A THESIS ENTITLED

'THE EVOLUTION OF GRAIN EDGE POROSITY'

by

DAVID MICHAEL DOWLING

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An investigation is made of porosity in polycrystals which have an idealised microstructure, comprising regular polyhedral grains of uniform size.

The stability of networks of grain edge pores is considered in Chapter Two. In this chapter a new model of interlinked grain edge porosity is derived on physically realistic grounds and takes into account the variation in the dihedral angle of the porosity along its length. The model also improves extant work by paying careful attention to the surface morphology of the porosity in the region of the grain corners, where grain edge tunnels interlink.

The relaxation of porous structures of general dihedral angle, to configurations of minimum energy, is the subject of Chapter Three. A mathematical model of the surface diffusion driven morphological changes in grain edge pores is developed. The model employs the sophisticated analysis of Chapter Two to describe the surface morphology of the porosity at any instant in time.

In the later chapters the surface diffusion shape change model is extended to include the effects of diffusion in the grain boundaries. Thus the diminution of pore volume, by the condensation of vacancies on the grain boundaries, together with the enhancement of shape changes, by the mechanisms of grain boundary diffusion and surface diffusion acting in parallel, is introduced into the model.

The results of a computer program capable of simulating the relaxation of both open, interlinked grain edge networks and closed, isolated edge pores is presented. The significance of these results to the phenomena of fission-gas release in nuclear fuels and sintering in ceramic polycrystals is discussed.
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1. GENERAL INTRODUCTION

1.1 The Aim of the Thesis

Porous structures which are encountered in polycrystalline materials, especially ceramics, exert considerable influence on their properties and uses. They can arise in several ways.

Porosity may develop during the manufacturing process for a material. Ceramic materials are usually fabricated by firing a compact of fine powder particles at high temperature. During the firing process the assembly of individual particles transforms into a single, coherent body. This phenomenon is known as 'sintering'. During sintering a well defined porous structure evolves between the particles forming the compact. The characteristic shape and extent of the porosity during the different stages of the process alters the rate at which densification occurs (Beeré, 1975).

Porous structures may also develop as a consequence of the in-service conditions to which a material is subjected. Uranium dioxide (UO$_2$) fuel used in nuclear reactors for the generation of electricity provides an example of this (Turnbull and Tucker, 1974). Fracture surfaces of UO$_2$ fuel viewed under the scanning electron microscope reveal it to be riddled by a labyrinth of interconnected tunnels and isolated voids, formed by the release of fission-gas during irradiation.

The object of the Thesis is to present a detailed theoretical study of the evolution of porous structures in polycrystalline materials. The occurrence and nature of all such porosity will be reviewed fully later in this chapter. However, before proceeding, it is essential to adumbrate the microstructural character of polycrystals and ceramics.
1.2 Ideal Crystals and Real Polycrystals

The model of an ideal crystal is a material of infinite extent isolated from all external sources of energy. Its constituent atoms or ions are ordered such that all attractive and repulsive forces between them are balanced. This high degree of order leads to a structure which is regular and periodic. A particular crystal structure is characterized by a 'unit cell', which completely specifies the relative positions of the atoms in the structure. The unit cell when repeated in three dimensions generates the complete crystal and in an ideal crystal such repetition is supposed to extend throughout all space. Crystals are categorised as 'ionic', 'covalent' or 'metallic', depending upon the nature of the interatomic forces.

The structure of a real crystalline material however, whilst still depending on its atomic make-up, is additionally affected by the method of its formation, its subsequent treatment and its final external conditions. These factors can lead to perturbations of its ideal structure, which in turn influences its physical properties and appearance. Many types of defects may occur in a real crystal, certain of which will be discussed in detail later. As a start, however, an obvious distinction between a real crystalline material and an ideal crystal is the presence of surfaces. The outer extremities of a real crystal constitute an abrupt end to its essentially periodic structure. Interior surfaces across which there is a marked change in crystal orientation may also be present, having occurred during fabrication. A complete real crystal may thus comprise a mosaic of many small crystallites or 'grains'. Such a structure is termed 'polycrystalline' and the interfaces between contiguous
crystallites are known as 'grain boundaries'.

Commonly the formation of metallic polycrystals occurs during the cooling of a 'melt' of the liquid metal. In these circumstances solidification occurs when small crystals are nucleated in the melt. They then grow at the expense of the surrounding liquid until all atoms become an integral part of the solid structure. Usually many nuclei are formed and these grow into a mass of fine grains. Often the nuclei grow rapidly along certain crystallographic directions and more slowly along others, resulting in a structure of long branching arms, called 'dendrites', extending from each nucleus. As cooling continues the growth of dendrites from one nucleus is inhibited by the mesh of dendrites emanating from neighbouring nuclei. At this point the remaining liquid freezes in the spaces between the branches, producing a polycrystalline structure, with one grain formed about each nucleus.

1.3 Ceramic Polycrystals

A ceramic or ceramic material is not well-defined. The term 'ceramic' is derived from 'Keramos', the Greek word for potters' clay or ware made from clay and fired. By natural extension of this meaning the word has come to embrace all products made from fired clay, such as bricks, tableware, sanitary ware and electrical porcelain. During the last century, however, products made from silica, using the same process of shaping a moist batch, drying it and firing it, also became known as ceramics. And still more recently, the phrase 'new ceramics' has been coined to describe products made from the whole field of inorganic, non-metallic, crystalline materials, fabricated by the
same general process. Thus ceramic, whilst still retaining its original sense of a product made from clay, has tacitly come to include all products distinguished by the special way in which they are manufactured. Included amongst these new ceramics are materials now being used in electrical and electronic, high temperature and nuclear engineering, such as gallium arsenide, Sialon and uranium dioxide (New Scientist, 1984).

A modern ceramic object is manufactured by firstly obtaining a fine powder of material, either by pulverising the raw material or by deliberate chemical synthesis. The powder is then compacted into the shape of the object required. This is achieved in different ways, depending on the amount of liquid which is added to assist the process. In 'slip casting' a suspension of the powder is poured into a mould, later the liquid is drawn off, leaving a shell of consolidated powder on the wall of the mould. If less liquid is used, a stiff, plastic mix of powder and liquid can be 'extruded' into the required shape by forcing it through the orifice of a die. Dry or nearly dry powders can be consolidated by 'pressing' them into a metal die. The object formed by one of these methods is then dried, after which it is fired. Firing consists of heating the object to a temperature high enough to cause it to change physically and chemically into a hard, brittle, chemically resilient body, without causing it to melt completely. The overall process taking place during firing is the sintering phenomenon mentioned above. However, this process seldom proceeds to the extent that the fired product is completely free of porosity.
1.4 The Morphology of Polycrystalline Grains

1.4.1 Surface Energy Considerations

Evidently the microstructure of polycrystalline materials fabricated from the melt or from powder compacts are similar in nature, both being primarily assemblies of grains. To understand the nature of porosity which occurs in these materials a discussion of the form assumed by the grains and the way in which they fill space is pre-requisite.

The 'radial' dimensions of metallic grains have been measured to range between $10^{-2}$m and $10^{-4}$m (Cottrell, 1975). The size of a grain is then much larger than that of an atom (which is typically $10^{-10}$m in radius (Tennent, 1976)), though sufficiently small for atomic forces to be significant in determining their surface morphology. For at the boundaries between grains atomic order is necessarily disturbed as a result of the discontinuity in the crystalline structure. This disturbance results in the atoms local to the boundary being in a high energy configuration. It is the attempted minimisation of this energy within a polycrystalline aggregate that controls the grain morphology, an effect often visualised as being driven by surface tension. An obvious analogy can be drawn here by considering the behaviour of a surface of water. The surface of a large volume of water, such as that contained in a full bucket, sets itself level under the influence of gravity. The surface of water in a capillary, however, is curved, due primarily to the effect of surface tension. The morphologies of other chemically diverse systems are also dictated by surface tension. Examples include cells in biological tissues and bubbles in soap froths. D'Arcy Thompson in his elegant treatise 'On Growth and Form'(1942)
describes numerous and varied phenomena governed by surface tension from the world of biology.

1.4.2 The Variation of Surface Energy

The membranes between bubbles in a soap froth clearly all possess the same specific free energy. However, both experimental and theoretical evidence shows that the free energy of a grain boundary depends on the orientation difference between the lattice planes of the contiguous crystallites which form the boundary (McNutt, 1968). The dependence is such, however, that the free energy increases rapidly for the first few degrees of misalignment in any direction, until it reaches a maximum value. Thereafter it changes much more slowly. It is therefore normal, and for the purposes of this discussion, quite satisfactory, to consider the grain boundary energy to be independent of orientation difference, and to assume that all boundaries possess the same specific free energy. Under this assumption a single isotropic grain boundary surface tension may be used in the ensuing calculations, in place of the specific free energy of the boundary.

1.4.3 The Conditions for Minimum Energy

With the assumption of homogeneous surface energy, together with further assumptions about the way in which grains pack together, it is possible to predict the equilibrium configuration of a crystalline grain.

Equilibrium is usually intended to refer to the situation of lowest free energy. Generally a body will tend to lower its total free energy by reducing the area of its grain boundaries. However, situations arise where the net grain boundary energy is not a minimum but the assembly is metastable (Ahmed, 1984). In
this case the definition of equilibrium is taken to be that average grain shape no longer changes with time. Here only the ideal case in which each grain assumes an area of least grain boundary area appropriate to its volume will be considered.

Surfaces of least area enclosing a given volume are known as 'minimal surfaces'. The sphere is probably the simplest example of a minimal surface. It has the smallest area of all forms enclosing the same volume and is exemplified by a single, free, weightless soap bubble. In a fully dense polycrystal, however, the grains are subject to the constraint that they must fill space. This cannot be done by an assembly of spheres, however small. The geometrical situation pertaining in a dense body of grains is much closer allied to an array of bubbles in a soap froth. The soap froth analogy is of great assistance in understanding the behaviour of grain boundaries in a polycrystal, since in both cases the same two shape determining factors pertain. These are:-

(1) Space must be filled, and

(2) The energy, or area of surface (grain boundary or soap film) must be minimised.

To elaborate, consider space divided into a number of separate parts, such that each partition is in equilibrium with all others. In a polycrystal the partitions will be grains and the surfaces of the partitions grain boundaries. The grain boundaries must meet in line in order to divide the space. The minimum number of grain boundaries which can achieve this is clearly three. Three is also the maximum number which can intersect and remain stable. It is found that more than three
boundaries meeting one another in a line will instantly dissociate (Ahmed, 1984). For instance, if four grain boundaries come together, they will quickly separate into two triple junctions joined by a single boundary. By considering either surface energy or surface tension, it can easily be shown that such a configuration is one of minimum energy when the angles between each boundary are equal. Therefore, it follows that a 'grain edge' is formed by the intersection of three grain boundaries meeting in equal angles of 120°.

The minimum number of grain edges required to form a 'grain corner' is four. Four is also the maximum number which is stable. This has been elegantly demonstrated by the Belgian philosopher, Plateau, (Plateau, 1873) in his now classical experiments with soap films. The work of Plateau has been summarised in English by many authors, including Isenberg (1978). Since the surface energies of each of the six grain boundaries meeting at a grain corner are assumed to be equal, it follows that the corner is symmetric and the four edges point to the apices of a regular tetrahedron. The angles between the edges can be shown geometrically to be the supplement of \( \cos^{-1} \left( \frac{1}{3} \right) \), that is 109°28'.

Thus the fundamental structural unit of minimum surface energy in a polycrystal is a grain composed of:

(2a) edges formed by the intersection of three grain boundaries mutually inclined at 120°, and

(2b) corners formed at the intersection of four grain edges mutually inclined at 109°28'.

The conditions (2a) and (2b) above are known as Plateau's rules for minimum energy.
1.4.4 Possible Idealised Grain Shapes

There are a number of plane-faced, regular polyhedra which come close to satisfying conditions (1) and (2) above but which do not comply completely. The edges of the pentagonal dodecahedron (shown in Figure 1.4.1) meet in angles of 108°, not far from the characteristic angle of 109°28′ and the faces meet at an angle not far removed from 120°. A small curvature of the faces would be sufficient to turn it into a stable configuration adhering to Plateau's rules. However, space cannot be filled by an assembly of pentagonal dodecahedra alone, the interstices remaining must be filled by small tetrahedra and hexahedra. An assembly of rhomic dodecahedra or tetrakaidecahedra (shown in Figures 1.4.2 and 1.4.3, respectively) will fill space entirely but neither comply completely with Plateau's rules for minimum energy.

It has been shown by Smith (1964) for instance, via the topological formulae due to Euler relating the number of faces, edges and corners of a polyhedron, that the ideal grain satisfying Plateau's rules must possess 13.39 faces, 5.10 edges per face and 22.79 corners. It follows then that no assembly of regular, plane-faced polyhedra of one type will fill space and conform to the conditions of minimum energy. The number of faces, edges per face and corners of the regular polyhedra mentioned above, together with the average values for cells observed in metals, soap froths and vegetable matter and those of the ideal are given below in Table 1.1. These data are based on those compiled by Smith (1964).
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Table 1.1

1.4.5 Kelvin's Minimum Energy Tetrakaidecahedron

The tetrakaidecahedron (Figure 1.4.3) may be thought of as an octahedron truncated at each of its six apices, normal to the line joining the apex with its centre of mass, forming a cell of fourteen sides - six square and eight hexagonal. The angles between its edges are 90° and 120°, and the angle between its faces are 125°16' and 109°28'. Table 1.1 shows the tetrakaidecahedron to possess topological features close to those of real materials. Furthermore, Lord Kelvin (Thompson, 1888) has shown that a simple distortion of the tetrakaidecahedron to what he called the minimum area tetrakaidecahedron will also satisfy the geometrical conditions of Plateau. The distortion consists of curving the edges so that all their junctions have the prescribed angles and introducing a double curvature into the hexagonal faces. The square faces are kept planar but are made
cushion-shaped. Kelvin's minimum area tetrakaidecahedron is illustrated in Figure 1.4.4.

To understand the geometry of Kelvin's minimum area tetrakaidecahedron, consider a surface in equilibrium curved under the influence of surface-tension. It is easily shown (Isenberg, 1978), that any point, p, on the surface, the difference in pressure, P, between the two sides is given by the well known Laplace-Young equation:

\[
P = \gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \]  
\[
P = \gamma K \]  

Here \( \gamma \) is the tension in the surface, \( K = \frac{1}{r_1} + \frac{1}{r_2} \) is the net curvature (twice the mean curvature) of the surface at \( p \), \( r_1 \) and \( r_2 \) being the principal radii of curvature of the surface at \( p \). The latter quantities, \( r_1 \) and \( r_2 \), are the largest and smallest radii of curvature of all curves through \( p \), formed by the intersection of the surface with those planes containing the normal to the surface at \( p \). They can be shown to be mutually perpendicular in direction (Lowry and Hayden, 1971).

In the absence of gravitational effects the extraneous pressure, \( P \), will be uniform over the whole surface, and with the assumption of isotropic surface tension this implies that such surfaces of minimum area are also surfaces of constant net curvature, \( K \). It is known from differential geometry (Struik, 1961) that a surface of minimum area passing through a closed curve in space is a surface of zero net curvature, and the geometer usually takes the definition of a minimal surface to be one of zero net curvature. However, such a surface is only minimal with respect to the area it encloses. Here, following Almgren (1983) the definition of minimal is extended to cover
situations in which the surface is minimal with respect to the volume it contains and is taken to be a surface of constant net curvature. However, in the case of an aggregate of ideal regular grains, where there is no pressure-difference, the net curvature is indeed zero.

For a surface \( z = f(x,y) \), defined relative to orthogonal cartesian coordinate axes \( ox, oy, oz \),

\[
K = \frac{\partial^2 z}{\partial x^2} \left[ 1 - \left( \frac{\partial z}{\partial y} \right)^2 \right] - 2 \frac{\partial z}{\partial x} \frac{\partial^2 z}{\partial x \partial y} + \frac{\partial^2 z}{\partial y^2} \left[ 1 - \left( \frac{\partial z}{\partial x} \right)^2 \right] \frac{1}{\left[ 1 + \left( \frac{\partial z}{\partial y} \right)^2 + \left( \frac{\partial z}{\partial x} \right)^2 \right]^{3/2}} \tag{1.2}
\]

The equation (1.2) is quoted by Isenberg (1978). Kelvin (Thompson, 1888) attempted to solve the homogeneous form of equation (1.2) for a hexagonal face of his minimum area tetrakaidecahedron. He predicted that the face is convoluted, assuming a wave configuration. This solution is only approximate and has been improved recently by Ahmed (Ahmed, 1984), who has also considered the surface morphology of irregular tetrakaidecahedra. In a bimodular array of such grains the hexagonal faces are again convoluted and the square faces planar with curved edges. It is worth noting that the hexagonal faces, which are the boundaries between grains of different sizes have associated net curvatures which are positive as seen from within the smaller grains. This suggests that once a bimodular array is formed by disturbing a unimodular array, the larger grains will grow further by a ripening process. However, the radii of curvature are very slight compared with the grain 'radii' and thus, except in materials of very fine grain size, these do not give rise to
driving forces of any significance. Thus tetrakaidecahedral grains are essentially stable in most materials.

1.5 The Occurrence of Grain Edge Porosity

This understanding of an idealised model of the microstructure of polycrystals paves the way for a discussion of the grain edge porosity occurring in these materials. Porosity in polycrystalline materials is encountered chiefly in two distinct situations: during the sintering and hot pressing of powder compacts (Coble, 1961) and during the irradiation of ceramic nuclear fuels (Tucker and Turnbull, 1975).

1.5.1 A Phenomenological Description of Sintering

It has been mentioned before that the term 'sintering' applies to the phenomenon whereby an aggregate of fine powder particles transforms to a strong, dense, polycrystalline product, after prolonged heating below the melting point of the particles. The driving force for sintering is provided by the excess of surface energy which an unsintered or partly sintered material possesses compared with when it is in a fully dense condition. A reduction of excess surface energy can be achieved by a number of different methods of material transport and these are discussed in Chapter Three. However, from the point of view of their effect on the geometry of the porosity throughout a compact, they may be divided into two types:

1. Those which produce densification (or a reduction in pore volume) and,

2. Those producing surface rounding (or a change in pore surface morphology).
The transport of matter, that is the movement of an atom from one position in the material lattice to an adjacent position, may equally be regarded as the transfer of a 'vacancy' - the absence of an atom - in the reverse direction. For simplicity throughout the present work, all atomic movements will be described in terms of vacancies rather than atoms. A vacancy transferred from a source on the pore-solid interface to a sink elsewhere on the interface will only cause surface rounding, whether it is transported via the pore surface, the volume of the grain or the grain boundary. A vacancy transported from a source on the pore-free surface to a sink in the bulk of the solid or to another surface will cause densification.

The sintering process may be considered in three stages (White, 1967) during each of which the porosity assumes physically different forms.

In the initial stage of sintering, the particles, which at first are only touching, begin to fuse together and necks of material are created between adjacent particles. This results in the formation of grain boundaries between adjacent particles and a network of connected pores throughout the assembly. As the necks continue to thicken, more grain boundary is created between neighbouring particles, which become flattened and faceted. At this stage, the grain boundary energy is sufficiently significant to produce local atomic shuffling in an attempt to minimise the total grain boundary and surface area of the compact. If the original particles are polycrystalline, the tendency to minimise their grain boundary area results in grain growth and the dissolution of all grain boundaries except those created between the necks. The geometry at this stage is then that of an
aggregate of polyhedral grains surrounded by a framework of channels lying along three grain edges and interlinking at four grain corners. If the material is created from particles of mono-crystals no grain growth occurs but the structure is identical to that described above. The grain boundaries created between the necks are effectively pinned by the surrounding porosity and cannot at this stage be removed by grain growth.

In the intermediate stage of sintering, the aggregate attempts to minimise its total surface energy by the shrinkage of the interlinked pores. This densification occurs by the transfer of vacancies from the tunnel walls to a sink within the material, such as the grain boundaries. The decrease in surface area of porosity is accompanied by an increase in grain boundary area, but in such a way as to seek a net reduction in total surface energy. Simultaneously, this energy can be further reduced by surface rounding. Thus, the interconnected porosity will attempt to adjust its shape to an equilibrium, minimum energy configuration appropriate to its volume at that instant. It is of importance to determine the morphology of this configuration, since the sintering potential of the pores is sensitively dependent on it (Beere, 1975). A calculation of this is made in Chapter Two.

The second stage of sintering gives way to the final stage when the porosity has pinched-off, becoming closed, almost spherical, pores at grain corners. Rayleigh (1892) has shown the intrinsic instability of cylindrical surfaces long compared to their circumference. Similar instabilities are inherent in long, narrow tunnels along grain edges, which become constricted and eventually close. This can occur by surface rounding alone. However, shorter, bulbous tunnels are made unstable as
densification changes their shape. Thus, long, slender pores will close first, followed by progressively shorter, more open porosity. During the final stage of sintering the isolated, grain-corner pores continue to shrink, by the transfer of vacancies to the bulk of the material, until theoretically at least a completely dense polycrystalline aggregate is formed. In practice, however, this theoretical density is rarely achieved.

'Hot-pressing', sometimes known as 'pressure assisted sintering', refers to the process of sintering under the application of an external pressure. The action of pressure may help to achieve greater densification.

1.5.2 A Phenomenological Description of Fission-Gas Release

Interlinked porous structures similar to those which are a feature of the intermediate stage of powder sintering are encountered in the microstructure of uranium dioxide fuel for nuclear reactors, undergoing irradiation. An explanation of these structures has been given by Tucker (1970) and Turnbull and Tucker (1974). Stable gaseous fission products, typically xenon and krypton, formed during the irradiation, are insoluble in the \( \text{UO}_2 \) crystal lattice. Consequently, single atoms of fission-gas diffuse from the interiors of the grains of fuel to their boundaries, where they tend to precipitate into lenticular shaped bubbles. At this stage the grain edges are free of pores. As the grain face bubbles continue to collect gas atoms they grow and eventually those nearest the perimeter spill onto the grain edges. Here they take up the shape of cigar-like bubbles, sited symmetrically along the edges like beads on a string. This configuration is energetically most favourable, representing a net
reduction in the total surface energy. These grain edge pores are continually fed by a flux of gas atoms, in time they coalesce, and in this way a continuous structure of connected pores evolves along the grain edges. The existence of such a network provides an easy path by which fission-gas can flow and be quickly released from the body of the fuel.

When the fuel has been vented in this way, the fission-gas pressure may no longer be sufficient to balance the surface tension in the tunnel walls and the tunnels may be expected to shrink and collapse in a manner similar to the intermediate stage of sintering. However, the diminution of pore volume occurs by the transfer of vacancies from the surface of the porosity to the grain boundaries. Simultaneously to this process, grain face bubbles accumulate further gas atoms. Those near the perimeter may coalesce with the grain edge tunnels, when they will discharge their gas. This gas will swiftly egress via the network of tunnels. However, when a grain face bubble is emptied, it too is left unsupported by gas pressure and will tend to sinter and coalesce with the tunnels. Consequently, the flow of gas from grain boundary bubbles to the grain edge tunnels is accompanied by a flux of vacancies from the shrinking grain face pores to the tunnel walls. Whether the grain edge tunnels grow or shrink and pinch-off after venting will depend on the relative magnitudes of the competing vacancy fluxes.

If the tunnels collapse the result will be a line of pores decorating the grain edge, smaller and fewer in number than at the outset (White and Tucker, 1983), but as fission-gas continues to diffuse to the exterior of the grains the pores will again grow and interlink. In principle, this process may be repeated ad
infinitum. However, in reality, the interconnected pores tend eventually to assume an equilibrium configuration, similar in appearance to those encountered in the intermediate stage of sintering. This sequence causes a significant expansion in the volume of the fuel and tends to keep the fuel in close contact with the cladding by which it is contained in the reactor. The intimate contact of the fuel with its cladding is important at high reactor temperatures when such contact provides better thermal conduction away from the fuel to the surrounding coolant, and consequently the fuel does not melt. However, too great a volume increase may damage the fuel's cladding. To determine the extent of this swelling is therefore of great technological importance.

The existence of vented networks demonstrates the stability of such structures. The scanning electron micrograph, Plate 1, of a fracture surface of irradiated \( \text{UO}_2 \) provides evidence of this. Whether the interlinked tunnels can sustain a truly stable morphology will be governed by the balance of surface tension forces and fission-gas pressure. In this situation the porosity will feel no tendency to change shape and a mathematical description of such interconnected structures follows in Chapter Two. Interconnected structures may also exist in a pseudo-stable state in which their shape changes so slowly that to all intents and purposes they may be regarded as stable. This situation is considered in Chapter Three.

1.6 **Some Thermodynamic Considerations**

In this section the ideas of 'chemical potential' are developed, since chemical potential is a concept which is evoked often throughout the rest of the Thesis.
1.6.1 The Thermodynamic Equilibrium of Atoms and Vacancies

Clearly, the ideal model of the crystal lattice does not suffice to explain all the important properties of crystalline materials. The existence of vacancies in a real crystal has been alluded to above. To consider a vacancy as an entity is in principle no different to considering porosity itself. In either case it is easier to identify the space which should normally be occupied, but is not, rather than a point in the structure by which the space is delineated. The occurrence of a vacancy is explained by the theory of statistical thermodynamics. The formation of a vacancy is a process which requires energy to be added to the crystal lattice. Its existence also introduces a degree of disorder into the crystal lattice. At sufficiently high temperatures this increase in entropy of the lattice compensates for the increase in its energy. In fact, the free energy of the lattice reaches a minimum at a certain concentration of defects. Since, in this state, the crystal is in equilibrium with its environment, this concentration is known as the equilibrium concentration, and it can be shown (Blakemore, 1974) that within a crystal containing \( n_A \) atoms the equilibrium concentration of vacancies, \( n_V \), is

\[
\frac{n_V}{n_V + n_A} = e^{-Q/\sigma}
\]

Here \( Q \) is the energy associated with the formation of each vacancy and \( \sigma \) is equal to the product of Boltzmann's constant, \( k \), and the absolute temperature, \( T \), of the crystal, thus

\[
\sigma = kT
\]
It is apparent from equations (1.3) and (1.4) that a certain number of vacancies will exist in thermodynamic equilibrium at all temperatures above absolute zero.

1.6.2 Chemical Potential

It is helpful to have some means by which to quantify the tendency of a vacancy to move from one position in the lattice to another. A suitable parameter must be defined at a point and be independent of the size of the crystal. The parameter employed for this purpose is chemical potential, which is usually denoted by the symbol \( \mu \). In a 'quasi-ideal' crystal, that is one which contains only atoms of one species, vacancies and no grain boundaries or other defects, reference can be made to the chemical potential of either an atom, \( \mu_A \), or a vacancy, \( \mu_V \). These have been defined by Herring (1951) as:

\[
\mu_A = \left( \frac{\partial G}{\partial n_A} \right)_T, P, n_V
\]

\[
\mu_V = \left( \frac{\partial G}{\partial n_V} \right)_T, P, n_A
\]

where \( n_A \) and \( n_V \) are the number of atoms and vacancies, respectively, in a crystal at constant temperature, \( T \), and pressure, \( P \). The symbol, \( G \), represents the Gibbs free energy of the crystal, hereafter referred to simply as its free energy.

