CHAPTER III

THE GEOMETRY OF CELLULAR PATTERNS

Before we turn to the physical processes of two dimensional coarsening we need to discuss a few basic mathematical relations describing general coördination number three networks. We also present the basic evolution equation describing bubble growth, (von Neumann's law), since its derivation is essentially geometrical and will therefore obtain to any purely diffusive surface tension driven system.

III.a Basic Mathematical Relations

The properties of a connected network consisting of vertices, edges, cells (or faces), and polyhedra (in three dimensions) may be briefly encapsulated in the Euler Relation,[51] which states that

$$N_{vertices} - N_{edges} + N_{cells} - N_{polyhedra} = 1. \tag{III.1}$$

In two dimensions there are no polyhedra so the Euler Relation reduces to

$$N_{vertices} - N_{edges} + N_{cells} = 1. \tag{III.2}$$

Another basic relation, the average number of sides per cell, $< n >$, in an infinite lattice of coordination number 3 may be derived as follows. Each vertex is shared by 3 cells and each cell has $< n >$ vertices on average, so

$$N_{vertices} = \frac{1}{3} < n > N_{cells}. \tag{III.3}$$

Each edge is shared by two cells so

$$N_{edges} = \frac{<n>}{2} N_{cells}.$$

(III.4)

Applying Euler's Relation we obtain that

$$\frac{1}{3} <n> N_{cells} - \frac{1}{2} <n> N_{cells} + N_{cells} = 1.$$

(III.5)

In the limit of a large system,

$$\lim_{N_{cells} \to \infty} \frac{1}{6} <n> = 1.$$

(III.6)

So the average number of edges per cell $<n>= 6$.[98] In three dimensions there is an extra degree of freedom, so the equations are underdetermined. If the average number of faces per grain is $<f>$ and the average number of sides per face is $<n_f>$ then for an infinite froth the quantities are related as:

$$<n_f> = 6 - \frac{12}{<f>}.$$

(III.7)

III.b Von Neumann's Law

The simplest and most beautiful theoretical result for the dynamics of the soap froth is due to von Neumann, who, in a comment to a presentation by Smith argued that the rate of increase or decrease of a bubble's area should depend only on the bubble's number of sides.[181]

Let us first discuss the driving force behind cell growth and shrinkage, pressure driven diffusion. If a film between two bubbles has a radius of

curvature ρ, and occupies an angle ϕ its length, ℓ is, to lowest order, $\ell = \rho\phi$. For a small change in normal radius, x, $\frac{d\ell}{dx} = \phi$. But $\phi = \arcsin\frac{\ell}{\rho} \sim \frac{1}{\rho}$ to lowest order. So $\frac{d\ell}{dx} \sim \frac{1}{\rho}$. Since the surface tension σ is a force per unit length, the pressure difference required to sustain the curvature is $\Delta P = \sigma\frac{d\ell}{dx} \sim \frac{\sigma}{\rho}$.

The same basic derivation holds for grain growth in polycrystals and for similar reasons. We follow the argument given by Plateau.[189] A curved film has a larger surface energy than a flat film, and a curved grain boundary has a higher surface energy than a flat grain boundary. In a grain there is no surface tension *per se* but there is a surface energy– atoms at the surface of the grain have a higher energy than those in the bulk. An atom sitting in a convex portion of grain surface is more exposed to defects, and hence has a higher energy than an atom sitting across the grain boundary in a concave section of surface. Thus it is energetically favorable for atoms to jump across the grain boundary from convex to concave surfaces. The energy difference is proportional to the surface curvature so the basic result is that energy driven diffusion results in a local boundary velocity, $\vec{v}$, at a point $\vec{x}$, of

$$\vec{v}(\vec{x}) = \mu(\vec{x})\frac{\hat{n}(\vec{x})}{\rho(\vec{x})}, \qquad \text{(III.8)}$$

where $\mu(\vec{x})$ is the local mobility which may depend strongly on time, temperature (activation energy) and boundary orientation (anisotropy), $\hat{n}(\vec{x})$ is the unit normal to the surface, and $\rho(\vec{x})$ the local curvature.[172] If the temperature is high enough that $kT >> $ orientational anisotropy, and the boundary mobility is constant in time (no zone refining effects), then averaging over a large number of grain orientations reduces the surface energy to an effective

