GRAIN GROWTH
IN
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MODELLING GRAIN GROWTH AND SOAP FROTH COARSENING: PAST, PRESENT AND FUTURE

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ABSTRACT

We review recent progress in understanding the coarsening of two-dimensional soap froth and idealized grain growth (Potts) models. These are found to be similar in the small anisotropy limit. We also discuss coarsening in lipid monolayers, magnetic bubbles and three dimensional soap froth.

INTRODUCTION

Grain growth is an example of the general tendency of systems which divide space into cells and have a positive interfacial energy associated with their mutual boundaries, to lower their total energy, by coarsening. This coarsening proceeds by the elimination of cells (grains). If it continues without limit, we may study its asymptotic properties. If the structure approaches a statistical steady state in which only the length scale changes, we call it a **scaling state**. It is be characterized by the average cell diameter, <d> defined as:

$$<a> \equiv \frac{\pi}{4} <d>^2, \tag{1}$$

where <a> is the average area per cell. Under rather general assumptions, grain growth in a scaling state has $<d> \propto t^{\beta}$, where $\beta=0.5$ in either two or three dimensions, by simple dimensional arguments. However, we have no *a priori* reason to expect the existence of a scaling state.

There is a long history of measurements of the exponent β for polycrystalline solids [1,2] which we shall not attempt to summarize. Usually the measured $\beta << 0.5$.

Bragg had used floating rafts of uniform sized bubbles to model coarsening as early as 1942, however, his results were more suggestive than quantitative [3]. Smith explored coarsening in detail [4], using two-dimensional (two-d) soap froth, measuring $\beta=0.5$. After various challenges this result has recently been confirmed. In the next section we summarize the experimental work which has followed Smith's lead during the intervening years.

Mean field theories, 'exact' boundary dynamics models, vertex models and the Potts model have all been used to simulate grain growth in a highly idealized form. We shall summarize this work. Although there is no complete equivalence between the soap froth, the boundary dynamics model and the Potts model, their results have now been shown to be quite similar in the appropriate limits.

SOAP FROTH: EXPERIMENT AND SIMULATION

A detergent soap froth, trapped between two glass plates forms a two-d pattern which coarsens. The average diameter and the distribution functions for the structural properties of interest (e.g. the topological distribution function, $\rho(\mathbf{n})$, the fraction of cells with n sides) are easily measured. We define the topological moments,

$$\mu_m \equiv \sum_{n=3}^{\infty} \rho(n)(n - \langle n \rangle)^m. \qquad (2)$$

The second moment μ_2 about its mean (which is fixed at six in two-d by geometrical constrains) roughly characterizes the degree of disorder in the pattern.

Two factors cause misleading effects in the coarsening of froth. First, initially well ordered (mostly hexagonal) patterns, exhibit large **transient effects** as they disorder. Second, apparently small **Plateau borders** (triangular liquid filled structures at the vertices between cells [5]) can have large effects: simple models neglect these entirely.

Figure 1 illustrates, for both experiment (a) and simulation (b), the large transients before μ_2 reaches its scaling state value of 1.5 (as originally observed by Smith). The distribution functions exhibit exponential cutoffs for large n and large area [6]. However, even these expected results, suggestive of a scaling state, failed to give $\beta=0.5$. This, and other anomalies, have now been attributed to Plateau border effects [7,8].

New experiments in which the borders were kept to a minimum size yield $\beta=0.5$ [9,10,11] and new simulation techniques using boundary dynamics methods in which von Neumann's law is used to evolve the area of