Such a definition may appear at first sight to be formal and unhelpful. However, physically it simply represents the free energy of an atom or vacancy at a given position in the crystal lattice, at constant temperature and pressure. Its definition is
analogous to that of other potential-type functions. Any such function can be regarded as the derivative of an energy term with respect to the number of entities being moved. The difference in potential between one position and another represents the amount of work involved in moving unit number of the entity between two positions. In the case of electrical potential, for example, the amount of work done in moving a quantity of charge, $q$, between two points which differ in electrical potential by $dV$ is $qdV$.

The difference in chemical potential of an atom or vacancy in two positions in the lattice is equal to the amount of work required to transfer the atom or vacancy from the position of lower chemical potential to that higher chemical potential. As is the case for all potential functions only differences in potential between one point and another are of consequence; the zero of potential is always arbitrary. If the change in chemical potential associated with the movement of an atom or vacancy between positions is negative the change in free energy is also negative, and the change will occur spontaneously. If the chemical potential difference is positive the free energy change is also positive and work must be done to effect the change. A crystal lattice will be in chemical equilibrium if there is uniformity of chemical potential throughout the lattice, that is when $dG = 0$, namely when the free energy of the lattice is a minimum.

1.6.3 Chemical Potential Immediately Below the Surface of a Pore

Consider the small element of pore surface $A B C D$, shown in Figure 1.6.1. The sides of the element $AB$ and $BC$ are arcs which subtend angles $d\phi_1$ and $d\phi_2$ at their
respective centres of curvature, $O_1$ and $O_2$. The principal radii of curvature associated with arcs $AB$ and $BC$ are $r_1$ and $r_2$ respectively. Let the surface be displaced a small distance, $dr$, normal to itself, whilst under the influence of an applied pressure-difference, $P$, between its two sides. The new position of the surface is labelled $A'B'C'D'$.

Within a quasi-ideal material the change in position of the surface occurs by atoms in the surface being displaced by vacancies. As the surface moves, its area and hence its surface energy increases. This increase in energy is supplied partly through the work done by the excess pressure and partly by the exchange of atoms for vacancies.

Let the increase in surface area of the element of pore be $dA$, and the volume bounded by the old and new positions of the surface $A'B'C'D$ and $A'B'C'D'$ be $dV$. Then the amount of energy which must be supplied by the exchange of atoms and vacancies is

$$\gamma dA - PdV,$$

where $\gamma$ is the tension in the surface. The energy obtained by the local shuffling of atoms, which is tantamount to the movement of an atom from a position in the surface of the porosity, with potential $\mu_S^A$, to a position of lowest potential, $\mu_0^A$, within the bulk of the material is

$$\mu_S^A - \mu_0^A.$$

Accompanying such a movement of atoms through the lattice will be the movement of a vacancy, from a position of lowest potential, $\mu_0^V$,
to a position in the surface of potential, $\mu_s$. The energy required
to achieve such a movement is

$$\mu_v - \mu_s.$$

Therefore the energy obtainable by this process of the
exchange of an atom for a vacancy is

$$\mu_s^A - \mu_s^V - (\mu_o^A - \mu_o^V).$$

If it requires $dN$ atoms to be replaced by vacancies to affect the
change in position of the surface, then

$$\gamma dA - P dV = (\mu_s - \mu_o) dN,$$

where $\mu_s = \mu_s^A - \mu_s^V$ and $\mu_o = \mu_o^A - \mu_o^V$. Assuming the volume of
an atom and a vacancy to be the same and equal to $\Omega$, then

$$\gamma dA - P dV = (\mu_s - \mu_o) \frac{dV}{\Omega} \text{ or}$$

$$\mu_s - \mu_o = (\gamma \frac{dA}{dV} - P) \Omega \quad (1.5)$$

It remains to calculate the changes in area $dA$ and volume
dV. From Figure 1.6.1 it can be seen that

$$dA = [(r_1 + dr)(r_2 + dr) - r_1 r_2] d\phi_1 d\phi_2$$
$$= (r_1 + r_2) dr d\phi_1 d\phi_2 \quad \text{and}$$
$$dV = r_1 r_2 dr d\phi_1 d\phi_2$$
Therefore

\[ \frac{dA}{dV} = \frac{1}{r_1} + \frac{1}{r_2} = K, \quad (1.6) \]

where \( K \) is the net curvature of the surface. Substituting equation (1.6) into (1.5) gives

\[ \mu_S - \mu_0 = (\gamma K - P) \Omega \]

Following the literature, (Herring, 1951; Balluffi and Siegle, 1957; Eadie, Wilkinson and Weatherley, 1974) the quantity \( \mu_S = \mu_A - \mu_V \) will be called simply the chemical potential immediately below the pore surface and \( \mu_0 \) will be regarded as the arbitrary zero of this potential, taken to be that immediately below a large, flat surface under no pressure-difference. Therefore

\[ \mu_S = (\gamma K - P) \Omega \quad (1.7) \]

In the absence of an applied gas pressure-difference equation (1.7) reduces to

\[ \mu_S = \gamma K \Omega \quad (1.8) \]

the well known Gibbs-Thompson relation (Mullins, 1957; Shewmon, 1963; Kuczynski, 1972). It should also be noted that for a surface supported in equilibrium by a gas pressure-difference, \( P \), (for which \( \mu_S = 0 \)) equation (1.7) reduces to the Laplace-Young equation (1.1).
2. THE EQUILIBRIUM MORPHOLOGY OF INTERLINKED GRAIN EDGE POROSITY

2.1 Introduction

2.1.1 The Soap Film Analogy

The array of bubbles forming a soap froth is an analogy which yields useful information about the nature of the material grains in a polycrystal aggregate. Likewise soap film analogies have been exploited usefully in understanding the structure of interlinked grain edge porosity (Tucker and Turnbull, 1975). It has long been known that a soap film drawn between two rigidly supported discs will take up the configuration of a catenoid of revolution (Poynting and Thompson, 1905). This is a configuration of constant curvature and net minimum area. In this equilibrium shape the net surface tension forces, which tend to contract the film, are just balanced by the excess pressure of the entrained air, which tends to make the film expand. Such films however are stable only under certain conditions. In the case of a cylindrical film, for example, if the end supports are moved slowly apart, the film will collapse, when its length exceeds its circumference (Rayleigh, 1892). Electron micrographs of irradiated UO₂ show many of the surfaces of tunnels to be anticlastic, similar to those of catenoidal soap films, and it is therefore reasonable to assume that interlinked grain edge tunnels are subject to similar instabilities. However, such interlinked structures are not held open by rigid supports, but instead appear to be sustained by the attachment of one tunnel to others at grain
corners. Tucker and Turnbull (1975) have demonstrated that a soap film stretched between four discs, supposedly situated at the mid-points of the edges forming a grain corner, can take up a stable configuration. They have shown further that stable configurations can also exist when one support is removed and another corner unit added. In principle, a complete network of interlinked cylindrical tunnels can be constructed in this way and such a construction is topologically similar to a network of interlinked porosity.

However, the morphology of interlinked structures arising in polycrystals is complicated by their intersection with grain boundaries. The existence of the surface energy of the three grain boundaries associated with a grain edge along which a tunnel lies lends the porosity a triangulated appearance. The dihedral angle subtended by the surfaces of the pore at their intersection with the grain boundary depends on the relative magnitudes of the specific grain boundary surface energy, \( \gamma_g \), and the specific free surface energy, \( \gamma_s \). In effect these constitute surface tension forces which in equilibrium balance forming the semi-dihedral angle \( \theta_0 \) given by the expression

\[
\theta_0 = \cos^{-1}\left(\frac{\gamma_R}{2\gamma_s}\right). \quad (2.1)
\]

The case for which grain boundary surface-tension and pore surface tension are equal, that is when \( \theta_0 = \pi/3 \), has been modelled by Tucker and Turnbull (1975), using soap films. The angle \( \theta_0 \) is a characteristic of a particular material and for example in \( \text{UO}_2 \) it has been measured to be approximately 50° (Reynolds, 1967).
2.2 Sintering Models

2.2.1 Non-Equilibrium Models

Several authors have turned their attention to understanding the nature of interlinked porosity such as that arising during the second stage of powder sintering and gas-release from nuclear fuels. The earliest endeavours comprise models of very idealized geometry. Most of these have assumed the grain boundary energy to be zero and the porosity to be circular in cross-section.

In 1961, Coble presented his kinetic theory of the intermediate stage of sintering. His model is constructed of cylindrical pores situated along the edges of identical tetrakaidecahedral grains. The motivation for sintering is taken to be the surface-tension due to the curvature of the cylindrical pores. In calculating the rate of exchange of vacancies between the pore surface and the grain faces, Coble (1961) simplifies the geometry still further. He neglects the shape effects at grain corners and assumes the grain faces to be circular, surrounded by toroidal porosity. From his model Coble (1961) is able to calculate the sintering rate of pores, that is the rate of change of volume fraction of porosity.

Later in 1974, Turnbull and Tucker published their model of fission-gas swelling in UO$_2$. This improves slightly Coble's treatment of sintering. The vacancy fluxes are also calculated assuming the grain faces to be circular and the porosity to be toroidal and it is also supposed that sintering is driven by the curvature of the tunnel walls. However, this curvature is taken
to be that of a toroid rather than a cylinder. Turnbull and Tucker (1974) also neglect the effect of the morphology of the corners where four tunnels converge but in their case calculate the sintering rate assuming the volume of this junction to be a sphere.

2.2.2 Equilibrium Models

Neither the model of Coble (1961) nor that of Turnbull and Tucker (1974) addresses the problem of determining the equilibrium morphology adopted by interlinked grain edge structures. The exact equilibrium shapes of interconnected pores are difficult to calculate, since their surfaces possess complex, anticlastic curvatures. The first attempts to determine equilibrium configurations, made by Beere (1973), were entirely numerical. He devised two alternative, fundamental units of porosity from which a network of interconnected pores can be constructed along the edges of tetrakaidecahedral grains. The first unit is composed of a sphere surmounted by four conical frustra. The second is an octahedral unit abutted by four frustra of triangular prisms. These are illustrated in Figure 2.2.1(a) and (b). Beere then computed the dimensions of the basic unit of given volume fitted around a grain of constant edge length, which minimises the free energy of the pore surface and associated grain boundary. The results of these calculations indicate the existence of a minimum value of fractional porosity (the ratio of pore volume to initial grain volume) below which no equilibrium structure can exist. However, neither basic corner unit suffices generally to describe porosity of any dihedral angle. The sphere and conical frustra best describe materials
with low or zero grain boundary energy and dihedral angle of about 180°. The octagon and triangular frustra are most appropriate to porosity with near planar surfaces as found in materials of dihedral angle around 60°.

Later Beere (1975) developed a model incorporating a more realistic unit of porosity suitable for dihedral angles of any value. Based on his earlier models this basic corner unit comprises a central octahedron, its alternate faces surmounted by frustra. The exposed faces of the frustra and the octahedron are curved so that their surfaces meet at a constant angle at their intersection with the grain boundary (see Figure 2.2.1(c)). In cross-section the frustra are curvilinear triangles, the dihedral angles of which approximately ensure the balance of grain boundary and pore surface-tension forces. Again, Beere (1975) was able to compute, numerically, the dimensions of such a unit for which the free energy of the pore surface and associated grain boundary is a minimum, subject to the constraint that pore volume, grain edge length and dihedral angle remain constant. Again his results demonstrate the existence of a minimum percentage volume of porosity below which interlinked structures are unstable.

The first attempt to determine the equilibrium morphology of interlinked grain edge porosity analytically was made by Tucker and Turnbull in 1975 in their model of porosity in nuclear fuel. They considered the changes in energy associated with the virtual displacement of an infinitesimal element of pore surface, under the action of an internal gas pressure, and were able to derive a differential equation which attempts to describe the minimum energy configuration of interlinked grain edge structures. Their derivation of this equation of equilibrium is based on the
established derivation for the equation governing the equilibrium of a soap film of revolution (Isenberg, 1978). However, the intersection of grain edge structure by the grain boundaries complicates this treatment considerably and Tucker and Turnbull (1975) found it necessary to make certain simplifying assumptions to render the problem tractable. These assumptions are discussed below. However, their work has formed the foundation of the subsequent treatments of this subject made by Tucker and White (1979) and Rinous, Tucker and Crocker (1982). The latter attempted to describe the morphology of interlinked tunnels in materials of non-uniform grain size.

All three models, however, can be criticised for embodying the same set of assumptions. For they assume the cross-section of the tunnel perpendicular to the grain edge to be a curved triangle, the sides of which are three identical circular arcs. This has the advantage that the morphology of the porosity is described by a profile in a single plane, taken by Tucker and Turnbull (1975) to be the plane bisecting adjacent grain boundaries. The profile in any other plane is simply generated by a rotational transformation. In practice, however, there is no reason to assume such an exact geometry. Furthermore, these arcs are assumed to join in a dihedral angle $2\theta_0$. The magnitude of the angle $\theta_0$ was taken to be that given by equation (2.1). The model of Tucker and Turnbull (1975) and later that of Tucker and White (1979) assumed this dihedral angle to be constant along the length of the tunnel. However, $2\theta_0$ is the dihedral angle which the tunnel cross-section must assume in the plane perpendicular to the line of intersection of the tunnel surface in the grain boundary, in order for the surface tension forces to balance in this plane. An equilibrium tunnel is not cylindrical but anticlastic, flaring outward towards the grain corners.
Therefore, at any point along its length, the plane normal to the grain edge (in which the profile is supposed to be a curved triangle) will not in general be perpendicular to the line of intersection of the tunnel in the grain boundary. Thus the angle $2\theta$ at which the sides of the curved triangles meet will depend on the gradient of the profile, $\frac{dy}{dx}$, at each point along the length of the tunnel. This problem was recognised by Rinous et al (1982) but was not treated in detail. For, considering such a variation in $\theta$, gives rise to a system of two simultaneous differential equations, rather than just one, and these have no simple analytic solution.

In addition to these simplifying assumptions, Tucker and Turnbull's (1975) original derivation of the equilibrium equation, when calculating the decrease in grain boundary area by the virtual expansion of the pore volume, assumed the surface to move outward in a direction approximately normal to the grain edge. Again, this ignores the non-cylindrical nature of the tunnel surface.

2.2.3 Early Treatments at the Grain Corner

A further important criticism can be made of the models of Tucker and Turnbull (1975), Tucker and White (1979) and Rinous et al (1982), for each made considerable approximations when modelling how tunnels converge at grain corners.

In the original model of Tucker and Turnbull (1975) and the later model of Rinous et al (1982), no attempt was made to ensure that the four tunnels converging at a grain corner did so smoothly at every point. They assumed that the tunnels joined one another smoothly only in the planes of the grain boundaries. Furthermore, they assumed the volume of the junction to be filled
by a regular, plane-faced octahedron, with the tunnels surmounting its alternate faces. This resulted in there being abrupt steps in the surface of the porosity at the corner. The model also tends to under-estimate the volume of the corner region. An accurate knowledge of this volume is important when calculating the fractional volume of the porosity, and particularly so when attempting to ascertain the minimum fractional volume below which these structures are unstable. But perhaps the greatest shortcoming of this model is that the resulting corner is constructed of surfaces of zero mean curvature. The surface curvature of the tunnels associated with the corner may differ considerably from zero. If this were to occur in reality, the difference in chemical potential between the surfaces of the tunnels to those of the corner would give rise to a tendency for the pore morphology to change until both the corner and its associated tunnels possess the same uniform curvature. In this true equilibrium configuration the magnitude of the surface curvature of the porosity should lie somewhere between that of the catenoid-like surfaces of the tunnels and that of the planar surfaces of the octahedron in the model.

In recognition of this fact Tucker and White (1979) attempted to improve the model at the grain corner, assuming it to be constructed entirely of catenoid-like surfaces. However, their approach was still only approximate, since they supposed the junction to be filled by four right, circular cones, each of which subtended a solid angle of $\pi$ at its apex. The net surface curvatures of the structures calculated via this improved model showed good agreement with those calculated via a much simpler model of interlinked porosity - the so-called 'toroid' model.
The 'toroid' model was devised by Tucker in 1979 and will be described in detail in Chapter Four. However, the essence of the model is that the fourteen faces of a grain are represented by identical circles, each of which subtends a solid angle of $2\pi/7$ at the grain centre. The porosity surrounding each face is constructed of three identical surfaces, which are each segments of a toroid. This simple model has the advantage that it is computationally much less demanding than the more sophisticated models but yet, under certain circumstances, yields values of surface curvature and fractional volumes close to those given by the model of Tucker and White (1979).

It is the aim of this chapter to present a model of the equilibrium morphology of interlinked grain edge porosity, which is derived on a physically sound basis and which attempts to overcome the shortcomings of earlier work on the subject. However, the model used is still slightly approximate in so far as it retains the assumption that the tunnel cross-section perpendicular to the grain edge is formed by the intersection of three identical circular arcs.

The following sections include a new derivation of the ordinary differential equation governing the equilibrium profile along the length of a tunnel. This takes account of the fact that the dihedral angle subtended by the surfaces of a tunnel at its intersection with the grain boundaries varies along its length. An equation relating the value of this angle to its value $\theta_0$ at the mid-point of the tunnel and the gradient of its profile is also derived. This yields a coupled system of two ordinary differential equations, the solution of which is, of
course, dependent on the boundary conditions implicit in the model. A fresh treatment of the way in which four tunnels interlink at grain corners is also included, from which the appropriate boundary conditions are chosen. The model is then used to derive the relationship between the fractional volume of the pores and the chemical potential associated with their surfaces. This potential is useful in determining the propensity of the porosity to sinter. A description of the numerical solution of the equations is also included.

2.3 The Derivation of the Equilibrium Equations

2.3.1 Preliminaries

In attempting to describe the structure of the grain edge porosity, each grain is considered to be a regular tetrakaidecahedron, so that in the absence of porosity the grains pack together to form an entirely dense polycrystal. Such a structure, described in section 1.4.4, is close to one of minimum energy. This is because the three grain boundaries forming a grain edge intersect with approximately threefold symmetry and each grain corner, which is formed at the point where four adjacent grains meet, possesses approximately tetrahedral symmetry. In the ensuing calculation the structure is taken to possess exactly these symmetries without distortion of the grain edges or surfaces. The tunnels are also taken to be symmetric about the mid-point of the grain edges.

The equation describing the equilibrium profile of the grain edge tunnel, in the plane bisecting adjacent grain boundaries, is derived by applying the principle of Virtual Work to an infinitesimal increase in the volume of the porosity.
The derivation relies critically on four assumptions:

(i) the stability of the network as a whole is achieved by the interlinkage of tunnels one with another,
(ii) each grain edge is formed by the intersection of three grain boundaries mutually inclined at angles of $\frac{2\pi}{3}$ radians,
(iii) the cross-section of a tunnel in the plane normal to the grain edge is a curvilinear triangle, the sides of which are three identical circular arcs, and
(iv) the grain boundary and free surface tensions are isotropic.

To apply the Principle of Virtual Work consider the element of surface $A B C D$ shown in Figure 2.3.1, which is displaced a small distance, $\delta n$, along its outward facing normal, under the influence of a pressure-difference, $P$, between its two sides. The new position is labelled $A' B' C' D'$. In order to apply the principle the changes in energy due to:

2(a) the increase in free surface from $A B C D$ to $A' B' C' D'$,
2(b) the corresponding decrease in grain boundary area, and
2(c) the work done by the excess pressure acting on the underside of the surface in moving the element outwards,

must be considered.

To this end it is convenient to define two sets of cartesian co-ordinate axes $Ox, Oy$ and $Ox^*, Oy^*$, as shown in Figure 2.3.2. The axis $Oy$ is in the plane bisecting adjacent grain
boundary planes, whilst $Oy^*$ is in the plane of the grain boundary itself. Both axes $Ox$ and $Ox^*$ are coincident with the grain edge. The origin of both coordinate systems is taken to be the mid-point of the grain edge, that is the mid-point of the tunnel. Co-ordinates $(x,y)$ and $(x^*,y^*)$ describing the tunnel profiles in the two planes are related as follows:

\[ x^* = x \quad \text{and} \quad (2.2(a)) \]

\[ y^* = \xi y \quad , \quad (2.2(b)) \]

where it may be shown geometrically that

\[ \xi = \frac{\sqrt{2}}{\sqrt{3}} \frac{\sin(\theta - \frac{\pi}{6})}{(1 - \frac{2}{\sqrt{3}} \cos \theta)} \quad (2.2(c)) \]

Here $\theta$ is the semi-dihedral angle of the cross-section of the tunnel in the plane perpendicular to the grain edge at $x$, shown in Figure 2.3.2.

Associated with any point, $p$, on the profile in the $x,y$-plane are the principal radii of curvature $r_1$ and $r_2$. The radius $r_2$ relates to the profile in the $x,y$-plane. The radius $r_1$ pertains to the pore section in the plane normal to both the $x,y$-plane and the pore surface at the point $p$. It is simply related to the radius of curvature, $r$, of the pore cross-section in the plane normal to the grain edge, by Menseur's Theorem (Struik, 1961). These radii of curvature may be written

\[ r_1 = \frac{y}{\cos \phi} = \frac{y}{\sqrt{3}} \quad (1 - \frac{2}{\cos \theta}) \quad \text{and} \quad \frac{1}{\cos \phi} \quad (2.3(a)) \]

\[ r_2 = \left[1 + \left(\frac{dy}{dx}\right)^2\right]^{\frac{3}{2}} \frac{\left(\frac{d^2y}{dx^2}\right)^{-1}}{2} \quad (2.3(b)) \]
The angle \( \phi \) shown in Figure 2.3.2 is given by the expression

\[
\phi = \tan^{-1}\left(\frac{dy}{dx}\right).
\]  

(2.3(c))

In the following calculation tunnel morphologies are sought corresponding to a particular constant net surface curvature, \( K \). In doing this it is assumed that at equilibrium the change in surface energy due to a small increase in the volume of the tunnel is matched by the work done by an excess internal pressure, \( P \), necessary to cause its surface to expand. As stated in Chapter One, this pressure is related to the net curvature by the expression

\[
P = Y_s K
\]

The separate contributions to the energy balance will now be derived assuming that all terms of third order and higher are negligible.

2.3.2 The Energy Required to Increase the Free Surface Area

Let \( \Delta A \) and \( \Delta A' \) be the areas of the surface elements \( A B C D \) and \( A' B' C' D' \), respectively. Then, referring to Figure 2.3.3(a) and using formula (1) given in Appendix 1, the increase in free surface area \( \Delta s \) is

\[
\Delta A_s = \Delta A' - \Delta A
\]

\[
= D \left\{ [y + \delta y] + \delta n(\cos \phi - \delta \phi \sin \phi) \right\}^2
\]

\[
- [y + \delta n \cos \phi]^2 - (y + \delta y)^2 + y^2 \right\}
\]

\[
= 2 D \delta n(\delta y \cos \phi - \delta \phi y \sin \phi)
\]
where

\[ D = \frac{\frac{3(\theta - \frac{\pi}{6})}{6}}{(1 - \frac{2}{\sqrt{3}} \cos \theta) \sin \phi} \]

Clearly from Figure 2.3.2(b)

\[ \delta \phi = \frac{FF}{r_2} = \frac{\delta y}{r_2 \sin \phi} \]

which gives

\[ \Delta A_s = 2D \delta n \delta y (\cos \phi - \frac{\sqrt{3}}{r_2}) \]  

If \( \Delta E_s \) is the energy required in increasing the area of the small element of free surface, then

\[ \Delta E_s = \gamma_s \Delta A_s = 2\gamma_s D \delta n \delta y (\cos \phi - \frac{\sqrt{3}}{r_2}) \]  

2.3.3 The Energy Gained by the Decrease in Grain Boundary Area

Let \( \Delta A_g \) be the total grain boundary area consumed by the outward movement of the free surface. Since, according to equations (2.2) a point \((x,y)\) in the plane \(EE'FF'\) corresponds to a point \((x,\xi y)\) in the grain boundary, the co-ordinates of points \(A, A', B\) and \(B'\) in the \(x^*,y^*-\)plane may be deduced. This enables the area of the quadrilateral \(AA'B'B\) to be calculated and it may be shown that, to second order, \(\Delta A_g\) is given by

\[ \Delta A_g = 3 \frac{\delta n \delta y \xi}{\sin \phi} \]

Therefore the energy gained by the decrease in grain boundary area is

\[ \Delta E_g = \gamma_g \Delta A_g = 3\gamma_g \frac{\delta n \delta y \xi}{\sin \phi} \]  

(2.4(b))
2.3.4 The Work Done by the Excess Pressure

If $\Delta W_p$ is the work done by the pressure-difference, $P$, in displacing the surface a distance $\delta n$ along the outward facing normal of the tunnels, then to second order accuracy

$$\Delta W_p = \delta n \Delta P = 2D \delta n \delta y y P \quad (2.4(c))$$

2.3.5 The Principle of Virtual Work

For the tunnel to be in equilibrium with the gas pressure-difference

$$\Delta W_p = -(\Delta E_s - \Delta E_g)$$

Thus from equations (2.4(a)), (2.4(b)) and (2.4(c))

$$2\gamma_s D(\cos \phi - \frac{y}{r_2}) - 3 \frac{\gamma_s \xi}{\sin \phi} - 2DPy = 0$$

and substituting for $r_2$ and $\phi$ from equations (2.3(b)) and (2.3(c)) the differential equation describing the equilibrium tunnel shape is

$$\frac{d^2y}{dx^2} \left[ 1 + \left( \frac{dy}{dx} \right)^2 \right] - \frac{1}{y} \left[ 1 + \left( \frac{dy}{dx} \right)^2 \right] + \frac{a}{y} + K = 0$$

where

$$a = \frac{2}{\sqrt{3}} \frac{\sin(\theta - \frac{\pi}{6}) \gamma_g}{\left( \theta - \frac{\pi}{6} \right) 2\gamma_s}$$

and $K$ is the net curvature of the free surface.
2.3.6 The Variation of Dihedral Angle

It was described in section 2.2.2 how, in the plane perpendicular to the line of intersection of the tunnel surface and the grain boundary plane, surface tension forces will balance provided \( \gamma_g/\gamma_s = 2 \cos \theta_0 \). Here \( \theta_0 \) is the semi-dihedral angle \( P \ Q \ R \), depicted in Figure 2.3.4(a). In this figure the plane \( P \ Q' \ R' \) is perpendicular to the grain edge, and it is clear that the angle \( \theta \) in this plane differs in general from \( \theta_0 \). In fact, they are equal only at the mid-point of the tunnel, where due to the symmetry of the porosity, the gradient \( \frac{dy}{dx} \) is zero. It is necessary therefore to relate the angle \( \theta \), at any position along the grain edge to the characteristic angle \( \theta_0 \).

