CHAPTER II
HISTORY

The oldest reference to the behavior of a froth that this author has been able to find is in Robert Boyle's *New Experiments.*[35] In a discussion of the effects of a vacuum on a fluid Boyle notes that small bubbles form within the fluid, rise to the top and clump into bubble rafts. Later on he describes the bubbling of human urine under vacuum and notes that the froth coarsens and collapses over time. Doubtless a thorough search in the literature would reveal other studies. Matzke quotes Hooke, and Lewis quotes Leeuwenhoek as the first to have considered froth as a model for aggregates of cells.[108,138,140,161]

II.a Basalts

Geology is a generous source of examples of cellular patterns, as two recent articles in Scientific American pointed out.[128,222] Examples range in scale from millimeters to miles, with a variety of origins, the most common being convective cells and fracture patterns in rock.

The earliest well known investigations of two dimensional cellular patterns are studies not of froths but of the fracture patterns in basalts, in particular the large region of fractured basalt known as the Giant's Causeway in northern Ireland (See Frontispiece and Fig. 4 (C)).[40,55] The most significant of these is Reverend Dr. Samuel Foley's account of 1694.[65] This works contains, among other things, the first distribution function (albeit a qualitative one) calculated for a two dimensional network of grains: "We found none at all Square, but almost all Pentagonal or Hexagonal; only we observed that a few had seven sides; and many more Pentagons than Hexagons; but they were all irregular, for none that we could observe had their sides of equal breadth."[65] In this short passage, the reverend doctor has already established two of the most important characteristics of equilibrated cellular patterns, that they have more five-sided than six-sided grains and that they are strongly irregular. In particular that they are not merely a poor approximation to an hexagonal array. This basic observation would be neglected for the next few hundred years.

The history of attempts to explain the fracture pattern in basalts is long, and need not detain us, except to note that the study of the origin of these patterns continues to the present.[214] The other point to note is the apparent universality of these patterns. Pieri, in his article on the fracture patterns in the crust of the moon, Europa, presents a helpful summary of the various types of geological patterns, including basalt fracture, large scale straight cracks with coördination number four, and a few models.[191]

II.b Biology

A complete survey of the study of polyhedral structures in biology would take many hundred pages. We can only briefly outline a few of the major ideas and efforts to connect the soap froth to biological tissues, focusing on those that emphasize two dimensional patterns.

Fig. 2 Stages in the Development of a Geranium. Various stages in the development of a geranium embryo showing similarity to a bubble raft (From Souèges 1923).[213]

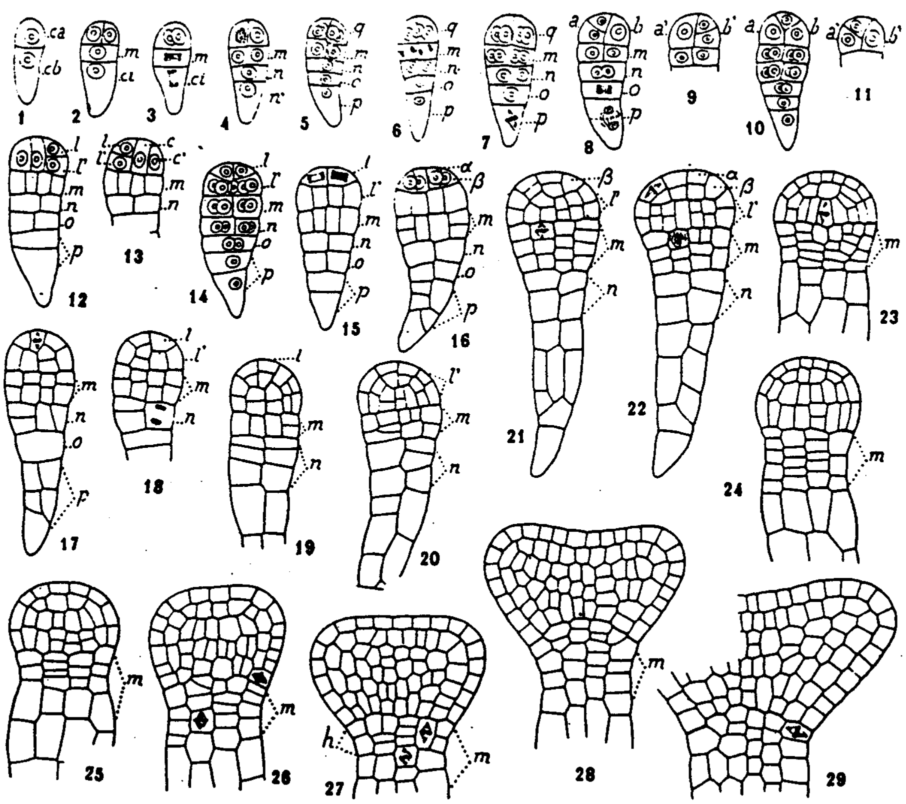
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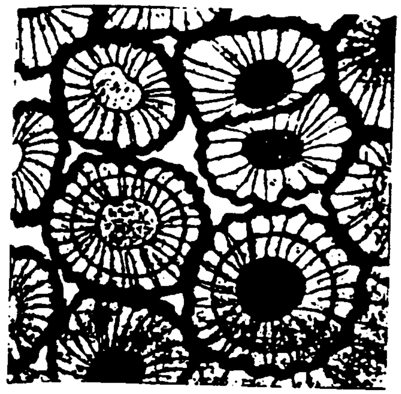
Fig. 3 Grain Growth in Calcium Carbonate. (A) Early stage of grain growth, (B) Developed grains (C) Coarsening. (D) Sample of clam shell showing similar polygonal patterning (Redrawn from D'Arcy Thompson 1942).[230]

