Mathematical modelling and numerical simulation of viscous sintering processes
van de Vorst, G.A.L.; Mattheij, R.M.M.

Published: 01/01/1995

Document Version
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the author's version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
RANA 95–14
October 1995

Mathematical Modelling and Numerical Simulation of Viscous Sintering Processes

by

R.M.M. Mattheij
G.A.L. van de Vorst
Reports on Applied and Numerical Analysis
Department of Mathematics and Computing Science
Eindhoven University of Technology
P.O. Box 513
5600 MB Eindhoven
The Netherlands
ISSN: 0926-4507
Mathematical Modelling and Numerical Simulation of Viscous Sintering Processes

R.M.M. Mattheij
Department of Mathematics and Computing Science
Eindhoven University of Technology
P.O. Box 513, 5600 MB Eindhoven, The Netherlands,
G.A.L. van de Vorst*
Department of Systems Research and Development
Agrotechnological Research Institute (ATO-DLO)
P.O. Box 17, 6700 AA Wageningen, The Netherlands.

In memory of Alan Tayler, a dear colleague and friend

Abstract

The objective of this research is to develop reliable numerical methods to predict the deformation of an incompressible Newtonian viscous fluid region (Stokes Flow) driven by surface tension. In particular this mathematical model describes the physical processes that appear when a compact of glassy particles is heated to such a high temperature that the glass becomes a viscous creeping fluid. As a result, the particles are joining together so that the cohesion of the compact is increasing with time. This phenomenon is usually called viscous sintering and e.g. appears in the production of high-quality glasses. From the methods developed, theoretical insights can be obtained about the densification kinetics of such a compact. Therefore, a numerical simulation program is developed which calculates the deformation of a representative two-dimensional or an axisymmetric unit cell of the compact. A Boundary Element Method is applied to solve the integral equations arising from the Stokes problem and the time integration is carried out by a variable step, variable order Backward Differences Formulae method.

1 Viscous Sintering and its Applications

Sintering, in general, is the process in which a granular compact of metals, ionic crystals or glasses, consisting of many particles, is heated to such a high temperature that sufficient mobility is present

*Correspondence should be send to this author
to release the excess free energy of the surface of the compact, thereby joining the particles. As a result, the cohesion of the compact increases with time. There are three types of sintering processes; ones without a liquid phase (solid-state sintering), ones with a limited (< 10%) liquid phase (liquid-phase sintering) and finally processes with a liquid phase only (e.g. viscous sintering). One may additionally apply pressure (hot-pressing), carry out chemical reactions (reactive sintering) or both during sintering. For a general overview on ceramic processing we refer to Reed [37, p.110]; comprehensive reviews about sintering phenomena can be found in Exner [9] and Sōmiya and Moriyoshi [42].

Here we only consider the case of sintering when the material transport is caused by a volume flow driven by surface tension. We shall assume the volume flow to be Newtonian and incompressible. Sintering processes of this type occur in the sintering of amorphous materials such as glasses; at sintering temperature glasses appear to behave reasonably well like incompressible Newtonian viscous fluids (cf. De With and Corbijn [53]). Because of this, the process is usually referred to as viscous sintering.

A recent technological application in which viscous sintering occurs, is the production of high-quality glasses (monoliths) which cannot be manufactured in a traditional way. For example, glasses with a component preferentially evaporating at high temperatures, have to be produced at temperatures lower than the temperatures at which glasses are produced normally, and so sintering must be applied in their manufacturing. One of the characteristics of sintering is that it occurs at a relatively low temperature; the particles are already coalescing at one-half to two-thirds of the melting temperature. In this way, also glasses with an extremely high melting temperature can be produced by applying the sintering technique at a substantially reduced temperature. In the traditional glass manufacturing contamination of the glass melt occurs by corrosion of the melting crucible. Since this happens more easily at higher temperatures, sintering can be applied in the production of glasses, free of such crucible contaminants; this is particularly important in manufacturing some high technology materials.

One method for making a monolith is the viscous sintering of a glassy compact produced in a controlled manner by the so-called sol-gel technique. In sol-gel processing, colloidal particles in a suspension, a sol, are heated or mixed with a liquid (acid or basic). This causes the particles to aggregate or polymerize and form a giant aggregate or molecule that extends completely throughout the sol; the substance is said to be a gel. The fundamental importance of this technique is the ability to tailor the microstructure on molecular length scales. For example, a wide range of gel structures can be obtained by varying the pH of the liquid.

The next step is the drying of the gel, i.e. the solvent has to be removed. This can be performed in a conventional way by removing the remaining liquid phase (alcohols and water) at ambient or moderate temperature (< 100°C) which results into a considerable shrinkage of the gel network. Moreover, because of the relatively large structure of the gel compared to the pore sizes (1-50 nm), the drying has to be performed extremely slowly to avoid cracking of the gel. For example, the drying of even small monolithic pieces can take a period from a few days to even months. Finally, one obtains what is called a xerogel. A much faster method is hypercritical drying. This is achieved by heating up the gel above the critical temperature in an autoclave with excess solvent. This excessive liquid evaporates and produces a high pressure on the gel preventing premature drying of the gel. When the system has exceeded these critical conditions, the
pressure is released by keeping the temperature above the critical point. Then an extremely light material is obtained from which most of its volume is taken up by air: this is normally called an aerogel. When the aerogel is heated to a sufficiently high temperature, the viscosity of the glass becomes low enough for surface tension acting on the interior surface of the gel to cause the gel to collapse into a hopefully dense and homogeneous glass from which the fibres can be drawn. This technique has been used in the production of glass fibres for the telecommunications industry. In figure 1 an example of a partially densified aerogel is plotted which is obtained by moving the aerogel through a hot zone (from Mulder et al. [32]).

A schematic overview of the above described sol-gel processing is given in figure 2 including powder forming, monoliths, fibres and thin film coatings (obtained from Brinker [6]). The latter application of sol-gel processing has become both a very popular and important research subject during the last decade. The sprayed gel layers are only a few hundred nanometers thick, hence the solvent evaporates easily and one obtains a xerogel film which is sintered thereafter. Applications for these sol-gel coatings can be found in optics (especially anti-reflective coatings for silicon solar cells, glasses and plastics), in electronic and sensor devices, in corrosion resistance and in strengthening (see also figure 2). Sol-gel techniques and their applications are extensively discussed in the books of Brinker and Scherer [7], Klein [25] and Paul [34]; more about the sintering aspect can be found in the reviews of both James [22] and Orgaz [33].

2 Theoretical Studies on Viscous Sintering

Most studies on viscous sintering aim at better insights in the densification kinetics of the gel (compact). In particular, one is interested in the shrinkage rate as a function of important vari-
Figure 2: A schematic overview of sol-gel processing for ceramics which includes powder forming, monoliths, fibres and thin film coatings (after Brinker [6]).

ables involved such as viscosity and particle size, thus reflecting how time, temperature and microstructure influence the development of the densification process. One wants to know what kind of structural configuration leads to a higher free energy of the gel and hence to a higher densification rate. Moreover, one is interested to find controlling factors which influence not only the processing time and temperature, but also the bubbles and properties of the finally obtained densified glass. Overviewing the literature, it appears that over the years a great deal of experimental evidence has been gathered by sintering scientists, but also that it has been very difficult to produce sophisticated mathematical models which have some predictive power.