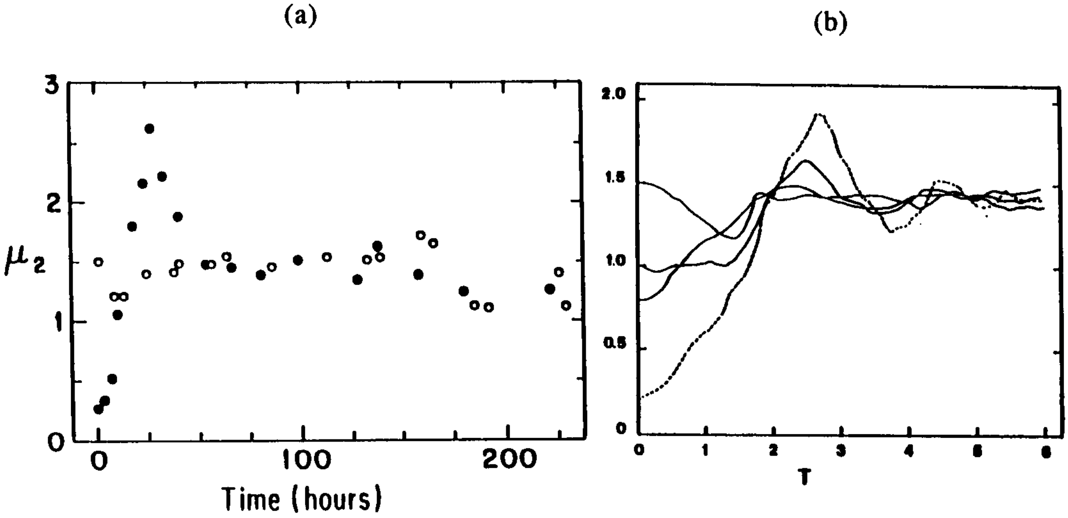
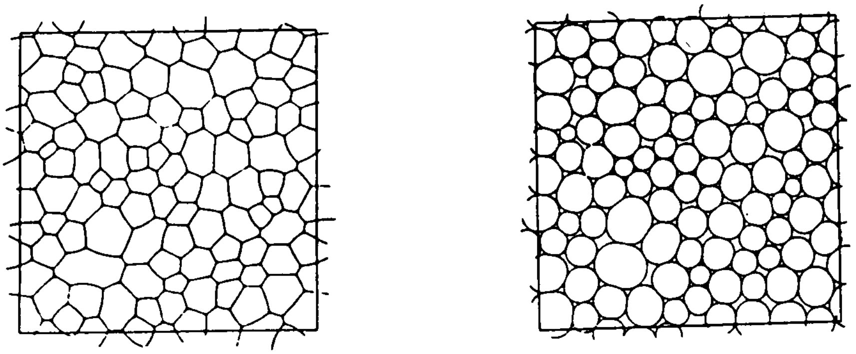


Figure 1. (a) Approach to a scaling state for the two dimensional soap froth--by Stavans and Glazier [9]. Solid circles indicate an initially ordered froth, open circles an initially disordered froth. (b) Computer simulation of the approach to a scaling state for the two dimensional soap froth--by Weaire and Lei [28]. Different lines show evolution for patterns with different initial degrees of disorder.



$\phi = 1.0$

$\phi = 0.90$

Figure 2. (a) Computer simulation of a dry soap froth (gas fraction $\varphi=1.0$) and (b) a wet froth with finite Plateau borders (gas fraction $\varphi=0.90$)--by Bolton and Weaire [8]. Note the presence of four-fold Plateau Borders.

each bubble, together with relevant theorems, have enabled us to understand the role of the Plateau borders [7,8,12,13,14].

Figure 2 (a) and (b) shows some of the elegant structures produced by the computer simulations. While inadequate in size to determine β unambiguously, they offer many insights into the coarsening process and its underlying topological events.

MEAN FIELD THEORIES

One approach to the modelling of coarsening is to decompose it into two processes, a growth law defining the rate of growth or shrinkage of a grain as a function of its area and number of sides, and a set of scattering processes which occur when grains disappear. When these processes are applied directly to the distribution functions (with or without correlations) the result is a mean field theory of master equation type. There were many early attempts to write such models for grain growth using growth laws based on bubble radius. These were unsuccessful, because, as von Neumann showed [15], the rate of growth of a two-d bubble depends only on its number of sides:

$$\frac{da_n}{dt} = \kappa(n-6), \qquad (3)$$

where a_n is the area of a single n-sided bubble.

Fradkov *et al.*, Beenakker, and Marder all studied models of this type [16,17,18]. The first two also looked at evolution on a topological network, where side rearrangement was restricted to neighbouring bubbles. None of these models gave the correct distribution functions in the scaling state, because all assumed incorrect forms of the redistribution correlations. They did, however, successfully reproduce the transients observed in the disordering of a pattern, and perforce the existence of a scaling state with $\beta=0.5$. They also yielded distribution functions with exponential cutoffs. Recently Stavans *et al.* have shown that if the correct correlations are used, the mean field theory can yield the observed distribution functions [6]. Purely statistical approaches to determining scaling state distributions also have a long history, and have recently had some success [19,20,21,22].