(A)



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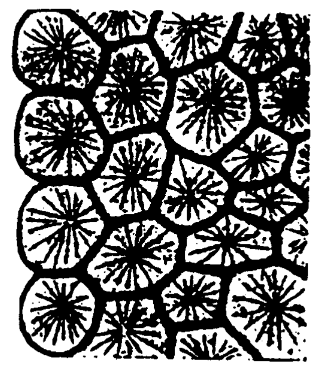

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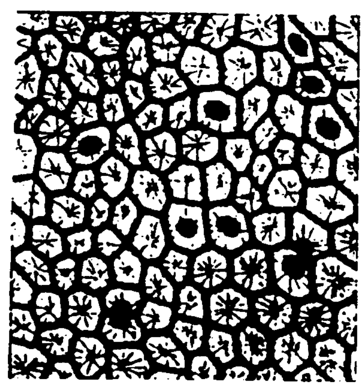

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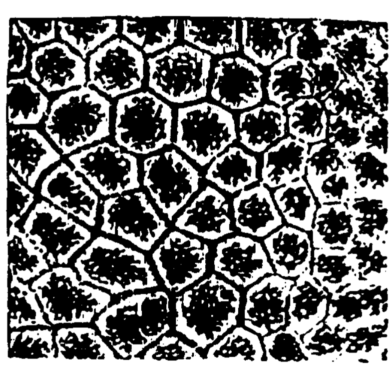
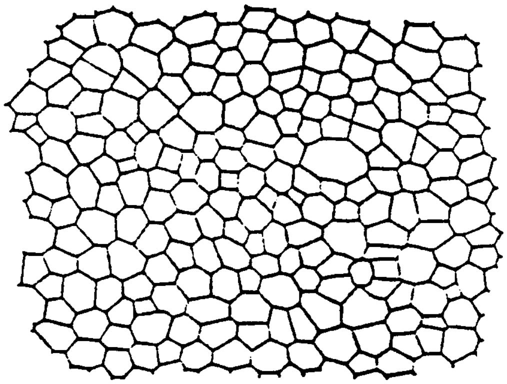


II.b.i D'Arcy Thompson

The obvious similarity in appearance between the cells of a soap froth and the cells in a living organism lead to many attempts to connect the two more formally. The resemblance may, indeed, be striking, as in the development of the geranium (Fig. 2).[213] Sir D'Arcy Thompson expressed the analogy succinctly: "surface tension is of great, and is probably of paramount importance" in the determination of the shapes of simple organisms and cells.[230] He therefore discussed at length the mathematics of minimal surfaces and of surface tension, and catalogued almost every conceivable analogy between bubbles and living forms. He connected the scission of an isolated bubble or floating oil drop to the division of cells,[232,233,234] the pattern of two dimensional soap bubbles to the segmenting egg (p. 601), and honeycomb (p. 494), three dimensional froths to vegetable parenchyma (p. 544), and the tortoise (p. 518). He addressed in particular the analogy between grain growth in molluscan shell and a model system of calcium carbonate crystals growing in albumin (see Fig. 3). The list could be extended to nearly arbitrary length. The fundamental weakness of Thompson's approach, which carries over to later writers as well is an obsession with the crystal, with a regularity and symmetry which he assumed to be the Platonic form for imperfect natural structures. Sir D'Arcy had no room for probability in his ordering of the natural world. For him, disorder was merely a deviation to be characterized and dealt with as an unavoidable inconvenience, but not of interest in itself.