The development of a deterministic description of the viscous flow of a structure as complicated as a dried gel (xerogel or aerogel) is out of the question, even when restricted to a simple Newtonian constitutive model. The structure is simply too stochastic for such an attempt to be successful. Hence, the first attempts describing sintering phenomena dealt with the behaviour of simple systems only, like the coalescing of two spheres, or the sintering of a sphere onto a flat surface, hoping to recover the phenomenological behaviour for macroscopic systems by these so-called unit problems. In sintering literature these models are also used, with varying degrees of success, as a diagnostic tool to decide which driving force is responsible for a particular sintering process.
This approach goes back to 1945, when Frenkel [10] described the early stage of the coalescence of two equal spherical particles. He introduced the empirical rule, which is used in most mathematical models of viscous sintering to date, that the work done by surface tension in decreasing the total surface area is equal to the total energy produced by dissipation of the flow. So in applying this energy balance one has to know beforehand both the shape deformation and the description of the governing flow field during sintering. However, this shape and flow field evolution are unknown and therefore he used approximate descriptions which only allow to predict rough estimates of the coalescence rate of the spheres. In Van de Vorst [46] it is shown that the famous and widely used Frenkel rule, viz. the width of the neck growing between the two spheres is proportional to the square root of the time, does not fit at all with the numerical solution. This guessing of the geometrical deformation and/or flow field is applied in most of the theoretical studies, cf. Kingery and Berg [24], Exner and Petzow [8], Mackenzie and Shuttleworth [31] and Scherer [39]-[41] (see also below).

An important improvement in the analytical solution of the above mentioned unit problems was presented by Hopper [13]-[16]. Starting from by the surface curvature driven Stokes's flow equations, without any assumption on the shape deformation and flow field, Hopper solved two unit problems analytically, viz. the coalescence of two equal cylinders (Hopper [13, 14]) and the coalescence of a cylinder on a half-space (Hopper [16]). He applied a conformal mapping technique to solve the Stokes equations in which the time evolution of the shape was described in terms of an equation of motion involving the mapping function. Inspired by Hopper's work, Richardson [36] was able to solve the unit problem of the coalescence of two unequal cylinders.

Application of computational methods by which the viscous sintering process of unit problems is simulated, is relatively recent. Generally, these numerical simulations are carried out by successively solving the Stokes problem for the present level geometry, and employing a time step to predict the next level geometry. The first numerical simulation of a unit problem of viscous sintering was carried out by Ross et al. [38]. They considered the sintering of an infinite line of equal cylinders and performed their simulation by employing a Finite Element Method (FEM). Jagota and Dawson [18, 20] also applied the FEM for two axisymmetric problems: the sintering of two spheres and an infinite line of spheres. Jagota and Dawson [19] used the behaviour of the two coalescing spheres to describe the densification of a powder compact. In that model, the particle packing is modelled as a framework of links between the touching spheres and the development of those links are described by considering the behaviour of the two coalescing spheres separately. Recently, Jagota [21] extended the model to simulate the viscous sintering of two equal glass coated spherical particles (two-phase sintering).

Kuiken [28] considered two-dimensional domains with a rather moderately varying curvature. He used an integral formulation based on the stream function and vorticity function and solved the resulting equations by employing a Boundary Element Method (BEM). The most important advantage of the BEM with respect to the FEM is that the dimensionality of the problem is reduced by one, i.e. the two-dimensional fluid domain is replaced by a boundary curve which makes the moving boundary problem easier to solve from a computational point of view.

In recent years, significant progress has been made in the numerical simulation of unit problems. In Van de Vorst et al. [43]-[46], we reported about the successful solution of the sintering problem for arbitrarily shaped two-dimensional and axisymmetric finite fluid bodies with even
pores inside. In those papers, the Stokes problem is described by another integral formulation, based on boundary distributions of single- and double layer hydrodynamical potentials (cf. subsection 3.2). The advantage of this formulation is that both the surface velocity and tension are the primary variables, i.e. after solving these equations the flow field for the surface is obtained directly. Moreover, a sophisticated (implicit) time integration scheme can be incorporated in the numerical scheme which allows for simulating the deformation of sharp curved geometries adequately. Using this solution method, the densification of all kinds of finite fluid domains can be simulated. However, due to the small size of such a pore domain compared to the whole gel structure, the mathematical model has to be improved in order to get rid of effects in the densification simulations that are to be attributed to the tension of the outer boundary of such a fluid domain (cf. section 5). Because of this we require another, more advanced, mathematical model.

A more sophisticated approach to describe the sintering phenomenon is the determination of a representative unit cell within the gel and to consider the densification of it. This unit cell has to be chosen so that it reflects the sintering of the gel as a whole realistically. Such a unit cell may consist of a number of particles, depending on the microstructure; this cell is also referred to as a meso-cell (De With [52]). Examples of this approach are in fact the analytical densification models developed by Mackenzie and Shuttleworth [31] and Scherer [39].

The model of Mackenzie and Shuttleworth [31] (MS-model) is generally accepted for the late-stage viscous sintering. In this model, the densification results from the shrinkage of uniform spherical pores distributed throughout the gel. Hence the MS-model is also referred to as the closed pores model. The representative unit cell is an individual spherical pore for which the flow field can be calculated analytically. The MS-model leads to an equation for the sintering time necessary to reach a particular density of the gel.

Scherer [39] developed the so-called open pores model, which assumes the gel to be a regular three dimensional array of interconnected liquid cylinders, and considered its shrinkage. This model was used by Scherer to analyze the early and intermediate stages of the sintering of gels. For the unit cell representing this structure, Scherer took a cubic array consisting of intersecting cylinders on all the edges from which the total surface was calculated. After applying Frenkel’s energy balance, he obtained an analytical relationship between the relative density and the time. However, the model breaks down when the pore is trapped in each cell during the late sintering stage. Scherer’s main result is a graph showing the density of the gel as a function of time which is very close to the predicted densification rate of the MS-model. In [40], Scherer extended his model to bimodal pore-sizes distributions. In [41], Scherer and Garino present analysis for the sintering kinetics of porous glass layer on a rigid substrate (i.e. thin film coatings).

In Van de Vorst [49], a mathematical formulation is presented that can be used to simulate the densification of a two-dimensional arbitrary shaped unit cell numerically. Therefore, it is assumed that the structure of the gel can be described by a periodic continuation of this particular unit cell as time evolves, hence the unit cell has to be representative for the gel. The flow of the pores in the unit cell is described in terms of an integral formulation with kernels that incorporate the two-dimensional lattice assumption of the gel. It appears that the strength of the formulation is that one does not have to know the tension distribution on the boundary of the unit cell since this tension is canceled out in the equations.

