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THE STRUCTURE OF CONSTITUTIVE LAWS FOR THE SINTERING OF FINE GRAINED MATERIALS

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Abstract—This paper examines the general structure of constitutive laws for the sintering of fine grained materials for situations where power-law creep and grain-boundary diffusion are the dominant mechanisms of deformation and densification. The description of grain-boundary diffusion accepts an interface reaction. Constitutive laws for general multiaxial stress states are expressed in terms of scalar potential functions. Bounds to the potential are obtained which take into account the coupling between power-law creep and diffusion.

INTRODUCTION

Ceramic and intermetallic components are often manufactured using a power route. Compacts of near net shape are heated to high homologous temperatures, with or without the application of pressure, where they densify and the individual particles bond together. Hot isostatic pressing is becoming increasingly popular as a means of providing dense fine grained components, particularly in the manufacture of composite systems. Power processing also provides an attractive means of manufacturing complex shaped components from more conventional materials. The material is then generally compacted to the required density at low temperatures and only sintered for a sufficient period of time to allow sufficient diffusion to occur for the particles to bond together.

Ashby and co-workers [1–3] have identified the different mechanisms of densification for the full range of processing routes identified above and developed micromechanical models for simple applied stress states. It is convenient to divide the process of densification into two stages. The first stage describes the early phase of densification when the porosity is connected and discrete necks exist between the particles. For relative densities (density of compact/density of fully compacted material) greater than about 0.9 the porosity closes leaving isolated near equilibrium shaped pores between the grains. The material has then entered stage 2. The different mechanisms of densification identified by Ashby [1–3] are shown diagrammatically in Fig. 1. If the material is compacted at low temperature or sintered with the application of increasing pressure at elevated temperature then densification proceeds by time independent plastic deformation, which is localised in the contact region of the particles during stage 1 and extends through the entire compact during stage 2. At high homologous temperature densification can proceed by power-law creep or the direct diffusional transport of material, with the exact mechanism depending on the applied pressure, temperature, material system and extent of densification. The major characteristics of densification by power-law creep are directly equivalent to those of plasticity, with deformation being confined to the particle contacts during stage 1 and spreading through the entire component during stage 2.

Diffusional mechanisms tend to be favoured at low pressures and in fine grained materials, particularly in ceramic systems. The dominant path for diffusion can either be through the grain or along the grain boundary, with the overall rate of the process either controlled by the rate of diffusion or the rate at which any interface reactions are overcome when material is either added to or removed from a grain boundary [4, 5].

The constraint imposed by the can during hot isostatic pressing can result in the development of complex multiaxial stress states within the sintering compact and distortion of the finished component. Residual stress states can be generated in composite systems as a result of the differential rates of sintering as material densifies around the reinforcing phase. Full multiaxial constitutive laws are required to fully evaluate the evolution of microstructure, component shape and internal stress fields in each of these situations. Fleck et al. [6] have provided appropriate
equations for stage 1 for a perfectly plastic material, while Gurson's model [7], which was originally developed to describe void growth in ductile materials, is appropriate for stage 2. Kuhn and McMeeking [8] have evaluated the stage 1 response for a power-law creeping material and Cocks [9], McMeeking and Sofronos [10], Duva and Crow [11] and Ponte Castanada [12] have examined the material response during stage 2. McMeeking and Kuhn [13] have developed a constitutive model for stage 1 when grain-boundary diffusion is the controlling mechanism.

In the present paper we examine the general structure of constitutive laws for the sintering of fine-grained materials in terms of scalar stress and strain-rate potentials and develop general bounds for these potentials which incorporate a description of the coupling between the different mechanisms. In the process we develop models for grain-boundary diffusion controlled sintering in stage 2 and for situations where an interface reaction controls the rate of sintering in both stages 1 and 2. The constitutive laws for the microscopic response are presented in the following section, which are expressed in terms of microscopic convex potentials. The existence of a convex potential for the macroscopic response is obtained from a variational argument due to

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![Fig. 1](image_url). It is convenient to divide the process of densification into two stages. In stage 1 the porosity is connected and discrete necks exist between the particles. In stage 2 the residual porosity is in the form of small isolated voids (after Ashby [3]).
Needleman and Rice [14] and its extension to interface reaction controlled creep as described by Cocks [15]. A series of bounds are then developed directly from the convexity conditions for the microscopic potentials and these are then employed to evaluate the full range of mechanisms described above.