THE POTTS MODEL AND ANISOTROPY

The two-d Potts model simulation is one of the most extensively studied models for coarsening in two dimensions. As shown in figure 3, each grain is defined as the region of a lattice in which vertices have a given value of "spin" $\sigma(i, j)$. Bonds between unlike spins cost energy. Like spins do not interact. The Hamiltonian is simply the surface energy:

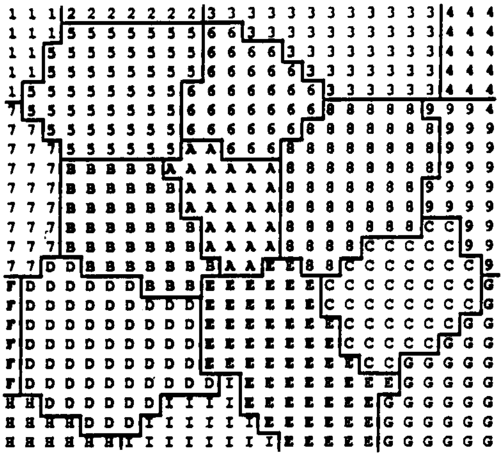


Figure 3. Detail of a Potts model lattice showing spin types and grain boundaries.

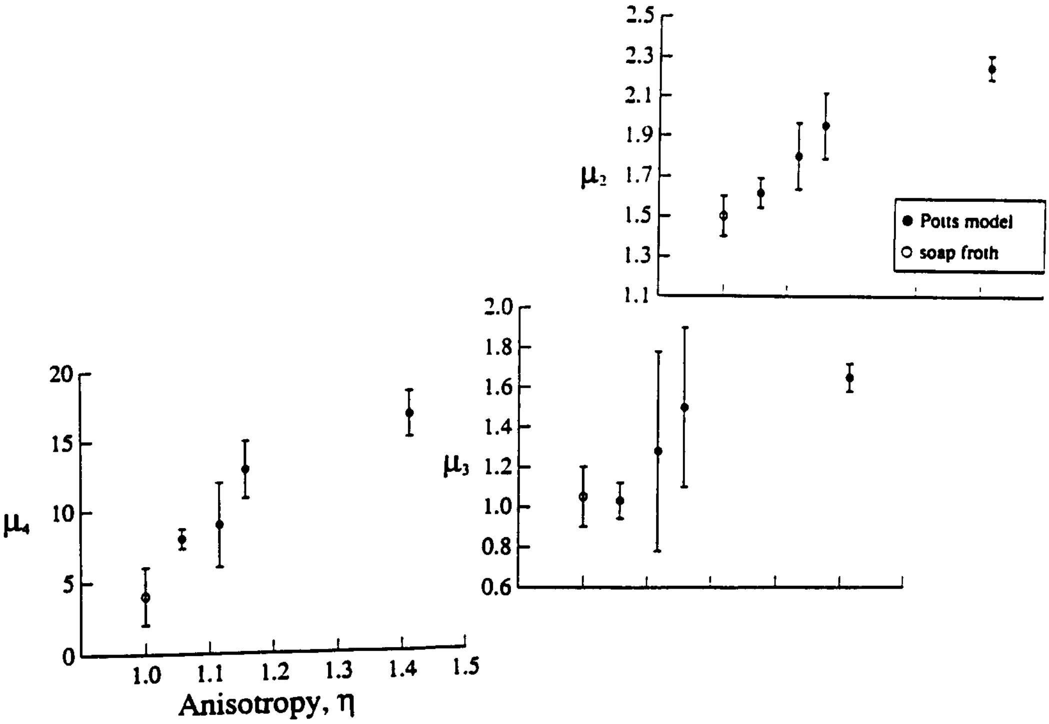


Figure 4. Comparison of topological moments for the two-dimensional soap froth and the Potts model, plotted as a function of anisotropy--by Holm *et al.* [24].

$$\mathcal{H} = \sum_{(i,\, j)\ (i',\, j')\ \text{neighbours}} 1 - \delta\sigma(i,\, j),\, \sigma(i',\, j'). \qquad (4)$$

In a zero temperature simulation we repeatedly select a site at random and assign it a new spin if the change reduces the energy. This may be extended to standard finite temperature Monte Carlo simulation. The lattice has a surface energy that depends on boundary orientation. We define the **anisotropy** (η) as the ratio between the highest surface energy per unit length and the lowest.