In section 3 we briefly outline some mathematical models which are applied to simulate vis-
cous sintering. First we start with an outline on the mathematical formulation that is used for the viscous sintering phenomenon in general (subsection 3.1). Secondly, we consider the derivation of the integral formulation that is used to simulate the deformation of the so-called unit problems (subsection 3.2). Finally in subsection 3.3 we consider the formulation to simulate the densification of unit cells. The numerical solution technique applied to solve the various models is outlined in section 4. Finally we demonstrate the capabilities of these models when simulating some viscous sintering problems in section 5.

3 Mathematical Models for Viscous Sintering

In this section we briefly outline the two mathematical models which are being used to simulate the deformation of unit problems and the densification of unit cells respectively. However, we start with the derivation of the governing flow field equations and boundary conditions that have to be satisfied in both cases.

3.1 Field Equations for Viscous Sintering

We consider an incompressible Newtonian fluid which is characterized by the dynamic viscosity $\eta$, the surface tension $\gamma$ and the magnitude of the body say through its cross-section, e.g. the length $\ell_0$. The velocity of the fluid is denoted by $v$ and the pressure by $p$. A simply connected region of fluid is defined by a closed curve $\Gamma$ and the interior area is denoted by $\Omega$. In the case of a multiply connected domain, the region is bounded externally by $\Gamma_0$, internally by $\Gamma_1, \ldots, \Gamma_M$: the complete boundary will be denoted by $\Gamma$. The orientation of the boundary is taken so that on progressing by $\Gamma$, the fluid region $\Omega$ lies at the left hand side.

In general the motion of the flow field during the sintering stage can be described by the incompressibility condition and the Navier-Stokes equation, cf. Van de Vorst [47]. Carrying out a dimension analysis on the latter equation yields two characteristic numbers, i.e. the Reynolds number $Re$ and the Froude number $Fr$ which are defined by

$$Re = \frac{\rho \ell_0 \gamma}{\eta^2} \quad \text{and} \quad Fr = \frac{\gamma^2}{g \ell_0 \eta^2},$$

where $g$ is the acceleration of gravity and $\rho$ is the density of the fluid. Considering the magnitude of the characteristic parameters involved for a typical sintering system of a glassy aerogel the following holds: the particles are of a few micrometer in size or smaller ($\ell_0 \approx 10^{-6}$), the density $(\rho)$ of the gel is approximately $10^2$ kg m$^{-3}$ (Fricke [11]), the viscosity $\eta \approx 10^8$ N m$^{-2}$ (Reed [37, p.462]) and the surface tension $\gamma \approx 10^{-1}$ N m$^{-1}$ (Paul [34, p.125]). From these numbers it follows that the the Reynolds number is of order $10^{-21}$ and the Froude number is of order $10^{-13}$. Hence both the convective and gravitational forces can be ignored in comparison to the viscous forces in the dimensionless Navier Stokes equation so that this equation reduces to the so-called Stokes creeping flow equation, i.e.

$$\Delta v - \text{grad } p = 0,$$

(3.1)
together with the incompressibility condition
\[ \text{div } \mathbf{v} = 0. \] (3.2)

During the sintering stage, the fluid can be assumed to be Newtonian, hence the following dimensionless stress tensor \( T \) holds
\[
T_{ij}(p, \mathbf{v}) = -p \delta_{ij} + \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right),
\] (3.3)

where \( \delta_{ij} \) is the Kronecker delta.

As we already mentioned in section 1, the driving force of sintering is the excess free energy of the surface of the compact. Physically, a molecule in the interior of the fluid is completely surrounded by other molecules so that these molecules have an (equal) average attraction in all directions. On the other hand, a molecule at the surface will be subjected to a net inwards attraction. Therefore, the fluid surface will always tend to contract to a shape with the smallest possible surface area. Hence a viscous blob will transform itself through time into a sphere, since that shape minimizes the outer surface occupying a certain amount of matter. The work required to decrease the surface area is called the free surface energy. In the two-dimensional case which we will mainly consider, the boundary condition in the normal direction for a free fluid surface (Batchelor [2, p.150]) is given by
\[
T_{ij} n_j = -\kappa n_i = b_i
\] (3.4)

where \( n \) denotes the outward normal and \( \kappa \) is the curvature of the boundary curve, which is taken positive for a convex boundary curve as is considered from the interior of the fluid. Here a repeated index in an expression denotes a summation over all possible values of that index (Einstein summation convention). Moreover the vector \( b \) will be referred to as the body force further on.

When the boundary curve is written in parametric form, say \( \mathbf{x} = \mathbf{x}(s) \), we obtain for the curvature the following expression,
\[
\kappa(s) = \frac{x_1'' x_2'' - x_1' x_2'}{(x_1')^2 + (x_2')^2}^{\frac{3}{2}},
\]
where ' denotes the derivative with respect to \( s \).

In the case of a multiply connected region, we assume the normal component of the stress vector to be proportional to the local curvature of the inner hole boundaries too. Thus we exclude the case that holes can move as a consequence of buoyancy or that there is an extra stress component due to a gas inside those holes. This is a reasonable simplification, since we observed that the force due to gravity can be neglected. Furthermore, we assume that gas inside the interior holes vanishes by diffusion into the glass; so this effect will not be included in the mathematical model.

If we were to solve the Stokes problem for a fixed domain outlined above, we would find, in general, a non-zero flow field on the boundary curve, which would mean an inflow through one part of the boundary and an outflow elsewhere. This is unphysical since we have a material boundary; hence the fluid domain is moving. The time-dependency does not appear explicitly in the
Stokes equation (3.1). Because of this we define a kinematic constraint that describes the movement of the fluid domain. This treatment is also called a quasi-static approach. The kinematic constraint we used to describe the motion of the fluid domain in time is the so-called Lagrangian representation of the movement of a material fluid particle, i.e.

\[
\frac{dx}{dt} = v(x) \quad (x \in \Gamma).
\] (3.5)

The above equation expresses the trajectories of the material particles. The disadvantage of the Lagrangian representation is that nodal points needed for numerical approximation do not remain uniformly distributed during the shape evolution. Hence a number of redistributions of the (collocation) points has to be carried out, cf. section 4. From equation (3.5), a system of (nonlinear) ordinary differential equations can be obtained which describes the trajectories of the nodal points. In section 4 we discuss the solution of this system of nonlinear equations.

From the outline above it is clear that we are only interested in the evolution of a particular, initially prescribed, fluid domain. Hence we only need the boundary of the flow field of the evolving shape. Therefore we reformulate the problem as an integral equation over the boundary: we transform the two-dimensional creeping flow equations with boundary conditions into an equivalent set of integral equations. In subsection 3.2 we will deduce the formulation for a blob of fluid which is applied to simulate the so-called unit problems. The mathematical formulation used to simulate the densification of unit cells is discussed in subsection 3.3.

### 3.2 Integral Formulation for a Finite Domain

In order to keep the outline simple, we consider a two-dimensional viscous fluid blob with no internal pores inside; the consequences on the model when the fluid includes pores or the axisymmetric case are discussed at the end of this subsection. So let \( \Omega \) be a simply connected domain surrounded by a closed curve \( \Gamma \) in the plane \( \mathbb{R}^2 \) in the following sense: let \( \Gamma \) be a Lyapunov surface, i.e. the normal vector is continuously varying.