Consider Figure 2.3.4(b), which shows in detail the geometric relationship between angles \( \theta \) and \( \theta_0 \). The planes \( P \ S \ T \) and \( P \ S' \ T' \) are coincident with \( P \ Q \ R \) and \( P \ Q' \ R' \), respectively in Figure 2.3.4(a) and are related by a rotation through an angle \( \phi^* \) about the normal to the grain boundary at \( P \). The angle \( \phi^* \) is that which the tangent to the line of intersection of the pore surface in the grain boundary at \( P \) makes with the grain edge. The triangle \( P \ T \ T' \) lies in the tunnel surface and \( P \ S \ S' \) in the plane of the grain boundary. It follows that \( S \ S' \ T' \ T \) lying perpendicular to the line \( P \ S \) is a rectangle and therefore

\[ \tan \theta = \frac{P \ S'}{P \ S} \tan \theta_0 = \frac{P \ S'}{\cos \phi^* \tan \theta_0} . \]

From equations (2.2) it follows that

\[ \tan \phi^* = \frac{dy^*}{dx^*} = \xi \frac{dy}{dx} \]

and it may be shown that the angles \( \theta \) and \( \theta_0 \) are related by the
expression

\[
\tan \theta = \tan \theta_o \left[ 1 + \xi^2 \left( \frac{dy}{dx} \right)^2 \right]^{-\frac{1}{2}}
\]

Thus to summarise, the equilibrium morphology of the porosity in the x,y-plane is described by the system of equations

\[
\frac{d^2 y}{dx^2} \left[ 1 + \left( \frac{dy}{dx} \right)^2 \right]^{-\frac{3}{2}} - \frac{1}{y} \left[ 1 + \left( \frac{dy}{dx} \right)^2 \right]^{-\frac{1}{2}} + \frac{\alpha}{y} + K = 0, \quad (2.5(a))
\]

where

\[
\alpha = \frac{2}{\sqrt{3}} \frac{\sin \left( \theta - \frac{\pi}{6} \right)}{\left( \theta - \frac{\pi}{6} \right)} \cos \theta_o \quad (2.5(b))
\]

and

\[
\tan \theta = \tan \theta_o \left[ 1 + \frac{4}{3} \frac{\sin^2 \left( \theta - \frac{\pi}{6} \right)}{2 \left( \frac{dy}{dx} \right)^2} \right]. \quad (2.5(c))
\]

It remains to consider in detail the manner in which the tunnels interlink at grain corners and so to specify the boundary conditions under which equations (2.5(a)) and (2.5(c)) are to be solved.

2.4 Boundary Conditions, The Treatment at the Grain Corner and Fractional Volume

2.4.1 The Boundary Conditions

The assumption that the grain edge tunnels are symmetric about the mid-point of the grain edge (x = 0) leads immediately to the boundary condition:

\[
\frac{dy}{dx} = 0 \quad \text{at} \quad x = 0 \quad (2.6(a))
\]
Assumption (i) of section 2.3.1 asserts that stable interlinked networks are sustained by the four tunnels which converge at a grain corner giving support to one another. Accordingly, this situation must be reflected in the second boundary condition to which equations (2.5(a)) and (2.5(c)) are subject. To this end it is necessary to consider the region of the corner closely.

In the present treatment a unit of porosity is constructed at the grain corner about the octahedral building block used by Tucker and Turnbull (1975). Such a building block is shown in Figure 2.4.1(a). The four converging tunnels surmount its alternate faces. The triangle A B C in Figure 2.4.1(a) represents one such face. The tunnel surmounting the face A B C has its axis perpendicular to the face at the point O₁. The point O₁ is located at the intersection of the medians of the triangle A B C. The lines O₁A, O₁B and O₁C represent the lines of intersection of the grain boundaries forming a grain edge with the octahedral building block. This construction leads to a corner region which has tetrahedral symmetry. Though precisely such symmetry is not found in a material composed of the ideal tetrakaidecahedral grains, the construction is adequate in view of the already approximate nature of the model.

Figure 2.4.1(b) depicts the resulting construction. This figure shows also the tunnels interlinking smoothly at points such as C,D and E in the planes of the grain boundaries. Imposing this requirement leads to the boundary condition that is sought. The section in the plane through the point C and the grain edge, that is in the plane of the grain boundary, is shown in Figure 2.4.1(c). The gradient of the tunnel, tan ψ, at the point
0 \_1 (x = x_n) in this plane is easily deduced from the geometry of the tetrahedron, leading to the equation:

\[
\tan \psi = \left. \frac{dy^*}{dx^*} \right|_{x^* = x_n} = \xi \left. \frac{dy}{dx} \right|_{x = x_n} = \frac{1}{\sqrt{2}}
\]

Therefore the required boundary condition is given by

\[
\frac{dy}{dx} = (\xi_n \sqrt{2})^{-1} = s_n \text{ at } x = x_n \quad (2.6(b))
\]

where the notations \( \xi_n \) and \( s_n \) have been introduced for convenience in the calculations which follow. The quantity, \( \xi_n \), denotes \( \xi(\theta_n) \), where \( \theta_n \) is found by substituting the condition (2.6(b)) into equation (2.5(c)) yielding

\[
\tan \theta_n = \frac{\sqrt{2}}{\sqrt{3}} \tan \theta_0
\]

In principle then, the solutions of the system of simultaneous equations (2.5(a)) and (2.5(c)) subject to the boundary conditions (2.6(a)) and (2.6(b)) lead to the equilibrium profile which is sought. However, the value of \( x_n \) in equation (2.6(b)) is unknown and for this reason it is convenient to introduce the alternative condition

\[
y = b \quad \text{at} \quad x = 0. \quad (2.6(c))
\]

By so specifying \( b \), the minimum neck height of the tunnel, the system (2.5(a)) and (2.5(c)) can be solved, subject to the 'initial' conditions (2.6(a)) and (2.6(c)). For a given choice of \( b \) there are two values of \( x_n \) at which the condition (2.6(b)) is met. In practice, however, for a given curvature, only a limited range of values of \( b \) yield values of \( x_n \) at which the condition can be fulfilled. Outside this range the tunnel shapes...
calculated never achieved the gradient required by the condition
and therefore are not encountered in interconnected pore networks.

From the knowledge of $x_n$ and $y_n$ obtained in this way
the grain edge length, $\ell$, indicated in Figure 2.4.1(c) may be
calculated from the equation

\[ \ell = 2\left[ x_n + \frac{1}{(\sqrt{2})} y_n \right] \tag{2.7} \]

2.4.2 The Treatment at the Grain Corner

The construction of the grain corner region
described above differs from the model of the region used by
Tucker and Turnbull (1975) only in that now the value of the
dihedral angle $2\theta$ of the tunnels at the corner is different to
that at the mid-point of the tunnels, and without further
modification, it will suffer from those undesirable features
described in section 2.2.3. To avoid introducing these errors
here, those faces of the octahedral building block which are not
surmounted by tunnels are assumed instead to distort so that they
follow the shape of the tunnels surmounting their neighbouring
faces. Thus the resulting corner region has no discontinuities
in its surface. Furthermore, the distorted surfaces of the
octahedron are assumed to possess the same curvature and thus
chemical potential as the surfaces of the neighbouring tunnels.

In Figure 2.4.2(a) the triangle B C D represents one of
the exposed surfaces of the octahedron, whilst arcs BC, CD and DB
indicate the shapes of the surfaces of three of the tunnels
converging at the corner to which the corner region must join
smoothly. To describe the surface of the distorted face of the
octahedron it is convenient to define an axis $O_1Z$, normal to the
face B C D of the planar octahedron, having its origin at
the intersection of the medians of the triangle B C D. The shape of the curved surface B P C D is described by equation (1.2), due to Thompson (1887). Provided the surface gradients are sufficiently small, that is $|\nabla z|^2 < 1$ equation (1.2) reduces to Poisson's equation

$$\nabla^2 z = K .$$ (2.8)

Here $K$ is the surface curvature as defined in equations (2.5).

The solution to equation (2.8) is a linear combination of the solution to Laplace's equation $\nabla^2 z = 0$ and a particular integral of Poisson's equation (2.8). Using the solution to Laplace's equation in cylindrical polar co-ordinates $(z, r, \phi)$ given by Butkov (1968), the solution to equation (2.8) may be written

$$z = \sum_{n=0}^{\infty} \left( a_n \cos n \phi + b_n \sin n \phi \right) + \frac{Kr^2}{4} ,$$ (2.9)

where $\frac{Kr^2}{4}$ is the particular integral. Clearly the surface has three-fold symmetry and this must be reflected in the solution to equation (2.9), which must also be even in $\phi$. In the face of these constraints equation (2.9) reduces to

$$z = \sum_{n=0}^{\infty} a_n \cos 3n \phi . r^{3n} + \frac{Kr^2}{4} .$$ (2.10)

However, the geometry of the surface is such that no analytic expression for the unknown coefficients $a_n$ ($n = 0, \ldots, \infty$) is readily available. However, a good approximation to the sum of the infinite series can be obtained by truncating the series after four terms and calculating the values of $a_n$ ($n = 0, 1, 2, 3$) by imposing conditions on the height and
derivative of the surface $B C D P$ at points such as $D$ and $C$ shown in Figure 2.4.2.(a).

At the point $P$, where the surface $B P C D$ meets the tunnel surmounting the adjacent face $A B C$ of the octahedron, the profile of the porosity should be continuous and smooth. Therefore, using the notation of the Figure 2.4.2(b), the following conditions apply:

$$z = H \cos \eta = \left[ 1 - \frac{1}{2} \xi_n \right] y_n \cos \eta$$

and

$$\frac{\partial z}{\partial r} \bigg|_{\phi=0} = \tan \left[ \eta - \tan^{-1}(S_n) \right]$$

$$= \frac{\sqrt{2} - 4S_n}{4 + \sqrt{2} S_n}$$

Here the angle $\eta = \tan^{-1}(\frac{1}{2\sqrt{2}})$ is deduced from the geometry of the octahedron and $\xi_n$ and $S_n$ are given earlier in section 2.4.1.

The situation at the point $D$ is most easily seen by referring back to Figure 2.4.1(b). At this point, the porosity is intersected by a grain boundary. The porosity is also symmetric about the plane normal to the grain boundary, through the point, $0$, located at the centre of the octahedron. In this plane the balance of surface tension demands that the dihedral angle of the porosity at $D$ is $2 \theta_o$. Therefore at $D$,

$$z = 0$$
and

\[ \frac{\partial z}{\partial r} \bigg|_{r=\pi} = \tan(\theta_0 - \tan^{-1}\left(\frac{1}{\sqrt{2}}\right)) \]

\[ = \frac{\sqrt{2} \sin \theta_0 - \cos \theta_0}{\sqrt{2} \cos \theta_0 + \sin \theta_0} . \]

The directions \( \phi = 0 \) and \( \phi = \pi \) are shown in Figure 2.4.2(b).

These conditions lead to a set of four simultaneous linear equations which easily yield values of \( a_n \) \( (n = 0, 1, 2, 3) \). It is worth noting that since each triangular surface element has three-fold symmetry they will have been matched exactly to the tunnel shapes at six points.

2.4.3 The Fractional Volume of the Porosity

The volume, \( V_t \), of a tunnel is given by the integral

\[ V_t = 2 \int_0^{x_n} A(x)y^2(x)dx, \]

where

\[ A(x)y^2(x) = \frac{3(\theta - \frac{\pi}{6})}{(1 - \frac{2}{\sqrt{3}} \cos \theta)^2} \left[1 - \frac{2 \cos \theta \sin(\theta - \frac{\pi}{6})}{\sqrt{3}(\theta - \frac{\pi}{6})}\right] y^2 \]

is the cross-sectional area of a tunnel.

The volume of a corner, \( V_c \), is equal to the volume of the regular octahedral building block plus the volume of the four caps, formed by the surfaces which smoothly link the tunnels.
The volume of the octahedron is given by the formula

$$V_{\text{oct}} = \frac{\sqrt{2}}{3} [\sqrt{3} y_n]^3$$

$$= \frac{\sqrt{2}}{3} \left[ 2\sqrt{3} \left( 1 - \frac{(1 - \cos(\theta - \frac{\pi}{6}))}{(1 - \frac{2}{\sqrt{3}} \cos \theta)} \right) y_n \right]^3.$$

The additional volume associated with the caps is most conveniently calculated in the two stages. Consider one such cap, as depicted in Figure 2.4.3(a). Its volume is equal to the volume contained between the curved surface of the cap B P C D (shown in Figure 2.4.3(a)), plus three times the volume of the segment B P C C1. The segment B P C C1 is bounded by the intersection B P C of the cap surface with the converging tunnel, the curved boundary, B C1 C, of the normal projection of the cap on to the face, B D C, of the regular octahedron, and the edge, B C, of this face. Thus if w(r,φ) is the equation of the plane through B P C, the volume, V_{cap}, contained between the cap and the face of the octahedron is given by

$$V_{\text{cap}} = \int \int z r d\phi d\theta + 3 \int \int w r d\phi d\theta$$

BC1CC2DC2 BC1CB

The volume V_{c} of the corner is then given by the expression

$$V_{\text{c}} = V_{\text{oct}} + 4V_{\text{cap}}.$$

In a compact of tetrakaidecahedral grains every grain possesses 36 edges and 24 corners, but since each edge is shared
by 3 grains and each corner by 4 grains, the volume of porosity, \( V_p \), associated with each grain is
\[
V_p = 12V_t + 6V_c
\]

The volume increase of a compact of grains due to the existence of edge porosity is quantified by the fractional swelling, \( \frac{\Delta V}{V_o} \), defined as the ratio of the volume of porosity per grain to the original volume of the grain:
\[
\frac{\Delta V}{V_o} = \frac{V_p}{8\sqrt{2} \ell^3} - \frac{V_p}{V_p}
\] (2.11)
Here \( 8\sqrt{2} \ell^3 \) is the volume of a tetrakaidecahedron of side \( \ell \).

Finally in this section two parameters, which are useful in the ensuing discussion, are defined. The original grain edge length, \( \ell_o \), before swelling occurred is given by the expression
\[
\ell_o = \ell(1 + \frac{\Delta V}{V_o})^{\frac{1}{3}}
\] (2.12)

The radius of a sphere \( a_o \), with a volume equivalent to that of the tetrakaidecahedral grain before swelling is given by
\[
a_o = \sqrt{2} \ell_o \left(\frac{3}{\pi}\right)^{\frac{1}{3}} = \sqrt{2} \ell \left[\frac{3}{\pi \left(1 + \frac{\Delta V}{V_o}\right)}\right]^{\frac{1}{3}}
\] (2.13)

2.5 Numerical Methods, Results and Discussion

2.5.1 The Numerical Solution of the Equilibrium Equations

Equations (2.5(a)) and (2.5(c)) and conditions (2.6(a)) and (2.6(c)) can be rewritten in terms of the dimensionless co-ordinates
\[
X = Kx \quad \text{and} \quad Y = Ky
\]
In this co-ordinate system the morphology of the interlinked
porosity is described by the equation

\[
\frac{d^2Y}{dx^2} \left[ 1 + \left( \frac{dY}{dx} \right)^2 \right]^{2/3} - Y^{-1} \left[ 1 + \left( \frac{dY}{dx} \right)^2 \right] + \alpha Y^{-1} + 1 = 0 \tag{2.14(a)}
\]

and

\[
\tan \theta = \tan \theta_0 \left[ 1 + \frac{4}{3} \frac{\sin^2 \left( \theta - \frac{\pi}{6} \right)}{(1 - \frac{2}{\sqrt{3}} \cos \theta)^2} \left( \frac{dY}{dx} \right)^2 \right]^{1/2} \tag{2.14(b)}
\]

subject to the conditions

\[
Y = B = K_b \quad \text{at} \quad x = 0 \quad \text{(2.15(a))}
\]

and

\[
\frac{dY}{dx} = 0 \quad \text{at} \quad x = 0 . \quad \text{(2.15(b))}
\]

Similarly the condition 2.6(b) becomes

\[
\frac{dY}{dx}_n = S_n \quad \text{at} \quad x = x_n . \quad \text{(2.15(c))}
\]

Still \( \alpha \) is defined by equation (2.5(b)). The effect of such a transformation is to normalise the net surface curvature of the porosity to be unity. There is now no need to specify absolutely the pressure-difference between the two sides of the free pore surface (the net curvature and pressure are related via \( P = K_y g \)). In addition, the general qualitative behaviour of the porosity is more readily interpreted in this dimensionless co-ordinate system.

The numerical solution to the equilibrium equations was found by a predictor-corrector type algorithm. A value of \( Y \), namely \( Y_{i+1} \) was predicted from equation (2.14(a)) using the last calculated value of theta, \( (\theta_i) \) (initially \( \theta = \theta_0 \)). Next a value of theta, \( (\theta_i + 1) \), was calculated via equation (2.14(b)) and hence a corrected value of \( Y \) \( (Y_{i+1}^c) \) was computed via equation (2.14(a)), using \( \theta = \theta_{i+1} \). Clearly this procedure
can be repeated and repeated, in practice though good agreement between successive iterates of \( Y \) was found after only one such cycle.

The solution of equation (2.14(a)) was found by a fourth order Runge-Kutta method. The procedure was started under the initial conditions (2.15(a)) and (2.15(b)) and allowed to proceed until \( \frac{dY}{dx} \) became equal to \( (\sqrt{2}x)^{-1} \), as required by the boundary condition (2.15(c)). The solution to equation (2.14(b)) was found by the Method of False Position. However, \( \theta = \frac{\pi}{6} \) will always satisfy equation (2.14(b)) and this solution was excluded before the iterative root finding scheme was implemented in the following way. Equation (2.14(b)) can be rewritten

\[
\tan^2 \theta \left[ 1 + \left( \frac{\sqrt{3} \sin \theta - \cos \theta}{\sqrt{3} - 2 \cos \theta} \right)^2 \left( \frac{dY}{dx} \right)^2 \right] - \tan^2 \theta_0 = 0
\]

i.e.

\[
\tan^2 \theta \left[ (\sqrt{3} - 2 \cos \theta) + (\sqrt{3} \sin \theta - \cos \theta)^2 \left( \frac{dY}{dx} \right)^2 \right]
- \tan^2 \theta_0 \left( \sqrt{3} - 2 \cos \theta \right)^2 = 0
\]

or

\[
(\sqrt{3} - 2 \cos \theta) \left\{ \tan^2 \theta \left[ 1 + \left( \frac{\sqrt{3} + 2 \cos \theta}{\sqrt{3} \sin \theta + \cos \theta} \right)^2 \right] - \tan^2 \theta_0 \right\} = 0
\]

Therefore either

\[
(\sqrt{3} - 2 \cos \theta)^2 = 0,
\]
which has the solution $\theta = \pi/6$,
or
\[
\tan^2 \theta \left[ 1 + \left( \frac{\sqrt{3} + 2 \cos \theta}{\sqrt{3} \sin \theta + \cos \theta} \right)^2 \left( \frac{dY}{dx} \right)^2 \right] - \tan^2 \theta_0 = 0 . \tag{2.16}
\]

Solving equation (2.16) rather than (2.14(b)) ensures that Method of False Position will converge. The volume of the porosity was evaluated using the method of Undetermined Coefficients to give a quadrature formula of fourth order.

Before proceeding to discuss the results of these calculations and their implications for the sintering phenomenon and the fission-gas release process, consider the form of equations (2.14(a)) and (2.14(b)) in detail. For the case when the grain boundary energy is infinitesimally small compared to the free pore surface energy and the semi-dihedral angle of the porosity tends to $90^\circ$ the system (2.14(a)) and (2.14(b)) reduces to the single equation

\[
\frac{d^2Y}{dx^2} \left[ 1 + \left( \frac{dY}{dx} \right)^2 \right] - \frac{3}{2} \left[ 1 + \left( \frac{dY}{dx} \right)^2 \right]^{-\frac{1}{2}} + 1 = 0 \tag{2.17}
\]

The first term of equation (2.17),

\[
\frac{d^2Y}{dx^2} \left[ 1 + \left( \frac{dY}{dx} \right)^2 \right]^{-\frac{3}{2}},
\]

is recognisable as the principal curvature $\frac{1}{r_2}$, in the $(x,y)$-plane. The second term is also indentifiable as the curvature of the porosity $\frac{1}{r_1}$, in the meridian plane, that is the second principal curvature of the surface. Therefore, equation (2.17) simply states that, in this case, the equilibrium configuration of the porosity is one of uniform net surface
curvature and hence uniform surface chemical potential. This result is to be fully expected in view of the discussion in Chapter One.

However, when the semi-dihedral angle, \( \theta_0 \), of the porosity differs from 90°, which is the case for most materials, the net surface curvature of the porosity that should be expected by considering the analytical geometry of this surface where it intersects the \((x,y)\)-plane is given by the expression

\[
\frac{d^2y}{dx^2} [1 + \left( \frac{dy}{dx} \right)^2]^{-\frac{3}{2}} - y^{-1} \left( 1 - \frac{2}{\sqrt{3}} \cos \theta \right) \left[ 1 + \left( \frac{dy}{dx} \right)^2 \right]^{-\frac{1}{2}} + 1 = 0, \quad (2.18)
\]

where the angle \( \theta \) is related to \( \theta_0 \) by equation (2.14(b)). The second curvature term above is obtained from the earlier equation (2.3(a)). The total expression (2.18), though the exact statement of the net curvature for points on the pore surface in the \((x,y)\)-plane, clearly differs from equation (2.14(a)). In this case a simple interpretation of the two curvature terms in equation (2.14(a)) is not possible, since the model is not derived by considering an elemental area of infinitesimal extent in two directions. Instead the expression (2.14(a)) for \( k \) represents an 'average' curvature over the whole surface element of the pore surface shown in Figure 2.3.1. It is a limitation of the model which requires only this 'average net curvature' to be uniform and not the curvature at every point on the surface.
2.5.2 Results and Discussion

Figure 2.5.1 shows a plot of $K_{a_0}$, the dimensionless curvature of the porosity versus $\Delta V/V_0$, its fractional volume, also a dimensionless quantity. The parameter, $a_0$, is the radius of a spherical grain which has a volume equivalent to that of a tetrakaidecahedral grain of edge length $l_Q$ before swelling, and is defined by equation (2.13). It is used in preference to $l_Q$ mainly to facilitate a comparison of the present model of interlinked porosity with the simpler 'toroid' model proposed by Tucker (1979), in which grains are assumed to be almost spherical. The figure gives insight into the way in which in irradiated $\text{UO}_2$ interlinked porosity is inclined to collapse. The chemical potential, $\mu_s$, immediately below the surface of such a pore is given by the Gibbs-Thompson relation (1.8), so that

$$K = \frac{\mu_s}{\gamma_s \Omega}$$

where $\Omega$ is the atomic volume of the material. The 'curvature' $K_{a_0}$ is therefore a measure of the tendency of the porosity to sinter. For a network of pores with high positive surface curvature, which has been vented of its gas, will have a high propensity for vacancies to diffuse away from the pores to nearby sinks, such as grain boundaries, and for the network to collapse or sinter.

Each curve in Figure 2.5.1, irrespective of the value of the semi-dihedral angle of the porosity $\theta_o$ ($50^\circ < \theta_o < 90^\circ$), exhibits the same characteristic features. Evidently in each case there exists a minimum value of fractional volume below which
interlinked porosity cannot occur. Physically then there is a threshold volume below which there is insufficient porosity to interlink in a viable equilibrium configuration. The curves are of the same general shape - convex with respect to the ordinate axis, curling over from the abscissa to terminate at a point where the tunnels have pinched-off into isolated pores at grain corners. These isolated pores are spherical tetrahedra in shape and for this geometry the volume of the porosity can easily be calculated via formulae due to Clemm and Fisher (1955). The curvature of these pores can also be determined. Clearly Figure 2.5.1 shows good agreement between the analytically computed values of fractional volume and those obtained from the numerical model; with the possible exception of the case for which $\theta_0 = 90^\circ$.

The discrepancy between the analytic and numerical solutions in this case is, in fact, not surprising, since as the dihedral angle increases the corners become more bulbous, the surface displacements are therefore large and the solution to Poisson's equation is no longer a good description of the surface at the corner. Actually the volume is underestimated and consequently the difference between the analytical and numerical solution increases with increasing $\theta_0$. The numerically and analytically found values of $K \alpha_0$, for the limiting case when the porosity has pinched-off, also shows relatively good agreement and in the worst case, $\theta_0 = 50^\circ$, differ only by a small percentage of their true value.

The tunnel and corner profiles in the $(x,y)$-plane, shown in Figure 2.5.2, illustrate the different shapes exhibited by the porosity. The profiles depicted in the figure are of the porosity corresponding to points $A_i$ and $B_i$ ($i = 1, 2, 3$)
marked on the curves in Figure 2.5.1. Although these are all equi-potential surfaces, it is not immediately obvious whether they are all stable configurations. The tunnel profiles, $A_4$, on the lower section of the 'potential curves' are in general narrow with long edges and of low surface curvature. These structures are very stable and for reasons which will be discussed later are energetically most favourable. Similar structures also predominate in reality. The potential curves meet the abscissa at a value of $\Delta V/V_0$ for which the tunnels have zero curvature. They have not collapsed but are anticlastic - possessing curvatures which are equal and opposite in mutually orthogonal directions. Configurations on the upper arm of the curves in Figure 2.5.1 are bulbous, dumbell-shaped and at the extreme points such as E, completely separate pores at grain corners. They have high surface curvatures and surface chemical potentials and if stable would have a greater propensity to sinter.

Tucker (1979) and Rinous et al (1982) have argued that when the volume fraction of porosity exceeds the minimum at which interlinkage can arise then two possible configurations of uniform curvature can result, corresponding for example to the points C and D on the $\theta = 50^\circ$ curve in Figure 2.5.1. The structures C and D have the same fractional volume but different uniform curvatures. However, it has been argued by these authors that a tunnel newly formed by the coalescence of a line of individual bubbles, of volume slightly above the minimum stable volume, can attempt to take up a configuration of higher curvature, corresponding to a point such as D on the upper part of the curve in Figure 2.5.1, just above the value of curvature for minimum
swelling. The profile of a similar configuration is illustrated in Figure 2.5.2 for the point B₁. This configuration is however one of unstable equilibrium and cannot be sustained for the following reasons. If, as this configuration is approached, the neck at the mid-point of the tunnel, ₀, is slightly narrower than that required for equilibrium, the corners will expand at the expense of the tunnel length, in order to reduce their curvature, until the system collapses into isolated pores at grain corners, similar to but smaller than those corresponding to the point E in Figure 2.5.1. Alternatively, if the tunnel neck is larger than it need be for equilibrium, the corners will lose material to the length of the tunnel and take up a configuration similar to that at point C on the lower part of the curve in Figure 2.5.1. The profile A₁ illustrated in Figure 2.5.2 is such a configuration. Apparently then inter-connected porous networks corresponding to points between E and the minimum are unstable and any disturbance, however slight, will lead to the system collapsing or attaining a lower curvature configuration.

Qualitatively the present work exhibits no marked difference to the previous work of Tucker and Turnbull (1975) and Tucker and White (1979). Clearly Figure 2.5.3 shows some quantitative differences, notably in the value of the minimum swelling. The present work suggests interlinked porosity exists at generally lower volume fractions than previously expected by Tucker and White (1979). For the case illustrated in Figure 2.5.3 when θ = 50°, the value of semi-dihedral angle pertaining to UO₂ nuclear fuel, the present work shows porosity to be inherently unstable for volume fractions below 6.0% rather than below 6.9%, the value predicted by the 'catenoid' model of Tucker and White (1979). Since there
is good agreement between the values of fractional volume obtained via the numerical calculation and the analytic calculation for the limiting case when the porosity constitutes closed pores at grain corners, there is every reason to believe in the validity of the present results. The difference in the results is the combined effect of a number of improvements in the model. Firstly, the improvement in the equation governing the equilibrium shape of the porosity, secondly the precise treatment of the way in which the dihedral angle $2\theta$ varies along the length of a tunnel, and lastly, though probably most significantly, the more accurate way in which the pore surface at a grain corner and its volume are calculated. Each of these factors contributes to the general improvement in the results.