The anisotropic Potts model agrees qualitatively with the isotropic two-d soap froth. For most lattices the grains coarsen and the distribution functions reach a scaling state with $\beta=0.5$ [9,10]. However, high anisotropy (e.g. $\eta=1.24$) lattices produce frozen patterns and the scaling states of moderate anisotropy lattices (e.g. $\eta=1.15$) have distribution functions broader than in soap froth, e.g. $\mu_2=2.4$ rather than the 1.5. Also, the disordering process takes more time than in soap froth and the grain boundaries do not have uniform curvature. In these respects the Potts model resembles metallic grain growth more than soap froth [1,2,23].

The time for diffusion along a grain boundary in the model is long compared to the diffusion time across the boundary; this is reversed in the soap froth case. Thus the soap froth is equilibrated while the Potts model and real metals are not.

In figure 4 we plot the topological moments of the scaling state distributions for each lattice type. All three moments increase monotonically with the anisotropy. Any reasonable extrapolation of the Potts model results to $\eta=0$ would agree with the soap froth [24]. Evolving to large grains does not remove anisotropy effects, because pattern evolution is driven by side redistribution on bubble disappearance, which always occurs at the length scale of the lattice.

Fradkov *et al.* [16] measured $\mu_2=2.9\pm0.8$ for two-d grain growth in $Al+10^4$ Mg foil at 460°C, close to the high anisotropy limit for the Potts model. Thus it seems that the lattice anisotropy is the chief cause of discrepancies between the Potts model and soap froth.

VERTEX MODELS

Fullman proposed a third type of simulation [25] which has been pursued by Kawasaki and others [26]. The vertices at which cells meet are treated as pseudo-particles with well defined mobilities (velocity/force) and subject to forces determined by the positions of the neighbouring vertices. The connections between the vertices are assumed to be straight and the deviations from the ideal 120° angles are related to an effective curvature, but these derivations have not yet been made rigorous. The great advantage of this method is that it is computationally efficient. Fullman did his computations by hand. The models reach a scaling state with $\beta=0.5$, but the scaling state distribution functions, in spite of the presence of many free parameters, never come close to the experimental results. Typically $\mu_2=2.8\pm0.5$.

WHERE WE STAND

We can now say that we understand the evolution of an ideal soap froth from a theoretical, experimental and computational perspective. The experimental results of Glazier *et al.* [9,10] and Stavans [11] make it clear that ideal froth reaches a scaling state characterized by a growth exponent of $\beta=0.5$ and well defined moments with $\mu_2=1.5$. Both the boundary dynamics model of Weaire *et al.* [7,8,12,27,28], that of Frost and Thompson [23] and the zero anisotropy limit of the Potts model can reproduce these results. Recent work on mean field theories by Stavans *et al.* has shown that the distribution functions can also be obtained by a mean-field theory [6]. Thus we have an adequate understanding of ideal two-d grain growth. However, we need direct extensions of our models and experiments to include true metallic anisotropy, impurity pinning, zone refining, and other secondary effects.

LIPID MONOLAYERS

When a monolayer of an amphiphilic molecule (e.g. pentadecanoic acid) floats on a water surface it can undergo a two-d phase transition from a gas to a liquid. Adding a dye that is fluorescent only in the liquid phase makes domains visible [29]. When the pressure is gradually increased through the phase transition, small bubbles of gas appear, surrounded by a continuous background of liquid. Sometimes the gas bubbles contain small liquid drops, but these do not seem to affect the subsequent evolution [30]. The basic topology is identical to that of the soap froth. However, the weak repulsive dipole interaction which prevents bubbles from coalescing also allows the formation of labyrinthine stripe patterns [31] with a weak crumpling transition seen in magnetic bubbles [32]. Depending on the liquid fraction, the pattern may contain separated, round gas bubbles as shown in figure 5 (a), or polygonal, close-packed bubbles as shown in figure 5 (b). For large fluid fractions the bubbles interact with a background mean field. This is the Lifschitz-Slyozov limit, a radius-based model of form:

$$\frac{da(r)}{dt}=\kappa'\left(\left\langle\frac{1}{r}\right\rangle-\frac{1}{r}\right), \tag{5}$$

where $\left\langle\frac{1}{r}\right\rangle$ is a mean radius characterizing the effective pressure in the system and a(r) is the area of a bubble of effective radius r (as defined in

