spherical-bubble foams already suggests that there may be some sort of criticality in foamy systems. The arrangement of bubbles in polyhedral foams also seems like a ripe place to look for various equilibrium configurations that may change qualitatively as a function of some parameter.

The parameter which controls whether one has a foam with spherical bubbles or a foam with cells is the fraction of interfacial material (the liquid fraction in wet foams). For an arrangement of spheres of the same size, the limit of the liquid fraction at which the bubbles can remain spherical is 26% (as the ideal packing fraction for spheres is 74%) [5]. However, bubbles in a foam are not all of equal size and the arrangement of those bubbles is not necessarily in such a way as the obtain the ideal packing fraction.

For wet foams, drainage under gravity is an important mechanism toward the coarsening of the foam. It results in a liquid fraction which varies over the vertical coordinate. For a column of foam which is initially all at the same liquid fraction, the liquid and bubble phases will separate out. However, it is possible depending on the initial parameters that there will still be a cellular foam at

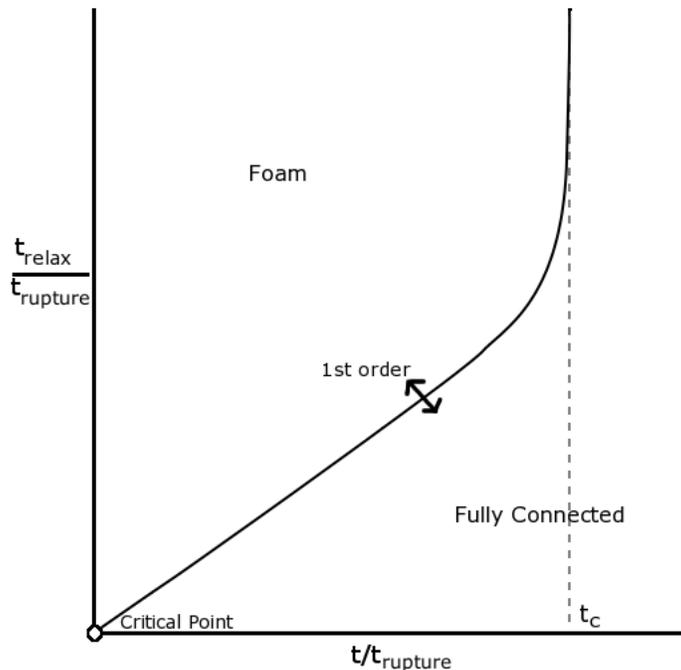


Figure 3: This is a sketch of a possible phase diagram for a coarsening foam with both relaxational dynamics and rupture. For a system with rupture, the foam will eventually vanish - that is, there will be a bubble the size of the system at some finite time. As the rupture time tends toward infinity however, the foam will coarsen with time but the time for a bubble the size of the system to appear will scale with the system size. A potential third axis to consider in this phase space is the liquid fraction, which affects whether the coarsening occurs as  $t^{1/3}$  or  $t^{1/2}$ .

the top or bottom of the column in equilibrium. This is a consequence of capillary forces in the bubble walls - there is a balance between the gravitational forces acting on the liquid in the bubble walls and the capillary forces [5]:

$$\rho g = -\frac{\partial \sigma}{\partial z r_p} \quad (6)$$

where  $\sigma$  is the surface tension and  $r_p$  the radius of the Plateau channel where bubble walls intersect (which is a function of liquid fraction). The consequence of this is that there are four possible outcomes for a foam in equilibrium - either there are no regions of bulk phase of either the gas or the liquid, there is a bulk region of the liquid in equilibrium with the foam, there is a bulk region of the gas in equilibrium with the foam, or there are bulk regions of both liquid in gas with the foam in between. The phase diagram for this system can be determined by looking at the maximum and minimum liquid fractions. If there exists a liquid fraction greater than 26% in the column, that can be seen as a bulk liquid phase. If the liquid fraction drops beneath the amount necessary to sustain the thinnest possible film walls (this depends on material the foam is composed of, and will be called  $\epsilon_c$ ) then there is a bulk gas phase[5]. The phase diagram for this system is in terms of the initial liquid fraction and a dimensionless variable  $P = \frac{\sigma}{K\rho g R_0 L_0}$  ( $K \propto 1/\sqrt{n_p}$ , where  $n_p$  is the number of channels per bubble), and is shown in figure 4. In order to understand the variable  $P$ , it may be helpful to think of it as the ratio of the bubble pressure due to surface tension (which scales as  $\sigma/R$ ) and the gravitational pressure  $\rho g L_0$ .