It is also encouraging that the simpler and computationally less demanding 'toroid' model (Tucker, 1979) gives quantitatively similar results for low values of curvature, as seen in Figure 2.5.4. In fact, better agreement is given with this model than with the other 'catenoid' models (Tucker and Turnbull, 1975, Tucker and White, 1979) for small curvatures and though it is vastly different for higher values of $K$, because the 'toroid' model cannot go unstable, this is of little consequence, since it is argued above that real materials favour equilibrium configurations of lowest curvature where the agreement is good.

2.5.3 Significance to Sintering and Gas-Release

The rate at which sintering will occur depends upon the chemical potential-difference between the tunnel surfaces and the grain boundary sinks. In the absence of externally applied stresses, the grain boundary potential is determined from the stresses on it caused by the surface tension in the surrounding
tunnel walls. Clearly the surface tension forces hold the boundaries in compression and therefore the vacancy potential of the boundaries is always negative. Although, as shown in Figure 2.5.3, the pore surface potential, $\mu_g$, can also become negative (Tucker and Turnbull, 1975, Tucker and White, 1979), the grain boundary potential will always be the smaller. Consequently, during the intermediate stage of the processes interconnected porosity will always tend to sinter spontaneously.

The curves in Figure 2.5.1 suggest that this sintering process continues until the threshold fraction volume below which the porosity cannot remain interconnected is achieved. Below this minimum value surface diffusion will cause 'necking' to begin at the mid-point of the tunnels and the network will collapse into isolated pores at the grain corners. At this point the final stage of sintering begins and the sintering rate changes. This change is governed by the changes in chemical potential at the surface of the porosity and the rapid change in its surface geometry affects the rate of surface diffusion (Beere, 1975).

The fact that stable configurations of interconnected porosity exist above a minimum value of fractional volume also indicates that the process of 'pumping-up' grain edge porosity by the generation of fission-gas, described in Chapter One, is necessarily limited to volumes lower than this minimum. At these low volumes, when tunnels are formed by the coalescence of grain edge bubbles, the entrained fission-gas leaks out through the developing interconnected network of porosity. The newly formed tunnels are therefore essentially unsupported by any gas pressure and shrink by a mechanism equivalent to the intermediate stage of sintering. If the rate at which this occurs offsets the rate at
which the porosity is inclined to enlarge by the 'pumping-up' mechanism of gas release, then the tunnels will not grow and a stable configuration will never be achieved. This could be a mechanism of delaying fission-gas release in nuclear fuels.

Sintering also plays a role in the continued swelling of uranium dioxide beyond the initial level at which stable tunnels can form. Once stable interlinked porosity has been achieved, developing grain face bubbles may come into contact with and join the grain edge tunnels. This then constitutes a flux of vacancies into the tunnels from the grain faces and if sintering is not sufficient will result in the growth of the tunnels. The values of chemical potentials arising from the present calculations therefore provide important information on the contribution of sintering processes to gas release and swelling in UO$_2$ nuclear fuels.
3. A SURFACE DIFFUSION SHAPE CHANGE MODEL OF GRAIN EDGE POROSITY

3.1 Introduction

Chapter Two has been concerned with calculating the equilibrium configuration of porosity occurring in the microstructure of powder compacts. Throughout the chapter it was tacitly assumed that material particles are sufficiently mobile for grain edge pores to relax to configurations of minimum surface energy. However, no mention was made of the possible mechanisms of material transport by which this can occur. These will be discussed below.

Mankind has long been sintering ceramics and metals. From as early as the iron age he has unwittingly made use of the phenomenon in the manufacture of his artifacts. In the last four decades, or so, enormous steps forward have been taken in the technology of sintering and the manufacturing processes utilizing it. However, these advances have been largely due to experiment and empiricism and man's understanding of the fundamental mechanisms involved in the process is still in its infancy.

Detailed investigations were not attempted until the 1920's. Thummler and Thomma (1967) give references to the work of the early pioneers of the field in a comprehensive review of the sintering process. However, it was not until 1945 that significant headway was made. Then, Frenkel (1945) made the first effort to elucidate the mechanistic theory of sintering analytically but Kuczynski (1949) was the first to achieve major success. Kuczynski's work remains as a standard and only relatively minor refinements have been made to it since.
All authors are agreed that the motivation for sintering in an assembly of powder particles is an excess of surface energy and the sintering phenomenon occurs to reduce the net interfacial energy of the system. It is not clear from the literature, however, by which mechanism or mechanisms of material transport it occurs. It is reasonable to believe that different mechanisms are dominant in the sintering of different types of materials and at different stages of any one material.

3.1.1 Sintering Mechanisms

It has long been suggested (Thummler and Thomma, 1967; Kuczynski, 1949) that the formation of a common interface between material particles, in the initial stage of sintering, can occur by one or more of the following mechanisms:

(i) Evaporation and condensation.
(ii) Viscous or plastic flow.
(iii) Volume diffusion.
(iv) Grain boundary diffusion.
(v) Surface diffusion.

Mechanisms (i) and (v) alone are incapable of producing the shrinkage of porosity encountered during the later stages of sintering but each merits some consideration. For this purpose many authors, following Frenkel (1945), have attempted to determine a kinetic law for the growth of the region of contact, or neck, between two spherical particles, or a spherical particle and a plate, of the form:

\[ \frac{b}{a} = ct^n \]

(3.1)

Here, \( \frac{b}{a} \) is the ratio of the radius of the neck to the initial radius of the particle, shown in Figure 3.1.1(a), t is isothermal
time and \( c \) is a constant incorporating temperature, particle size and material properties. The exponent \( n \) is intended to characterize the transport mechanism. For diffusive processes \( c \) will contain the relevant diffusion coefficient. A log-log plot of experimental measurements of \( \frac{b}{a} \) versus \( t \) can therefore yield some useful information. Its slope will give the exponent \( n \) and its intercept the diffusion coefficient for the process. Comparisons of the values of \( n \) found experimentally with those derived theoretically can give an insight into the processes involved. In addition, the values of diffusion coefficients calculated from the intercepts of such plots and those found by other experimental methods can be compared. Relationships in the form of equation (3.1) have been derived by Kuczynski (1949) for most of the mechanisms listed above.

### 3.1.2 Evaporation – Condensation

Material transport via a vapour phase by means of evaporation followed by re-condensation has been suggested by Kuczynski (1949). This mechanism alone cannot cause pore shrinkage but can cause grain growth, or coarsening. Kingery and Berg (1955) have observed that the early stages of the sintering of sodium chloride occurs by an evaporation-condensation process.

However for metallic polycrystals, which possess very low vapour pressures, the process has not been seriously considered. The relationship found by Kuczynski (1949) in the form of equation (3.1) with \( n = \frac{1}{3} \) has never been reported for metals (King, 1968).

### 3.1.3 Plastic and Viscous Flow

Plastic flow, due to the motion of slip dislocations through the material lattice, driven by surface tension forces has also been considered (Early, Lamel and Ansell,
as a mechanism by which sintering can occur. In polycrystalline materials, however, the existence of lattice defects constitute a serious obstacle to the motion of dislocations. The stress necessary to move a dislocation in the presence of such defects is often greater than that which can normally be provided by surface tension forces at low temperatures. Thus the likelihood of plastic deformation causing sintering is slight, especially in large grained material.

Explanations of sintering invoking a plastic flow mechanism are now largely discounted except during hot pressing. Theories of hot pressing by plastic flow are usually based on that of McKenzie and Shuttleworth (1949), taking the driving force to be the applied pressure and not surface energy.

Newtonian viscous flow of material similar to that occurring in fluids was proposed by Frenkel (1945). He envisaged a flow of matter with a velocity gradient, or strain rate, linearly proportional to the stresses due to surface energy. For an assembly of two spherical grains of material he related the coefficient of viscosity to the self-diffusion coefficient and derived a relationship in the form of equation (3.1) with the exponent n equal to $\frac{1}{3}$. Such a law is in agreement with evidence of Kuczynski (1949) and Kingery and Berg (1955), who have investigated the sintering of small glass beads. Furthermore, Brett and Siegle (1966) have observed that inert markers in fibres of glass migrate into the region of the neck as the fibres are sintered together. This evidence lends support to the idea that sintering in glass occurs by a mechanism of viscous flow.
On the other hand, the $t^1$ law has never been confirmed for polycrystalline solids (Watson and Shewmon, 1966). Nor did Brett and Siegle (1966) find that markers in rods of nickel were transported to the neck region during sintering. Consequently, they drew the conclusion that, for nickel, sintering does not occur by a net, macroscopic flow of material but by a process of diffusion. Other authors (Alexander, Kuczynski and Dawson, 1951) have reached the same conclusions — that sintering does not occur by a mechanism of Newtonian viscous flow, unless a glassy phase, which can behave as a fluid, is present in the material at sintering temperature.

3.1.4 **Diffusive Mechanisms**

In view of the foregoing it is expedient to consider the process of diffusion in some detail. Diffusion is easy to envisage in liquids and gases, where atoms are mobile and bound only weakly to one another. The way in which atoms migrate in the solid state is less obvious. What follows will be concerned with the motion of atoms of one species amongst themselves. This is usually referred to as self-diffusion. It is distinct from chemical diffusion, which refers to the process in which atoms of one species migrate into a structure of atoms of a different species. Hereafter 'diffusion' will be used to mean 'self-diffusion'.

Atoms in a solid are not stationary but perform rapid oscillations about a mean, lattice position. Usually the amplitude of this motion is small. However, by heating for example, it is possible for an atom to acquire sufficient energy to increase appreciably the amplitude of its oscillations. Such an atom may gain enough momentum to be displaced from its lattice
site to a position elsewhere in the material matrix. A jump of this type constitutes the basic mechanism of diffusion but it can take a number of forms.

An atom which resides at a lattice point adjacent to a vacancy might jump to fill the vacant site. This is known as the Schottky mechanism of diffusion. An atom might also be displaced to the position in the lattice which is not normally occupied — an interstitial position. This is the Frenkel mechanism of diffusion. Diffusion may also occur by the simultaneous movement of a number of atoms located in a ring or by adjacent atoms simply exchanging positions. However, the cooperative movement of several atoms is unlikely and the most energetically favourable mechanisms are those suggested by Schottky and Frenkel. The energy of a material lattice will not increase if an atom jumps to an adjacent vacancy. Consequently, the most probable mechanism for the diffusion of atoms is via vacant lattice sites. This is always possible since a certain number of vacancies exist in a material at all temperatures above absolute zero.

In the Schottky mechanism an atom which has jumped to a neighbouring vacancy site can jump again if a vacancy exists adjacent to its new position. However, this is unlikely since vacancies do not occur with equal probability throughout the lattice. It is most likely that a vacancy will exist at the lattice point just left by the excited atom. For this reason then there is a good chance that the atom will jump back to its original position. Successive movements of atoms are thus correlated with one another. Before moving to other lattice points an atom might vacillate between neighbouring sites for some considerable time. The movement of a vacancy however is not
correlated. A vacancy, which is surrounded by identically sited atoms, has an equal chance of moving in all directions. It is convenient therefore to consider diffusion as a flux of vacancies, the net effect of which is to attempt to smooth out differences in their concentrations. The motion of vacancies is random and their net movement down a concentration gradient does not imply a preferred direction for their movement. They move in such a way only because more vacancies exist at the top of a concentration gradient than at the bottom. A gradient of vacancy concentration can be regarded as a gradient of chemical potential and in general diffusion can be thought of being brought about by inhomogeneities of vacancy chemical potential.

Above it has been convenient to discuss the diffusive process in terms of the movements of atoms and simply to regard a vacancy as the absence of a atom. However, in an ionic crystal the displacement of an anion or cation alone would result in the crystal acquiring extra energy owing to an imbalance of electrical charge. Consequently in a crystal comprised of say equal amounts of two species, a vacancy must consist of an anionic and cationic vacancy pair. The vacancy mechanism of diffusion is therefore made up of a jump of a cation to a cationic vacancy and an anion to an anionic vacancy. In crystals of other stoichiometries vacancies exist in such a way as to maintain electrical neutrality. Although it is worthwhile to keep this in mind, the present discussion will revert to a consideration of the movement of atoms and atomic vacancies only.

In principle vacancies can be created in a number of ways, the simplest being by transferring an atom from the interior of a material to its surface. Similarly, the vacancy can be removed
by filling it with an atom from the surface. The surface of a material can therefore act as both a site for vacancy creation - a vacancy source - and a site for vacancy annihilation - a vacancy sink. In a polycrystal there are various other possible vacancy sources and sinks and these have been analysed by Coble (1958). In the case of two contacting spherical grains the concave surface of the neck is a region of high surface curvature, giving rise locally to tensile stresses directed radially outwards. The neck surface is therefore a region of high potential from which vacancies will diffuse. Ultimately, however, vacancies must be destroyed at sinks - regions of lower chemical potential. There exist two possible sinks to which vacancies can flow. One is provided by the convex free (sphere) surface, giving rise locally to compressive stresses. A second is provided by the region of contact between the grains - the grain boundary. Under the effect of surface tension this is subject to compressive stresses acting perpendicular to its plane giving rise to a low chemical potential. Vacancies annihilated at the grain boundary can cause the growth of the neck width and the approach of the grain centres causing the system to shrink. This phenomenon is known as Nabarro-Herring Creep or 'diffusional viscosity'. The phrase 'diffusional viscosity' is coined since no external stress is necessary to bring about the deformation and the macroscopic manifestations are identical to those of viscous flow. However, it can be shown that the strain rate of the deformation is dependent on the inverse square of the length of the diffusive path. The deformation will become slower and effectively stop as the diffusive path becomes longer. This is not the case for Newtonian viscous flow.
The several paths by which vacancies can travel from the tensile neck region to the free surface and grain boundary sinks are shown in Figure 3.1.1(b) and will be discussed below.

3.1.5 Volume Diffusion

Volume diffusion, lattice diffusion or bulk diffusion refers to the motion of vacancies through the interior of the material. Paths 1 and 2 in Figure 3.1.1(b) show the vacancy flux path, via the material lattice when the vacancy sink is the free surface and grain boundary respectively. Only the second mechanism can directly cause the system to shrink and powder compacts to densify.

The role of volume diffusion has been considered by many authors. The case when the sink for vacancies is provided by the free surface has been studied by Kuczynski (1949) who derived a neck growth law in the form of equation (3.1). The case in which the sink for vacancies is provided by the grain boundary has been investigated by Kingery and Berg (1955), who also derived a power relation for the rate of neck growth between two spheres. Each derivation gives \( n \) to be \( 1/5 \). The authors compare experimental observations of sintering metals with their analytical results. Both sets of experimental results yield values of \( n = 1/5 \) and both yield values of diffusion coefficients which agree with those for the respective processes when measured directly. They draw the same conclusion - that the early stage of sintering of metals occurs by volume diffusion. Their work however leaves some confusion over the question of where vacancies flow preferentially. Furthermore, Coble (1958) has suggested that any agreement between bulk diffusion coefficients calculated via their sintering rate expressions and
those measured experimentally may be purely fortuitous, this good fortune being due to the similarity between the diffusion coefficients for the two processes. In conclusion Coble gives his favour to the model of Kingery and Berg.

Johnson and Clarke (1964) and Wilson and Shewmon (1966) have attempted to derive sintering rate expressions due to volume diffusion, which incorporate contributions to both the free surface and grain boundary sinks. However, each of these models can be criticized for making considerable assumptions about the nature of the geometry of the system. King (1968) was able to relax the assumptions and make a rigorous numerical simulation of the two sphere system but did not consider the grain boundary as a possible vacancy sink. Eadie et al (1974) have also presented a numerical solution to the volume diffusion problem considering both possible vacancy sinks but were unable to specify realistic boundary conditions.

3.1.6 Grain Boundary Diffusion

Grain boundaries of a crystal are regions of disordered atoms and might be expected to provide an easier diffusive path than its interior. However, their effectiveness to transport material is governed by their width. Experimental observations indicate that grain boundary regions are only three or so atom diameters wide and grain boundary diffusion is not thought to contribute greatly to the overall process. Though Wilson and Shewmon (1966) have suggested that grain boundary diffusion may contribute significantly to neck growth at low temperatures. Theoretical treatments of grain boundary diffusion are complicated by the fact that material diffusing down a grain boundary can also diffuse away from the plane of the boundary into the bulk of the
The problem of grain boundary diffusion will be tackled in detail in later chapters.

3.1.7 Surface Diffusion

At sufficiently high temperatures the surface of a material is disordered and liquid-like and the energy required to form a vacancy in it is less than that required in the bulk or on the grain boundary. Therefore the free surface of a material can be expected to provide another path for the movement of atoms.

Kuczynski (1949) has argued that at temperatures low compared to the melting point surface diffusion dominates volume diffusion. He reasons particularly that small particles which have a large surface to volume ratio, sinter by surface diffusion. Wilson and Shewmon (1966) suggest that surface diffusion is responsible for the initial stage of sintering and that small necks grow entirely by surface diffusion. Both Kuczynski (1949) and Wilson and Shewmon corroborate these ideas with experimental evidence.

Surface diffusion alone cannot account for shrinkage in a powder compact but it can cause neck growth and grain coarsening. It is generally regarded to be predominant during the initial stage of sintering of most materials (Wilson and Shewmon, 1966) when the grain boundary junction between the particle is small. Also it can never be completely disregarded, since matter arriving at the neck region by other methods of diffusion can be redistributed evenly by surface diffusion.

In regard to this then, a study of surface diffusion in sintering is worthwhile. There have been many such studies but no definitive model for the process has emerged. A number of workers have
followed Kuczynski's (1949) lead and derived sintering rate expressions, in the form of equation (3.1), appropriate to surface diffusion. Kuczynski's original expression gives \( n \) equal to \( 1/7 \), the work of Rockland (1966) and German and Lathrop (1978) is in agreement with this. However, Cabrera (1950) has obtained a fifth power relation, as has Schwed (1951) for certain circumstances. Pines (1954) has found a sixth power relation. As with the case of volume diffusion the power laws mentioned above have been derived making severe assumptions about the geometrical nature of the system, especially in the region of the neck. These assumptions have been discussed fully by King (1968). However, Nichols and Mullins (1965) have been able to relax these assumptions. They have rigorously derived a partial differential equation describing the normal rate of displacement of the surface of a volume of revolution due to surface diffusion. Such a model is appropriate to material possessing semi-dehedral angles of 90°. They have obtained a finite-difference solution of the equation for a number of geometries including cylindrical and tapered rods, lines of spheres and a sphere resting on a slab. Their solution for the latter two cases exhibit a power relation with \( n \) approximately equal to \( 1/6 \). In a separate study Nichols (1966) has obtained the solution for the coalescence of two touching spheres. Since the case of solid spheres is entirely equivalent to that of spherical voids for the process of surface diffusion, such solutions are of interest in the field of fission-gas swelling of nuclear fuels. Results of Nichols (reported by King (1968)) via the finite-difference scheme of Nichols and Mullins, indicate a power law rate expression with \( n \) lying between
German and Lathrop (1978) have presented a finite-difference solution of the same problem based on the equation of Nichols and Mullins which suggest a value of $n = 1/7$ to be representative of the initial stage of sintering by surface diffusion.

Clearly there is a plethora of models for the initial stage of sintering by surface diffusion and little consensus amongst them. Furthermore, few models of surface diffusion have been published for materials possessing semi-dihedral angles less than $90^\circ$. Of such material and both for models of surface diffusion and volume diffusion, Coblenz, Dynys, Cannon and Coble (1979) have this to say:

".... no models exist which treat the problem precisely: such calculations are badly needed, because approximate estimates indicate that order of magnitude changes in sintering rate may result".

In view of the discrepancies in the sintering rates predicted by the various surface diffusion models for materials with high dihedral angles and because of the dearth of models for materials with low dihedral angles, a rigorous approach to the problem is timely. It is the aim of the rest of this chapter to present a general analysis of the evolution of grain edge porosity, due to surface diffusion.

The following sections will include a derivation of the partial differential equation which describes the changing shape of the $(x,y)$-profile of grain edge porosity. Simulations of the relaxation of both interlinked and isolated pores of general triangulated geometry are presented. The analytical and
computational details necessary to perform these simulations are also included. Finally the effect of the size of dihedral angle of the pores on the rate of collapse or coalescence of different grain edge porosity is analysed.

3.2 The Treatment of Pore Surface Movement

The derivation of the equation describing the movement of the surface of a pore due to diffusion over its surface relies on the assumptions 2(b), 2(c) and 2(d) listed in Chapter Two for the derivation of the equilibrium equations. A further assumption is also necessary, that is:

3(a) the surface diffusion coefficient $D_s$ is isotropic.

It has been shown in Chapter One that a vacancy which is transferred from a point of zero curvature to a point of finite curvature on a surface acquires an associated chemical potential proportional to the curvature of its new position. On a surface then, a gradient of chemical potential, the driving force for diffusion over the surface, will be associated with a gradient of the curvature of the surface. Mullins (1957) has derived an expression relating the flux of atoms per unit length, per unit time, $J$, over the surface to its curvature, $K$.

$$J = \frac{B}{\Omega} \nu_s K,$$

(3.1(a))

where

$$B = \frac{4}{\frac{D_s \delta \Omega}{\sigma}} \quad \text{and} \quad \sigma \text{ is defined by equation (1.4)}.$$

$$\nu_s K = \frac{\partial K}{\partial S}$$

(3.1(b))
is the curvature gradient with respect to $s$, the length of the surface profile. In the cartesian coordinate system defined previously and shown in Figure 2.3.2, $s$ is given by

$$ds^2 = dx^2 + dy^2.$$  

For a pore of triangular cross-section its curvature, $K$, at any point $(x(s), y(s))$ along its profile is given by equations (2.14(a)), (2.14(b)) and (2.14(c)) in Chapter Two.

### 3.2.1 The Derivation of the Equation of Motion

Following the approach of Nichols and Mullins (1964), consider again an element of pore surface $A B C D$, shown in Figure 3.2.1(a), which is displaced a small distance $\delta n$ along its outward normal to $A' B' C' D'$. Here the displacement is taken to be due to surface diffusion and to occur in an infinitesimal time $\delta t$. During this time a surface flux of atoms, $J$, will cross the edge of the element $A B$ of length $l_1$ at height $y_1$. A flux $J_2$ will cross the edge $C D$ of length $l_2$ at height $y_2$. Let the volume contained between the surfaces $A B C D$ and $A' B' C' D'$ be $\delta V$, then since no volume can be lost or gained by the mechanism of surface diffusion

$$\delta V = (J_1 l_1 - J_2 l_2) \Omega \delta t.  \hspace{1cm} (3.2)$$

It can be shown that for this geometry

$$l_i = 2 \phi(\theta_i) y_i, (i = 1, 2) \hspace{1cm} (3.3(a))$$

where

$$\phi(\theta) = \frac{(\theta - \frac{\pi}{6})}{(1 - \frac{2}{\sqrt{3}} \cos \theta)} \hspace{1cm} (3.3(b))$$

Substituting from equations (3.1(a), (b), (c)) and (3.3) into
equation (3.2) gives the expression

\[
\frac{\delta V}{\delta t} = 2B[\phi(\theta_2) y_2 \frac{\partial K_2}{\partial S} - \phi(\theta_1) y_1 \frac{\partial K_1}{\partial S}]
\]

\[= 2B \delta(\phi(\theta) y \frac{\partial K}{\partial S}) . \quad (3.4)
\]

It now remains to calculate the volume \(\delta V\). This volume is equal to the sum of the volumes of the segments similar to \(efgh'g'f'e'\), shown in Figure 3.2.1(a). In the notation of the figure, the volume \(V'\) of such a parallelepiped is given by

\[V' = \Delta A(w)r \delta w \cos \epsilon , \quad (3.5)
\]

where \(\Delta A(w)\) is the area \(ehh'e'\). It is shown in Chapter Two, section 2.3.3, that the grain boundary area \(AB'B'A'\) is given by

\[\delta n \delta s \xi ,
\]

where \(\xi\) is defined by equation (2.2(c)). In general it is convenient to write

\[\Delta A(w) = \delta n \delta s \xi(w) , \quad (3.6(a))
\]

where \(\xi(w)\) is such that \(y_w\) and \(y\), defined in Figure 3.2.1(b), are related by the expression

\[y_w = \xi(w) y . \quad (3.6(b))
\]

The form of function \(\xi(w)\) can be deduced by applying the Cosine Rule to triangle \(PQR\) in Figure 3.2.1(b), giving

\[y_w^2 = r^2(1 + \frac{4}{3} \cos^2 \theta - \frac{4}{\sqrt{3}} \cos \theta \sin w) . \quad (3.6(c))
\]
Here \( r \) is the radius of curvature defined in Section 2.3.1.

Whence from equations (2.3(a)), (3.6(b)) and (3.6(c))

\[
\xi(w) = (1 + \frac{4}{3} \cos^2 \theta - \frac{4}{\sqrt{3}} \cos \theta \sin w)(1 - \frac{2}{\sqrt{3}} \cos \theta)^{-1} . \tag{3.7}
\]

It should be noted that on the grain boundaries, where \( w = \frac{2\pi}{3} - \theta \) and \( \frac{\pi}{3} + \theta \), equation (3.7) reduces to equation (2.2(c)) and \( y_w = y^* \). Also applying the Sine Rule to triangle P Q R in Figure 3.2.1(b) gives

\[
\sin \varepsilon = -\frac{2}{\sqrt{3}} \frac{r \cos \theta}{y_w} \cos w .
\]

Hence substituting for \( \frac{r}{y_w} \) from equations (3.6) and (3.7) the relation

\[
\cos \varepsilon = \frac{(1 - \frac{2}{\sqrt{3}} \cos \theta \sin w)}{\xi(w)(1 - \frac{2}{\sqrt{3}} \cos \theta)} \tag{3.8}
\]

is obtained. Combining equations (3.5), (3.6(a)), (3.6(b)), (3.7) and (3.8) to give \( V' \), and integrating over the whole range of \( w \) gives the elemental volume \( \delta V \) in the form

\[
\delta V = \frac{\delta n \delta s}{(1 - \frac{2}{\sqrt{3}} \cos \theta)} \int_{\frac{\pi}{3} - \theta}^{\frac{\pi}{3} + \theta} (1 - \frac{2}{\sqrt{3}} \cos \theta \sin w) \, dw
\]

\[
= \frac{2 \delta n \delta s y}{\Psi(\theta)} \tag{3.9(a)}
\]

where \( \Psi(\theta) = \left\{ \frac{(1 - \frac{2}{\sqrt{3}} \cos \theta)^2}{[\theta - \frac{\pi}{6} - \frac{2}{\sqrt{3}} \cos \theta \sin (\theta - \frac{\pi}{6})]} \right\} . \tag{3.9(b)}
Combining the expression for $\delta V$ with equation (3.4) gives the equation of the normal velocity of the pore surface at the point $y(s)$, as

$$\frac{\partial n}{\partial t} = B \psi(\theta) \frac{1}{y} \frac{\partial}{\partial s} \left( \Phi(\theta) y \frac{\partial K}{\partial s} \right) . \quad (3.10)$$

It is interesting to note that when $\theta_0$ is equal to $\frac{\pi}{2}$ radians and the porosity is circular in cross-section equation (3.10) reduces to

$$\frac{\partial n}{\partial t} = B \frac{1}{y} \frac{\partial}{\partial s} \left( y \frac{\partial K}{\partial s} \right) . \quad (3.11)$$

This is the familiar form derived by Nichols and Mullins.