Many authors attribute the following analysis and the resulting integral formulation to Ladyzhenskaya [29] (1963), but, actually, it was Lorentz [30] who in fact derived this formulation, back in 1896. Here we will closely follow the derivation of the integral equation as can be found in Ladyzhenskaya [29].

We introduce the vector field \( u_k(x, y) \) and the scalar function \( q_k(x, y) \) satisfying the following Stokes problem

\[
\triangle u_k(x, y) - \text{grad} q_k(x, y) = \delta(x - y)e_k
\]

\[
\text{div} u_k = 0.
\] (3.6)

Here \( k = 1, 2, e_k = (\delta_{1k}, \delta_{2k})^T \) is the \( k^{th} \) unit vector of an arbitrarily chosen Cartesian coordinate system, \( y \) is an arbitrary point in the plane \( \mathbb{R}^2 \) and \( \delta(x - y) \) is the Dirac delta function. Physically, these equations may be interpreted as the velocity at \( x \) induced by a two-dimensional unit point force in the \( e_k \)-direction concentrated at the point \( y \). This solution is also referred to as a flow due a Stokeslet. The problem (3.6) can be solved uniquely using the requirements

\[
u^*_f(x, y) = O(\log |x - y|) \quad \text{and} \quad q^*(x, y) = o(1), \quad (|x| \to \infty),
\]
and applying a Fourier transformation. We obtain

\[ u_j^k(x, y) = -\frac{1}{4\pi} \left[ \delta_{jk} \log \frac{1}{|x - y|} + \frac{(x_j - y_j)(x_k - y_k)}{|x - y|^2} \right], \quad (3.7) \]

\[ q_j^k(x, y) = -\frac{x_k - y_k}{2\pi|x - y|^2}. \]

This solution is called the fundamental singular solution of the Stokes problem. The functions (3.7) are also the solutions to the adjoint system,

\[ \nabla_y u^k(x, y) + \text{grad}_y q^k(x, y) = \delta(x - y)e^k, \]

\[ \text{div}_y u^k = 0. \quad (3.8) \]

By \( (\ )_y \) we mean that the differentiation is carried out with respect to \( y \). Furthermore, we require the so-called Green’s formulae corresponding to the Stokes problem.

**Theorem 3.1 (Green’s Formulae)** Let \( u, v \) be two arbitrary solenoidal vector fields and let the scalar functions \( p, q \) be sufficiently smooth. Then, the following integral identity holds for those functions,

\[ \int_{\Omega} \left[ \left( \Delta u_i - \frac{\partial p}{\partial x_i} \right) u_i - \left( \Delta u_i + \frac{\partial q}{\partial x_i} \right) v_i \right] \, d\Omega = \int_{\mathcal{G}} \left[ \mathcal{T}_{ij}(p, v) u_i n_j - \mathcal{T}_{ij}(-q, u) v_i n_j \right] \, d\Gamma. \quad (3.9) \]

The proof of this theorem can be found in Ladyzhenskaya [29].

We replace \( u \) and \( q \) in the Green’s formulae by the fundamental singular solutions \( u^k(x, y) \), \( q^k(x, y) \) of (3.7) and consider those as a function of \( y \), to be the solution of the adjoint system (3.8). Furthermore, we require that \( v, p \) satisfy the Stokes problem outlined in the previous section. Hence we obtain the following Fredholm integral equation of the second kind,

\[ v_k(x) = \int_{\mathcal{G}} \mathcal{T}_{ij}(-q^k, u^k) v_i n_j \, d\Gamma_y - \int_{\mathcal{G}} \mathcal{T}_{ij}(p, v) u^k n_j \, d\Gamma_y, \quad (3.10) \]

for any \( x \in \Omega \). Substitution of the fundamental solution (3.7) into equation (3.3) yields

\[ \mathcal{T}_{ij}(-q^k, u^k)_y = -\frac{(x_i - y_i)(x_j - y_j)(x_k - y_k)}{\pi|x - y|^4}. \]

Note that \( \mathcal{T}_{ij}(p, v)n_j \) is given by the boundary condition (3.4), i.e. \( \mathcal{T}(p, v)n = b \).

When \( x \) in equation (3.10) approaches the boundary the following integral formulation can be deduced, assuming this boundary being “smooth”

\[ c_{ij} v_j(x) + \int_{\mathcal{G}} q_{ij}(x - y)v_j(y) \, d\Gamma_y = \int_{\mathcal{G}} u_{ij}(x - y)b_j(y) \, d\Gamma_y. \quad (3.11) \]

Here \( c_{ij}, q_{ij} \) and \( u_{ij} \) are given by

\[ c_{ij} = \begin{cases} \delta_{ij} & x \in \Omega, \\ \frac{1}{2} \delta_{ij} & x \in \Gamma, \\ 0 & x \in \Omega^c, \end{cases} \]

\[ q_{ij}(x - y) = \frac{r_i r_j}{\pi R^4} r_k n_k, \]

\[ u_{ij}(x - y) = \frac{1}{4\pi} \left[ -\delta_{ij} \log R + \frac{r_i r_j}{R^2} \right], \quad (3.12) \]
where \( r_i = x_i - y_i \), \( R = \sqrt{r_1^2 + r_2^2} = |x - y| \) and \( \Omega' \) is the complementary region of \( \Omega \cup \Gamma \). When \( x \in \Gamma \) the integrals are to be understood as Cauchy principal values. The integral at the right-hand side in equation (3.11) is the so-called single-layer hydrodynamic potential and the other integral is called the double-layer hydrodynamic potential; equation (3.11) is usually referred to as the integral equation of single- and double-layer potentials.

It can be shown that the integral formulation (3.11) has a unique solution up to an arbitrary rigid-body motion. Because of this, we have to prescribe or remove these degrees of freedom from the formulation in order to obtain a fully determined problem.

There are mainly two approaches to make the above integral equation uniquely solvable. The first method is related to the approach employed by Hsiao, Kopp and Wendland [17]. In Van de Vorst et al. [44], three additional variables are added to the integral equation which prescribe the rigid-body movements. In order to achieve a full rank system, three integral constraints are included. The translation freedom is prescribed by considering the flow stationary at a reference point inside the fluid. This point is usually taken equal to the centre of mass. With regard to this point the boundary flow field is computed. Substitution of the reference point as the \( x \)-argument into the integral equation yields two integral constraints which have to be satisfied. The third integral constraint is derived by taking the inner product of the velocity field and the tangential vector along the boundary curve equal to zero.

The other method is to "remove" the eigenvalue of the double-layer hydrodynamic potential that causes this null space, i.e. \(-\frac{1}{2}\), and construct a "deflated" operator. The advantage of deflation is that the number of unknowns does not change and that we do not have to seek extra integral constraints: it is a purely mathematical approach. For example, this approach can be achieved by Wielandt's deflation (Wilkinson [51, p.596]) which is extensively discussed in two recently published books by Kim and Karrila [23] and Pozrikidis [35] respectively. This method "replaces" the deflated eigenvalue by zero without affecting the other eigenvalues; this is an important property when a iterative solution methods are applied, cf. Kim and Karrila [23]. Furthermore, this technique can be used to make the integral equation uniquely solvable (range completion).

