Sintering of Non-Uniform Porous Materials

Problem Presented by
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Problem Outline

In the manufacturing of optical fibers it is necessary to produce cylindrical blanks of solid glass with prescribed axisymmetric optical properties. The process consists of depositing SiO_2 by a combustion procedure onto the blank to create a highly porous material. This material is then heated to a sufficiently high temperature for the SiO_2 to fuse together and densify removing all the voids in the process. The behavior of the porous glass in the heating step of the process, called sintering, was the main topic of the workshop discussions. There is a large literature on the general area of sintering, particularly related to metallic powders (e.g. [1]), however this is not very applicable. For these optical blanks the densification typically involve changing the density by a factor of five, much larger than in powders, and glass can be modeled well by a Newtonian fluid in the situations of interest, rather than having to consider solid/solid diffusion and other phenomena relevant to metals.

The basic theories underlying the process of sintering glass are presented in Scherer [2] and Mackenzie and Shuttleworth [3] which we briefly review.

The theory of [2] represents the highly porous material as a uniform lattice of cylindrical rods. The model takes a simple expression for the rate of energy dissipated in a uniformly shortening viscous rod and equates this to the rate of change of surface energy due to surface tension in a uniform rod. This gives an expression relating the length of the rods to their surface area which then leads to a simple algebraic expression for the density as a function of time.

In the model of [3] the material is assumed to be at a much later stage of sintering, when the voids in the material are isolated. The model therefore looks at each individual spherical bubble of a void and balances the forces due to surface tension on the bubble surface with the viscous dissipation of the surrounding glass. The surrounding glass is taken to be of finite extent to account for adjacent bubbles. Again simple expressions can be found for the resulting density as a function of time.

The current practice is to take these two models and to fit them together at some suitable point in time where the densities are taken to be equal. This results in a "kink" in the graph where the rate of densification changes suddenly due to the change in the model.

Three specific problems were posed by Dr. Abbott to direct the work and these can be paraphrased as

1. The conventional model of the sintering has two different steps in the behavior with a jump between. Is there a better model and is there some smooth transition?
2. The existing model (basically contained in [4]) of an inhomogeneous material experiencing transient stresses uses an analogy with stresses created in a material by thermal contraction or expansion. Is this consistent with what actually happens and what are the resulting limitations of the model?
3. In practice the combustion process creates a layered blank with significant changes in density through the layers. How do these changes affect the sintering and, in particular, when do they accelerate or inhibit the sintering process?

During the workshop a number of ideas were generated which partially answer these questions. The main approach was to attack the modelling of the process from first principles and to compare the resulting behavior with that predicted by the existing theories.

Deposition

The electron micrographs of the material at various stages of the sintering and the existing literature indicated that there were several length scales involved within this type of sintering and these can be exploited.

The deposited SiO_2 is highly porous with a void fraction over 80%. This high void fraction appears to be due to the fact that the SiO_2 is created in the flame as small spheres of between 0.1 and $0.001\mu m$. As these move toward the blank they flocculate. Because of the high temperatures in the flame and the observed flocs, the process may be approximated by spheres diffusing in a turbulent flow that adhere on impact. The resulting flocs have the classical shape of long chains of spheres. The chains appear to be up to 1.0μm in length and it is these flocs that are deposited, adhering to one another, to create the initial highly porous material.

Initial Heating

When heat is applied to this porous material the viscosity of the glass decreases. Motion then occurs due to the surface tension forces generated by the convoluted geometry. In determining this motion it is first necessary to consider the existing theory concerning the behavior of viscous material subjected to surface tension with changing geometry. Here the work of Hopper [5], who considers the interaction of two cylinders of glass which initially touch, is relevant. This work has been used previously to consider the problem of fusing two optical fibers to create splices. For the present problem this work indicates that if the typical sphere is of size d with glass of viscosity μ and surface tension coefficient γ, then the spheres in a chain will create a thread of viscous material in a time of around $\mu d/\gamma$. In practice this corresponds to a very small time compared to the full sintering process. Hence the spheres are quickly eliminated. Note that there will be some shrinkage of the structure during this process.

Significant Densification Phase

A slower process must now take over as the previous stage has eliminated the smallest radii of curvature (where the spheres join) when the threads form. The next stage is then similar to that used by [2] with threads shrinking. It was noted, however, that there are two ways in which the thread can shrink. The first is by a process in the thread itself as in [2], and the other is by a process where threads cross. The first is identical to that described in [2] and assumes that the thread has no external force acting and that the thread is uniform along its length with viscosity and surface tension balancing. The second was modeled as a thin thread of viscous material adjacent to a pool of the same material.

There has been significant work done on modelling of long thin viscous fibers under the influence of both an external force along the fiber and surface tension (in fact gravity is usually also included in such model). The behavior of such fibers under stretching is stable while compressive forces can result in buckling, and this may be of particular interest when considering non-uniform densification later. References that might be useful in this area are [6], [7], and [8].