GOVERNING EQUATIONS FOR PLASTICITY, POWER-LAW CREEP AND DIFFUSION

The general situation examined in this paper is shown diagrammatically in Fig. 2. A body of total volume $V$ contains grains of volume $V_m$, pores of combined volume $V - V_m$ and surface area $A_p$ and grain boundaries of total area $A_b$. The body is subjected to a stress $\Sigma_{ij}$ and deforms at a rate $\dot{E}_{ij}$. An element of material within a grain experiences a stress $\sigma_{ij}$. If the grain material can only deform by time independent plastic straining, plastic straining can only occur when the stress is at yield, i.e. when

$$f(\sigma_{ij}) = \vec{\sigma} - \sigma_0 = 0$$

where $\vec{\sigma}$ is a homogeneous function of degree one in stress and $\sigma_0$ is the material yield strength. At yield the plastic strain-rate vector is normal to the yield surface in stress space, Fig. 3,

$$\dot{\epsilon}_{ij} = \lambda \frac{\partial f}{\partial \sigma_{ij}} = \lambda \frac{\partial \vec{\sigma}}{\partial \sigma_{ij}}$$

where $\lambda$ is a plastic multiplier.

In the present paper we do not examine the response of a perfectly plastic material directly, but determine the response as the limiting case of a power-law creeping material. We describe the creep response in terms of two convex potential functions, $\phi_c$ and $\psi_c$, such that

$$\dot{\epsilon}_{ij} = \frac{\partial \phi_c}{\partial \sigma_{ij}}; \quad \sigma_{ij} = \frac{\partial \psi_c}{\partial \dot{\epsilon}_{ij}}$$

where

$$\phi_c = \frac{1}{n + 1} \dot{\epsilon}_0 \sigma_0 \left( \frac{\vec{\sigma}}{\sigma_0} \right)^{n+1}$$

and

$$\psi_c = \frac{n}{n + 1} \dot{\epsilon}_0 \sigma_0 \left( \frac{\dot{\epsilon}}{\dot{\epsilon}_0} \right)^{n(n+1)}$$

In these expressions $\dot{\epsilon}_0$ is the uniaxial strain-rate at a stress $\sigma_0$ and $n$ is a creep exponent. These dual potentials are related to the energy dissipation rate per unit volume, $d$, through the relationship

$$d = \dot{\phi}_c + \dot{\psi}_c.$$
plated out onto the boundary the grains on either side move apart at a rate \( v_n \). If \( j_s = \Omega I_x \) (where \( x \) is in the range 1, 2 and refers to the local coordinate system) is the volumetric flux crossing unit length of grain boundary, matter conservation requires that

\[
\frac{\partial j_s}{\partial x_n} + v_n = 0. \tag{5}
\]

Following Ashby [4] Cocks [15] introduced the effect of an interface reaction into the kinetic equation for diffusion in the following manner

\[
\dot{j}_s = -\frac{D_b \delta_b \delta (\mu - \mu_0)}{kT} - \frac{\delta}{\partial x_n} \frac{\partial (\mu - \mu_0)}{\partial x_n} \tag{6}
\]

where \( D_b \) is the grain-boundary diffusivity, \( \delta_b \) is the thickness of the grain boundary, \( k \) is Boltzman’s constant, \( T \) is the absolute temperature, \( \mu \) is the excess chemical potential of an atom in the boundary

\[
\mu = -\sigma_s \Omega \tag{7}
\]