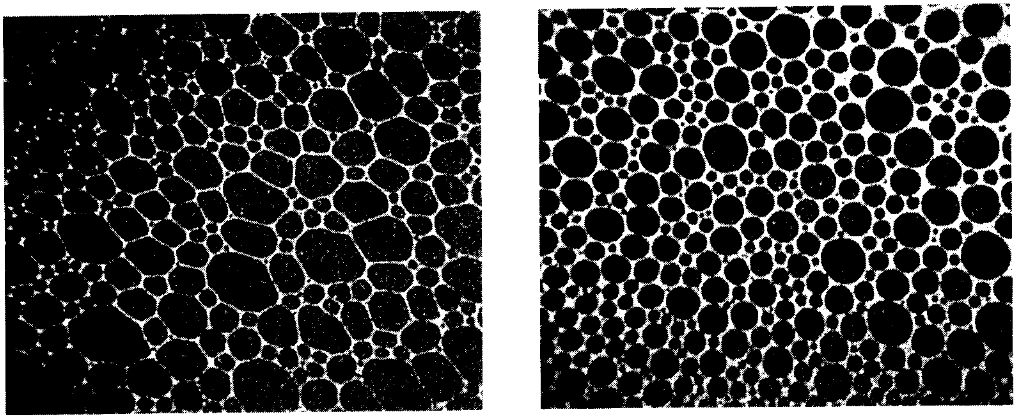
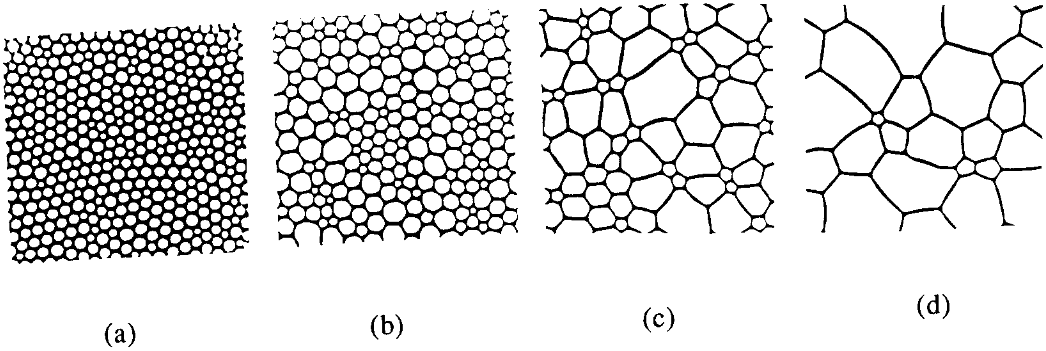


Figure 5. (a) Separated lipid monolayer bubbles, and (b) close packed lipid monolayer bubbles--by Berge *et al.* [9,30].



(a) (b) (c) (d)

Figure 6. Evolution of a magnetic froth with increasing applied magnetic field (a) H=0 Oe., (b) H=54.1 Oe., (c) H=73.8 Oe., (d) H=85.2 Oe.--by Molho [9,39].

equation 1) [33]. In the long-time limit the growth exponent differs from that for von Neumann's law, yielding $\beta=0.33$ [34].