The thickening of the thread is assumed to be driven by surface tension around it with no exteral forces acting on it as in [2], but it is also drawn into the pool by the curvature,

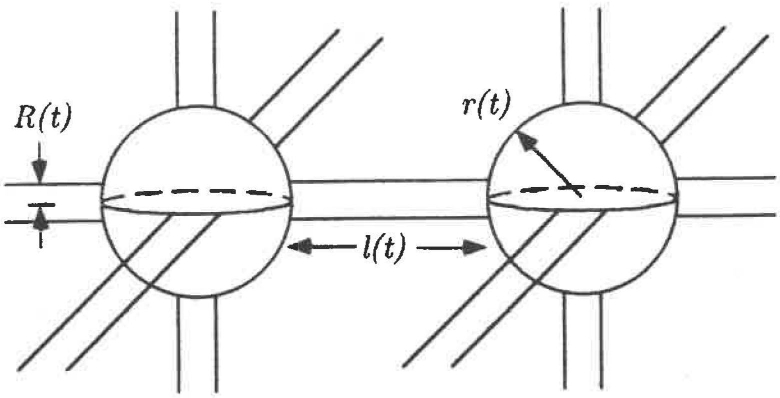

Figure 1: Thread Geometry.

and hence a surface tension force, along the thread. The speed at which this second process occurs is taken to be λ (a quantitative value for λ was not found).

This model gives the local behavior of the threads and their intersection points. To homogenize the model, some local structure must be assumed and the cubic structure of [2] is reasonable for this calculation. Other assumptions would give slightly different geometric factors but would have the same quantitative effects. Taking l to be the length of each thread, R to be the radius of each thread, r to be the radius of the intersection points with an initial configuration $l = l_0$, $R = R_0$, $r = r_0$ at $t = 0$, we have the situation shown in figure 1. The rate of change of l is governed by two parts namely that due to the model in [2] and that due to absorption into the intersection points:

$$\frac{dl}{dt} = -\frac{l\gamma}{\mu R} - \lambda.$$

Conservation of mass at the intersection points and in the linking threads gives

$$\frac{d(4\pi r^3/3)}{dt} = -\frac{d(2\pi\ R^2 l)}{dt} = \lambda,$$

and finally the geometry gives

$$\rho = \rho_G \frac{\pi r^3/6 + 3\pi\ R^2 l}{(r + l/2)^3},$$

where ρ_G is the density of solid glass and ρ is the average density of material made by the glass structure and the air. Note that this model would appear to be valid only while $l \gg R_0$ (so that the threads are reasonably approximated by long rods) and $R_0 \ll r$ (so that the threads are significantly smaller than the droplets formed intersection points). Two reasonable limits to consider are $\lambda \rightarrow 0$, which results in the model of [2], and $R \sim R_0$, where the intersection absorption of the threads dominates. A simple model of this behavior considers the case where λ dominates and is constant. In this case the glass thread length and the average density of the glass are given by

$$l = l_0 - \lambda t$$

$$\rho = \rho_G \frac{\frac{\lambda}{8r_0^3}t + \frac{\pi}{6} + 3\pi \left(\frac{R_0}{r_0}\right)^2 \left(\frac{l_0}{r_0} - \frac{\lambda}{r_0}t\right)}{\left(\left(\frac{3\lambda}{4\pi r_0^3}t + 1\right)^{1/3} + \frac{l_0}{2r_0} - \frac{\lambda}{2r_0}t\right)^3}$$

Whatever the particular model used, it breaks down when the assumption that the threads are long and thin becomes invalid (i.e., when $R \sim l$). At this point the structure no longer consists of thin threads shrinking but enters a stage where the intersections become close packed spheres. It does not seem possible to get an analytic model of the transition to this later stage. In addition, due to the distribution of initial lengths of threads and intersection points the details of the transition will be smoothed spatially.

Final Densification Phase

This final stage is equivalent to that considered by the model in [3].

Non-Uniform Stress Distributions

In discussing the problems involved in describing non-uniform sintering it is necessary to consider how it will affect the two distinct phases of significant densification and final densification previously identified as important.

It is worth starting with comments concerning the existing model as presented in [4]. To give insight into the behavior predicted by this model the equations were solved numerically. An example of the results generated using a cylindrically symmetric blank with a sinusoidal initial variation in the density ρ was solved and this showed the same behavior as that encountered in [4]. This model is based on the final densification phase and looks at the collapse of bubbles in the glass. The collapse of each bubble is taken to be a local phenomena with the bubbles sufficiently far from each other so that they can be considered in isolation. The crucial interaction between bubbles comes from the dependency of this collapse on the "pressure" in the glass. This pressure is taken from a large-scale problem containing many bubbles. An investigation of the model shows that this long range stress field generated due to the deformations created by the collapsing bubbles is in fact an elastic stress field. In this way the problem is equivalent to stresses in a thermally shrinking material. There was significant disquiet that the model exhibits elastic properties rather than exhibiting viscous behavior on all scales.