Fig. 4 Sample Two Dimensional Cellular Patterns. (A) Section of the epithelium of a cucumber (From Lewis 1925).[140] (B) Territorial patterns of mouthbreeder fish (From Hasegawa and Tanemura 1976).[105] (C) Detail of the fracture pattern of the Giant's Causeway (From Lewis 1949).[147] (D) Sample of Agfa color film photographic emulsion (From Lewis 1931).[142]



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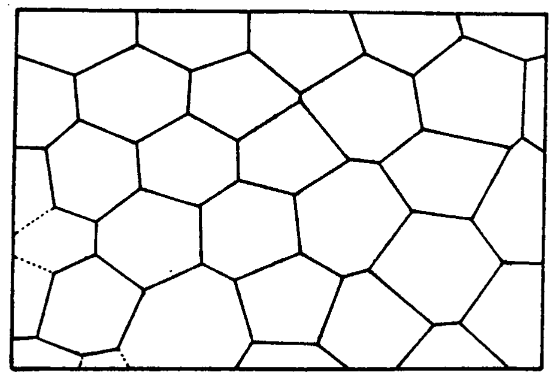

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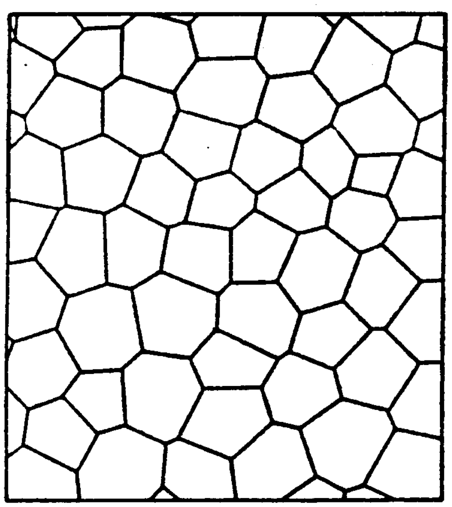

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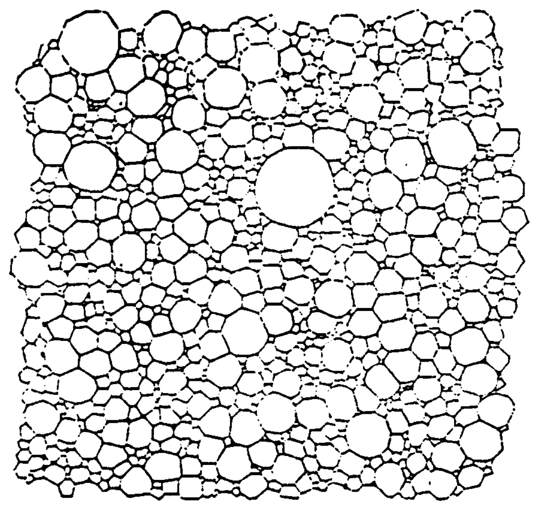


D

TABLE 1

LEWIS' DISTRIBUTION FUNCTIONS[147]

$\rho(n)$	n							
System	4	5	6	7	8	9	10	N
Cucumber Epithelium	0.02	0.251	0.474	0.224	0.03	0.001	-	1000
Wax Convection	0.023	0.357	0.377	0.220	0.023	-	-	300
Giant's Causeway	0.054	0.406	0.464	0.073	0.003	-	-	386
Dividing Cucumber	-	0.016	0.255	0.478	0.224	0.026	0.001	1000.
Eupatorium	0.026	0.265	0.436	0.238	0.034	0.001	-	1000

TABLE 2

LEWIS' LAW[147]