3.3 The Intersection of Pores and Grain Edges

Clearly, equation (3.10) is singular at the point where $y$ equals zero. Such a situation is encountered when considering the relaxation of an isolated pore, half such a pore is illustrated in Figure 3.3.1, where the three bounding surfaces of the pore meet at a point $P$ on the grain edge. Infinitesimally close to this point the lines of intersection of the pore surfaces with the grain boundaries approach linearity and the pore surfaces become planar. Here then the cross-section of the pore, in the plane perpendicular to the grain edge, is an equilateral triangle of semi-dihedral angle $\frac{\pi}{6}$ radians. Thus as the ordinate $y$ tends to zero the semi-dihedral angle of the porosity $\theta$ tends to $\frac{\pi}{6}$ radians, except in the case where $\theta_0 = 90^\circ$ when the cross-section of the porosity shrinks to a circle of zero radius. Also at the point $P$, for the general triangulated geometry, the value of the derivative of the curvature $\frac{\partial K}{\partial s}$ is unclear. In the
90° case its value is zero since such a profile is smooth and symmetrical at P. In the general situation for a solution of equation (3.10) to be mathematically tractable it is also reasonable to assume that $\frac{\partial K}{\partial s}$ is zero at P. Physically, this condition states that there is no flux of material passing point P, that is no material is lost or gained from the tip of the pore. With this information to hand a careful consideration of equation (3.10) in the limit of $y$ tending to zero is possible.

First consider the two limits:

\[
\lim_{\theta \to \frac{\pi}{6}} \psi(\theta) \quad \text{and} \quad \lim_{\theta \to \frac{\pi}{6}} \phi(\theta),
\]

where $\psi(\theta)$ and $\phi(\theta)$ are defined by equations (3.9(b)) and (3.3(b)) respectively. Invoking L'Hopital's Rule:

\[
\lim_{\theta \to \frac{\pi}{6}} \psi(\theta) = \lim_{\theta \to \frac{\pi}{6}} \frac{(1 - \frac{2}{\sqrt{3}} \cos \theta)^2}{\theta - \frac{\pi}{6} - \frac{2}{\sqrt{3}} \cos \theta \sin (\theta - \frac{\pi}{6})} = \frac{1}{\sqrt{3}}. \quad (3.12(a))
\]

and

\[
\lim_{\theta \to \frac{\pi}{6}} \phi(\theta) = \lim_{\theta \to \frac{\pi}{6}} \frac{\theta - \frac{\pi}{6}}{(1 - \frac{2}{\sqrt{3}} \cos \theta)} = \sqrt{3}. \quad (3.12(b))
\]

Now, expanding equation (3.10) gives

\[
\frac{\partial n}{\partial t} = B \psi \phi \left[ \frac{\partial^2 K}{\partial s^2} + \frac{1}{y} \frac{\partial y}{\partial s} \frac{\partial K}{\partial s} + \frac{1}{\phi} \frac{\partial \phi}{\partial s} \frac{\partial K}{\partial s} \right].
\]
Allowing \( y \) to approach zero and calling on equation (3.12) gives

\[
\frac{\partial n}{\partial t} \bigg|_{y=0} = B \left[ \frac{\partial^2 K}{\partial s^2} + \frac{\partial y}{\partial s} \frac{\partial K}{\partial s} y + \frac{1}{\sqrt{3}} \frac{\partial \phi}{\partial s} \frac{\partial K}{\partial s} \right]_{y=0}.
\]

Again, invoking L'Hôpital's Rule, the second term of the right-hand side above becomes

\[
\frac{\partial y}{\partial s} \bigg|_{y=0} \lim_{y \to 0} \frac{\partial K}{\partial s} \bigg|_{y=0} = \frac{\partial y}{\partial s} \bigg|_{y=0} \frac{\partial^2 K}{\partial s^2} \bigg|_{y=0}.
\]

The third term of the right-hand side is zero since \( \frac{\partial K}{\partial s} \bigg|_{y=0} = 0 \).

Therefore

\[
\frac{\partial n}{\partial t} \bigg|_{y=0} = 2B \frac{\partial^2 K}{\partial s^2}.
\] (3.13)

A knowledge of the behaviour of the curvature, \( K \), of the pore, defined by equation (2.5), as \( y \) tends to zero is also vital to the solution of equation (3.10). The second term of the curvature equation (2.5(a)), namely

\[
K_2 = \frac{1}{y} \left( [1 + (\frac{dy}{dx})^2]^{-\frac{1}{2}} - \alpha (\theta) \right),
\] (3.13(a))

is obviously singular at the pore tip when the denominator, \( y \), is zero. The question now is, what happens to the numerator in this limit. To answer this it is necessary to ascertain the value of the derivative, \( \frac{dy}{dx} \), as \( y \) approaches zero. It has been established earlier that when the ordinate, \( y \), tends to zero the
semi-dihedral angle $\theta$ tends to $\frac{\pi}{6}$ radians. Substituting this value of $\theta$ into equation (2.5(c)) gives

$$\left. \frac{dy}{dx} \right|_{y=0} = \frac{1}{2} [3 \tan^2 \theta - 1]. \quad (3.14)$$

(It should be noted that this derivative is infinite when $\theta = 90^\circ$.) Substituting $\theta = \frac{\pi}{6}$ and equation (3.14) into the equation (3.13(a)) for the second curvature term, shows that its numerator is also zero as $y$ approaches zero, since

$$\lim_{\theta \to \frac{\pi}{6}} \alpha (\theta) = \frac{2}{\sqrt{3}} \cos \theta,$$

where $\alpha$ is given by equation (2.5(b)). Therefore L'Hôpital's Rule is applicable to finding the limiting value of $K_2$ as $y$ tends to zero, that is

$$\lim_{y \to 0} K_2 = -\frac{d^2y}{dx^2} \left[ 1 + \left( \frac{dy}{dx} \right)^2 \right]_{y=0}$$

By differentiating equation (2.5(b)) twice, it can be shown that

$$\lim_{\theta \to \frac{\pi}{6}} \frac{\partial \alpha}{\partial \theta} = 0,$$

therefore

$$\lim_{y \to 0} K_2 = -\left[ \frac{d^2y}{dx^2} \left[ 1 + \left( \frac{dy}{dx} \right)^2 \right]_{y=0} \right] = K_1 \left|_{y=0} \right.$$

and

$$\lim_{y \to 0} K = 2 K_1 \left|_{y=0} \right.$$
Here $K_1$ is the first curvature term in equation (2.5(a)), namely

$$K_1 = \frac{d^2 y}{dx^2} [1 + \left( \frac{dy}{dx} \right)^2]^{\frac{3}{2}}.$$  \hspace{1cm} (3.14(a))

In summary then, the motion of the normal to a pore profile, in the plane bisecting adjacent grain boundaries is given by:

$$\frac{\partial n}{\partial t} = \begin{cases} B \psi(\theta) \frac{1}{y} \frac{\partial}{\partial s} \left( \phi(\theta) y \frac{\partial K}{\partial s} \right) & y \neq 0 \\ 2B \frac{\partial^2 K}{\partial s^2} & y = 0 \end{cases}$$ \hspace{1cm} (3.15(a))

where $K$ is given by

$$K = \begin{cases} K_1 + K_2 & y \neq 0 \\ 2K_1 & y = 0 \end{cases}$$ \hspace{1cm} (3.15(c))

and $K_1$ and $K_2$ are defined by equations (3.13(a)) and (3.14(a)). The equations above are subject to boundary conditions which must reflect whether the porosity is open or closed. These will be discussed later in the chapter.

3.4 Computational Method

Following the approach of Chapter Two, it is useful to make equations (3.15) dimensionless via the following transformations:

$$X = \frac{x}{a}$$ \hspace{1cm} (3.16(a))

$$Y = \frac{y}{a}$$ \hspace{1cm} (3.16(b))

$$S = \frac{s}{a}$$ \hspace{1cm} (3.16(c))

$$N = \frac{n}{a}$$ \hspace{1cm} (3.16(d))

$$K = \frac{\kappa a}{B t}$$ \hspace{1cm} (3.16(e))

$$T = \frac{B t}{a^4}$$ \hspace{1cm} (3.16(f))
Here 'a' is unit length. Then equations (3.15) become:

\[
\begin{align*}
\frac{\partial N}{\partial T} &= \begin{cases} 
\psi(\theta) \frac{1}{Y} \frac{\partial}{\partial S} (\phi(\theta) Y \frac{\partial \kappa}{\partial S}) & Y \neq 0 \\
2 \frac{\partial^2 \kappa}{\partial S^2} & Y = 0
\end{cases} \quad (3.17(a)) \\
\kappa &= \begin{cases} 
\kappa_1 + \kappa_2 & Y \neq 0 \\
2\kappa_2 & Y = 0
\end{cases} \quad (3.18(a))
\end{align*}
\]

where

\[
\kappa_1 + \kappa_2 \quad (3.18(a))
\]

with \( \kappa_1 \) and \( \kappa_2 \) defined by equations similar to (3.13(a)) and (3.14(a)).

A finite difference approach similar to that of German and Lathrop (1978) is adopted. First for ease of computation, it is convenient to recouch the expressions for \( \kappa_1 \) and \( \kappa_2 \) in terms of the parameter \( S \). Thus equations (2.14) become:

\[
\begin{align*}
\kappa_1 &= \frac{\partial^2 X}{\partial S^2} \frac{\partial Y}{\partial S} - \frac{\partial^2 Y}{\partial S^2} \frac{\partial X}{\partial S} \quad (3.19(a)) \\
\kappa_2 &= \frac{1}{Y} \left( \frac{\partial X}{\partial S} - \alpha(\theta) \right) \quad (3.19(b))
\end{align*}
\]

This parameterization has the advantage that only derivatives with respect to \( S \) need be calculated, all of which can be computed numerically to the same accuracy. Also, the first and second derivatives of \( X \) and \( Y \) with respect to \( S \) are not infinite; they fall in the interval \((-1, 1)\), which removes any complications posed by infinite derivatives of \( Y \) with respect to \( X \) at positions such as \( P \) in Figure 3.3.1 on the profile of a 90° pore.
At any point along the length of the profile $S$, its outward unit normal is $\hat{N}$, given by

$$\hat{N} = -\frac{dY}{dS} \hat{x} + \frac{dX}{dS} \hat{y},$$

where $\hat{x}$ and $\hat{y}$ are unit basis vectors in the direction of $OX$ and $OY$, respectively. The change in the profile coordinates, $(X(S), Y(S))$ with 'time' can now be written separately as:

$$\frac{\partial X}{\partial t} = -\frac{\partial N}{\partial t} \frac{\partial Y}{\partial S} = F(X, Y) ,$$

and

$$\frac{\partial Y}{\partial t} = \frac{\partial N}{\partial t} \frac{\partial X}{\partial S} = G(X, Y) .$$

(3.20(a))

(3.20(b))

The functions $F$ and $G$ have been introduced here for convenience.

The numerical solution to equations (3.20) can be found using the improved Euler Method, as follows. Let $(X_i^j(S), Y_i^j(S))$ be the coordinates of the $i^{th}$ point along the profile after a 'time' $T_j$ has elapsed. Let also

$$\Delta T_j = T_{j+1} - T_j . \ j = 0, 1, 2 ...$$

A first estimate $(\hat{X}_{i+1}^j, \hat{Y}_{i+1}^j)$ to $(X_i^{j+1}(S), Y_i^{j+1}(S))$, the position of the $i^{th}$ point after a further small period of time $\Delta T_j$ can be found simply by using the Euler approximation to the derivatives defined by equations (3.20), that is:

$$\hat{X}_i = X_i^j + F_i^j \Delta T_j ,$$

and

$$\hat{Y}_i = Y_i^j + G_i^j \Delta T_j .$$

(3.21(a))

(3.21(b))

Here

$$F_i^j = F(X_i^j, Y_i^j, T_j) = \frac{\partial N}{\partial t} (X_i^j, Y_i^j, T_j) \frac{\partial Y_i^j}{\partial S},$$

and

$$G_i^j = G(X_i^j, Y_i^j, T_j) = \frac{\partial N}{\partial t} (X_i^j, Y_i^j, T_j) \frac{\partial X_i^j}{\partial S}.$$
A second improved estimate of the coordinates \((X_i^{j+1}, Y_i^{j+1})\)
can be found by applying the trapezium formula for numerical
quadrature to equations (3.20). Thus

\[
X_i^{j+1} = X_i^j + \frac{1}{2}[F_i^j + \tilde{F}_i^j] \Delta T_j ,
\]

and

\[
Y_i^{j+1} = Y_i^j + \frac{1}{2}[G_i^j + \tilde{G}_i^j] \Delta T_j .
\]

where \(\tilde{F}_i^j = F(X_i^j, Y_i^j, T_j)\) and \(\tilde{G}_i^j = G(X_i^j, Y_i^j, T_j)\).

The quantities \(\tilde{F}_i^j\) and \(\tilde{G}_i^j\) are used as estimates of
\(F_i^{j+1}\) and \(G_i^{j+1}\), respectively. Combining equations (3.21)
and (3.22) gives

\[
X_i^{j+1} = \frac{1}{2}[X_i^{j+1} + X_i^Y + \Delta T_j \tilde{F}_i^j] ,
\]

\[
Y_i^{j+1} = \frac{1}{2}[Y_i^{j+1} + Y_i^Y + \Delta T_j \tilde{G}_i^j] .
\]

It remains to compute values of \(F_i^j\) and \(G_i^j\), which now only
contain derivatives with respect to \(S\). Consider then the
evolution of an initial profile defined discretely by

\[
\{X_i^0, Y_i^0, : Y_i^0 = f(X_i^0), i=1, ..., n\} ,
\]
such a profile is illustrated in Figure 3.4.1. After a time \(T_j\)
has elapsed the profile will have moved to the position described
by the set of coordinates

\[
\{(X_i^j, Y_i^j), i=1, ..., n\} .
\]

At all points the length of the profile \(S_i^j\) can be calculated
via

\[
S_i^{j+1} = S_i^j + [(\Delta X_i^j)^2 + (\Delta Y_i^j)^2]^{\frac{1}{2}}, i=1, ..., n-1
\]

where

\[
\Delta X_i^j = X_i^{j+1} - X_i^j , i=1, ..., n-1
\]

and

\[
\Delta Y_i^j = Y_i^{j+1} - Y_i^j , i=1, ..., n-1
\]
In general the \{S_i^j\}_{i=1,...,n} calculated thus will not be equally spaced and the numerical approximation to the derived functions of S will differ from one point to another along the profile's length. To avoid introducing such discrepancies unnecessarily and to facilitate speedy computation of the derivatives, it is expedient to express X and Y as function of S and evaluate them at equally spaced points \Delta S_j apart. There are a number of approximation techniques which will perform this task. However piecewise spline interpolation is the most suitable, for cubic splines guarantee that the approximation is smooth and has continuity of curvature at all points, \( S_i, i = 1, n \). Cubic spline interpolation also readily embodies the boundary conditions, since there is a degree of freedom in either the first or second derivative of the spline at its end points, \( S_1 \) and \( S_n \). The derivatives \( \frac{\partial X}{\partial S} \) and \( \frac{\partial Y}{\partial S} \) are given by

\[
\frac{\partial X}{\partial S} = [1 + (\frac{dy}{dx})^2]^{-\frac{1}{2}}, \quad \text{and} \quad \frac{\partial Y}{\partial S} = \frac{dy}{dx} [1 + (\frac{dy}{dx})^2]^{-\frac{1}{2}}.
\]

At \( S = 0 \), the mid-point of the porosity, symmetry requires \( \frac{dy}{dx} = 0 \) and hence

\[
\frac{\partial X}{\partial S}^1 = 1, \quad (3.24(a))
\]

and

\[
\frac{\partial Y}{\partial S}^1 = 0. \quad (3.24(b))
\]

At the tip of an isolated pore, for example, \( \frac{dy}{dx} \) is given by
equation (3.14). In general, however, \( \frac{dY}{dX} = \tan \psi \) and hence
\[
\frac{\partial X}{\partial S} n = \cos \psi
\]
and
\[
\frac{\partial Y}{\partial S} n = \sin \psi
\]

Values of the angle \( \psi \) for various cases of open and closed porosity will be given in the following section.

Otherwise, however, the first and second derivatives of \( X \) and \( Y \) can be calculated to order \((\Delta S_j)^2\) by the central difference formulae given in Young and Gregory (1972) namely

\[
\frac{\partial f}{\partial S}^j \approx \left[ -\frac{3}{2} f^j_i + 2f^j_{i+1} + \frac{1}{2} f^j_{i+2} \right] \frac{1}{\Delta S_j}, \quad (3.25(a))
\]

\[
\frac{\partial f}{\partial S}^i \approx \left[ -\frac{1}{2} f^j_{i-1} + \frac{1}{2} f^j_{i+1} \right] \frac{1}{\Delta S_j} \quad i=2, \ldots, n-1 \quad (3.25(b))
\]

\[
\frac{\partial f}{\partial S}^n \approx \left[ \frac{1}{2} f^j_{n-2} - 2f^j_{n-1} + \frac{3}{2} f^j_n \right] \frac{1}{\Delta S_j} \quad (3.25(c))
\]

The second derivatives of \( X \) and \( Y \) can also be found to second order in \( \Delta S_j \), via

\[
\frac{\partial^2 f}{\partial S^2}^j = \left[ f^j_i - 2f^j_{i+1} + f^j_{i+2} \right] \frac{1}{(\Delta S_j)^2}, \quad (3.26(a))
\]

\[
\frac{\partial^2 f}{\partial S^2}^i = \left[ f^j_{i-1} - 2f^j_i + f^j_{i+1} \right] \frac{1}{(\Delta S_j)^2} \quad i=2, \ldots, n-1 \quad (3.26(b))
\]

\[
\frac{\partial^2 f}{\partial S^2}^n = \left[ f^j_{n-2} - 2f^j_{n-1} + f^j_n \right] \frac{1}{(\Delta S_j)^2}. \quad (3.26(c))
\]
In the same manner as in Chapter Two values of the semi-dihedral angle $\theta_i^j$ can be found by solving equation (2.16), using

$$\frac{dY_i^j}{dx_i^i} = \frac{dY_i^j}{ds_i^i}, \quad i=2, \ldots, n-1.$$ 

Hence values of the curvature $K_i^j$ can be computed via (3.18) and (3.19). Then using equation (3.25(b)) the quantities $Z_i^j$ are evaluated as follows:

$$Z_i^j = \phi (\theta_i^j) Y_i^j \frac{\partial K_i^j}{\partial s_i^i}, \quad i=2, \ldots, n-1$$

and $Z_1^j = Z_n^j = 0$.

The last equations arise since symmetry requires $\frac{\partial K_i^j}{\partial s_i^i} = 0$ and volume conservation requires $\frac{\partial K_n^j}{\partial s_n} = 0$. Finally

$$\frac{\partial N_i^j}{\partial T_i} = \frac{\psi (\theta_i^j)}{Y_i^j} \frac{\partial Z_i^j}{\partial s_i^i} \quad \text{if } Y_i^j \neq 0,$$

or

$$\frac{\partial N_i^j}{\partial T_i} = 2 \frac{\partial^2 K_i^j}{\partial s_i^2} \quad \text{if } Y_i^j = 0,$$

The derivatives of $Z$ and $K$ above are found by equations (3.25) and (3.26) respectively.

New coordinates $(X_i^{j+1}, Y_i^{j+1})$ of the profile after 'time' $T_{j+1}$ are calculated via the improved Euler method described above. For the sake of stability of the algorithm the time step $\Delta T_j$ must be chosen such that the maximum distance moved by the profile during this 'time' period does not exceed $\Delta S_j$. That is

$$\Delta N_i^j = \delta \Delta S_j,$$
where $0 < \delta < 1$. Therefore

$$\Delta T_j = \delta \frac{\Delta S_j}{\max_i (\overline{\partial N_i})}.$$ 

In practice $\delta = 0.3$ guaranteed stable solutions. The accuracy of the scheme described above was monitored by checking that volume was conserved throughout the simulation. Consistency of the routine was established by observing the relaxation of a pore from ellipsoidal to spherical.

### 3.5 Applications

The numerical scheme described above has been employed to simulate the relaxation of porosity taking a number of different initial configurations. They are listed below:

(i)a The coalescence of two cigar-shaped pores.

(i)b The coalescence of a finite line of cigar-shaped pores.

(ii) The coalescence of an infinite line of cigar-shaped pores.

(iii) The ovulation of finite rod-like cylinders of triangulated cross-section.

(iv) The relaxation of tunnels held open at grain corners.

The boundary conditions for these situations differ. At the mid-point of the porosity symmetry will always demand that $\frac{dy_j}{dx} = 0$ and hence the boundary conditions are given by equations (3.24).

The conditions imposed on the derivatives at the right hand end of the porosity are given below in Table 3.1, for the various cases. For cases (i) and (iii) the conditions reflect the fact that the pores meet the grain edge at a point. Case (ii) requires periodic boundary conditions. The conditions for case (iv) have
been encountered in Chapter Two and demand that four tunnels join smoothly at grain corners. Here $\xi(\theta)$ is defined by equation (2.2(c)) and $\theta_n^j$ is found via equation (2.6b).

$$\frac{dY^j}{dx_n} = \frac{2}{\sqrt{3}} \cos \theta_n - [1 - \left(\frac{2}{\sqrt{3}} \cos \theta_n \right)^2]^{\frac{1}{2}}$$
$$\frac{dY^j}{dS_n} = \frac{2}{\sqrt{3}} \cos \theta_n - [1 - \left(\frac{2}{\sqrt{3}} \cos \theta_n \right)^2]^{\frac{1}{2}}$$

Table 3.1

<table>
<thead>
<tr>
<th></th>
<th>$\frac{dY^j}{dx_n}$</th>
<th>$\frac{dX^j}{dS_n}$</th>
<th>$\frac{dY^j}{dS_n}$</th>
<th>$\theta_n^j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) a,b</td>
<td>$-\frac{1}{2}[3\tan^2 \theta_n - 1]$</td>
<td>$\frac{2}{\sqrt{3}} \cos \theta_n^o$</td>
<td>$-\frac{1}{2}[3\tan^2 \theta_n - 1]$</td>
<td>$\frac{\pi}{6}$</td>
</tr>
<tr>
<td>(ii)</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>$\theta_n^o$</td>
</tr>
<tr>
<td>(iii)</td>
<td>$-\frac{1}{2}[3\tan^2 \theta_n - 1]$</td>
<td>$\frac{2}{\sqrt{3}} \cos \theta_n^o$</td>
<td>$-\frac{1}{2}[3\tan^2 \theta_n - 1]$</td>
<td>$\frac{\pi}{6}$</td>
</tr>
<tr>
<td>(iv)</td>
<td>$(\xi(\theta^j)\sqrt{2})^{-1}$</td>
<td>$[1 + 2\xi^2]^{\frac{1}{2}}$</td>
<td>$\sqrt{2}\xi[1 + 2\xi^2]^{-\frac{1}{2}}$</td>
<td>$\tan^{-1}\left(\frac{2}{\sqrt{3}} \tan \theta_n^o\right)$</td>
</tr>
</tbody>
</table>

The conditions placed on the ordinate $Y_n^j$ in all cases are given in Table 3.2. In addition it is well advised for the sake of accuracy to place conditions on the abscissae $X_n^j$. This can be done by assuming that the profile is linear, with slope $\frac{dY_n^j}{dx_n}$ between the coordinate point $(X_{n-1}^j, Y_{n-1}^j)$ and $(X_n^j, Y_n^j)$. In the case of a tunnel lying along a grain edge, the length of the grain edge $2L$ must remain constant throughout the evolution of the porosity. Therefore in the plane of the grain boundary,

$$\sqrt{2} \left(Y_n^j - Y_{n-1}^j\right) = X_n^j - X_{n-1}^j$$

and

$$Y_n^j = \sqrt{2} (L - X_n^j)$$
from which the conditions in table 3.2 can be found.

<table>
<thead>
<tr>
<th></th>
<th>$X_n^j$</th>
<th>$Y_n^j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>$X_{n-1}^j + Y_{n-1}^j / \tan \psi$</td>
<td>0</td>
</tr>
<tr>
<td>(ii)</td>
<td>$a$</td>
<td>$Y_{n-1}^j$</td>
</tr>
<tr>
<td>(iii)</td>
<td>$X_{n-1}^j + Y_{n-1}^j / \tan \psi$</td>
<td>0</td>
</tr>
<tr>
<td>(iv)</td>
<td>$\frac{1}{3}(2L - \sqrt{2} \xi(\theta_{n-1})Y_{n-1} + X_{n-1})$</td>
<td>$\sqrt{2} \xi(\theta_{n-1})(L - X_n^j)$</td>
</tr>
</tbody>
</table>

Table 3.2

Here 'a' is unit length and $\tan \psi = \frac{dy_n^j}{dx_n}$.

3.6 Results and Discussion

In this section the results of the simulation of the relaxation of the various types of porosity specified in Section 3.5 and an analysis of them are presented. In the cases when the porosity is closed a measure of the accuracy of the simulation was attained by monitoring the volume of the porosity. In most cases the pore volume did not change by more than 1% of its initial volume, though in some cases, after very advanced times, this error increased to 5%. In the light of this it is expected that the simulations of open porosity are achieved to similar levels of accuracy.

3.6.1 The Coalescence of Two Cigar-Shaped Pores

The Figure 3.6.1 shows the way in which two initially cigar-shaped pores of 70° cross-section coalesce with time. Nichols and Mullins (1965) and German and Lathrop (1978), who have performed similar simulations of the sintering of spherical particles, have reported a degree of 'undercutting' of
the pore surface in the neck region and this is also evident in
the case shown here.

Figure 3.6.2 shows the variation of the dimensionless
neck height, $Y$, versus the dimensionless time, $T$, for different
values of characteristic dihedral angle, $2\theta_o$. The variables, $Y$
and $T$, are normalised with respect to the initial 'radial'
distance, $d_b(\theta_o)$, of the pores. This dimension is shown in
Figure 3.6.3. In this case $Y$ and $T$ are defined as follows:

\begin{equation}
Y = \frac{y}{d_b(\theta_o)} \tag{3.27(a)}
\end{equation}

and

\begin{equation}
T = \frac{Bt}{d_b(\theta_o)^4} \tag{3.27(b)}
\end{equation}

where $y$ is the actual neck height at the real time, $t$. At
constant temperature, $B$ is a constant defined by equation
(3.1(b)). Initially each bubble is taken to be formed by the
union of three surfaces of a sphere, which intersect at the
prescribed dihedral angle $2\theta_o$. The radial dimension,
$d_b(\theta_o)$, of such a pore is related to the radius of curvature,
$r_b(\theta_b)$, of the spherical caps of which it is composed via the
equation:

\begin{equation}
r_b(\theta_b) = d_b(\theta_b) \sin \psi \tag{3.28}
\end{equation}

where $r_b$ and the angle $\psi$ are shown in Figure 3.6.3. The value
of this angle is related to the characteristic angle, $\theta_o$, of the
porosity by

\begin{equation}
\sin \psi = \left(1 - \frac{4}{3} \cos^2 \theta_o\right)^{-\frac{1}{2}} \tag{3.29}
\end{equation}
This relation is quoted by White and Tucker (1983) but may also be derived via equation (3.14). Evidently each curve in Figure 3.6.2 is defined by a power law of the form

\[ Y = C (\theta_o)^n (\theta_o) \],

(3.30)

where, for each value of \( \theta_o \) the exponent, \( n \), and coefficient, \( C \), are respectively given by the slope and intercept of the lines in the figure. Values of \( n \) and \( C \) for various \( \theta_o \) are given below in Table 3.3.