Non-Uniform Final Densification

In the final stages of densification a model with many bubbles is appropriate. On the large scale such a homogeneous model should consider the variables $B(\mathbf{x}, t)$ the typical radius of bubbles at a position $\mathbf{x}$ and at a time t, $p_B(\mathbf{x}, t)$ the pressure of the gas in the bubbles, $n(\mathbf{x}, t)$ the number density of bubbles, $\rho(\mathbf{x}, t)$ the average density of the material, and $p(\mathbf{x}, t)$ the pressure in the glass.

Now these are related by a number of un-controversial equations namely due to geometry

$$\rho = \rho_G(1 - 4\pi n B^3/3)$$

while if $\mathbf{u}$ is the velocity of the material the conservation of bubbles and material implies that

$$\frac{\partial n}{\partial t} + \nabla \cdot (n\mathbf{u}) = 0,$$
$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho\mathbf{u}) = 0.$$

It is then necessary to discuss how the bubbles shrink and a simple model is

$$\frac{\partial B}{\partial t} + \mathbf{u} \cdot \nabla B = F$$

where $-F$ is the bubble shrink rate. The precise functional form of F depends on the local approximations made. From hereon the equations in the model become more controversial. One possible example is to consider a simple bubble collapsing in an infinite region of glass with a known compressive stress, σ_g, at infinity, representing the long range stresses in the material, and the bubble at the pressure p_B. Taking spherically symmetric Stokes flow, we find that the bubble radius changes at a rate given by

$$F = \frac{3B}{4\mu}\left(p_B - \sigma_g - \frac{\gamma}{B}\right)$$

The model of the long range stresses can be extracted from multi-phase fluid models. A simple version of this is to assume that the glass can be considered to be incompressible and to be governed by Stokes flow. The notation used here is the usual convention such as found in Langlois [9]. To account for the effective compressibility of the material due to the changing bubble size, assume that if the resulting large scale flow of the glass is purely isotropic, then no stress will occur. This is equivalent to taking the large scale stress not to be generated by the actual strain rate

$$e_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)$$

but rather by an effective strain rate, $\tilde{e}_{ij}$, which is the actual strain rate minus any isotropic expansion on the region due changes in sizes of the bubbles, so that

$$\tilde{e}_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) - \frac{1}{3}\frac{\partial u_k}{\partial x_k}.$$

Using these ideas, which are equivalent to those of thermoelasticity, the stress problem can then be written as

$$0 = -\nabla p + \mu_e \nabla^2 \mathbf{u} + \frac{\mu_e}{3}\nabla(\nabla \cdot \mathbf{u}),$$

where μ_e is the effective viscosity of the material. Note that if μ_e varies spatially, perhaps due to a dependency on n and B, this equation needs to be modified. However, given the numerous approximations made it may be sufficient to assume it is constant at the value for glass without any bubbles.

Boundary conditions must be added to this model. The outer surface of the material will obviously move as the bubbles collapse so there will be the conventional kinematic condition (the normal velocity of the fluid on the boundary is the normal velocity of the boundary), and in addition the outer surface will have no tangential force and the normal force will be the external gas pressure (if using the previous effective strain rate to define the stresses care should be taken to use the correct definition of stress).

To see how the predictions of this model compared with those generated using [4] the system as outlined earlier with the cylindrical blank would require a numerical solution for the same physical situation. One significant difference is that if the initial density is specified, then this newer model also requires that either the initial bubble size or number density be given and the solution behavior depends on the form that is specified.

We also note that if the initial blank has uniform properties and it is either spherical or cylindrical then it will shrink uniformly in keeping with expected behavior. This is because in these special geometries the flow is insensitive to the precise force balance model used.

Non-Uniform Significant Densification

For the case where the material is still in a state where it is a fine network of thin thread with intersections there was little modelling progress. On the local level the non-uniformities result in forces being applied along the threads. This modifies the rate equations relating l to R. For the model in [2] this is relatively straightforward; however, the case where intersection dynamics are considered is less obvious.

To homogenize the model some local structure must again be considered. Here the cubic structure considered earlier is inappropriate. The thin threads can sustain tensile or compressive forces only, so a cubic structure will collapse if any shear force is applied. A more practical local structure is some tetrahedral lattice which will then account for shear forces through decomposition into various forces along the thread directions. The homogenized model must then allow for the length and radius of the threads along each of the edges of the tetrahedron. These quantities must be advected with the material in a manner similar to the model of the final densification. Such a model was considered to be extremely complex compared to the level of modelling required for other aspects of the process. In addition at all stages of the modelling we have assumed that the local structure is periodic whereas in practice there will be significant spatial variations in such properties as chain length, sphere sizes, bubble sizes and so on which will smooth much of the resulting behavior.

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