Berge *et al.* [30] find for a froth of round bubbles (liquid fraction 50%), $\beta=0.3$, with a power law tail in the distributions, such that $\mu_2=\infty$. In the close packed case (liquid fraction 25%) they observe $\beta=0.5$ and von Neumann distributions, with $\mu_2=1.4$. Stine, *et al.* [35] working with an intermediate fluid fraction, find $\beta=0.4$ and $\mu_2=1.95\pm0.6$, with distributions intermediate between Berge's two results. Apparently, the lipid monolayer interpolates between the von Neumann regime and the Lifschitz-Slyozov regime. While the filling fraction is not necessarily constant during a real experiment, it would be worth investigating the simplest combination of the two growth laws as an approach to a mean field theory:

$$\frac{da(n,r)}{dt} = \varepsilon\kappa(n-6) + (1-\varepsilon)\,\kappa\left(\left\langle\frac{1}{r}\right\rangle - \frac{1}{r}\right), \tag{6}$$

where a(n,r) is the area of a bubble with n sides and radius r, and ε increases from zero to one with the filling fraction. In experiments, changes in ε can cause substantial changes in the growth exponent, just as Plateau borders do in the soap froth.

MAGNETIC DOMAINS

That garnet films can produce a bubble pattern which coarsens has been known for a long time [36,37]. While the Hamiltonian contains a term proportional to the total boundary length in the froth, the dominant term is the dipole interaction between patches of bulk magnetization. An external magnetic field, **H**, applied to favour one direction of magnetization sets the balance between them, and hence a length scale. The patterns are static. An increasing applied field corresponds to the passage of time in soap froth as shown in figure 6. On the other hand, bubbles cannot nucleate when the applied field decreases. Instead, the walls crumple into a labyrinth. If the field is restored slowly, the original pattern is regained. The rate of coarsening diverges near an critical field strength. Near this field, the dominant process is the disappearance of small, uniform-sized, dipole-field-stabilized five-sided bubbles. Normal coarsening has recently been observed in ferrofluids, which also exhibit labyrinthine phases [38].

Weaire *et al.* [39] treat the long range interaction as a perturbation to a boundary dynamics soap froth model, where the dipole interaction is a function of the areas of the neighbouring bubbles. This simple model gives the correct qualitative loss of stability for few-sided bubbles, and reasonable values for the distribution functions and length scale as a function of **H**. It also correctly predicts the stabilization and clustered disappearance of small bubbles. It cannot, however, create the more exotic labyrinths and other textures which characterize magnetic bubble patterns, particularly when the applied field is decreased.

THREE DIMENSIONS

Most cellular materials and hence most applications for a theory of cellular patterns are three-dimensional. The problem is difficult both experimentally and theoretically. There is no equivalent to von Neumann's law since the growth rate of a bubble is not determined by its number of faces. The minimum information needed to determine the growth rate is not known. Rivier has suggested a reasonable *ad hoc* form for the three-d analog to von Neumann's law:

$$\frac{dv_f}{dt} = \kappa(< f > - f), \tag{7}$$

where f is the grain's number of faces, v_f its volume, and <f> is the mean for all grains.

The Potts model can be extended to three dimensions provided that sufficient computer time is available. Anderson, Grest and Srolovitz [40] have run simulations on an 100 x 100 x 100 lattice. For a high anisotropy lattice, grain growth ceases after a short time. For low anisotropy, $\beta=0.48\pm0.04$ and for moderate anisotropy $\beta=0.28\pm0.02$. They made a variety of distribution function measurements, obtaining <f>=12.9. The agreement with experimental values for metal grains is good with the residual discrepancy compatible with anisotropy effects.

Nagai *et al.* [41] used a simple vertex model to obtain a scaling state with <f>=13.6 and $\beta=0.5$. While the model permits larger patterns, its derivation is *ad hoc* and the agreement with the Potts model and metal grains is poor.

In metals, serial sectioning gives the length scale and two-d distribution functions. β varies between 0.25 and 0.5 (reassuringly it never exceeds 0.5), apparently due to impurity and anisotropy effects since it increases at higher temperatures [1]. Durian *et al.* [42] monitored the evolution of shaving cream using spectroscopy. Their froth reaches a scaling state with $\beta=0.47\pm0.05$. Film draining does not seem to be a problem, but their technique does not allow them to measure distributions. Perhaps the best experiment would use multiple samples of a photo-setting polymer froth, which could evolve and set, and then be sectioned and analyzed at leisure. Confocal microscopy is defeated by the froth's specular reflections. CAT, NMR, or even optical tomography, might be useful, provided that their rate of scanning is sufficiently fast compared to the rate of froth evolution.

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