This system seems very similar to binary alloys, in which at certain parameter ranges, a bulk phase

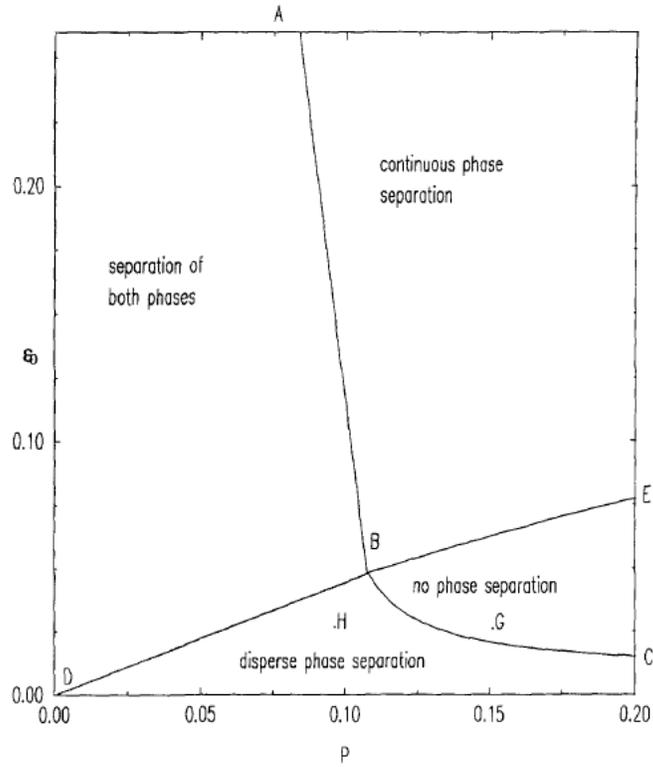


Figure 4: Phase diagram of a column of foam under gravity.  $P$  is a dimensionless number which is inversely proportional to the initial bubble radius and column height.  $\epsilon_0$  is the initial liquid fraction. Figure is from [5].

of one or the other constituent emerges, and at other parameter ranges there is only the mixed phase. Whereas in binary alloys the entropy of mixing causes the mixture of different atoms to be stable, in the case of dry foams this comes from capillary forces. There is also an interesting potential application in these different equilibria - if you create a foam from a solution that has two different surfactants which can stabilize bubble walls, but such that the surfactants have different  $\epsilon_c$ , then the creation of a column of foam from that solution will provide a means for separating them analogous to distillation, as the liquid fraction at which the foam vanishes for the two different surfactants will differ.

There is a question as to whether the point where the liquid fraction exceeds the ideal spherical packing is actually a phase transition or not. In the situation with a column of foam, there is a discontinuity of the behavior at this point, as spherical bubbles which form inside that region of  $\epsilon > 0.26$  will float up through the liquid and accrete at the line at which  $\epsilon = 0.26$ . So there will never actually be a region in equilibrium for which  $0.26 < \epsilon < 1$  in that system. However, in a foam without drainage, what is the equivalent point? There needs to be some discontinuous change in the mechanical or thermodynamic properties of the foam.