Here we prefer to apply the latter method to equation (3.11) for determining a solution (more details can be found in Van de Vorst [47]). The deflated equation obtained can be expressed by,

\[
c_{ij} v_j(x) + \int_{\Gamma} q_{ij}(x - y) v_j \, d\Gamma_y + \tilde{\varphi}^k(x) \int_{\Gamma} \tilde{\varphi}^k v_j \, d\Gamma = \int_{\Gamma} u_{ij}(x - y) b_j \, d\Gamma_y, \tag{3.13}
\]

where \( \varphi^k \) denotes the three linearly independent rigid-body motions,

\[
\varphi^k(x) = e^k \quad (k = 1, 2) \quad \text{and} \quad \varphi^3(x) = x_2 e^1 - x_1 e^2.
\]

The integral formulation above will be solved for a simply connected two-dimensional domain. The next step will be the extension to an integral formulation for a multiply connected domain, i.e. a fluid with pores inside. Let this domain be bounded externally by \( \Gamma_0 \) and internally by \( \Gamma_1, \ldots, \Gamma_M \). By \( \Gamma \) we denote the complete boundary. Note that we have chosen the orientation of the boundary so that on progressing on \( \Gamma \) the fluid region lies on the left hand side. This means that the outer boundary \( \Gamma_0 \) is considered in counter-clockwise direction and all the inner boundaries at \( \Gamma_m \) are passed through in clockwise direction. Hence, the normal vector is always pointing to the outward of the fluid.
The mathematical formulation can be obtained by formally applying the simply connected domain equation (3.13) to this multiply connected domain and deflating with respect to the rigid-body motions. However, to simulate the shrinkage or expansion of the pores, we have to model a sink point or a source point respectively inside the pores and carrying out a deflation with respect to the outward normal since this vector spans the zero-space of the adjoint system of equations (more details can be found in Van de Vorst [45],[47]). In all the holes we choose an arbitrary point: let \( z^m \) be a point in the inside area surrounded by \( \Gamma_m \) \((m=1, \ldots, M)\). Then the following formulation can be derived for the multiply connected domain,

\[
\frac{1}{2}v_i^m(x) + \sum_{k=0}^{M} \left( \int_{\Gamma_k} q_{ij}(x - y)v_j^k d\Gamma_y + n_i^m(x) \int_{\Gamma_k} \bar{q}_j(z^m - y)v_j^k d\Gamma \right) + \varphi_i^m(x) \int_{\Gamma_m} \varphi_j^m v_j^m d\Gamma = \sum_{k=0}^{M} \left( \int_{\Gamma_k} u_{ij}(x - y)b_j^k d\Gamma_y + n_i^m(x) \int_{\Gamma_k} \bar{u}_j(z^m - y)b_j^k d\Gamma \right),
\]

where \( x \in \Gamma_m \) and the superscript \( k \) of a vector denotes that this particular vector is part of the boundary \( \Gamma_k \). The kernels \( \bar{q}_j(z^m - y) \) and \( \bar{u}_j(z^m - y) \) are equal to

\[
\bar{q}_i = \sum_{m=0}^{M} \frac{1}{2\pi} \left( \frac{2(z_i^m - y_i)(z_j^m - y_j)n_j}{R^4} - \frac{\delta_{ij}n_j}{|z^m - y|^2} \right), \quad \bar{u}_i = - \sum_{m=0}^{M} \frac{z_i^m - y_i}{2\pi |z^m - y|^2}.
\]

For a three-dimensional domain the derivation of the various formulations are analogous to the two-dimensional case. Here, we will not consider these formulations further. The formulation for axisymmetric domains is outlined in Van de Vorst [48].

### 3.3 Integral Formulation for the Unit Cell Approach

In this subsection, we briefly present the mathematical model in terms of an integral equation, to describe the sintering of a representative unit cell of a two-dimensional periodic lattice of Stokes fluid. More precise details about the derivation of this formulation can be found in Van de Vorst [49].

The important assumption we use in the mathematical model presented here, is that we suppose that the sintering gel can be represented by a periodic continuation, in two directions, of a unit cell with a certain pores distribution at any stage during the densification process (cf. figure 3). So the shrinkage of that particular unit cell corresponds to the shrinkage rate of the whole gel in the two-dimensional plane. In fact, this is the same assumption which is used by the derivation of the analytical models of both Mackenzie and Shuttleworth [31] and Scherer [39] as are mentioned in section 2.

Let \( a^1 \) and \( a^2 \) be the time dependent basic vectors of the unit cell of the lattice (see figure 3). Hence the position of the \( \lambda^{th} \) lattice is given by

\[
X^\lambda = \lambda_1 a^1 + \lambda_2 a^2 \quad (\lambda_i = 0, \pm 1, \pm 2, \ldots).
\]

(3.15)
Denote by $\Gamma_0$ the outer boundary of the unit cell and let $\Gamma_1...\Gamma_M$ be all the pore boundaries. Moreover, let $x$ be a point on the boundary of a pore. Then, the following integral formulation for the velocity of the pores in the unit cell can be derived,

$$\frac{1}{2}v_j(x) + \sum_{m=0}^{M} \int_{\Gamma_m} q_{ij}(x - y)v_j(y) \, d\Gamma_y = \sum_{m=1}^{M} \int_{\Gamma_m} u_{ij}(x - y)b_j(y) \, d\Gamma_y. \quad (3.16)$$

The kernels $q_{ij}(x)$ and $u_{ij}(x)$ are given by the following expressions,

$$q_{ij}(x) = \frac{x_i n_j}{\tau} + \frac{1}{2|\tau|} \sum_{\lambda} \left[ -r_{ij}^\lambda n_i - \delta_{ij} r_k^\lambda n_k + \frac{2r_i^\lambda r_j^\lambda r_k^\lambda n_k}{r^2} (1 + |\tau|) \right] \exp \left( -\frac{\pi r^2}{|\tau|} \right) + \frac{1}{\tau} \sum_{\mu} \frac{1}{k^4} \left[ (1 + \frac{|\tau| k^2}{4\pi}) (k^2 (K_i^\mu n_i - \delta_{ij} K_j^\mu n_k) - 2K_i^\mu K_j^\mu K_k^\mu n_k) + k^2 K_i^\mu n_j \right] \exp \left( -\frac{|\tau| k^2}{4\pi} \right) \sin(x \cdot K^\mu). \quad (3.17)$$

and

$$u_{ij}(x) = \frac{\delta_{ij}}{8\pi} \left[ \log \left( \frac{r}{\pi} \right) - 2 - \gamma \right] - \frac{1}{8\pi} \sum_{\lambda} \delta_{ij} E_1 \left( \frac{\pi r^2}{\tau} \right) + 2 \left( \frac{r_i^\lambda r_j^\lambda}{r^2} - \delta_{ij} \right) \exp \left( -\frac{\pi r^2}{|\tau|} \right) + \frac{1}{4\pi r^2} \sum_{\mu} \frac{1}{k^4} (-\delta_{ij} k^2 + K_i^\mu K_j^\mu) \left( 4\pi + \tau k^2 \right) \exp \left( -\frac{\tau k^2}{4\pi} \right) \cos(x \cdot K^\mu), \quad (3.18)$$