Fig. 7 von Neumann's Law: Explanatory Diagram. A five-sided bubble, where α is the average central angle, β half the average internal angle of a polygonal approximation to the bubble, δ the difference between β and $60°$, ℓ the length of the side of the bubble, and ρ the radius of curvature of the side.
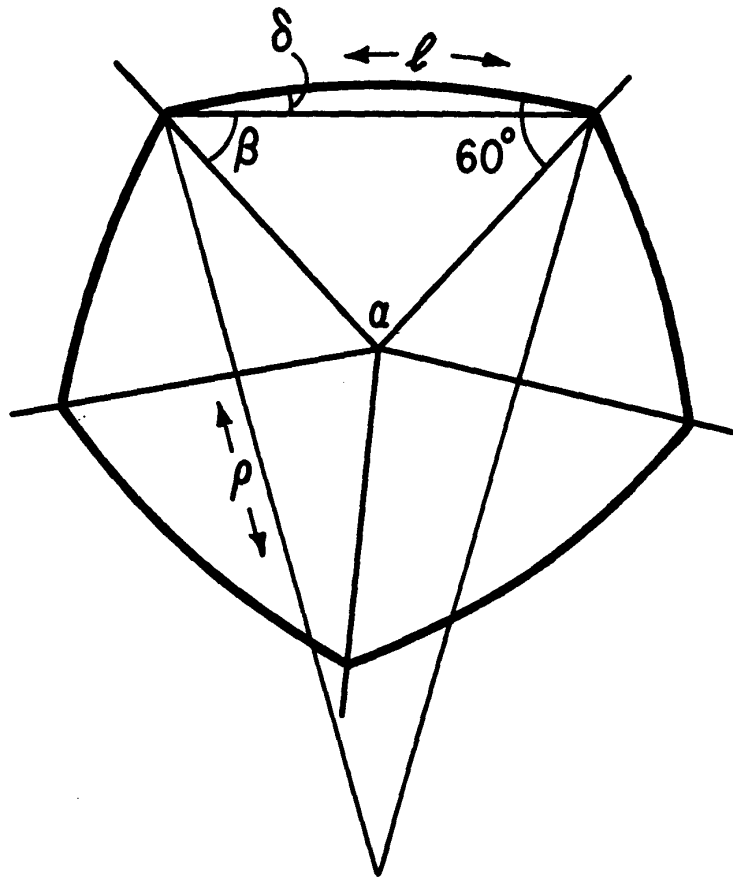
surface tension and differential pressure, and we can treat grain growth and soap bubble growth as identical. If $kT \approx$ orientational anisotropy, certain grain boundary orientations will be stabilized and grain growth will gradually slow, and may even stop at a finite grain size. If zone refining reduces or enhances the average boundary mobility, cessation of grain growth or explosive anomalous grain growth can result.

The remainder of the argument is purely geometrical and local. Von Neumann's derivation is economical and we follow it closely. We make the following hypotheses. 1) That vertex angles in a froth are 120°. 2) That all walls are sections of circular arcs. 3) That the pressure difference across a wall Δ P is proportional to one over the radius of curvature of the wall. 4) That the rate of gas diffusion across a wall is equal to its length times the pressure difference across it. 5) That pressure differences are small so that diffusion of gas is equivalent to diffusion of area.