\( \sigma_n \) is the stress normal to the boundary, \( \Omega \) is the atomic volume and \( \mu_i \) is the strength of the interface reaction, representing the additional chemical potential required to add an atom to, or remove an atom from, the boundary. The chemical potential \( \mu \) is negative for atoms added to a boundary and positive when atoms are removed. Cocks [15] proposed that \( \mu \) is only a function of the grain separation rate. It is then instructive to write \( \mu \) in the form of equation (3)

\[
\mu = -\sigma_s \Omega \tag{8}
\]

where \( \sigma_s \) is an interface reaction stress, which is determined from the local grain separation rate \( v_n \), using the following relationship

\[
\sigma_s = \frac{\partial \psi_s}{\partial v_n} \tag{9}
\]

where

\[
\psi_s = \frac{m}{m+1} v_n \sigma_0 \sigma \left( \frac{1}{\sigma_0} \right)^{m+1} \tag{9a}
\]

is a scalar convex potential, \( v_n \) is the separation-rate when \( \sigma_s = \sigma_0 \) and

\[
\sigma^2 = v_n \cdot v_n.
\]

Equation (6) can then be written in the form

\[
\dot{j}_s = \frac{\partial \phi_b}{\partial s_s} \tag{10}
\]

where

\[
\phi_b = \frac{1}{2} \delta_{s_s} s_s \quad \text{and} \quad s_s = \frac{\partial (\sigma_s - \sigma_e)}{\partial x_n}. \tag{10a}
\]

As for power-law creep dual potentials to \( \psi_s \), \( \phi_b \) exist

\[
\phi_i = \frac{1}{m+1} \sigma_0 v_n \left( \frac{\sigma}{\sigma_0} \right)^{m+1} \quad \text{and} \quad \psi_b = \frac{\sigma_s}{2 \sigma_0} \tag{11}
\]

where \( \sigma^2 = \sigma_i \cdot \sigma_e \), which are related to \( \psi_s \) and \( \phi_b \) according to the relationships

\[
v_n \sigma_i = \phi_i + \psi_i, \tag{12}\]

\[
\dot{j}_s \, s_s = \phi_b + \psi_b. \tag{13}
\]

Continuity of flux requires that

\[
\mu - \mu_e = -\gamma_s (\kappa_1 + \kappa_2) \Omega = -\sigma_e \Omega \tag{14}
\]

along the collection of arcs, \( \Gamma \) where the grain boundaries meet any free surfaces, such as at the apex of a shrinking pore, where \( \gamma_s \) is the surface free energy, \( \kappa_1 \) and \( \kappa_2 \) are the principal curvatures of the adjoining surfaces and \( \sigma_e \) is the resulting capillarity stress.

We assume throughout this paper that grain boundaries, including the interparticle interfaces, slide freely with respect to each other. The effect of a finite sliding resistance could readily be incorporated in the potential functions and the bounds generated in this paper, but as noted by Fleck [16] and Kuhn and McMeeking [8] inclusion of this effect does not significantly affect the form of the constitutive relationships. We do not fully model the effect of surface diffusion on the sintering process. In the general results presented in the following section we assume that the shape of any pores are known and that the angles that the surfaces make with any intersecting grain boundaries retain their equilibrium values throughout the sintering process.

### THE MACROSCOPIC POTENTIAL

In this section we generalize the result of Hill [17] for the macroscopic potential to the class of problem represented by Fig. 2. Let \( \sigma^*_p \) be a stress field within the body that is in equilibrium with an applied stress \( \sigma^*_p \), a surface tension force per unit length, \( \gamma^*_p \), on the surface of the pores of total area \( A_p \) and a grain-boundary tension force per unit length, \( \gamma^*_s \), on the grain boundaries of total area \( A_b \). \( \Sigma^*_p \) must also satisfy the requirement that \( \sigma^*_p = \sigma^*_s \) where the grain boundaries meet any pores. Further, let \( \varepsilon^*_p \) and \( v^*_p \) represent the strain-rate and velocity fields that are compatible with the remote strain-rate \( \dot{E}_i \).