<table>
<thead>
<tr>
<th>( \theta_o )</th>
<th>50°</th>
<th>60°</th>
<th>70°</th>
<th>80°</th>
<th>90°</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>0.191</td>
<td>0.186</td>
<td>0.180</td>
<td>0.171</td>
<td>0.144</td>
</tr>
<tr>
<td>( C )</td>
<td>0.528</td>
<td>0.677</td>
<td>0.875</td>
<td>1.110</td>
<td>1.130</td>
</tr>
<tr>
<td>( \frac{dY}{dT} )</td>
<td>31.0</td>
<td>121.0</td>
<td>138.0</td>
<td>152.0</td>
<td>166.0</td>
</tr>
<tr>
<td>( \frac{1}{n} )</td>
<td>5.24</td>
<td>5.38</td>
<td>5.55</td>
<td>5.85</td>
<td>6.95</td>
</tr>
<tr>
<td>( C \frac{1}{n} )</td>
<td>0.035</td>
<td>0.122</td>
<td>0.476</td>
<td>1.930</td>
<td>5.910</td>
</tr>
</tbody>
</table>

Table 3.3

The values of exponents, \( n(\theta_o) \), given here have been calculated at fairly advanced 'times' for which the ratio, \( Y \), of neck height to initial pore 'radius' has developed to a value in the range \( 0.1 < Y < 0.7 \). The case for which \( \theta_o = 90° \) can be compared with existing data provided by the numerical models of Nichols and Mullins (1965) and German and Lathrop (1978). Both of these models have predicted values of \( \frac{1}{n} \) of approximately 7 for large neck to initial radius ratio, \( Y \). This compares favourably with the results of the present model and with the analytical models derived by Nichols and Mullins (1965) and King (1968). However,
the values of \( n \) and \( C \) reported here are not purported to be definitive but represent an average value of the quantity observed over a long 'time' cycle, calculated via a least squares fit to the data \((Y, T)\).

Also given in Table 3.3 are values of the rate of change of the dimensionless neck height, \( Y \), with dimensionless time, \( T \), for the different values of \( \theta_0 \). These values are calculated via the equation

\[
\frac{dY}{dT} = n \frac{Y}{T} \quad (3.31)
\]

However it is difficult to compare these rates directly since, for different values of \( \theta_0 \), the variables, \( Y \) and \( T \), have been normalised with respect to different 'radii', \( d_b(\theta_0) \). For the purpose of making some comparisons of the rates of coalescence, however, suppose that the kinetics of the coalescence of two grain edge bubbles are similar to that of a long or near infinite line of bubbles held open at a grain corner. This assumption can be justified later. Suppose further that the coalescing bubbles eventually develop into a parallel-sided grain edge tunnel of length \( L \). It is intended to compare the rate at which two cigar-shaped grain edge bubbles coalesce to form such a tunnel against the rate at which two spherical bubbles develop into a cylindrical tunnel of equal volume. To this end, let the radius of the cylindrical tunnel be \( r_T(90^\circ) \) and the radius of the triangulated tunnel be \( r_T(\theta_0) \), then neglecting the volume of porosity at the grain corners

\[
\pi r_T^2(\theta_0) f_T(\theta_0) L = \pi r_T^2(90^\circ) L ,
\]
where the factor \( f_T(\theta_o) \) is proportional to the cross-section area of the tunnel. This factor can be derived via equations (2.3(a)) and (2.10(a)) and has been evaluated by White and Tucker (1983) for various values of \( \theta_o \). Therefore

\[
\frac{r_T(\theta_o)}{r_T(90^\circ)} = \left( \frac{1}{f_T(\theta_o)} \right)^{\frac{3}{4}}, \quad (3.32)
\]

and referring to equation (2.3(a)) this gives

\[
\frac{y_T(\theta_o)}{y_T(90^\circ)} = \left( \frac{1}{f_T(\theta_o)} \right)^{\frac{3}{4}} \left( 1 - \frac{2}{\sqrt{3}} \cos \theta_o \right), \quad (3.33)
\]

where \( y_T \) is the usual height of the tunnel from its axis in the plane bisecting adjacent grain boundaries. If the grain edge is completely occupied by two bubbles of 'radius' \( d_b(\theta_o) \) then the grain edge, \( L \), is equal to \( 4d_b \) and if these bubbles eventually coalesce to form a tunnel of volume equal to that of a cylindrical tunnel of radius \( r_T(90^\circ) \) then

\[
\frac{4}{3} \pi f_E(\theta_o) r_b^3(\theta_o) = \pi r_T^2(90^\circ) 2d_b(\theta_o). \quad (3.34)
\]

Here \( r_b(\theta_o) \) is the radius of curvature of the bubble and \( f_E(\theta_o) \) is a factor given by White and Tucker (1983), for the evaluation of the volume of the bubble. The radius, \( d_b \), of a cigar-shaped pore and its radius of curvature, \( r_b \), are related via equations (3.28) and (3.29). Therefore substituting for \( d_b \) into equation (3.34) gives

\[
\frac{d_b(\theta_o)}{d_b(90)} = \frac{(1 - \frac{4}{3} \cos^2 \theta_o)^{\frac{3}{4}}}{f_E(\theta_o)^{\frac{3}{4}}}, \quad (3.35)
\]

since by volume conservation:

\[
r_T(90^\circ) = \frac{\sqrt{2}}{\sqrt{3}} d_b(90^\circ). \quad (3.36)
\]
The rate at which the neck of the coalescing bubbles eventually achieve the configuration of a parallel-sided tunnel can be measured by the ratio:

\[
\frac{d[y_\text{T}]_{\theta_0}}{dt} = \frac{dV}{dt} \theta_0 \cdot \frac{y_T(90^\circ)}{y_T(\theta_0)} \frac{d_b(90^\circ)}{d_b(\theta_0)}^{3}, \tag{3.37}
\]

where

\[
y_T(90^\circ) \quad \text{and} \quad \frac{d_b(90^\circ)}{d_b(\theta_0)}
\]

are given by equations (3.33) and (3.35) respectively.

Therefore:

\[
\frac{d[y_\text{T}]_{\theta_0}}{dt} = \frac{dV}{dt} \theta_0 \cdot \frac{f_T(\theta_0)^{\frac{1}{2}}}{f_T(\theta_0)^{\frac{1}{2}}} \left[ \frac{f_E(\theta_0)^{\frac{1}{2}}}{f_E(\theta_0)^{\frac{1}{2}}} \right]^{3} \frac{d[y_\text{T}]_{90^\circ}}{dt}
\]

A comparison of these rates is given below in Table 3.4

<table>
<thead>
<tr>
<th>( \frac{d[y_\text{T}]_{\theta_0}}{dt} )</th>
<th>50°</th>
<th>60°</th>
<th>70°</th>
<th>80°</th>
<th>90°</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{d[y_\text{T}]_{90^\circ}}{dt} )</td>
<td>0.015</td>
<td>0.130</td>
<td>0.275</td>
<td>0.561</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 3.4

It is evident from this comparison that the lower the semi-dihedral angle of the porosity the slower is the rate at which pores will coalesce to form networks of interlinked tunnels.
This may not be a surprising result, since the radius of curvature, \( r_b(\theta_0) \), of a cigar-shaped bubble of volume equivalent to that of a spherical bubble of radius \( r_b(90^\circ) \) is related via

\[
\frac{1}{r_b(\theta_0)} = f_E(\theta_0) \frac{1}{r_b(90^\circ)}
\]

and, since values of \( f_E(\theta_0) \) given by White and Tucker (1983) are always less than or equal to unity, the curvature and hence surface chemical potential is always less for the lower angled bubble.

3.6.2 Lines of Cigar-Shaped Pores

Figures 3.6.4 and 3.6.5 respectively show the coalescence of a line of four cigar-shaped pores and an infinite line of pores each with semi-dihedral angle 70°. Figure 3.6.6 shows a plot of \( Y \) versus \( T \) for these two cases together with that for the coalescence of two bubbles. In the case of the line of four bubbles the neck height, \( Y \), has been measured at the centre of the line of pores. Table 3.5 gives the value of the exponent, \( n \), in the rate equation (3.30).

<table>
<thead>
<tr>
<th>Number of bubbles in line</th>
<th>2</th>
<th>4</th>
<th>( \infty )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>0.180</td>
<td>0.187</td>
<td>0.218</td>
</tr>
</tbody>
</table>

Table 3.5

Now the rates of coalescence can be compared directly, since the variables, \( Y \) and \( T \), have been normalised with respect to the same 'radius', \( d_b(70^\circ) \), in each case. It can be seen from Figure 3.6.6 that the development of the neck between adjacent bubbles
is slowest in the line of four bubbles and fastest in the line of two bubbles. The rapidity with which the two pores coalesce is accounted for by the following reasoning. Initially the pores are symmetrical about the plane, $\Sigma_1$, orthogonal to the grain edge, through the points A and A' shown in Figure 3.6.1. At this time the curvature gradient of the pore surface across the 'circumference' of the pore in the plane $\Sigma_1$ is zero. However, after only a short time as the region of the neck grows, the symmetry of the pore is lost and a non-zero curvature gradient across the circumferential line in the plane $\Sigma_1$ results in a non-zero flux of vacancies across it. In the case of an infinite line of bubbles, however, the periodicity pertaining ensures that the flux across the circumference of the pore in the plane, $\Sigma_2$, orthogonal to the grain edge through the points B and B' marked in Figure 3.6.5 is always zero and the neck region is fed by fewer vacancies than the line of two bubbles. Hence in this case coalescence is slower. In view of this one might expect the neck region in the line of four bubbles to grow still faster than the neck region in a line of two bubbles. In fact, as can be seen to some extent from Figure 3.6.4, the necks at positions C and D in the line grow at different rates. The neck at position C grows slower than at position D. At the latter position the situation compares to a line of two bubbles, whereas at position C the situation is more comparable with an infinite line of bubbles. As shown by Figure 3.6.6, the rate at which the neck grows at position C is even slower than for the necks in an infinite line of bubbles. This perhaps explains the persistence of large numbers of closed chains of pores observed in irradiated UO$_2$ (Plate 1.1). It can also be seen that the rate of coalescence
of two pores is not vastly different to the rate of coalescence of an infinite line of pores, hence vindicating the analysis of Section 3.5.1.

3.6.3 The Ovulation of a Grain Edge Tunnel

Figure 3.6.7 shows the pinching-off of a grain edge tunnel of 70° cross-section held open by neighbouring tunnels at grain corners. This ovulation occurs in the region of the grain corner caused by the gradient of surface curvature from the corner region to the length of the tunnel. Figure 3.6.8 shows a plot of Y, the ratio of the minimum neck height of the tunnel to the initial minimum neck height, versus dimensionless time, T, for three values of θ₀: 50°, 70°, 90°. The porosity in each simulation has approximately the same fractional volume of 10% and the same initial neck height of unity. The plot demonstrates the fact that interlinked porosity of low dihedral angle takes longer to pinch-off than porosity of higher dihedral angle. This result concurs with the findings of White and Tucker (1983), who assert that the time to pinch-off, t₀, of a tunnel of radius of curvature, rₜ, in the plane orthogonal to the grain edge varies with the fourth power of this radius, thus

\[ t₀ = a₁(θ₀) \frac{1}{B} rₜ^4 \]

where a₁ is a constant and B is defined by equation (3.16).

Alternatively

\[ a₁ = \frac{t₀ B}{rₜ^4} = \frac{t₀ B}{\sqrt{\frac{4}{3}} (1 - \frac{3}{\sqrt{3}} \cos θ₀)^4} \]

\[ = T₀ (1 - \frac{2}{\sqrt{3}} \cos θ₀)^4 \]
since the height of the tunnel, \( y_T \), is related to the radius of curvature by equation (2.3(a)). Here \( T_0 \) is the dimensionless time to pinch-off. Figure 3.6.8 yields values of \( a_1 \) equal to 4.1 for \( \theta_0 = 90^\circ \) and 0.1 for \( \theta_0 = 50^\circ \). These values compare with those reported by White and Tucker (1982) of approximately 5 for \( \theta_0 = 90^\circ \) and 0.04 < \( a_1 < 0.4 \) for \( \theta_0 = 50^\circ \). In fact a value of \( a_1 = 0.2 \) was found by White and Tucker (1983) to yield realistic results in their fission-gas release model of \( \text{UO}_2 \).

3.6.4 The Ovulation of Rod-Like Porosity

Figure 3.6.9 shows the ovulation of a long sausage-shaped pore lying along a grain edge, the tip of which is inclined at the constant angle prescribed by the balance of surface tension forces and given by equation (3.14). This simulation is intended to demonstrate qualitatively the evolution of the remanent grain edge porosity after the collapse of a grain edge tunnel. It is worthwhile noting that a relatively large proportion of the grain edge is left free of porosity after such a pore tends towards an equilibrium configuration. In the situation of fission-gas release this may leave sufficient grain edge unoccupied on which further migrating grain face bubbles can collect. This possibility was overlooked by White and Tucker (1983) in their description of the evolutionary cycle of grain edge porosity.

3.6.5 Significance to Gas-Release and Sintering

In the work presented here no attempt has been made to follow uninterrupted the evolutionary cycle of grain edge porosity from a long or near infinite line of pores through the configuration of a slender parallel-sided tunnel to its eventual collapse again into smaller grain edge and corner pores. In
principle there is no objection to performing such a simulation bar its large demand on processor time, and this would provide a useful starting point for further work on fission-gas swelling. However, the separate simulations of the individual parts of the fission-gas release process presented in Sections 3.6.1, 3.6.2, 3.6.3 and 3.6.4 taken together yield useful information on the whole life-cycle.

The results of Section 3.6.1 have demonstrated the significant contribution of the first stage of the gas-release process, that of the coalescence of edge pores, to the overall time that the porosity remains open. In their model of fission-gas release White and Tucker (1983) have proposed a theory of percolation of fission-gas through grain edge tunnel networks, in which they define the probability, p, of finding a tunnel open in terms of $t_0$ - the time taken by a tunnel to pinch-off. Their definition of $t_0$ ignores the time taken by the grain edge pores to coalesce in the first instance, which it is clearly shown in Section 3.6.1 varies with dihedral angle, and is most significant for porosity of low dihedral angle such as that found in irradiated UO$_2$. In turn this has a bearing on the effective-diffusion coefficient for fission-gas through grain edge tunnels, defined by White and Tucker via the probability, p.

The results of Section 3.6.3 suggest that the rate of sintering of pores of low dihedral angle are significantly less than those for higher dihedral angle, it taking $\frac{30}{4} = 7$ times longer for a $50^\circ$ tunnel to collapse than for a $90^\circ$ tunnel of the same fractional volume. This result is pertinent in view of the non-cylindrical nature of pores in most materials and must be significant in sintering models which predict the time taken to achieve theoretical density.
4. A MODEL OF FISSION-GAS SWELLING AND SINTERING INCLUDING GRAIN BOUNDARY DIFFUSION

4.1 Introduction

Tacit in the previous chapter was the assumption that diffusion over the grain boundary and through the bulk of the material is infinitesimally slow compared to diffusion over the surface of the porosity. In practice this is seldom true, especially since the diffusion coefficients for the three processes often have quite different temperature dependences (Shewmon, 1963). Therefore the assumption made in Chapter Three cannot be true at all temperatures. In this Chapter the additional effects of including grain boundary diffusion will be considered. The treatment is still not entirely general in that the influence of volume diffusion is not considered. However, its inclusion will in essence simply further enhance the effects, identified below, of diffusion over the grain faces.

4.1.1 The Effects of Grain Boundary Diffusion

The grain boundary can act as a source or sink where vacancies can be created or annihilated. Primarily grain boundary diffusion provides a mechanism by which vacancies can be transferred between the grain faces and the tunnel walls. By this process volume can be lost from the porosity at the same time as it attempts to adjust its shape by surface diffusion and sintering results. The converse can also occur resulting in the swelling of the porosity, as during fission-gas release in ceramic nuclear fuels.
The grain boundary can also play a secondary role by providing an alternative route by which vacancies participating in the primarily surface diffusion controlled shape changes can travel. The effect of this is to enhance the rate at which this shape changing process proceeds.

It is intended in this Chapter to incorporate these two effects into the dynamic surface diffusion shape change model developed in the previous chapter. However, only the 90° case for which the grain boundary energy is small compared to the free surface energy is considered. This proviso is made mainly for the sake of simplicity, but without great loss, since the qualitative behaviour of porosity of more general geometry is similar to the special case to be considered here.

4.2 The Principle of the Calculation

From Fick's second law of diffusion (Shewmon, 1963) it is possible to derive the continuity equation for the chemical potential, \( \mu \), at any point in the grain boundary. This is quoted by Spight and Beere (1975) as

\[
D \nabla^2 \mu - \frac{\partial \mu}{\partial t} = 0 \quad , \quad (4.1(a))
\]

where

\[
D = \frac{D_g \delta g}{\Omega \sigma} \quad (4.1(b))
\]

Here \( D_g \) is the grain-boundary self diffusion coefficient, \( \delta g \) is the width of the boundary and \( \Omega \) the atomic volume. At constant temperature, \( \sigma = kT \) is also a constant, defined earlier by equation (1.4). In the steady state, when stress redistribution is complete and adjacent boundaries remain in contact with one
another at all times, vacancy formation must occur at a constant rate, $\beta$, per unit area, or annihilation rate $-\beta$, per unit area, over the entire boundary. Therefore the continuity equation above reduces to:

$$\nabla^2 \mu + \beta' = 0$$  \hspace{1cm} (4.2)

where

$$\beta = D\beta'$$  \hspace{1cm} (4.3)

In order eventually to compute the vacancy production/annihilation rate, $\beta$, the solution of (4.2) is sought subject to the appropriate boundary conditions at the perimeter where the grain boundaries meet the grain edge tunnels. With this there is the complication that there is a variation of chemical potential, $\mu_\delta$, over the surfaces of the tunnels forming the perimeter of the grain face.

To overcome the difficulties posed by solving equation (4.2) subject to the complex condition at the perimeter of the grain face, the problem can be considered in two separate parts. Firstly, it can be envisaged that a radially symmetric sintering flux over the grain boundary will result in a gradient of potential between the tunnel surface and the boundary, arising from a mean potential, $\bar{\mu}$, in the pore surface. Secondly, variations about this mean will give rise to a flow of vacancies via the grain boundary from regions of high potential in the pore surface to regions of lower potential. Shape changes controlled by surface diffusion will also occur as a result of this variation in pore surface potential, $\mu_\delta$. 
These problems will be dealt with separately below.

4.3 Grain Boundary Diffusion Due to a Constant Potential in the Pore Surface

To render this problem tractable it is necessary to employ the geometrically simple 'toroid' model (Tucker, 1979) of grain edge porosity. In view of the good agreement, demonstrated in Chapter Two for high pore volumes of this model with the more realistic models, the validity of the ensuing calculation is not impaired greatly.

In the 'toroid' model the ideal grain has fourteen faces each of which is assumed to be identical and circular and to subtend a solid angle of $2\pi/7$ steradians at the grain centre. In the absence of any porosity the cone which has its apex at the grain centre and its base forming a grain face of radius $R$ has a volume which is one fourteenth of the overall volume of the grain. Such a cone is depicted in Figure 4.3.1, the angle $\phi$ shown in the figure is of magnitude $\sin^{-1}(6/7) = 59.0^\circ$. However in the calculations which follow $\phi$ is taken to be equal to $60^\circ$.

The surface $A B C D$ depicted in Figure 4.3.1 represents the upper surface of the interlinked grain edge porosity surrounding half of the grain face $A D$ shown in the figure. It is the segment of the surface of the toroid formed by rotating a circle of radius, $b$, and centred at $O'$ about the axis $O E$. The surface intersects the plane of the grain boundary in the semi-dihedral angle $\theta$. Hereafter in this chapter $\theta$ will be taken to be $90^\circ$.

Assuming the geometry of the 'toroid' model equation (4.2) can be solved. The circular symmetry of the grain faces allows equation (4.2) to be rewritten as:

$$\frac{1}{r} \frac{d}{dr} \left( r \frac{du}{dr} \right) + \beta' = 0$$

$$0 \leq r < a$$

(4.4)
subject to the conditions that:

\begin{align*}
  \text{(i) } & \quad \mu = \bar{\mu} = \text{constant at } r = a \\
  \text{and (ii) } & \quad \frac{du}{dr} = 0 \quad \text{at } r = 0.
\end{align*}

The radius 'a' is marked on Figure 4.3.2, which shows half the grain boundary plane surrounded by 90°-toroidal porosity of radius b. Integrating equation (4.4) gives:

\[ r \frac{du}{dr} = -\beta' \frac{r^2}{2} + A. \]

Condition (ii) implies that the constant \( A = 0 \). Integrating further gives:

\[ \mu = -\beta' \frac{r^2}{4} + B. \]

Condition (i) implies that

\[ B = \bar{\mu} + \beta' \frac{a^2}{4}. \]

and therefore that

\[ \mu = \bar{\mu} + \frac{\beta'}{4} (a^2 - r^2). \quad (4.5) \]

Before proceeding to calculate the flux of vacancies over the grain boundary due to the gradient of potential \( \mu \), defined by equation (4.5), the unknown rate of formation or annihilation, \( D\beta' \), must be calculated. This is done by applying the Principle of Virtual Work to a small increase in the volume of the porosity.
In the following derivation this change in volume is assumed to occur by the work of a fission-gas pressure in which case the porosity is inclined to swell rather than to sinter. It may equally be thought to occur by an externally applied pressure, such as during hot-pressing, or simply by the excess pressure due to the tension in the surface of the porosity.

4.4 To Calculate the Rate of Production or Annihilation of Vacancies

Consider the changes in energy when work done by the fission-gas pressure, \( P \), causes the volume of the porosity to swell by a small amount, \( dV \). This occurs by vacancies 'running' over the grain boundary to the free surface of the tunnel and 'plating out' a layer of atoms of uniform thickness, say \( dh \), on the grain boundary. The growth of the porosity causes an increase in free surface area and hence free surface energy, which is accommodated by the expenditure of energy due to the work of the gas-pressure, and the decrease in potential energy of the vacancies on the grain boundary.

4.4.1 The Work Done by the Fission-Gas Pressure

The work done by the fission-gas pressure, \( \Delta W_p \), is

\[
\Delta W_p = PdV = P \frac{dV}{dh} dh
\]  

(4.6)

4.4.2 The Change in Potential Energy

The change in the potential energy, \( \Delta E_\mu \), on the grain boundary is

\[
\Delta E_\mu = \int_{r=0}^{r=a} [\mu(r) - \overline{\mu}] dN.
\]
Here $dN$ is the number of vacancies contained in a small annulus of grain boundary of uniform thickness, $dh$, and radial width, $dr$.

The volume of such an annulus is

$$\pi [(r + dr)^2 - r^2] \, dh = 2\pi r \, dr \, dh.$$ 

It follows that

$$dN = \frac{2\pi r \, dr \, dh}{\Omega},$$

and

$$\Delta E = \frac{2\pi dh}{\Omega} [\int_0^a \mu(r) r \, dr - \bar{\mu} \int_0^a r \, dr]$$

$$= \frac{\pi dh}{\Omega} \frac{\beta' a^4}{8}.$$  \hspace{1cm} (4.7)

since

$$\mu(r) = \bar{\mu} + \frac{\beta'}{4} (a^2 - r^2).$$

### 4.4.3 The Increase in Free Surface Energy

The increase in free surface energy, $\Delta E_f$, is given by

$$\Delta E_f = \gamma_s \frac{dA}{dh} = \gamma_s \frac{dA}{dh} \, dh.$$  \hspace{1cm} (4.8)

There is no associated decrease in grain boundary energy since this has been assumed to be negligible.

### 4.4.4 The Principle of Virtual Work

The work done by the fission-gas pressure is equal to the changes in energy, and therefore collecting together equations (4.6), (4.7) and (4.8) gives

$$P \frac{dV}{dh} = \gamma_s \frac{dA}{dh} + \frac{\pi \, dh}{\Omega} \frac{\beta' a^4}{8}.$$
Solving the equation above for \( \beta' \), gives

\[
\beta' = - \frac{8}{\pi a^4} \frac{dV}{dh} \left( \gamma_s \frac{dA}{dV} - P \right) \Omega .
\]

Equation (1.6) states that \( \frac{dA}{dV} = \overline{K} \), and therefore that

\[
\beta' = - \frac{1}{\pi} \frac{dV}{dh} \frac{8}{a^4} \overline{\mu} .
\]

Now the change in volume, dV, of the porosity associated with one grain face, that is the change in one sixth of the volume of the toroid, is equal to the layer of atoms plated out on the grain boundary. Therefore, if db is the small increase in the radius of the porosity, it follows that

\[
dV = \pi(a - db)^2 \, dh \equiv \pi a^2 \, dh ,
\]

and

\[
\frac{dV}{dh} = \pi a^2 .
\]

Consequently,

\[
\beta' = - \frac{8}{a^2} \overline{\mu} . \tag{4.9}
\]

In the absence of a fission-gas pressure, P, in the tunnel, the excess pressure associated with the porosity is due entirely to the tension in the surface, \( \gamma_s \), and the mean chemical potential, \( \overline{\mu} \), in the surface is given by the Gibbs-Thompson relation

\[
\overline{\mu} = \overline{K} \gamma_s \Omega , \tag{4.10}
\]
where $\bar{K}$ is the average curvature of the porosity. This curvature is calculated below for the toroidal geometry. In the case when a fission-gas pressure, $P$, (or externally applied pressure, $-P$) is present

$$\bar{u} = (\bar{K} \gamma_s - P) \Omega \quad .$$

(4.11)

4.5 The Average Potential in the Surface of a Toroid

The average curvature, $\bar{K}$, of a body of volume, $V$, and surface area, $A$, is given by

$$\bar{K} = \frac{dA}{dV}$$

(see equation (1.6)). The surface area and volume of the segment of the toroid shown in Figure 4.3.1 is given by Tucker (1979) as

$$A_t = 2\pi b (R\phi - b \sin \phi) \quad (4.12)$$

and

$$V_t = \pi b^2 (R\phi - \frac{2}{3} b \sin \phi) \quad .$$

(4.13)

The expression (4.13) was originally misquoted by Tucker (1979) but was later corrected by Tucker and White (1979). For the grain face and porosity illustrated in Figure 4.3.2, $R = a + b$. Since during the swelling or sintering process the grain edge length $2\pi(a + b)$ remains approximately constant then

$$\frac{da}{db} = \frac{db}{da} = -1$$
Therefore differentiating expressions (4.12) and (4.13) with respect to \(b\) gives

\[
\frac{dA_t}{db} = 2\pi[(a + b) \phi - 2b \sin \phi] \tag{4.14}
\]

and

\[
\frac{dV_t}{db} = 2\pi[(a + b) \phi - b \sin \phi] \tag{4.15}
\]

Dividing equation (4.14) by equation (4.15) and substituting \(\phi = \frac{\pi}{3}\) gives

\[
\bar{K} = \frac{dA_t}{dV_t} = \frac{2[(a + b) \frac{\pi}{3\sqrt{3}}b]}{b[(a + b) 2\pi - 3\sqrt{3}b]} \tag{4.16}
\]

and it is convenient to introduce the notation

\[
\bar{H} = \bar{K}a = \frac{2}{p} \frac{(1 + p) \frac{\pi}{3\sqrt{3}}p}{(1 + p) 2\pi - 3\sqrt{3}p} \tag{4.17}
\]

where \(p = \frac{b}{a}\).

