CHAPTER IX

THREE DIMENSIONAL FROTHS

IX.a Some Thoughts On Three Dimensional Froths

While we have briefly discussed two dimensional sections of three dimensional materials, our previous discussion has focussed on true two dimensional coarsening, like that found in a flat soap bubble cell or a thin metal film. For most applications, however, coarsening occurs in an open geometry in three dimensions and it is the real three dimensional properties, not the properties of sections which are important. In spite of the importance of the problem few detailed studies of the development of true three dimensional structures exist. In the 1940's Marvin and Matzke did some beautiful work on the shapes resulting when spherical lead shot is subject to high pressure and reduced to a dense polygonal mass,[158,160] Matzke *et al.* studied the shape distribution of carefully stacked regular soap bubbles,[161,162] and Lewis studied the shape distributions of three dimensional biological cells.[140,144,147] In the first two cases the systems were not allowed to coarsen in time, either by the nature of the material (lead shot) or the design of the experiment. In the last, biological constraints on the growth of vegetable cells (mitosis of large cells) introduced additional processes which are not typical of normal coarsening. The one complete study of an evolved froth is that of White and Van Vlack,[250] who studied the area and side distributions of a slowly cured polymer foam. Unfortunately, as we mentioned earlier, it appears that the foam had not reached a true scaling state. In addition, Williams' and

Smith measured the shape distribution in Al-1.2%Sn,[252] using stereographic pairs taken with X-rays and viewed under a microscope. Earlier work on grain shapes was done by Desch in β-brass,[54] and Scheil and Wurst in ingot iron.[24] None of these studies examined the dynamics of the pattern evolution.

Theoretical studies of regular and pseudo-regular polyhedral packings are more common, beginning with Lord Kelvin's famous paper demonstrating that a modified tetrakaidekahedron is the minimal regular packing.[120] The distributions produced by plane sections of regular three dimensional packings have also been extensively studied. Fortes and Ferro have enumerated the allowed three dimensional polyhedra, in order to define the elementary three dimensional processes.[72,73] Besides the studies of Blanc and Mocellin and Carnal and Mocellin on two dimensional sections, direct simulations of three dimensional coarsening are few. Kurtz and Carpay go to great length to develop the formalism for a true topological mean field theory, but then make a variety of *ad hoc* assumptions that greatly reduce the usefulness of their model.[132] The generality of the various radius based mean field theories means that their predictions are usually independent of dimension, and so they may be considered three dimensional models, but the only true three dimensional models of grain coarsening are the Potts model simulations of Anderson *et al.*.[12,15] Without more detailed experimental data, it is difficult to evaluate the accuracy of their results.

Except for the Potts model studies, none of this work is of the sort to appeal to a physicist. Besides the now discredited idea that a froth was an imperfect realization of an optimal regular packing, the work on three dimensional froths has concentrated on details and special cases with little effort to elucidate general principles.

IX.b Why is the Three Dimensional Case Difficult?

Why is the three dimensional case so relatively neglected? The basic problem is experimental. It is much harder to measure a three dimensional than a two dimensional structure. Just recording the state of the system in an unambiguous way becomes difficult. Measuring the volume of foam grains with a syringe or the volume of metal grains by serial sectioning is extraordinarily tedious and slow, while the much broader range of shapes possible in three dimensions means that many more bubbles need to be analyzed to obtain reasonable statistics. Small wonder that most researchers have contented themselves with examining the two dimensional sections of three dimensional materials. This method has two unfortunate consequences. First, since sectioning is destructive, it is impossible to follow the evolution of a pattern. Second, the distribution functions of the two dimensional section are only second order dependent on the real three dimensional distributions. For example, a section of a perfectly regular tetrakaidekahedral packing can result in broad area and number of sides distributions in the section.[53] It is not surprising therefore, that all the mean field theory models which give (or assume) log-normal area distributions agree reasonably well with the experimental results. They essentially describe the process of taking two dimensional sections rather than the properties of the materials being modeled.

Besides the virtual absence of good experimental data, any theory of the three dimensional froth faces an even more serious obstacle. The basic equations which allow one to write mean field theories for two dimensional froths, von Neumann's law, and the rule that $<n>=6$, both fail in three dimensions. In fact, the average number of faces, $<f>$ of bubbles in a three dimensional froth can vary considerably, though most experiments yield a value near 14. Instead the relation is

$$<n>=6-\frac{12}{<f>}, \tag{IX.1}$$

which adds an inconvenient level of self consistency to any models. Similarly, in three dimensions the average surface curvature of a bubble with tetrahedral angles (109.5°), is not determined solely by its number of sides. Rivier has proposed patching things up with the relation

$$\frac{dA_f}{dt}=\kappa(<f>-f), \tag{IX.2}$$

but his argument is not entirely convincing,[198] and at best applies only to ensembles of bubbles. An additional problem is that the basic scattering processes and elementary shapes are much more complicated. There are many different types of fourteen-sided bubbles, for example. Trying to simulate two dimensional sections in the manner of Carnal and Mocellin's and Blanc and Mocellin's phenomenological mean field theories, though extremely successful at giving distributions does not help us understand the real physics of the three dimensional froth. Non 120° angles and spontaneous nucleation of bubbles at vertices, remove the characteristic geometrical constraints which are typical of two dimensional froths, without suggesting any way to recover their three dimensional equivalents, and leave us without either von Neumann's law or rates for the elementary processes.