The principle of virtual power then gives

\[
\Sigma^*_p \dot{E}_i = V^{-1} \left\{ \int_{v_n} \sigma^*_p \varepsilon^*_p \, dV + \int_{A_b} \sigma^*_s v^*_s \, dA \right. \\
+ \int_{A_p} \gamma^*_p \varepsilon^*_p \, dA + \gamma^*_s v^*_s \sin \theta \, d\Gamma \\
+ \int_{A_b} \gamma^*_s \varepsilon^*_s \, dA + \int_{A_p} \gamma^*_p \varepsilon^*_p \, dA \right\}
\]
where \( \sigma^* \) is an arbitrary distribution of interface reaction stresses, \( e^*_\alpha \) is the axial (stretch) strain in the surface of a pore or in the plane of a grain boundary and \( \theta \) is the dihedral angle, the angle a surface makes with an intersecting grain boundary. In the derivation of the term containing \( \sin \theta \) in equation (15) it was assumed that the dihedral angle retains its equilibrium value as material is plated out onto a grain boundary. The quantities \( k_i^\gamma \) and \( k_j^\gamma \) are the principal curvatures in the plane of the boundary and in the derivation of the term relating to these curvatures it was assumed that material is added evenly to each grain either side of a grain boundary. The last term is integrated over the length \( \Gamma_b \), where more than two boundaries meet where the sum \( \Sigma_x \) is made over all the adjoining grain boundaries. In the derivation of this term we have limited our attention to triple grain junctions, assuming that the boundaries lie at 120° with respect to each other. The result can be readily generalised to other geometric arrangement of grains but this is unnecessary for the purposes of this paper.

The last five terms of equation (15) are in addition to those previously introduced by Needleman and Rice [14] and Cocks [15]. These contributions relate to the increasing internal surface and grain-boundary area as the body deforms; i.e. from the stretching of the surfaces and boundaries due to power-law creep of the grains and from the plating of material on the boundaries (additional terms would be required in the above expressions if we were to consider the influence of surface diffusion on the sintering process). They are included here for completeness and largely determine the sintering potential in a given situation. The other three terms are of more practical interest and we mainly concentrate on these in the bulk of this paper.

Following Needleman and Rice [14] the first integral on the right hand side of equation (12) becomes

\[
\int_{\Delta_b} (\sigma^*_\alpha - \sigma^*_\alpha)v^*_{\alpha} dA = \int_{\Delta_b} \sigma^*_\alpha s^*_{\alpha} j^*_{\alpha} dA + \int_J \gamma^*_\alpha m^*_{\alpha} j^*_{\alpha} d\Gamma
\]  

(16)

where \( j^*_{\alpha} \) represents the flux pattern responsible for the velocities \( v^*_{\alpha} \) and \( s^*_{\alpha} \) is related to the stress field \( \sigma^*_\alpha \) and distribution of interface reaction stresses \( \sigma^*_\alpha \) through equation (10). The vector \( m^*_{\alpha} \) represents the normal to the arc of intersection of a boundary facet with a pore directed into the plane of the intersecting facet.

If we now identify the fields \( \epsilon^*_{\alpha}, v^*_{\alpha}, j^*_{\alpha} \) with the actual fields obtained when the body creeps at a rate \( \dot{E}_\alpha \) under a stress \( \Sigma_{\alpha} \), the fields \( \sigma^*_\alpha, \sigma^*_\alpha \) and \( s^*_{\alpha} \) with \( \delta_{ij}, \delta_{\alpha}, \) and \( \delta_{ij} \) respectively, \( \Sigma^*_\alpha \) with \( d\Sigma_{ij} \) and set \( \sigma^*_\alpha \) equal to zero, equations (15) and (16) become

\[
\dot{E}_{ij} d\Sigma_{ij} = V^{-1} \left\{ \int_{\Delta_b} \dot{\epsilon}_{ij} d\sigma_{ij} dV + \int_{\Delta_b} j_{ij} ds_{ij} dA \right\}
\]

\[
= V^{-1} \left\{ \int_{\Delta_b} v_n d\sigma, dA \right\}
\]

\[
= V^{-1} \left\{ \int_{\Delta_b} d\phi_{ij} dV + \int_{\Delta_b} d\phi_{ij} dA \right\}
\]

\[
= \frac{\partial \Phi}{\partial \Sigma_{ij}}
\]  