where $\cdot$ is the inner product, $E_1(x)$ denotes the Exponential integral, which is defined by

$$E_1(x) = \int_1^\infty e^{-x/t} \, dt,$$

and $\gamma = 0.5772156649 \ldots$ is Euler's constant. The other variables $r_j, r$ and $k$ in equations (3.17) and (3.18) are subsequently equal to $r_j^\lambda = x_j - X_j^\lambda$, $r = |x - X^\lambda|$ and $k = |K^\mu|$, where $K^\mu$ is a vector in the so-called reciprocal lattice space and is denoted by

$$K^\mu = \mu_1 b_1 + \mu_2 b_2 \quad (\mu_i = 0, \pm 1, \pm 2, \ldots). \quad (3.19)$$
The vectors \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \) are the basic vectors of the unit cell of the reciprocal lattice which are defined as
\[
\mathbf{b}_1 = \frac{2\pi}{\tau} \begin{pmatrix} a_2^1, -a_1^2 \end{pmatrix}^T, \quad \mathbf{b}_2 = \frac{2\pi}{\tau} \begin{pmatrix} -a_2^1, a_1^2 \end{pmatrix}^T,
\] (3.20)
and \( \tau \) is the total surface area of one cell, i.e. \( \tau = a_1^1 a_2^2 - a_1^2 a_2^1 \). Note that the following relation is satisfied between the basic vectors of the original and the reciprocal lattice,
\[
\mathbf{a}^i \cdot \mathbf{b}^j = 2\pi \delta_{ij}.
\] (3.21)
Moreover, we remark that when the kernel of equation (3.18) is considered as a velocity field \( u^k_i = u_{ik} \), then this is the fundamental solution of the flow due to a lattice of point forces in the \( \mathbf{e}_k \) direction in the two-dimensional plane.

As in the two-dimensional formulation, we have to deflate the integral equation (3.16) with respect to the outward normal; this in order to accomplish that the pores in the inside of the unit cell are vanishing.

Here we will only give the resulting integral formulation after the deflation has been carried out,
\[
\frac{1}{2} v_i^m(x) + \sum_{k=0}^{M} \int_{\Gamma_k} q_{ij}(x^m - y) v_j^k \, d\Gamma_y + (1 - \delta_{0m}) n_i^m(x) \int_{\Gamma_m} \bar{q}_j(z^m - y) v_j^m \, d\Gamma
\]
\[
= \sum_{k=1}^{M} \int_{\Gamma_k} u_{ij}(x^m - y) b_j^k \, d\Gamma_y + (1 - \delta_{0m}) n_i^m(x) \int_{\Gamma_m} \bar{u}_j(z^m - y) b_j^m \, d\Gamma,
\] (3.22)
where \( q_j \) and \( \bar{u}_j \) are the fundamental solutions for a lattice of sink or source points (cf. Van de Vorst [49]). Here the superscript \( m \) denotes that the particular variable is lying on the boundary of hole \( \Gamma_m \). Note that the contribution of the cell boundary \( \Gamma_0 \) for the right-hand side is not included, since it can be shown that this particular integral is equal to zero for every arbitrary periodic force \( \mathbf{b} \). This is a very nice property, because we cannot give an expression for the force on the outer boundary anyway. The above integral formulation is applied to simulate the densification of the unit cell in the Stokes flow with vanishing holes in the inside.

4 Numerical Solution

The governing integral formulations (3.13), (3.14) and (3.22) which are obtained from the various models as discussed above, are all solved by applying a BEM. Hence the boundary is discretized into a set of nodal points, say \( N \); the boundary curve \( \Gamma \) is replaced by a polygon through these nodal points. Moreover, the integral formulation is enforced on the polygon for each of the collocation points. This results into a square full rank system of 2N linear algebraic equations with 2N unknowns denoted as,
\[
\mathcal{H}(x) \mathbf{v} = \mathcal{G}(x) \mathbf{b}(x).
\] (4.1)
Figure 4: The development of the largest absolute eigenvalue (solid line) compared to the absolute eigenvalue second in magnitude (dotted line) of the numerically obtained (exact) Jacobian of two equal coalescing cylinders is showing stiffness in the initial stage of the coalescence. The jumps in the magnitude of the eigenvalues are caused by node redistributions.

Here $\mathbf{x}$ is a vector of length $2N$ consisting of all successive collocation points, viz.

$$
\mathbf{x} = \begin{bmatrix} x_1^1, x_2^1, x_1^2, x_2^2, \ldots, x_1^N, x_2^N \end{bmatrix}^T,
$$

whereas the vectors $\mathbf{v}$ and $\mathbf{b}$ represent the corresponding boundary velocity and tension respectively. The vector $\mathbf{b}$ is known (cf. equation (3.4)): this vector is approximated by fitting a quadratic polynomial through three successive collocation points. The unknowns $\mathbf{v}$ are obtained after solving the linear square full rank system (4.1) by Gaussian elimination with partial pivoting (LU-decomposition). Books that describe the implementation of the BEM are for example Banerjee [1], Becker [3] and Brebbia et al. [4, 5].

After solving the system (4.1) we have to perform a time step. Using the kinematic constraint (3.5) for each collocation point together with equation (4.1), yields the following nonlinear system of ODE with dimension $2N$,

$$
\frac{d\mathbf{x}}{dt} = \mathcal{H}^{-1}(\mathbf{x}) \mathcal{G}(\mathbf{x}) \mathbf{b}(\mathbf{x}).
$$

(4.2)

It appears that the ODE above may be *stiff* for a certain type of shapes (e.g. shapes which are having cusp-like regions). To demonstrate the stiffness of (4.2), we consider the evolution of the coalescence of two equal cylinders that already make a line contact with each other initially.
These coalescing cylinders demonstrate the deformation phenomena very well. In the early stage of the coalescence, the boundary curvature is very large in the region where both cylinders are touching (almost a cusp); in later stages the shape is becoming “smoother”, i.e. the curvature is only moderately varying everywhere.

In figure 4 we have plotted the development of the absolute value of the two eigenvalues largest in magnitude, say $\lambda_1, \lambda_2$ with $|\lambda_1| \geq |\lambda_2|$, of the numerically obtained (exact) Jacobian matrix $\mathcal{J}(x)$ of the ODE (4.2), i.e.

$$
\mathcal{J}(x) = \frac{\partial}{\partial x} \left( \mathcal{H}^{-1}(x) \mathcal{G}(x) \mathcal{b}(x) \right),
$$

(4.3)
after every successful integration time step. From the difference in size of both the eigenvalues at the initial stage of the coalescence, we conclude that there are smoother modes (of the linearized problem) that ask for larger steps on an interval that is substantially larger than $O(\lambda_1^{-1})$; hence the ODE is stiff in that region. Because of this, we have used the variable step, variable order BDF-method, as is implemented in the solver LSODE, cf. Hindmarsh [12]. Since the BDF-method is an implicit linear multistep method, the corrector equation has to be solved by some iteration method. In LSODE this is performed by applying a modified Newton iteration. This implies that the code requires the Jacobian matrix (4.3) of the ODE.