$< a_n >$	n								
System	a_4	a_5	a_6	a_7	a_8	a_9	a_{10}	a_{11}	a_{12}
Cucumber Epithelium	2.0	3.0	4.0	5.1	5.9	6.4	6.7	-	-
Photographic Emulsion	1.3	3.1	6.6	11.1	16.1	23.1	29.7	35.5	42.7
Eupatorium	2.9	5.9	9.0	13.1	18.2	18.8	-	-	-

II.b.ii Lewis and the Cucumber

One of those heavily influenced by Sir D'Arcy's program to attempt physical explanations of biological structure was Frederic T. Lewis, of the Harvard Medical School. His lifetime study was the analogy between living cells and soap froths in both two and three dimensions, by means of which he hoped to demonstrate that surface tension was the chief factor determining the organization of cellular aggregates.[140,141,142,143,144,145,146,147] While much of his writing was devoted to three dimensional structures, he recognized that the two dimensional case was more susceptible to experiment, hence an abiding interest in two dimensional layers of cells, first in the retina, then in human epithelium (surface tissue), a variety of plants and finally in the skin of the cucumber (See Fig. 4 (A)). In approach he followed Sir D'Arcy in positing an ideal regular lattice, either hexagonal in two dimensions or tetrakaidekahedral in three dimensions and regarding all actual observations as imperfect realizations of the ideal. Lewis had a strong distaste for disorder, "Yet, whether certain cells surpass others by accelerated growth or are reduced in size by division, the effect upon the uniform hexagonal mosaic is the same; it becomes a heterogeneous mess."[144] This obsession with order led to an emphasis on the geometry of regular polyhedra and a certain tendency to mysticism, particularly in his later papers. Thus many of his writings are of more historical than scientific interest today. However, Lewis was also a careful observer, and his desire for order never prevented him from recording the real disorder in his samples, nor from attempting to explain the origins of that disorder. His calculations of the distribution of areas and number of sides of the skin of the cucumber were the first real hard data gathered in the field of cellular patterns, presenting results not only for biological materials but also Bénard-Marangoni convection, photographic emulsion (Fig. 4 (D)) and basalt fracture. Table 1 summarizes his results for cucumber (Fig. 4 (A)), convection in wax, the Giant's Causeway (Fig. 4 (C)), and the *Eupatorium* plant. His studies have inspired many investigators, including Occelli, Guazzelli and Pantaloni who have recently reexamined the cellular patterns present in Bénard-Marangoni convection.[104,185,251]

It is important to notice that in all of these systems, the number of six-sided domains is greater than the number of five-sided domains, and that the cutoff for both many and few-sided domains is very sharp. We will see later how these results for patterns in which there are intrinsic limits placed on the range of areas, e.g. by cell division or wavelength selection in convection, compare to theory and experiment for froths and other unrestricted coarsening.

Lewis is best remembered for his empirical determination of the relation between the number of sides of a cell and its area. We summarize his results in Table 2.

On the basis of this data he concluded that the average area of a cell was a simple linear function of its number of sides, i.e.:

$$< a_n >= c_1 + c_2 * n, \qquad \text{(II.1)}$$

where a_n is the area of an n-sided cell and c_1 and c_2 are fitting parameters. This relation is known as "Lewis' Law," It has been elevated to the status of a general principle by some later writers,[134,198,201] casting undeserved opprobrium on Lewis, because it seems to be essentially never true for coarsening systems, failing for both soap froths and metal grains, (though it is approximately correct for domains with between five and eight sides). To be fair to Lewis, he proposed it only for the specific case of cucumber epithelium, and noted himself that cells with many sides were smaller than predicted by the linear relation. In this case he was less literal minded than the majority of his followers.

Another relation first proposed by Lewis is the inverse correlation between a cell's number of sides, n, and the number of sides of its neighbors, m(n).[142] In its basic form his conclusion was that

$$m(n) = c + \frac{d}{n}, \tag{II.2}$$

where c and d are constants. Aboav discovered independently a slightly more elaborate version of this harmonic relation in the soap froth, which is usually known as the Aboav-Weaire Law.[9,8]

Studies continue to the present on the significance of cellular patterns in the configurations of animal cells, e.g. in the human retina.[257] Cellular patterns have also attracted interest from population biologists, for example studying the polygonal territories of mouthbreeder fish (see Fig. 4 (C)).[105] Many of the methods we will discuss are also used by sociologists and geographers interested in the distribution and allocation of resources.[89]