So far in Section 4.3 the variation in chemical potential, \(\mu\), over the grain boundary arising from a constant potential, \(\bar{\mu}\), maintained in the pore surface has been calculated. The potential, \(\mu(r)\), is given by equation (4.5). In Section 4.4 the rate of production, \(\beta\), or annihilation, \(-\beta\), has been calculated from the potential, \(\mu\), and is expressed by equations (4.3) and (4.9), in terms of the mean potential, \(\bar{\mu}\). In turn the potential \(\bar{\mu}\) is given by equations (4.10) and (4.11) in terms of the average curvature, \(\bar{K}\), in the surface of the porosity. This curvature is calculated in Section 4.5. In the following section (4.6) the contribution made by grain boundary diffusion to the transport of
vacancies from sources in the pore surface to sinks in the same surface is calculated. This vacancy flux arises from a variation of chemical potential in the pore surface.

4.6 Surface Diffusion Enhanced by Grain Boundary Diffusion

In this section an effective surface-diffusion coefficient, \( D^*_S \), is calculated for the mechanism by which vacancies are transferred from positions of high potential in the pore surface to positions of lower potential, now that pure surface diffusion is enhanced by the transfer of vacancies via the grain boundary.

Consider the cylindrical tunnel of length \( L \) and radius \( b \), shown in Figure 4.6.1. The grain boundary dimensions 'a' and 'L' are shown in the figure. A sinusoidal variation of chemical potential, \( \mu_S \), over the tunnel surface of the form

\[
\mu_S = \bar{\mu} + \mu_0 \cos \frac{\pi x}{L}
\]

(4.18)

has been chosen. This choice is made intentionally for, theoretically at least, any variation of potential can be constructed from such a periodic function using Fourier-like techniques.

In the grain boundary the chemical potential must satisfy the elliptic form of equation (4.1(a)), since now the requirement is that vacancies have not been created or destroyed on the grain boundary. Therefore, the solution is sought of the equation

\[
\nabla^2 \mu = 0 \quad , \quad 0 < x < L, \; 0 < y < a
\]

(4.19)

subject to the condition at the perimeter where the grain boundary and tunnel meet that

\[
(1) \quad \mu(x,0) = \bar{\mu} + \mu_0 \cos \frac{\pi x}{L}
\]
and the periodic conditions:

\[(ii) \frac{\partial u}{\partial y} \bigg|_{x,a} = 0 \]

\[(iii) \frac{\partial u}{\partial x} \bigg|_{0,y} = 0 \]

\[(iv) \frac{\partial u}{\partial x} \bigg|_{L,y} = 0 \]

The solution to equation (4.19) satisfying conditions (i) to (iv) can be found from Carslaw and Jaeger (1980) to be

\[\mu(x,y) = \bar{\mu} + \mu_o \cosh \frac{\pi a}{L} (1 - \frac{y}{a}) \cos \frac{\pi x}{L} \cosh \frac{\pi a}{L} \]

\[= \mu_o \frac{D \cosh \frac{\pi a}{L} (1 - \frac{y}{a})}{\cosh \frac{\pi a}{L}} \sin \frac{\pi x}{L} \quad . \]

4.6.1 The Flux Due to Grain Boundary Diffusion

Due to the symmetry of the present model the number of vacancies which are transported from positions of high potential in the pore surface to position of lower potential amounts to the number of vacancies which cross the line perpendicular to the grain edge through the middle of the grain boundary.

The flux per unit length, \(J_g\), of vacancies over the boundary across any line perpendicular to the grain edge is given by the expression:

\[J_g(x,y) = -D \frac{\partial u}{\partial x} (x,y) \]

\[= \frac{\pi}{L} \mu_o \frac{D \cosh \frac{\pi a}{L} (1 - \frac{y}{a})}{\cosh \frac{\pi a}{L}} \sin \frac{\pi x}{L} \quad . \]
The constant \( D \) is defined by equation (4.1). The flux crossing a line, \( x = \frac{L}{2} \), through the middle of the grain boundary is, therefore

\[
J_g \left( \frac{L}{2}, y \right) = \frac{\mu_0}{L} D \frac{\cosh \frac{\pi a}{L} (1 - \frac{y}{a})}{\cosh \frac{\pi a}{L}}.
\]

Thus the total number, \( Q_g \), of vacancies crossing the grain boundary at \( x = \frac{L}{2} \) per unit time is

\[
Q_g = \frac{\mu_0}{L} D \int_0^a \frac{1}{\cosh \frac{\pi a}{L}} \cosh \frac{\pi a}{L} \left(1 - \frac{y}{a}\right) dy
\]

\[
= \mu_0 D \tanh \frac{\pi a}{L}. \quad (4.21)
\]

For well-developed porosity the length \( L \) in the model can be identified with half the length of the grain edge, because of the periodicity of the cosine term in condition (i). Roughly then there are five edges per face of length \( 2L \) associated with an area \( \frac{\pi a^2}{5} \), where \( a' \) is the grain face radius. Since in the model an area of \( 2aL \) is associated with the whole tunnel and \( L = \frac{\pi a'}{2} \), it follows that \( \frac{\pi a}{L} = \frac{5}{2} \) and thus \( \tanh \frac{\pi a}{L} = 1 \). These values will be assumed in the subsequent calculations.

4.6.2 The Flux Due to Surface Diffusion

According to Mullins (1957), the flux per unit length, \( J_s \), over the pore surface due to surface diffusion is given by

\[
J_s = \frac{B}{\Omega} \frac{\partial k}{\partial s} = \frac{B}{\Omega} \frac{\partial k}{\partial x}. \quad (4.22)
\]

Here \( K \) is the net curvature of the pore surface and \( B \) has been
defined earlier by equation (3.1b). Since

\[ K = \frac{\mu_s}{\gamma_s \Omega} + \frac{p}{\gamma_s} \]

then equation (4.22) becomes

\[ J_s = -\frac{B}{\gamma_s \Omega^2} \frac{\partial \mu_s}{\partial x} \cdot \left( s \right) \]

Therefore the total number, \( Q_s \), of vacancies crossing the pore surface at \( x = \frac{L}{2} \), per unit time is

\[ Q_s = -\frac{B}{\gamma_s \Omega^2} \frac{\partial \mu_s}{\partial x} \bigg|_{x = \frac{L}{2}} \]

\[ = 2\pi b \left( \frac{B}{\gamma_s \Omega^2} \frac{\mu_0}{L} \right) \]

(4.23)

4.6.3 The Total Contribution of Both Grain Boundary and Surface Diffusion

The total number of vacancies, \( Q \), crossing the pore surface and three associated grain boundaries at \( x = \frac{L}{2} \), per unit time is:

\[ Q = Q_s + 3Q_g \]

\[ = 2\pi b \left( \frac{\mu_0}{L} \right) \frac{B}{\gamma_s \Omega^2} + 3\mu_o D \]

\[ = \frac{\mu_0}{L} \left( 2\pi b \frac{B}{\gamma_s \Omega^2} \left[ 1 + \frac{3 \Omega^2 \gamma_s D}{5p} \right] \right) \]

(4.24)

where \( p = \frac{b}{a} \). This number of vacancies, \( Q \), being transported by the combined processes of surface diffusion and grain boundary
diffusion can be treated as though they are being transferred by a single mechanism of enhanced surface diffusion. Then from equation (4.23), the number of vacancies, $Q^*$, crossing the pore surface at $x = \frac{L}{2}$ by the enhanced surface diffusion, per unit time is

$$Q^* = 2\pi b^* \frac{B^*}{\gamma_s} \frac{\pi \mu_o}{L},$$

(4.25)

where

$$B^* = \frac{D^*_s \gamma_s}{\delta} \frac{4}{3} \Omega^3$$

and $D^*_s$ is the diffusion coefficient for the process. Equating expressions (4.24) and (4.25) gives

$$B^* = B[1 + \frac{3}{5\pi} \frac{1}{p} \frac{D^*_s \delta_s}{\Omega^3}],$$

(4.26a)

where $\delta_s$ is the thickness of the surface layer in which diffusion occurs, and has been assumed to be equal to $\Omega^3$, the interatomic spacing. It is convenient at this juncture to introduce the notation

$$B^* = CB$$

(4.26b)

where

$$C = 1 + \frac{3}{5\pi} \frac{1}{p} \frac{D^*_s \delta_s}{\Omega^3}.$$  

(4.26c)

In the following section the contribution made by this grain boundary diffusion enhancement to the morphological changes in the porosity is included in the model developed in Chapter Three, together with the contribution made to change in volume of the
porosity associated with the production or annihilation of vacancies on the grain faces and the diffusion of vacancies to or from the pore walls via the grain boundary.

4.7 The Derivation of the Equation Describing the Changing Shape and Volume of Porosity Due to Surface Diffusion and Grain Boundary Diffusion

Consider again the small element of pore surface A B C D shown in Figure 3.2.1. The surface has been displaced a small distance $\delta n$ along its outward normal to A' B' C' D'. In this chapter the displacement is taken to be due to the combined effects of the following three mechanisms:

(i) enhanced diffusion over the surface of the pore,
(ii) the increase in volume due to vacancy diffusion into the pore from the grain boundaries, and
(iii) the increase in volume due to the formation (or annihilation) of vacancies on the grain boundaries.

The increase in volume of a complete elemental segment of porosity bounded by three surfaces similar to A B C D will be denoted by $\delta V$ and is obtained by referring to the equation following equation (3.8). Thus with the notation used previously

$$\delta V = 2\pi y \delta n \delta s$$

for the case when $\theta = 90^\circ$. The separate contributions to the change in volume $\delta V$ made by the three mechanisms listed above will be labelled $\delta V_i$ ($i = 1, 2, 3$) respectively and will be assumed to occur in a small time $\delta t$.

4.7.1 The Change in Volume Due to Surface Diffusion

In time $\delta t$, the contribution $\delta V_1$ is obtained from equation (3.4) with $\theta = 90^\circ$, namely

$$\delta V_1 = 2\pi B^\delta (y \frac{dK}{ds})$$

(4.28)
4.7.2 The Change in Volume Due to Vacancy Diffusion into the Porosity

The increase in volume of a single toroid of porosity due to diffusion over all six associated grain faces is

\[ 6(2\pi a J_b \mid r=a) \Omega \delta t \]

where \( J_b \) is the flux of vacancies diffusing over the edges of each of the upper and lower surfaces of a grain face.

Substituting \( J_b = -D \frac{du}{dr} \mid r=a \) the above expression becomes

\[-12\pi a \Omega (D \frac{du}{dr} \mid r=a) \delta t = -48\pi D\Omega \bar{\mu} \delta t \quad . \quad (4.29)\]

The increase in volume of the whole porosity per unit length of grain edge is then

\[ -\frac{24}{(a + b)} D\Omega \bar{\mu} \delta t \]

since each grain edge is of length \( 2\pi(a + b) \) in the 'toroid' model. Therefore \( \delta V_2 \), the volume increase associated with the short length of grain edge, \( dx \), is given by

\[ \delta V_2 = -\frac{24}{(a + b)} D\Omega \bar{\mu} \delta t \] dx

\[ = -\frac{24}{(a + b)} D\Omega \bar{\mu} \cos \phi \delta t \] ds , \quad (4.30)

where \( \phi = \tan^{-1} \left( \frac{dy}{dx} \right) \) and \( ds^2 = dx^2 + dy^2 \).
4.7.3 The Change in Volume Due to the Formation of Vacancies on the Grain Boundary

Figure 4.7.1 shows the increase in volume, $\delta V_3$, due to the separation of the grain boundaries caused by the formation (or annihilation) of vacancies there. In the figure $\delta y_3$ represents the increase in height of the porosity occurring by this mechanism in time $\delta t$. The resulting change in the circumference, $\delta C$, of the porosity is given by

$$\delta C = 2\pi(y + \delta y_3) - 2\pi y = 6\beta\Omega\delta t,$$

since $\beta$ vacancies of volume $\Omega$ are produced uniformly over the whole area of either side of each of three grain boundaries. This gives

$$\delta y_3 = \frac{3\beta \Omega \delta t}{\pi},$$

and the change in volume, $\delta V_3$, due to the separation of the grain boundaries associated with the production of vacancies, is thus

$$\delta V_3 = 2\pi y \delta y_3 \, dx$$
$$= 6\beta \Omega y \cos \phi \, \delta t \, ds. \quad (4.31)$$

However, by equations (4.3) and (4.11),

$$\beta = \frac{-D\delta\mu}{a^2}$$

and therefore

$$\delta V_3 = \frac{-48}{a^2} D \Omega \frac{-\mu}{a} y \cos \phi \, \delta t \, ds. \quad (4.32)$$
4.7.4 The Combination of the Three Mechanisms

The change in volume, $\delta V$, due to the compound effect of the three mechanisms described above is given by

$$\delta V = \sum_{i=1}^{3} \delta V_i.$$

Therefore combining equations (4.27), (4.28), (4.30) and (4.32) gives

$$2\pi \delta n \, ds = 2\pi B^* \delta (y \frac{\partial \mu}{\partial s}) \, \delta t$$

$$- \frac{24}{(a + b)} D \omega \delta t \, ds \cos \phi$$

$$- \frac{48}{a^2} D \Omega \delta t \, ds \cos \phi,$$

or

$$\frac{\delta n}{\delta t} = \frac{B^*}{y} \frac{\partial}{\partial y} (y \frac{\partial \mu}{\partial s}) - \frac{24D\omega}{\pi} \left( \frac{1}{a^2} \cos \phi + \frac{1}{2(a + b)} \frac{\cos \phi}{y} \right). \tag{4.33}$$

In the absence of a fission-gas pressure, $P$, or an externally applied pressure, $-P$, the chemical potential $\mu$ is given by equations (4.10) and (4.16), so that

$$\frac{\delta n}{\delta t} = \frac{B^*}{y} \frac{\partial}{\partial y} (y \frac{\partial \mu}{\partial s}) - \frac{24D\omega^2 y \bar{K}}{\pi} \left( \frac{1}{a^2} \cos \phi + \frac{1}{2(a + b)} \frac{\cos \phi}{y} \right). \tag{4.34}$$

4.7.5 The Dimensionless Equation

Again following the approach of previous chapters it is convenient to make equation (4.34) dimensionless, via the
following transformations:

(a) \( X = \frac{x}{a_0} \),

(b) \( Y = \frac{y}{a_0} \),

(c) \( S = \frac{s}{a_0} \),

(d) \( N = \frac{n}{a_0} \),

(e) \( \kappa = \frac{Ka_0}{a_0} \), and

(f) \( T = \frac{B^* t}{a_0^4} \).

(4.35)

Here \( a_0 \) is the radius of the grain boundary before any volume change.

It is related to the radius, \( a \), of the grain boundary surrounded by toroidal porosity of fractional volume \( \frac{\Delta V}{V_0} \) by the formula given by Tucker (1979)

\[
a = q a_0 \quad , \quad (4.36)
\]

where

\[
q = [1 + \frac{\Delta V}{V_0}]^{\frac{1}{3}}
\]

Substituting equations (4.35) into equation (4.34) gives

\[
\frac{\partial N}{\partial T} = \frac{1}{Y} \frac{\partial}{\partial S} \left( Y \frac{\partial K}{\partial S} \right) - \frac{24Dn^2}{\pi B^* \gamma_s K a_0} \left( \cos \phi + \frac{1}{2q(1 + p)} \frac{\cos \phi}{Y} \right),
\]

where \( P = \frac{b}{a} \). The coefficients \( D \) and \( B^* \) are given by equations (4.1) and (4.26), respectively, and therefore

\[
\frac{\partial N}{\partial T} = \frac{1}{Y} \frac{\partial}{\partial S} \left( Y \frac{\partial K}{\partial S} \right) - \frac{24}{\pi C D_s \delta_s \gamma} \frac{\partial}{\partial S} \left( 1 + \frac{q}{2q(1 + p)} \frac{1}{Y} \right), \quad (4.37)
\]

since \( \cos \phi = \frac{\partial X}{\partial S} \) and where \( \overline{H} \) is defined by equation (4.17). The coefficient \( \delta_s \) is the thickness of the surface in which diffusion occurs and has been assumed to be equal to \( \Omega \beta \).
At any instant, the parameter, $p$, can be calculated from the fractional volume, $\frac{\Delta V}{V_0}$, of the porosity. For the 'toroid' model this is given by the expression

$$\frac{\Delta V}{V_0} = \frac{V_t}{V_c - V_t}, \quad (4.38)$$

where $V_t$ is the volume of the segment of the toroid shown in Figure 4.3.1 and given by equation (4.13). The volume $V_c$ is that of the cone $OFG$, also shown in the figure, and is equal to $\frac{1}{\sqrt{3}} \pi(a + b)^3$. Substituting the expressions for $V_t$ and $V_c$ into equation (4.38) leads to the following cubic equation in $p$:

$$[(\pi - \sqrt{3})(1 + \frac{\Delta V}{V_0}) - \sqrt{3} \frac{\Delta V}{V_0}] p^3$$

$$+ [\pi(1 + \frac{\Delta V}{V_0}) - 3\sqrt{3} \frac{\Delta V}{V_0}] p^2$$

$$- 3\sqrt{3} \frac{\Delta V}{V_0} p - \sqrt{3} \frac{\Delta V}{V_0} = 0. \quad (4.39)$$

To complete the specification of the problem it remains to calculate the fractional volume, $\frac{\Delta V}{V_0}$, of the porosity at any instant, 'T', during its evolution.

4.7.6 The Change in Fractional Volume of the Porosity

Only mechanisms (ii) and (iii) above contribute to the overall change in volume of the porosity. Mechanism (i), surface diffusion, can effect only local changes in the volume of a pore and overall, and matter cannot be lost or gained by the pore surface due to this mechanism.

In a small time $\delta t$, the change in volume of the porosity associated with the grain boundary by diffusion of vacancies over the boundary (mechanism (ii)) is one sixth of expression (4.29), that is

$$\Delta V = -8\pi\Omega\mu \delta t, \quad (4.40)$$
since a single toroid of porosity is shared by six grain faces.

In the same time, the change in volume of the porosity due to the formation (or annihilation) of vacancies on one boundary (mechanism (iii)) is:

\[
\pi[(a + b)^2 - a^2] \left(\frac{-D\delta u}{a^2}\right) \delta t
\]

(4.41)

since \( \beta = -\frac{D\delta u}{a^2} \). Combining equations (4.40) and (4.41) gives the overall change in volume, \( \delta V \), of porosity associated with one grain boundary, thus

\[
\delta V = \pi(a + b)^2 \left(\frac{-D\delta u}{a^2}\right) \Omega \delta t
\]

(4.42)

or \( \delta V = \pi(a + b)^2 \beta \Omega \delta t \).

The latter expression can be expected, since \( \beta \) vacancies of volume \( \Omega \) are produced uniformly over an area of \( \pi(a + b)^2 \) in time \( \delta t \).

In the limit when \( \delta t \) tends to zero, equation (4.42) yields

\[
\frac{dV}{dt} = -8\pi \frac{(a + b)^2}{a^2} D \frac{\delta u}{\Omega} \Omega \delta t
\]

(4.43)

Equation (4.35) gives

\[
\frac{dt}{dT} = \frac{a^4}{B^*}
\]

where \( B^* \) is defined by equation (4.26). Therefore,

\[
\frac{dV}{dT} = \frac{dV}{dt} \cdot \frac{dt}{dT} = -8\pi \frac{(1 + p)^2}{C} \frac{D \frac{\delta u}{\Omega}}{\frac{D}{\delta s} \frac{\delta s}{\gamma S}} a^4
\]

\[
= -8\pi \frac{(1 + p)^2}{C} \frac{D}{\delta s} \frac{\delta s}{a} H a^4
\]
where \( \bar{H} \) is given by equation (4.17). The change in fractional volume of the porosity with dimensionless time, \( T \), is given by the expression 
\[
\frac{1}{V_0} \frac{dV}{dT} = \frac{1}{V_0} \frac{dV}{dT},
\]
where \( V_0 \) is the volume of the grain associated with one grain face. This volume is one fourteenth of the whole volume of the grain before swelling and in the 'toroid' model is equal to the volume of the cone with circular base of radius \( a_0 \) and height \( \sqrt{3}a_0 \), namely \( \frac{\pi a_0^3}{\sqrt{3}} \). Therefore

\[
\frac{1}{V_0} \frac{dV}{dT} = \frac{-8\pi}{C} (1 + p)^2 \frac{D g \delta}{D s \delta} \bar{H} a_0^4 \frac{\sqrt{3}}{\pi a_0^3}
\]

\[
= -\frac{8\sqrt{3}}{C} \frac{D g \delta}{D s \delta} (1 + p^2) \bar{H} \frac{q}{q}.
\]

(4.44)

In view of the complexity of the foregoing calculation it is wise to recapitulate at this point.

The changes made to the shape and volume of grain edge porosity by the three separate mechanisms described in this chapter are modelled by the differential equation

\[
\frac{\partial N}{\partial T} = \frac{1}{Y} \frac{\partial}{\partial S} \left( Y \frac{\partial \kappa}{\partial S} \right) - \frac{24}{\pi C} \frac{D g \delta}{D s \delta} \bar{H} \frac{\partial X}{\partial S} \left( 1 + q \frac{1}{2(1 + p)} \frac{1}{Y} \right),
\]

subject to appropriate initial conditions. In the absence of fission-gas pressure or externally applied pressure at any instant in 'time', \( T \), the coefficient \( \bar{H} \) is given by

\[
\bar{H} = \frac{2}{p} \left[ \frac{(1 + p) \pi - 3\sqrt{3} p}{(1 + p)2\pi - 3\sqrt{3} p} \right].
\]

(4.46)

If a pressure, \( P \), acts from within the porosity or a pressure, \( -P \), is applied externally to the material, \( \bar{H} \) must be modified.
according to equation (4.12). In these cases \( \overline{H} \) is given by

\[
\overline{H} = \frac{2}{p} \left[ \frac{(1 + p) \pi - 3\sqrt{3} p}{(1 + p)2\pi - 3\sqrt{3} p} \right] \overline{q} \quad (4.47)
\]

Here \( P = \frac{P_o}{\gamma_s} \) is a 'dimensionless pressure'. The parameter \( p \) is the solution to the cubic equation:

\[
\left( (\pi - \sqrt{3}) (1 + \frac{\Delta V}{V_o}) - \sqrt{3} \frac{\Delta V}{V_o} \right) p^3
\]

\[
+ \left( \pi(1 + \frac{\Delta V}{V_o}) - 3\sqrt{3} \frac{\Delta V}{V_o} \right) p^2
\]

\[
- 3\sqrt{3} \frac{\Delta V}{V_o} p - \sqrt{3} \frac{\Delta V}{V_o} = 0 \quad , \quad (4.48)
\]

which is real, positive and less than unity. The parameter \( q \) is given by

\[
q = \left[ 1 + \frac{\Delta V}{V_o} \right]^3 \quad , \quad (4.49)
\]

and at any instant the fractional volume \( \frac{\Delta V}{V_o} \), is calculated via the following equation:

\[
\frac{d}{dT} \left[ \frac{\Delta V}{V_o} \right] = \frac{8\sqrt{3}}{C} \frac{D_\delta}{D_{\delta s}} \left( 1 + p^2 \right) \frac{\overline{H}}{q} \quad (4.50)
\]

The value of \( C \) is given by

\[
C = 1 + \frac{3}{5\pi} \frac{1}{p} \frac{D_\delta}{D_{\delta s}} \quad , \quad (4.51)
\]

where the ratio \( \frac{D_\delta}{D_{\delta s}} \) is a property of the material, which is temperature dependent.

In the following chapter equation (4.45) is solved for a range of values of the ratio \( \frac{R_\delta}{R_{\delta s}} \), which pertain to uranium dioxide nuclear fuel at various reactor operating temperatures.

The evolution of interconnected porosity from three different
initial stages of development is considered. The development and collapse of porosity from a line of newly interlinked bubbles, through cylindrical tunnels, to well developed, minimum area structures is followed. Fission-gas swelling and pressure-assisted sintering are modelled by the inclusion of a positive or negative pressure acting on the pore surface.

The solution is necessarily numerical and the computational strategy follows that developed in Chapter Three. The cubic equation (4.48) is solved by an iterative process, the Method of False Position, and the fractional volume, \( \left( \frac{\Delta V}{V_o} \right)_j \), at each discrete time step, \( T_j \), is calculated by the simple Eulerian approximation:

\[
\left[ \frac{\Delta V}{V_o} \right]_{j+1} = \left[ \frac{\Delta V}{V_o} \right]_j - \frac{8\sqrt{3}}{C} \frac{D_k}{\delta_s} \left( 1 + p_j \right) \frac{H_j}{q_j} \Delta T_j , \quad (4.52)
\]

where \( \Delta T_j = T_{j+1} - T_j \). It is clear that equation (4.45) is singular when \( Y = 0 \), such as at the tip where the surfaces of an isolated pore meets the grain edge. As \( Y \) tends to zero the limiting value of the first term of this equation, namely

\[
\frac{1}{Y} \frac{\partial}{\partial S} (Y \frac{8k}{8S}),
\]

has been found in Chapter Three, and is equal to

\[
2 \frac{8^2}{8S^2} \]

The principal curvature, \( \kappa_1 \), is defined by equation (3.19 (a)). The third term in equation (4.45) involves the quantity

\[
\frac{8x}{Y} \frac{8}{8S}, \text{ which is simply the principal curvature, } \kappa_2, \text{ for } 90^\circ
\]

porosity defined by equation (3.19(b)). In the limit when \( Y \) tends to zero, it is also shown in Chapter Three that this quantity becomes equal to \( K_1 \).
CHAPTER FIVE

5. THE APPLICATION OF THE MODEL OF FISSION-GAS SWELLING, GAS-RELEASE AND SINTERING

5.1 Introduction

In this chapter the results of simulating the kinetics of interconnected grain edge pores, including both the effects of surface diffusion and grain boundary diffusion according to the model developed in Chapter Four, are presented. The combined effect of these diffusive mechanisms on the fission-gas release process and the phenomenon of powder sintering is also discussed.

The evolution of porosity from three separate initial configurations is considered in an attempt to model distinct stages of the fission-gas release and sintering process. These initial configurations are:

(i) The coalescence or collapse of an initial line of five spherical bubbles held open at grain corners,

(ii) the relaxation or collapse of an initially cylindrical tunnel, and

(iii) the relaxation or collapse of an initially catenoidal tunnel.

Configuration (i) is included to offer an insight into the kinetics of the very beginning of the process of fission-gas swelling cycle, when interlinked structures are first formed by the coalescence of isolated grain edge pores. Consideration of the relaxation of a network of interlinked cylindrical tunnels as in (ii) is pertinent to both the intermediate stage of powder sintering and the intermediate stage of the release of fission-gas. The final stage of sintering begins when the interlinked networks have relaxed sufficiently to collapse again
into isolated pores. This type of collapse also marks the beginning of a new stage of the fission-gas release process, and for these reasons relaxation from the configuration (iii) is considered. Ideally in modelling the swelling process it would have been better to draw no distinction between the separate stages and to have followed the evolutionary cycle of the porosity uninterrupted from the initial configuration of a line of touching bubbles through to the collapse of the developing tunnels. However, the vast overhead in central processor time necessary to perform this computation prohibited such a simulation.