However, it is practically impossible to derive an analytical expression for the Jacobian. A numerical approximation of the exact Jacobian matrix (4.3) would be extremely time consuming: one Jacobian matrix evaluation requires the assembling and solution of the system of equations $2N$ times. Fortunately, it is not necessary to have exact Jacobian matrices anyway, since LSODE is using a modified Newton method, i.e. the same Jacobian matrix is used in subsequent (Newton) iterations and for several time integration steps. Therefore, we will use an approximation of the Jacobian matrix as follows:

$$
\delta \mathbf{v}_{j,k} \approx \mathcal{H}^{-1} \mathcal{G} \delta \mathbf{b}_{j,k}.
$$

(4.4)
Here the vector $\delta \mathbf{v}_{j,k}$ denotes the $(2j - k)^{th}$ column of the matrix $\mathcal{J}$ and $\delta \mathbf{b}_{j,k}$ is a sparse vector that containing the derivatives of $\mathbf{b}$ with respect to $x_k^j$ (only 6 non-zero elements). Hence the computing costs of this approximation will require six matrix-vector operations ($\sim 16N^2$) and $2N$ forward and backward substitutions of $\mathcal{G} \delta \mathbf{b}_{j,k}$ into the LU-decomposition. More details about this implementation can be found in Van de Vorst and Mattheij [48].

The collocation points of the boundary are (re)distributed after a certain number of time steps. In Van de Vorst and Mattheij [44], we proposed an algorithm for a fairly optimal node redistribution based on equidistributing the curvature of the boundary. The aim of that algorithm is twofold. First, the number and position of the discretization points are optimized, which is important because the computational costs per time step are proportional to $(2N)^3$. Secondly, the algorithm treats regions with a large curvature “cusp” so that the curvature of this particular region is preserved after the redistribution thus avoiding (numerical) oscillations in the computed velocity field.
5 Some Typical Results from the Numerical Simulation of Viscous Sintering

In this section we demonstrate the numerical simulation of some unit problems in viscous sintering by applying the formulation of subsection 3.2 and the densification of some unit cells by using the formulation of subsection 3.3. Especially we discuss the difference in densification behaviour of nonuniform sized pore distribution as obtained by both solution approaches.

5.1 Finite Domain Simulations

The first example we consider is the most fundamental unit problem in viscous sintering: the coalescence of two equal spheres which we also compare to the coalescence of two equal cylinders. Hence the fluid domain of both these problems is simply connected; however the two coalescing spheres represent an axisymmetric problem while the coalescing of cylinders is a two-dimensional fluid domain problem. Here, the contact radius between the fluid species will be denoted by $r$.

The development during sintering of this contact radius is of physical interest. The contact radius is a measure of how “strong” a sintering compact already is. When $r$ is small, a smaller force is necessary to break the contact between both spheres than for situations where the contact radius is larger, which occurs at later stages of the sintering process.

The collocation points of both starting shapes are obtained from Hopper’s analytical solution for the coalescence of two equal cylinders, cf. Hopper [14]. Hence for the initial stage we assume that the geometrical differences between two touching cylinders and two touching spheres can be ignored. Only nodal points from the first quadrant of this plane are needed because of the double symmetry of the body. This symmetry is preserved during the calculations. Here both the radius of the coalescing spheres and the coalescing cylinders are taken equal to 1; the initial contact radius is set equal to 0.15.

Figure 5 shows the simulation results of the coalescence of two equal spheres at subsequent times $t$; a picture of the deformation of two coalescing cylinders was already shown in figure 4. In figure 6 we have plotted the numerically obtained contact radius between both spheres (solid line). The contact radius development obtained by Jagota and Dawson [18], which they derived by employing a FEM, is plotted too. In the figure, this curve is referred to as the FEM solution (dashed line). As can be observed from figure 6, at later time stages the BEM and FEM solutions “match” reasonably well. During the initial time stage both solutions also match, however the FEM solution follows the contact radius development of two coalescing cylinders for a longer time period. Hence, the FEM approach obtains a faster rate of coalescence for the period $0.25 \leq t \leq 2.0$. In this figure we have also plotted the exact Hopper solution for the contact radius between two equal coalescing cylinders with initial radius 1 (circle marks), cf. Hopper [14]. The BEM-solution, when considered as a two-dimensional problem, is also shown (solid line). This solution is found by running our 2D-code with exactly the same program parameters for the mesh generation and the BDF time integrator as in the axisymmetric case. As can be seen from the figure, the solutions are almost identical; this gives some validation of the correctness of the axisymmetric results.

Another important issue in sintering research is the quantification of the rest-porosity of the
Figure 5: The coalescence of two equal spheres into one sphere preserving the amount of fluid.

gel after sintering. As we mentioned in section 2, the scientific interest in the densification process is mainly driven by the need to understand the magnitude of the driving force for this process and to deduce how the driving force and thus the densification rate are affected by the gel microstructure. A first attempt towards a numerical simulation of this process would be to consider the densification of a bounded domain with pores inside. Therefore we consider the shrinkage of the shape of figure 7. The starting fluid geometry represents a viscous cylinder with 9 uniformly sized cylindrical pores inside. The initial radius of the circular disk is equal to 1.3 and the pores have radius 0.2 each. The centres of the pores closest to the outer boundary are equally distributed on the circle with radius 0.8. The deformation of this geometry at subsequent periods of time is plotted in this figure too.

The density ($\rho$) of the shape at a particular time is found by dividing the surface occupied by fluid through the total area defined by the outer boundary. In figure 8 the numerically obtained density change is shown by a solid line as time evolves. Furthermore, we have plotted the density increase as predicted by the two analytic densification models which are mentioned in section 2 viz. the MS-model and Scherer's open pores model, to the numerical simulation results of two-dimensional shapes with pores inside. Although both analytical models were developed for
1.4

2 cylinders

- 2 spheres (BEM)

- 2 spheres (FEM)

- 2 cylinders (BEM)

- 2 cylinders (Exact)

Figure 6: A comparison between the contact radius $r$ for the sintering of two equal spheres obtained by both BEM and FEM. The matching of Hopper's exact solution and the BEM solution is also shown when the shape is considered two-dimensional (two equal coalescing cylinders).

A really three-dimensional sintering compact, the comparison with the numerical results should give some quantitative insight in the reliability and limitations of these approximations. Note that Scherer's equation has to be coupled with the MS-model to make this relation applicable for all densities. Therefore, we have used both the 2D and 3D MS-models, i.e. models in which the densification results from both uniformly sized and distributed cylindrical tubes and spherical pores respectively (cf. Van de Vorst [47]).