II.c Metallurgy

II.c.i The Classical Model of Grain Growth

By far the strongest impetus to the study of soap froths came from the study of metals. The fundamental analogy between the growth of grains in a metal and bubbles in a froth was first recognized by Smith.[206] In this picture each separately oriented grain in the metal was considered analogous to one bubble in the froth and the metal's grain boundaries to correspond to the soap films. The growth or shrinkage of a given bubble corresponded to the growth or shrinkage of the corresponding grain. There are differences, but the basic analogy between the migration of grain boundaries due to surface energy in a metal and the growth of bubbles due to surface tension driven diffusion in a froth is exact (as we discuss in our section on von Neumann's Law), and the comparison between the two systems has proved fruitful as a series of review articles by Smith attest.[207,208,209]

One basic difference between a two phase bubble system, where the walls are made of soap films, and the diffusing material is a gas, and a one phase metal system where the grain boundaries are simply collections of defects, is the rate of grain coalescence. In an ideal froth, walls do not break and there is no grain coalescence. In some metals, on the other hand, if two grains with nearly identical crystalline orientation touch, the boundary between them vanishes. When it occurs, coalescence provides an additional coarsening mechanism that favors the creation of many sided, large and irregularly shaped grains. Other differences between the froth and the metal

Fig. 5 Bubble Rafts. Regular hexagonal free floating bubble raft. Bubbles are 1.41mm in diameter (From Bragg and Nye 1947).[38]

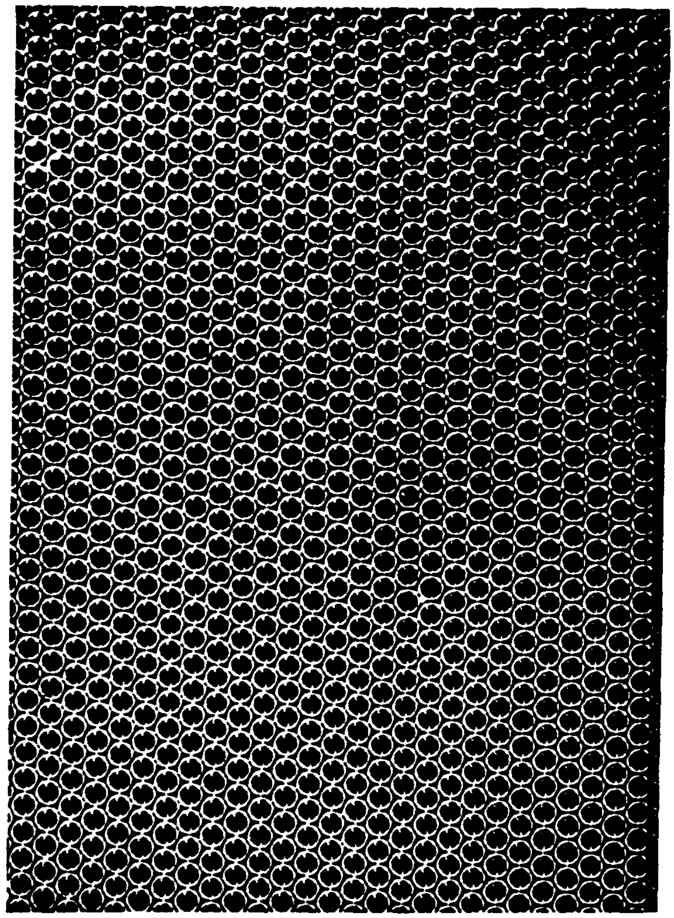
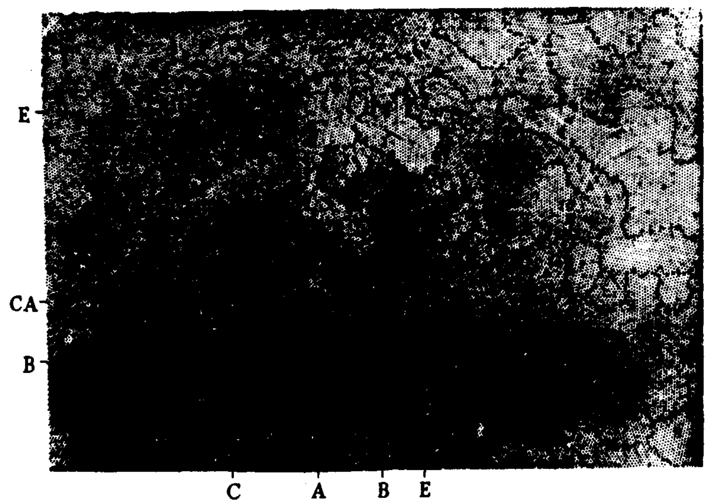