In every calculation reported in this chapter the initial porosity possessed approximately the same initial fractional volume of 28%. The simulations were performed for a range of the ratio of diffusion coefficients, \( \frac{D_{g}}{D_{s}} \). The range was chosen so as to pertain to uranium dioxide at typical reactor temperatures. The values of the ratio were calculated via the expressions:

\[
D_{g} \delta_{g} = 1.5 \times 10^{-3} \exp(-35 \times 10^{3}/T) \text{ m}^{2}\text{s}^{-1}
\]

and

\[
D_{s} \delta_{s} = 2.2 \times 10^{-5} \exp(-66 \times 10^{3}/T) \text{ m}^{2}\text{s}^{-1},
\]

given by Matthews (1979). Here \( T \) represents absolute temperature. Figures 5.1.1 shows the variation of \( D_{g} \delta_{g} \), \( D_{s} \delta_{s} \) and \( D_{g} \delta_{g}/D_{s} \delta_{s} \) against absolute temperature \( T \).

It can be seen from the figure that

\[
0.25 \leq \frac{D_{g} \delta_{g}}{D_{s} \delta_{s}} \leq 250
\]

when \( T \leq 1780K \) and \( T \geq 1275K \). Hereafter, for the sake of brevity, the ratio \( D_{g} \delta_{g}/D_{s} \delta_{s} \) will be denoted by the single symbol, \( R \). The simulations were performed for five values of \( R \), namely \( 0.0, 2.5 \times 10^{-1}, 2.5 \times 10^{0}, 2.5 \times 10^{1} \) and \( 2.5 \times 10^{2} \) with the exception in case (iii) when no further relaxation will
occur when \( R = 0.0 \) and there is no diffusion in the grain boundaries or when diffusion in the pore surface is infinitely fast compared to diffusion in the boundaries.

The effect of pressure on the surface of the porosity is also considered. Fission-gas swelling is modelled by incorporating a positive dimensionless pressure \( \bar{P} = \frac{Pa}{\gamma_s} \) (where 'a' is a characteristic length) into the curvature term of equation (4.47). Pressure assisted sintering is also modelled by the inclusion of a 'pressure', \( -\bar{P} \), equation (4.47). In the simulations presented these 'pressures' are given a magnitude equal to half that of the initial average 'curvature' of the porosity, \( \bar{H} = \bar{K}a \), in the absence of any pressure.

5.2 Results

5.2.1 The Evolution of a Line of Grain Edge Bubbles

As stated earlier the fission-gas release process begins with the coalescence of a line of grain edge bubbles. Figures 5.2.1(a) and (b) show the way in which grain edge porosity develops from such an array. In each case the last bubble in the chain is held open at the grain corner by interlinking with bubbles on neighbouring grain edges. The simulation represented by Figure 5.2.1(a) was performed for a ratio of the diffusion coefficients, \( R = 2.5 \times 10^{-1} \) and shows how initially diffusion in the surface of the pore attempts to smooth out the undulations in the surface of the newly coalesced bubbles. Surface diffusion continues in an attempt to achieve a cylindrical pore of nearly uniform curvature, but as time progresses the volume of the pore is lost by the diffusion of vacancies in the grain boundaries away from the surface of the pore. Eventually
the diminution of the pore is sufficient for it to pinch-off in
the manner shown in the third illustration of Figure 5.2.1(a).
Figure 5.2.1(b) shows the simulation repeated for
R = 2.5 \times 10^2. In this case it is evident that re-ovulation
occurs considerably more rapidly.

The variation of neck height of the porosity normalised
with respect to its initial neck height, with dimensionless time,
T, is shown in Figure 5.2.2. The figure illustrates clearly that
when R = 0, and diffusion in the grain boundaries is
infinitesimally slow, the necks between the bubbles continue to
grow until, at extended times, the porosity has passed through the
stage of a cylindrical pore, eventually to result in a stable
catenoidal configuration. Since initially the fractional volume
of the porosity (28%) is in excess of the threshold volume
fraction, calculated in Chapter Two, for which catenoidal
configurations are stable, the porosity will feel no tendency to
pinch-off. It is also evident from Figure 5.2.2 that even the
slightest degree of diffusion in the grain boundaries
significantly affects the normalised duration, T_0, for which the
porosity remains open. Thus for a constant value of
surface-diffusion coefficient, the figure demonstrates that the
effect of grain boundary diffusion is to reduce the actual
duration, t_0. Indeed it is interesting that, for
R \geq 2.5 \times 10^1, T_0 appears from the figure to reduce by an
order of magnitude as the speed of diffusion in the grain
boundaries increases by an order of magnitude, indicating, not
surprisingly, that in these regimes surface diffusion does not
contribute significantly to the collapse process. When R = 2.5
x 10^{-1} and to a lesser extent when R = 2.5 \times 10^0
however the tunnel initially attempts to seek by surface diffusion
the same equilibrium configuration as when \( R = 0 \), and this attempt has
the effect of prolonging the time to collapse.

5.2.2 The Relaxation of Cylindrical Grain Edge Tunnels

In this section the relaxation of a network of interlinked cylindrical edge tunnels is considered. The initial fractional volume of the network assumed throughout being 28% is such that the individual tunnels are not long and slender but short and squat. This initial value of percentage swelling was chosen intentionally to lie in the range (calculated in Chapter Two) for which, when the evolution of the network is dominated by surface diffusion, it will remain interlinked. Eventually, in this case, the network will relax to a structure of interconnected catenoidal tunnels. The development of this structure is 'driven' by the surface curvature gradient from the corner region to the length of a tunnel causing the tunnel to 'neck' at its centre and flare outward towards the grain corners. It was intended to examine the effect of diffusion in the grain boundaries on this regime. Even in the presence of rapid grain boundary diffusion, however, the relaxation of these networks of initially high percentage volume did not differ qualitatively from the relaxation of the longer, slender tunnels considered in Section 3.6.4 and illustrated in Figure 3.6.7, except for the case when \( R = 0 \), when pinch-off is never achieved. For this reason no further illustrations of pore shapes are included in this section.

Figure 5.2.3 shows the variation of the dimensionless neck height of the tunnels against dimensionless time. Here these parameters have been normalised with respect to the initial neck height of the tunnels. The figure demonstrates that relaxation
from these initial configurations is a slow process. In fact the
relaxations shown here have not progressed to a point where the
pores are about to pinch-off or become catenoid-like but still
these results represent a very considerable amount of
computation. It is evident again, however, that the effect of
grain boundary diffusion is to reduce the duration for which the
porosity remains open and in the case of irradiated nuclear fuels
this will inhibit the escape of fission-gas.

5.2.3 The Relaxation of Catenoidal Grain Edge Tunnels

In this section consideration of the evolution of
interlinked porosity is resumed at the stage when the edge pores
have become catenoidal. Figures 5.2.4(a) and 5.2.4(b) show the
diminution and eventual collapse of a catenoidal shaped grain edge
tunnel. The results illustrated in the figure are for the case
when \( R^* = 2.5 \times 10^2 \). The initial configuration of the tunnels
considered in the solution were calculated from the solution to
equations (2.14) with an initial neck height, \( B \), appropriate to a
fractional volume of 28%.

Figure 5.2.5 shows the variation of the ratio of the neck
height to initial neck height of the tunnels with normalised
time. The figure demonstrates that, for a given value of
surface-diffusion coefficient, the speed with which pinching-off
of the porosity occurs increases with increasing ratio, \( R \). The
figure also suggests in this case that for all the values of \( R 
\) shown the time for which the porosity remains open reduces by an
order of magnitude as the speed of diffusion in the grain
boundaries increases by an order of magnitude. It is interesting
to note that, in contrast to the configurations considered in
Figure 5.2.2, because the curvature of the initial pore surface
is almost constant surface diffusion appears to play virtually no part in determining the time to collapse, even at low values of R.

5.2.4 The Variation of Fractional Volume

In the model of fission-gas release and sintering, described in Chapter Four, the diminution in volume fraction of the porosity due to the transfer of vacancies by grain boundary diffusion, is determined from the mean curvature of the porosity (see equation (4.52)). At all times this curvature is assumed to be close to the mean curvature given by the 'toroid' model (Tucker, 1979). In view of the success of this model in predicting the curvature of catenoid porosity, described in Chapter Two, it is expected to approximate equally well to the curvature of the porosity at all the stages of evolution reported here. Therefore for a given ratio of the diffusion coefficients, R, the variation of the fractional volume of the porosity whether it has developed initially from configuration (i), (ii) or (iii) will be equivalent during an equivalent time period. The variation of the fractional volume of the porosity is shown in Figure 5.2.6 - the results shown in this figure have been taken from the relaxation of catenoidal porosity, described above. It must be borne in mind, however, that because of the limitations of the 'Toroid' model (Tucker, 1979) the values of fractional volume given for times at which the porosity has pinched-off may not be realistic.

5.2.5 The Effect of Pressure

In this section the results of incorporating an internal and external pressure acting on the surface of the porosity are reported. Again (i), (ii) and (iii) listed above are considered, but the simulations are performed only for
R = 2.5 \times 10^2. \ \text{In every instance the magnitude of the pressure acting on the surface of the porosity is given a value.}

\[ \bar{P} = \frac{P_a}{\gamma_s} = \frac{K_o a_0}{2}, \]

where \( K_o \) is the initial value of the mean curvature of the porosity, as calculated via the 'toroid' model of Tucker (1979).

A pressure acting from within the porosity, such as that encountered during fission-gas swelling in irradiated UO_2, is modelled by selecting a positive value of \( \bar{P} \). A pressure acting externally on the surface of the porosity, such as that applied during hot-pressing, is simulated using \(-\bar{P}\).

Figures 5.2.7(a), (b), (c), show the effects of these two types of pressure on the development of the neck region of the grain edge porosity from the initial configurations (i), (ii), and (iii) respectively. It is clear from these figures that porosity supported by entrained fission-gas takes longer to pinch-off and collapse than vented porosity of the same initial fractional volume. On the other hand porosity subjected to an externally applied pressure does indeed collapse faster than porosity unassisted by the action of pressure. Figures 5.5.8(a) and (b) show the variation of the fractional volume of porosity from initial configurations (i) and (iii) respectively.

5.3 Discussion

5.3.1 The Significance to the Fission-Gas Release Process

According to White and Tucker (1983) the fission-gas release process occurs by a repeated sequence of the following events. Grain edge bubbles are inflated continually by fission-gas generated intragranularly until inevitably the
situation is reached when the edge bubbles are just touching and they interlink. Following interlinkage the surface of the resulting tunnel will be smoothed by the tendency of surface diffusion to drive away material from regions of high net surface curvature to regions of lower curvature. Eventually this process will cause the tunnel to collapse into a string of larger bubbles, fewer in number and spaced wider than before. This coalescence-collapse sequence will be repeated and repeated by the continued production of fission-gas until eventually the re-formed tunnel is of such a size that it is stable and will no longer pinch-off. Then at any period during this sequence the times \( t_o \) and \( t_c \) can be defined as the duration for which the porosity remains open and closed, respectively. Then, according to White and Tucker (1983), the probability of finding a tunnel open is

\[
P = \frac{t_o}{t_o + t_c} = \frac{1}{1 + \frac{t_c}{t_o}}.
\]  

(5.1)

In determining \( t_o \) White and Tucker (1983) took no account of the effects of grain boundary diffusion such as those evident from Figure 5.2.2. In fact they calculated the value of this parameter based upon surface diffusion shape changes alone, and the present work demonstrates clearly that this in certain circumstances is erroneous. Figure 5.2.2 relates to the situation when the tunnels contain no internal gas pressure and shows that sintering is the predominant mechanism in tunnel collapse in these circumstances. It is clear, however, from Figure 5.2.8(a) that if the tunnels are gas-filled the effect of the gas pressure is to delay sintering. Indeed when the pressure
reaches a level sufficient to balance the surface tension forces in the tunnel walls no sintering will occur at all. In these circumstances the only effect of grain boundary diffusion is to enhance that of surface diffusion. It may be concluded therefore that early in the irradiation of UO$_2$ when gas is retained on the grain edges because the value of $p$ in equation 5.1 is so low (i.e. when $t_0 << t_c$ because of its sensitive dependence on tunnel radius as described in Section 3.6.3), the tunnel development model of White and Tucker (1983) is operative. However, as the tunnels get larger, $t_0$ and $p$ become larger, the gas escapes from the fuel more easily and the pressure in the tunnels falls. Grain boundary sintering collapse of tunnels then becomes the dominant mechanism, $t_0$ falls, $p$ falls and gas pressure builds up again. Thus embedded in what has hitherto been visualised as an exclusively volume increasing process is a mechanism which restricts volume increase beyond a certain level. This situation promotes better gas retention in irradiated nuclear fuel - a situation which is desirable in the nuclear reactor to minimise radiological hazards. However, if the fuel swelling does become so great that it is forced hard against its cladding, this has the effect of introducing an externally applied pressure, which according to Figure 5.2.7(c) again speeds up pinch-off. In turn this reduces $t_0$ and the effective diffusion coefficient for fission-gas release and promoting better gas retention. Thus dynamic equilibrium can be established between the competing processes - the situation that is probably observed in reality.

5.3.2 The Significance to Sintering

Figures 5.2.3 and 5.2.5 show that for a given surface-diffusion coefficient, the effect of diffusion in the
grain boundaries is to curtail the intermediate stage of powder sintering. Figure 5.3.1 shows the influence of the ratio of diffusion coefficients, $R$, on the percentage volume of the porosity, $\frac{\Delta V}{V_0}$, remaining after the collapse of catenoidal tunnels such as those encountered during the second stage of sintering. It is clear from this figure that, for a given speed of surface diffusion, the effect of grain boundary diffusion is to increase the volume of closed porosity existing as the final stage of sintering is entered. Indeed the figure suggests that when grain boundary sintering is the dominant mechanism in the collapse of interconnected edge porosity, networks of fractional volume below $\sim 15\%$ cannot be sustained. This is in contrast to the value of $\sim 9\%$ volume below which interconnected edge tunnels are unstable when their collapse is due purely to shape change effects driven by surface diffusion. During the process of grain growth, which follows the collapse of interconnected porosity in the sintering phenomenon, the existence of large pore fractions, $\frac{\Delta V}{V_0}$, promotes the likelihood of the grain boundaries breaking away from the closed pores and leaving them in the body of a grain. In this situation a high density final product becomes difficult to achieve, since such intragranular pores can only be removed by the mechanism of volume diffusion. Any reduction in the final density of the product will detrimentally affect its strength and is additionally disadvantageous in nuclear fuel, throughout which high thermal conductivity is essential to the safe and efficient operation of the reactor. However, Figure 5.2.8(b) indicates that the action of an external pressure is to reduce slightly the volume of closed porosity to be removed when the final stage of sintering commences. Furthermore, Figure 5.2.7(c) demonstrates
that for a given surface-diffusion coefficient, externally applied pressure also reduces the duration of the intermediate stage of sintering. The latter two observations indicate the usefulness of hot pressing.

5.4 General Conclusions and Further Applications of the Model

In Chapter Two a sophisticated model of the equilibrium morphology of minimum surface energy of interconnected grain edge porosity was developed, taking account of the variation in semi-dihedral angle of porosity along its length. The results demonstrate the existence of a threshold volume fraction of porosity below which these structures cannot be sustained. This finding concurs with earlier models of interlinked grain edge porosity but suggests further that the value of minimum swelling is generally lower than predicted previously. The model also vindicates the results given by the simpler 'toroid' model (Tucker, 1979) of interconnected grain edge porosity. Calculations using the surface diffusion driven shape change model reported in Chapter Three suggest that the coalescence of grain edge bubbles of low dihedral angle takes longer than for those of higher dihedral angle and that this process is a more significant part of the whole coalescence-collapse sequence during the fission-gas release than thought previously by White and Tucker (1983). It appears also that interconnected networks of low dihedral angle take longer to 'pinch-off' than those of higher dihedral angle and equivalent percentage volume, indicating that the duration of the intermediate stage of powder sintering is longer than predicted by earlier models of 90° porosity. In Chapter Four a model of the kinetics of the morphological changes and volume changes due to the combined effects of surface and
grain boundary diffusion was developed for 90° porosity. Results from the application of this model indicate that except when grain boundary diffusion is extremely slow, it is the diminution of pore volume due to such diffusion that is predominantly responsible for the collapse of the interconnected pore networks and not morphological changes driven by surface diffusion. The application of an external pressure assists the rate at which this collapse occurs, whilst internal gas pressure due for instance to entrained fission-gas tends to slow it down. When tunnel collapse is dictated by grain boundary diffusion the volume fraction of the resulting closed porosity is higher than when surface diffusion is dominant. In the latter circumstances the porosity will take up the equilibrium configurations calculated in Chapter Two as its volume falls until it collapses when the minimum volume for stable tunnels is reached.

The example calculations presented in Chapter Five, however, are not intended to be a complete exposition of the combined influences of grain boundary and surface diffusion on the sintering and gas-release processes, but to provide a foundation for a more thorough investigation.

For a start, a useful application would be to model the entire coalescence-collapse regime of the fission-gas release process, from a line of touching grain edge bubbles onwards. Since the physical, mathematical and computational models to do this have been developed fully during this present study, the only obstacle to this is the requirement of large amounts of computer time. Such a study might also be used to identify the separate contributions of surface and grain boundary diffusion at high, low and intermediate temperatures. For the analysis of the results
given in this chapter is to an extent artificial in that in practice changes in the ratio of diffusion-coefficients, $R$, occur through variation of temperature. Figures 5.1.1 show the dependences of $D_g \delta_g$, $D_s \delta_s$ and $R$ on temperature in UO$_2$ so in a given material, it is clearly not possible to maintain a value of $D_s \delta_s$ and independently vary $D_g \delta_g$.

An obvious extension of the model is to include the influence of grain boundary energy by generalising the value of the semi-dihedral angle of the porosity. This should present no particular difficulties mathematically, since the details of the 'toroid' model of general dihedral angle are given by Tucker (1979). It will however be computationally more demanding by virtue of the fact that at the dihedral angle each point along the length of a pore is given by the solution of the non-linear equation (2.14(b)).

Further extensions may be to include volume diffusion in the model and to apply the principles developed here to the coalescence and pinch-off of grain face porosity. The latter may then provide an understanding of the occurrence of snake-like tunnels on grain faces evident in Plate 1.1.
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APPENDIX 1

The Surface Area of a Small Segment of Tunnel

If $\Delta S$ is the surface area of a small segment of tunnel, then

$$\Delta S = 3 \int L(y) \, dS = 3 \int_{y_o}^{y_1} L(y) \frac{dy}{\sin \phi}$$

$$\Delta S = \frac{6(\theta - \frac{\pi}{6})}{1 - \frac{2}{\sqrt{3}} \cos \theta} \frac{1}{\sin \phi} \int_{y_0}^{y_1} y \, dy$$

$$= A \left[ y_1^2 - y_o^2 \right]$$

where

$$A = \frac{3(\theta - \frac{\pi}{6})}{(1 - \frac{2}{\sqrt{3}} \cos \theta)} \frac{1}{\sin \phi}.$$
Plate 1.1

Figure 1.4.1
A regular pentagonal dodecahedron

Figure 1.4.2
A regular rhombic dodecahedron
Figure 1.4.3

A regular tetrakaidecahedron
Figure 1.4.4

Kelvin's minimum area regular tetrakaidecahedron
Figure 1.6.1

The small element of surface used to derive equations (1.7) and (1.8)
The alternatives units of corner porosity devised by Beeré (1973 and 1975)
Figure 2.3.1

The surface element of grain edge tunnel used to derive the equation of equilibrium for such porosity
Figure 2.3.2

The sets of Cartesian axes $O_x$, $O_y$ and $Ox_\ast$, $Oy_\ast$ used to describe the pore morphology.
Figure 2.3.3

Details of the way in which a segment of tunnel moves outward, under the influence of the pressure-difference, \(P\), used to calculate the increase in free surface area due to such a movement.
Figure 2.3.4
Details of the geometric relationship between the angles $\theta$ and $\theta_o$, in the planes normal to the grain edge and normal to the line of intersection of the tunnel and grain boundary, respectively.
Figure 2.4.1

Details of the unit of porosity in the region of the grain corner, from which the right hand boundary condition is derived.
Figure 2.4.2

Details of way in which four tunnels meet at a grain corner, (a) shows the free surface of the octahedral building block distorted to follow the curvature of the tunnels, (b) shows the profile of the tunnel and corner in the (x,y)-plane.
Figure 2.4.3
Further details of the grain corner region
(a) The curved surface of the porosity at four grain corners, and
(b) its normal projection onto the octahedral building block.
Figure 2.5.1

The variation of the dimensionless surface curvature, $K_{a_o}$, of the grain edge porosity with its fractional volume, $\frac{\Delta V}{V_o}$, for $\theta_o = 50^\circ$, $70^\circ$ and $90^\circ$.

* represents analytic results when the porosity constitutes isolated pores of grain corners.
Figure 2.5.2
Profiles of grain edge tunnels for $\theta = 50^\circ, 70^\circ, 90^\circ$, corresponding to positions $A_i, B_i$, ($i = 1, 2, 3$) shown in Figure 2.5.1.
A comparison of the results of the present model with those of previous models, for $\theta_0 = 50^\circ$. 

Figure 2.5.3
Figure 2.5.4

A comparison of the 'toroid' model and the present model, for $\theta_0 = 50^\circ$. 

'Toroid' model (Tucker, 1979) 

Present model
The model of two spheres sintering

1. neck surface to sphere surface by means of volume diffusion
2. neck surface to grain boundary by means of volume diffusion
3. neck surface to grain boundary by means of grain boundary diffusion
4. neck surface to sphere surface by means of surface diffusion.
The small segment of porosity used to derive the equation of motion describing the morphological changes in the porosity, due to surface diffusion.

Figure 3:2.1(a)
The geometrical detail necessary to calculate the local change in volume of the small segment of porosity, due to surface diffusion.
Figure 3.3.1
An isolated grain edge pore.

Figure 3.4.1
The discretisation of the profile of an isolated grain edge pore, indicating the right hand boundary condition
\[ \frac{dy}{dx} = -\tan \psi. \]
The evolution due to surface diffusion of a grain edge bubble of semi-dihedral angle $\theta_o = 70^\circ$. 

Figure 3.6.1

Mid-point of pore

Dimensionless Time, $T = 2.42 \times 10^{-6}$

Dimensionless Time, $T = 4.17 \times 10^{-3}$

Dimensionless Time, $T = 8.33 \times 10^{-3}$
The neck growth time dependence of two coalescing cigar-shaped bubbles of different semi-dihedral angle, $\theta_o$. 

Figure 3.6.2
Figure 3.6.3

The relationship between the bubble 'radius', $d_b$, and its radius of curvature, $r_b$. 
Figure 3.6.4

The evolution due to surface diffusion of a line of 4 grain edge bubbles of semi-dihedral angle, \( \theta_o = 70^\circ \).
Figure 3.6.5

The evolution of a unit cell of an infinite line of grain edge bubbles of semi-dihedral angle $\theta_o = 70^\circ$. 
The neck growth time dependence of a line of \( k \) bubbles \((k = 2, 4, \infty)\), coalescing cigar-shaped bubbles of semi-dihedral angle 70°.
The evolution of a grain edge tunnel of semi-dihedral angle, $\theta_0 = 70^\circ$ and fractional volume, $\frac{\Delta V}{V_0} = 10\%$
Figure 3.6.8

The time dependence of the evolution due to surface diffusion of the neck region of a tunnel, for different values of $\theta_0$. 

$\theta_0 = 50^\circ$ $\theta_0 = 70^\circ$ $\theta_0 = 90^\circ$
Figure 3.6.9

The evolution due to surface diffusion of rod-like porosity of semi-dihedral angle $\theta_o = 70^\circ$
The 'toroid' model (Tucker, 1979) shown in section, where the tunnel surface ABCD is a segment of a toroid surrounding the grain face of radius $R$. 

Figure 4.3.1
Figure 4.3.2

Half a grain face surrounded by 90° - toroidal porosity of radius b.
Figure 4.6.1

The model of grain edge porosity used in calculating the effective diffusion coefficient, $D_s^*$. 
Figure 4.7.1

The increase in volume of the porosity due to the separation of the grain boundaries caused by the formation of vacancies there.
Figure 5.1.1(b)

Temperature dependence of the ratio \( R = \frac{D_R}{D_{ss}} \).
The evolution due to surface and grain boundary diffusion of a line of bubbles for the ratio, \( R = 2.5 \times 10^{-1} \).

Figure 5.2.1(a)

Dimensionless time, \( T = 0.216 \times 10^{-3} \)
Fractional volume, \( \frac{\Delta V}{V_0} = 23.5\% \)

\[ T = 0.690 \times 10^{-2} \]
\[ \frac{\Delta V}{V_0} = 10.9\% \]

\[ T = 0.792 \times 10^{-2} \]
\[ \frac{\Delta V}{V_0} = 6.5\% \]
The evolution due to surface and grain boundary diffusion of a line of bubbles for the ratio, $R = 2.5 \times 10^2$. 

**Figure 5.2.1(b)**
The time dependence of the evolution of the neck region of a line of interlinked bubbles for different values of the ratio, $R$. 

**Figure 5.2.2**
Figure 5.2.3
The time dependence of the evolution of the neck region of a cylindrical tunnel for different values of the ratio, $R$. 

\[ 10^0 \]

\[ 5 \times 10^{-1} \]

\[ 10^{-7} \quad 10^{-6} \quad 10^{-5} \quad 10^{-4} \quad 10^{-3} \]
The evolution due to grain boundary and surface diffusion of a catenoidal tunnel for the ratio, $R = 2.5 \times 10^5$. 

**Figure 5.2.4(a)**

Dimensionless time, $T = 0.0$

Fractional volume, $\frac{\Delta V}{V_o} = 28\%$

$T = 0.459 \times 10^{-5}$

$\frac{\Delta V}{V_o} = 17.9\%$
The evolution due to surface and grain boundary diffusion of a catenoidal tunnel for the ratio, $R = 2.5 \times 10^2$. 

Figure 5.2.4(b)
Figure 5.2.5

The time dependence of the evolution of the neck region of a catenoidal tunnel for different values of the ratio, $R$. 

$\text{DIMENSIONLESS TIME, } T$

$10^{-6}$ $10^{-5}$ $10^{-4}$ $10^{-3}$

$10^{-1}$ $10^{0}$ $10^{1}$ $10^{2}$ $10^{3}$ $10^{4}$ $10^{5}$ $10^{6}$

$\text{DIMENSIONLESS NECK SIZE, } Y$

$R = 2.5 \times 10^{-1}$

$R = 2.5 \times 10^{1}$

$R = 2.5 \times 10^{2}$
Figure 5.2.6
The time dependence of the fractional volume of the porosity for different values of the ratio, \( R \).
The effect of pressure on the evolution of the neck region of a line of bubbles, for the ratio $R = 2.5 \times 10^6$.
Figure 5.2.7(b)

The effect of pressure on the evolution of the neck region of a cylindrical tunnel, for the ratio $R = 2.5 \times 10^2$. 
The effect of pressure on the evolution of the neck region of a catenoidal tunnel, for the ratio $R = 2.5 \times 10^2$.
The effect of pressure on the variation in fractional volume of a line of bubbles when the ratio $R = 2.5 \times 10^3$. 

Fractional Volume, $\frac{\Delta V}{V_0}$
Figure 5.2.8(b)

The effect of pressure on the variation in fractional volume of a catenoidal tunnel when the ratio $R = 2.5 \times 10^2$
Figure 5.3.1
The volume fraction of porosity remaining after the collapse of catenoidal tunnels.