There is evidence of a transition in the behavior of foams without drainage or rupture at a gas fraction of 84% in two dimensions (which is close to the packing fraction for a hexagonal array of discs, 91%) at which point the mechanical properties change from jammed (cellular foam) to a granular fluid (circular bubble foam). In [3], using a bubble dynamics model, a two-dimensional sheared foam was simulated. The bubbles were represented by circles which repelled each other with a spring force when in contact and otherwise obeyed over-damped dynamics. At a liquid fraction of 16%, a phase transition was observed by examination of the static shear modulus  $G$ , which became zero as the liquid

fraction was increased past 16%. The observed scaling was as  $(0.16 - \epsilon)^{1/2}$ . The average number of contacts between bubbles also became zero at that point, dropping discontinuously from an average of four contacts to zero. This model did not take into account gas diffusion between bubbles in contact. Because of this, the initial distribution of bubble sizes was conserved throughout the simulation, which will certainly produce different critical liquid fractions for different distributions. This effect was noted in a followup paper [4], in which variations of the critical fraction between 15.5% and 18% were observed for different widths of bubble size distributions.

## Conclusions

Foams are a patterned structure whose existence in a system has consequences for its mechanical properties. A foam with a high liquid fraction tends to behave as a fluid and does not support shear waves. As the liquid fraction is reduced, the foam becomes a jammed system as the topological relations between the bubbles in the foam become frozen into place, and the foam behaves as a solid. This occurs at a critical liquid fraction which depends on the dimension of the foam and the distribution of bubble sizes, and is closely related to the optimal packing fraction of circular or spherical bubbles.

Foams tend to coarsen through gas diffusion and bubble rupture, but do so in a way that preserves the shape of the bubble size distribution function at long times. As foams are allowed to coarsen, they will not change qualitatively until the bubble size becomes comparable to the system size. This coarsening process can scale differently with time depending on the liquid fraction of the foam - bubbles in a foam with a high liquid fraction will scale as  $t^{1/3}$ . A foam with a small liquid fraction will have bubble radii which scale as  $t^{1/2}$ . Equilibrium without any coarsening is possible only if the bubbles are all the same size and are topologically the same (six-sided bubbles in two dimensions). For a foam in which rupture is a large contribution to the foam evolution, the scaling is not universal - exponents have been observed between 0.25 and 0.4 for different foams. Rupture will also produce a different distribution of bubble sizes and shapes, which can have consequences for the foam's mechanical properties.

For a draining foam, the liquid fraction is not constant over space in equilibrium. It is possible to consider the equilibrium distribution of the liquid fraction even if the foam is undergoing coarsening, as coarsening cannot change the liquid fraction on length scales larger than the bubble radii. The equilibrium state of a draining foam may or may not include regions which are pure liquid or pure gas, depending on the initial conditions of the foam - its initial gas fraction, bubble radius, and height.

These results give a set of guidelines that can be used to control the presence of foams in a material. Should foams be desired, the necessary elements are a liquid fraction smaller than 0.26 and minimal rupture of the bubble walls (which depends on the forces stabilizing the bubble wall). If one wishes to eliminate foams, inducing foam rupture is the fastest method as it will eliminate the foam in finite time. If the foam is a wet foam and can be drained, this can also be accomplished by placing the foam somewhere in the phase diagram for a draining foam such that separation of both phases will occur - by having a very long column of foam, by reducing the surface tension of the foam and thus reducing the capillary forces, or by increasing the density of the bubble wall material or gravitational acceleration (perhaps by centrifuging the system).

The behavior of foam coarsening near the large rupture time point bears further study - one might expect to observe universal scaling of the critical time at very small values of the inverse rupture timescale. Additionally, there remains a question of what is the physical rule for rupture rate. Although there is an argument from the behavior of soap bubbles to expect the rupture rate to be proportional to the perimeter of a bubble in two dimensions, the results from the numerical study by Chae and Tabor obtain the best fit to experimentally observed exponents when they use a perimeter-squared rule. It may be necessary to study the stability of thin films coated with surfactants in order to arrive

at the proper rupture rule.

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