We now make the following geometrical observations (See Fig. 7). The average central angle,α of a triangular wedge of an n-sided polygon is $\alpha = 360°/n$ so the average internal angle, β, is

$$\beta = 90°(1 - \frac{2}{n}).$$

(III.9)

The angle difference between the actual bubble angle and the polygon leaves, by hypothesis 1, an angle deficit to be made up by curvature:

$$\delta = 60° - \beta = 90°(\frac{2}{n} - \frac{1}{3})$$

(III.10)

to be made up by curvature, which gives, by hypothesis 2, a radius of curvature,

$$\rho = \frac{\ell}{360°(\frac{2}{n} - 1)},\tag{III.11}$$

where ℓ is the length of the circular arc over the side of the polygon. If we apply hypothesis 3 we find that

$$\Delta P \propto \frac{180°}{\ell}(\frac{6 - n}{3n}).\tag{III.12}$$

Noting that the diffusion of gas is towards the region with lower pressure, and applying hypotheses 4 and 5, we multiply by n sides and the length of each section of circular arc, ℓ, to obtain von Neumann's law, the rate of change of area, A_n of an n-sided bubble,

$$\frac{dA_n}{dt} = \kappa(n - 6),\tag{III.13}$$

where κ is a diffusion constant with the units of $\frac{area}{time}$.

Note that we have made no assumptions about the regularity of the froth since the lengths of the circular arcs cancel side by side. Thus the law is both exact and local for any pure diffusive system obeying our five hypotheses. If we had assumed an n-dependent typical internal angle, $\theta(n)$, for the froth, the derivation would follow as before to obtain the generalized result:

$$\frac{dA_n}{dt} = \kappa(3n(1 - \frac{\theta(n)}{180°}) - 6).\tag{III.14}$$

If the average internal angle of an n-sided bubble varies from bubble to bubble, this revised law provides a mechanism for a variation of growth rates within the population.

The only patterns that are stable under von Neumann's law are the perfect hexagonal lattice and the empty lattice. Introducing even a single defect pair into a perfect hexagonal lattice results in the collapse and eventual disappearance of all the bubbles in the lattice. Thus we know that the only possible type of equilibrium for the systems is one in which the average length scale grows continuously in time, but the normalized distribution functions ($\rho(n)$, the probability that a given bubble has n sides, $\lambda_n \equiv \frac{<a_n>}{<a>}$, the relative size of n-sided bubbles compared to the total population, etc.) and local correlations (e.g. $m(n)$, the average number of sides of a bubble next to an n-sided bubble), remain constant. We call this equilibrium, if it exists, a scaling state.

Von Neumann's law predicts that in a scaling state, i.e., when the functions describing the distribution of areas and number of sides are constant in time, the average area of a bubble, $< a >$ is proportional to the time, t. This result may be argued in several different ways,[94,157,172,173] but we find it simplest to derive as follows. Let A be the area of the entire system, N be the total number of bubbles, $\rho(n)$ and λ_n as above. Then the number of bubbles lost per unit time is the area lost by three-, four-, and five-sided bubbles per unit time divided by their mean areas,

$$\frac{dN}{dt} = - \sum_{n=3,4,5} \frac{\kappa \rho(n) N(n-6)}{\lambda_n < a >}. \qquad \text{(III.15)}$$

Substituting for $< a >$ we obtain

$$\frac{dN}{dt} = -N^2 \sum_{n=3,4,5} \frac{\kappa \rho(n)(n-6)}{\lambda_n A}. \qquad \text{(III.16)}$$

If the distribution functions are time independent, which is what we mean when we say we are in a scaling state, then the sum is a constant and

$$\frac{dN}{dt} \propto -N^2 \ \Rightarrow \ N \propto t^{-1} \ \Rightarrow \ <a> \propto t. \tag{III.17}$$

The modified version of von Neumann's law leads to the same result. Thus by itself, von Neumann's law predicts the asymptotic linear scaling of the froth. Alternative derivation of the growth exponent from the hypothesis of a scaling state have been given by Mullins and Weaire and Kermode.[173,242]

However, von Neumann's law is not a complete description of the dynamics of a froth. It describes only the growth of bubbles with fixed numbers of sides. During the evolution of a froth bubbles typically change their number of sides many times. In particular, whenever a bubble disappears some of its neighbors change their number of sides. Since average bubble area can only increase when bubbles disappear, von Neumann's law cannot provide a complete description of the coarsening process. Any complete description of the evolution of the soap froth must make additional assumptions about how side redistribution takes place. Such information can only come from direct experimental observations of real froths.