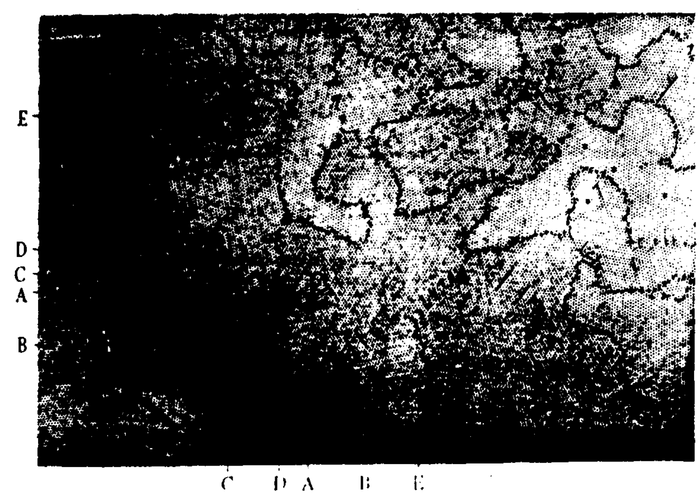
Fig. 6 Recrystallization of a Disordered Bubble Raft. The ordered raft is first shaken to produce a disordered pattern and then allowed to recrystallize. Bubbles are 0.60mm in diameter. (A) $t = 0$ minutes. (B) $t = 2$ minutes. (C) $t = 25$ minutes. Note the irregular shape of the grain boundaries (From Bragg and Nye 1947).[38]

A)

B)



C)



arise from a consideration of time scales. The soap froth's films relax very quickly in comparison to the diffusion time of the gas through the films. The films themselves adjust nearly instantaneously, and even the creep of the films on the walls of their container is fast compared to the diffusion time. Thus soap films always assume their equilibrium shape as minimal surfaces (circular arcs). In a metal this is not the case. The rate at which a grain boundary moves and equilibrates are nearly equal, so grain boundaries can be significantly irregular. Smith's great leap of faith was to assume that when the irregularities of the metal grains were averaged over a sufficiently large population, the differences would average out, and he conducted a series of experiments to show that this averaging did in fact occur.

In both two and three dimensions, the soap froth offers a number of significant advantages over the direct study of metals. The three dimensional structure of a metal is usually determined by serial sectioning, that is, taking a series of thin slices and reconstructing the three dimensional structure from the series of two dimensional images. Attempts at non-destructive measurements have been less successful.[252] Destructive measurements, besides being tedious, prevent the grains from being examined at different stages of growth, making it difficult to measure the basic dynamical laws governing grain coarsening. The three dimensional soap froth can, though with difficulty, be observed in situ.[161] In the case of the two dimensional froth, direct observation is trivial, while the surface preparation required to observe grain growth in metallic thin films or foils, can alter their evolution.

Another barrier to the understanding of metal evolution is the large range of secondary effects, orientational anisotropy, defect pinning, zone refining, vacancy migration, etc., which while interesting in their own right, tend to obscure the underlying dynamics. In the soap froth, such secondary effects are fewer in number, gravity driven thinning in three dimensions, wall breakage, and Plateau border thickening, so they should be easier to control for. Such are the historical motivations for the study of the soap froth as a model system.

II.c.ii Bragg's Model

Bragg put forward an alternative use of bubbles to model two-dimensional grain growth. Instead of looking at the growth or shrinkage of bubbles, Bragg used uniformly sized bubbles, free floating in rafts on water. Individual bubbles in a raft correspond to the atoms in the metal not to entire metallic grains. The orientation of the soap bubble grains corresponds precisely to the crystalline orientation of the corresponding grain. Since floating bubbles attract each other weakly at long range and repel strongly at short range, the analogy is reasonably exact.[18]

A typical experiment consisted of creating a large scale regular hexagonal bubble raft (see Fig. 5), shaking it to destroy the crystalline orientation and then monitoring the regrowth of hexagonal domains (Fig. 6). The observed behavior agreed quite closely with that seen in metals. In particular, the comparable diffusion times along and across grain boundaries resulted in much more irregular grain shapes than observed in soap froths (Fig. 6