It can be seen in figure 8 surprisingly well the results of Scherer's equation match with the 2D MS-model, i.e. the bullet line. Since the MS-model is based on cylindrical pores geometries and the starting geometry is likewise, we should have expected better likeness between both the numerical and analytical results. The 3D MS-model does not give a satisfactory result at all for this two-dimensional shape. Because of this, it will not be considered further. Moreover, the figure also shows a nearly linear shrinkage rate during a large period of time.

From the simulation results above we may draw the conclusion that the finite domain approach should give a good approximation of the densification rate of the sintering material in general. Hence we could also use this model to simulate another behaviour which cannot be investigated in through experiments: the vanishing order of nonuniformly sized and situated pores in the fluid during the densification process (which can affect this rate negatively or positively). This effect is important since sintering compacts normally do not have an uniformly sized pore distribution as we assumed for the previous example. One can consider three possible vanishing
Figure 7: The shrinkage of a circular disk with 9 uniformly sized cylindrical pores.

Figure 8: The numerical obtained density change of the geometry above compared with analytic densification rates from several models.
orders for the pores of a nonuniformly sized distribution: (1) the larger pores grow first at the expense of the smaller ones and shrink thereafter; (2) the larger pores shrink significantly faster than the smaller ones until they are all of the same size and (3) the pores are vanishing in order of size one after another: the smallest first followed by the larger ones.

In order to investigate this effect with the finite domain formulation, we consider the shrinkage of a fluid disk with initially 13 cylindrical pores as plotted in figure 9. The radius of the fluid disk is taken equal to 1 and the radii of the pores are varying between 0.08 and 0.23. Thus the largest pore is nearly 9 times the size of the smallest one. The figure shows that the initial larger sized pores are shrinking significantly faster compared to the smaller ones as time evolves. This phenomenon causes the numerically obtained densification rate of this geometry to differ much from the predictions derived by the various analytical models cf. Van de Vorst [47].

However, the vanishing order of the pores as suggested by the numerical simulations may not be valid in practice since the fluid domain obtains an extra tension due to the curvature of the outer circle boundary. This tension will influence the behaviour of the densification rate of the pores inside the fluid. Taking a very large domain with many pores inside will lead to a very large system of equations which requires a lot of memory and CPU times will become unacceptably large from a computational point of view. These problems were rather the reason to develop the unit cell model, whose formulation is discussed in subsection 3.3. In the following subsection some numerical results are given.

### 5.2 Densification by unit cells

In this subsection we demonstrate some simulation results obtained by applying the unit cell formulation as outlined in subsection 3.3. An overview of the simulation results obtained can be found in Van de Vorst [50].
Figure 10: The shape deformation of a unit cell with initial density $\rho_0$ equal to 0.25 at subsequent time steps.

Figure 11: The comparison of the analytic predicted densification rates from several models with the numerically obtained density change of various unit cells with one cylindrical pore and initial density $\rho_0$ equal to 0.25, 0.5, 0.75 and 0.9 respectively.
We start with considering a fluid with cylindrical pores of equal radius distributed uniformly in the two-dimensional plane. The initial size of the square unit cell is taken equal to 1 and the radius of the inner pore is varied to obtain a particular initial density. The density $\rho$ of the numerically calculated fluid domain at a particular time is found from dividing the surface occupied by fluid in the unit cell by the total area that surrounds the outer boundary of the cell.

The shape deformation of the unit cell with initial density of 0.25 is plotted in figure 10 at subsequent time steps. From this simulation it can be observed that the influence of the pores onto each other results into a smoother shape deformation during early stages. At higher initial densities it was observed that the pore shapes remains circular during the densification.

In figure 11 the numerically obtained density change for four of the considered unit cells above is compared to the various analytic densification models mentioned in section 2. The initial density $\rho_0$ of the unit cell of these four plots is subsequently equal to 0.25, 0.5, 0.75 and 0.9.

From the various plots showed in figure 11 it can be observed that the analytic predictions become better for increasing initial density. In particular, the densification rate predicted by the
Scherer–Garino equation [41] shows a very good likeness with the numerical results at initial densities higher than 0.75.

Next we investigate the effect of nonuniformly sized and distributed pores onto the densification behaviour. This is performed by the fluid lattice plotted in figure 12 at $t = 0.0$. Here we consider a unit cell of length 1 by 1 with 14 nonuniformly sized cylindrical pores from which the radii are varying between 0.025 and 0.225. The plots at various time steps of the deformed cell shape show that the pores vanish in order of size one after another: all pores are shrinking resulting in the vanishing of the smallest pores first, followed by the larger ones. Moreover, we observe from these pictures that the aspect ratio of the unit cell is changing which might be seen as an effect on the shrinkage of the entire viscous sintering body.

The behaviour of the pore vanishing is the opposite of the numerical results obtained for a finite two-dimensional fluid region with nonuniform sized pores as presented in the previous subsection. There, it appeared that the initially larger sized pores are shrinking significantly faster, compared to the smallest ones, as time evolves. Since the unit cell models incorporate the effect of the entire two-dimensional domain we believe that the vanishing order behaviour will be valid in reality; this is also the general opinion of most sintering scientists.
As we already mentioned, the sintering gel is an irregular particle packing consisting of a variety of particle sizes with (often) a non-spherical—(cylindrical) form. These irregularities may lead to rearranging the particles and opening and closure of pores induced by this rearrangement.

In the last example we demonstrate the topic of the rearrangement of particles in an irregular and unequally sized particle packing by the particle structure shown in figure 13. Here we consider a rectangular lattice with initial size 1 by 1.5; the initial radii of the various cylinders are ranging between 0.075 and 0.3. The deformed shape of this cell is also plotted at a number of subsequent time steps in the same figure. As can be observed from these pictures, during the early stage the L-shaped bridge of cylinders inside the cell is rearranging which causes the smaller (right) pore to grow a little at the expense of the larger one (left pore). Again it can be observed that after the initial time stage, when the particles have coalesced, the geometry evolves to a type we already encountered in the previous subsection.

The examples described above give a good impression of the simulation results that can be obtained by using the unit cell model. An overall view on the simulation results can be found in Van de Vorst [50].

6 Conclusion

The examples of section 5 demonstrate the capabilities of numerical simulations for obtaining insights in both pore size and pore distribution of the sintering gel. In particular the unit cell model is able to examine the microstructure evolution during the densification of a predefined pore size distribution. The next step in modelling viscous sintering would be to use the densification behaviour obtained by the unit cell model as a constitutive law to simulate a macroscopic sintering structure in which temperature gradients or external forces apply.

It is obvious, that some experimental verification has to be performed to justify the model presented. Starting in two-dimensions, such experiments should be utilized by considering the sintering of a packing of well-controlled glass fibres that will be compared with the numerical simulation of that particular packing. A first attempt of such an experiment is discussed in Van de Vorst [47] which shows a reasonable agreement between the experimental and numerical results. Another justification of our numerical approach is provided by the experiments of Korwin et al. [26, 27] and De With and Corbijn [53]. Korwin et al. performed experiments in which they considered the coalescence of two equally sized glass fibres. De With and Corbijn investigated the coalescence of a fibre on a glassy plate. The experimental results were compared with Hopper’s analytical solutions which showed a good to excellent agreement.

References