Computer time is the chief problem for the Potts model simulation (which is the one true three dimensional model which has been successfully implemented), especially because the fraction of volume affected by edge effects is much larger in three than in two dimensions. Equilibration times are similarly stretched out making very large systems imperative. Unfortunately, running long time montecarlo simulations on 1000 x 1000 x 1000 lattices is costly to say the least.

IX.c Existing Results

For detailed distributions broken down by topological categories of bubbles, we refer the reader to the papers of Matzke and Fortes and Ferro.[72,73,161] Rhines and Craig have measured the steady state face distribution in Aluminum.[194] Anderson, Grest and Srolovitz have summarized the existing data on metallic grain growth and the Potts model.[15] Besides the Potts model work, the only interesting theory for three dimensional grains is the topological mean field theory of Kurtz and Carpay.[132] Their comparisons to experiment are elaborate but not well chosen from a physicist's point of view, since they never really show that the model reproduces the most important characteristics of a real metal (for example the side distribution).[133]

IX.d Where do we go from here?

Fortunately many of the two dimensional models we have described can be extended in a straightforward manner to three dimensions. We describe briefly a few possible methods for extending simulations to three dimensions.

Three dimensional topological network models are no more difficult than network models in two dimensions, provided that we accept Rivier's three dimensional von Neumann's law. The scattering table is longer, but no more complicated in principle than in two dimensions, the chief inconvenience being that there are ten or more types of disappearing bubbles rather than three.

Three dimensional vertex models are extremely attractive because their dynamics is identical to that in two dimensions. If we select, for example, the model of Fullman, [86] we may immediately write the three dimensional equations of motion:

$$\vec{v}_i = \vec{\mathcal{F}}_i \frac{|\vec{\mathcal{F}}_i|}{\sum_{\substack{j=1,4 \\ neighbors}} (\vec{x}_i - \vec{x}_j) \cdot \vec{\mathcal{F}}}, \tag{IX.3}$$

where we define the force on a vertex j by

$$\vec{\mathcal{F}}_i = \sum_{\substack{j=1,4 \\ neighbors}} \frac{\vec{x}_i - \vec{x}_j}{|\vec{x}_i - \vec{x}_j|}. \tag{IX.4}$$

We note again that we have no *a priori* physical argument to derive these equations. However, their excellent agreement with two dimensional experiment suggests that if we accept them as phenomenologically correct we will not be too far wrong, especially since the work of Blanc and Mocellin and

Carnal and Mocellin indicates that three dimensional models are less dependent on details than two dimensional models. One minor difficulty in three dimensions is that it becomes much harder to define the inside and outside of a bubble. Perimeter tracing no longer works. Thus we need to set the dynamics on top of a topological network that we can use for bookkeeping purposes. Computationally, the effort goes up linearly in the number of vertices, allowing us to contemplate extremely large simulations, which should be able to reach the scaling regime in an unambiguous fashion. We are currently designing a model along these lines.

Boundary dynamic models also extend well from two to three dimensions with the added bonus that the underlying physics is correctly expressed. Indeed, we might hope to measure the three dimensional analogue to von Neumann's law from such a simulation. Laplace's law relating pressure differences to wall curvature is certainly true in three as well as two dimensions so there should be no surprises in the physics. Fortes and Ferro have described such a model but apparently never solved it numerically.[73] Once again the main problems are in bookkeeping. We need to maintain a topological network, and keep track of patches of two dimensional bubble walls, resulting in a computational load proportional to the total surface area of bubble in the system. Nonetheless, the method should still prove much more practical than Potts model simulations and should allow an empirical determination of an extended von Neumann's law.

Experimentally the picture is less promising. In principle it should be possible to determine the three dimensional structure of a froth using either CAT, NMR or optical tomography. Whether the needed accuracy of resolution is achievable, and if achievable compatible with the timescales of the coarsening process (true three dimensional imaging still uses the ancient method of serial sectioning–though in these cases non-destructive–and therefore remains painfully slow), are unsolved questions, because no one has ever tried the experiments. Clearly, any three dimensional tomographic experiment will generate vast quantities of image data. Nevertheless, the potential payoff would be large both in applications and in providing hard data to the theorists, and the experiment is worth trying. The biological possibilities are even more exciting. One might imagine, in the spirit of Lewis, that cancer cells with their fast division, would produce aggregates with different side distributions from normal cells, and hence provide a diagnostic tool. But such speculations lead us too far from our topic.