(C)). A defect of the model, the absence of a temperature to facilitate the motion of bubbles from one grain to another, can be simulated by applying constant small amplitude shaking. Such shaken systems have been studied by Fukushima and Ookawa, who have also made detailed studies of raft rheology and defect propagation.[66,67,68,69,70,71,177]

The chief disadvantage of such experiments is the difficulty of gathering adequate statistics. To obtain enough grains large compared to the bubble size requires a bubble raft composed of a prohibitively large number of bubbles. Nevertheless this alternative use of bubbles as a microscopic model is very appealing and deserves to be pursued further.

II.d Other Topics

Before we turn to a detailed description of the coarsening of the soap froth, we would like to mention two topics departing from the main focus of this thesis, but which have much intrinsic interest as part of the broader study of bubbles: the properties of soap films and the rheology of foams.

II.d.i The Properties of Soap Films

Early students of soap bubbles were much more interested in the behavior of single films or a few clumped bubbles than in the properties of froths. Newton was the first in a long chain of researchers who studied properties of an isolated soap film.[182] Plateau, the great master of the soap bubble, devoted nearly all of his monumental study of the properties of a weightless fluid to the equilibrium shapes of single films and the interactions among a few bubbles.[189,190] Even the method of producing a stable soap film was a subject of debate in the days before modern detergents.[36,56] In this century, the microscopic structure of films, and macroscopic properties like film draining, have received particular attention both theoretically and experimentally.[193] The classic guide to this material (including a complete bibliography) is Mysels, Shinoda, and Frankel, *Soap Films: Studies of their Thinning.*[176] We will return to their work when we consider possible explanations for the anomalous behavior observed by Glazier, Gross and Stavans in the long time evolution of two dimensional froths.

The stabilization of foams is a major industrial problem, and there is a large literature of engineering studies of foam stability. Since the chief mechanism for coarsening in three dimensions is gravity induced thinning and breakage, most of these studies focus on the properties of single films. Single soap films have been used for a variety of experimental and diagnostic purposes,[57] including recent studies at University of California, San Diego, on two dimensional shear flows.

We should also not omit to mention the less serious aspects of the 19th century's interest in bubbles. Boys' *Soap Bubbles: Their Colours and the Forces which Mold Them*,[176] in addition to a serious discussion of the properties of single bubbles, includes numerous party tricks, and even *Nature* was not averse to publishing accounts of the wonderful properties of soap bubbles, as observed at aristocratic soirées.[1,91]

II.d.ii Foam Rheology

Another topic of great technological importance is the rheology of foams, the behavior of foams subject to external forces. The best current review is Kraynik's thorough "Foam Flows."[126] Applications where foams are used industrially in conditions of large stress include for transporting of granular and high viscosity materials in pipes, as fire suppressants to smother flames, and in the manufacture of modern nuclear weapons.[21] Elucidating the properties of a true disordered froth subject to stress is difficult. Experimental results are limited and tend to focus on particular engineering applications rather than fundamental properties, though the work of Bragg on bubble rafts is very useful.[38]

Published theoretical studies of the rheology of foams cover almost as many methods of modeling as do those for grain growth. Weaire and collaborators have developed a small scale simulation of a fully disordered two dimensional froth, which shows interesting nonlinear and hysteretic effects.[240,241,243] There are also a number of studies of the principles of defect motion in froths, which can be compared directly to bubble raft and microsphere experiments.[19,171] Finally, Kraynik and his collaborators have developed an elaborate analytic theory for the properties of a perfect honeycomb with soap films described by realistic viscous equations.[125,129,130] Weaire has also examined this model.[239] They have even produced a movie of the stress response for different types of films and different lattice orientation, which exhibits an impressive variety of periodic and quasiperiodic motions.[127]

While we would not expect to find such elegant regularity in a real froth, the potential for complex self organized temporal behavior is an interesting possibility.

II.e Conclusion

The intent of this chapter has not been completeness, but an eclectic sampling of the variety of topics peripheral to our main theme of bubble growth. We hope that it provides some motivation to the study of the two dimensional soap froth (both as an unusually simple example of general grain coarsening and as a material worthy of study in its own right) and to the extension of the ideas developed working with the froth to more complicated systems.