(18)

where \( \Phi \) is the strain-rate potential for the deformation response of the body

\[
\Phi = V^{-1} \left\{ \int_{\Delta_b} \phi_{ij} dV + \int_{\Delta_b} \phi_{ij} dA + \int_{\Delta_b} \phi_{ij} dA \right\}
\]

\[
= \Phi_c + \Phi_b + \Psi \]  

(19)

Since \( \Phi_c, \Phi_b \) and \( \Phi \) are convex the potential \( \Phi \) is also convex, as are the potentials \( \Phi_c, \Phi_b \) and \( \Phi \).

Similarly we can identify \( \sigma^*_\gamma, s^*_\gamma, \sigma^*_\gamma, \gamma^*_\gamma, \gamma^*_\gamma \) with the actual fields \( \sigma_{ij}, s_{ij}, \sigma_{ij}, \gamma_{ij} \) and \( \gamma_{ij} \) for a body subjected to a stress \( \Sigma^*_\gamma = \Sigma_{ij} \) and \( v^*_{\gamma}, v^*_{\gamma} \) with \( \delta_{ij}, \delta_{ij} \) and \( \delta_{ij} \) and obtain the dual macroscopic potential

\[
\Psi = V^{-1} \left\{ \int_{\Delta_b} \psi_{ij} dV + \int_{\Delta_b} \psi_{ij} dA + \int_{\Delta_b} \psi_{ij} dA \right\}
\]

\[
+ \int_J \sigma_{ij} j_{ij} d\Gamma + \int_{\Delta_b} \gamma_{ij} \xi_{ij} dA + \int_{\Delta_b} \gamma_{ij} \xi_{ij} dA
\]

\[
+ \int_J \gamma_n v_n d\theta d\Gamma + \int_{\Delta_b} \gamma_n \frac{v_n}{2} dA
\]

\[
+ \int_{\Delta_b} \gamma_n \Sigma^* \frac{v_n}{2} d\Gamma \right\} = \Psi_c + \Psi_b + \Psi
\]  

(20)

where

\[
\Psi_c = V^{-1} \left\{ \int_{\Delta_b} \psi_{ij} dV + \int_{\Delta_b} \gamma_{ij} \xi_{ij} dA + \int_{\Delta_b} \gamma_{ij} \xi_{ij} dA \right\}
\]
In the above expressions we have included all the diffusional capillarity stress terms within the diffusion potential \( \Psi_s \) and not the interface reaction potential \( \Psi_r \). This provides a suitable structure for the development of the bounding theorems presented below; but it should be remembered that in situations where the interface reaction dominates the material response a sintering potential also exists. We address this problem in the following sections when we present detailed models for the different stages of sintering.

The stress can now be determined from the relationship

\[
\sigma_{ij} = \frac{\partial \Psi}{\partial \varepsilon_{ij}}
\]

with the macroscopic work-rate per unit volume given by

\[
D = \Phi + \Psi.
\]

**BOUNDING THEOREMS**

In this section we develop a number of upper and lower bound theorems for the potentials \( \Phi \) and \( \Psi \) in terms of assumed displacement, flux and stress fields. These bounds can be obtained by employing a set of variational arguments similar to those employed by Needleman and Rice [14] and McMeeking and Kuhn [13]. They can, however, be obtained more directly by making use of the convexity conditions for the microscopic and macroscopic potentials. We follow this route here. The general convexity condition we employ in this section is given in Appendix A.

**Kinematic bounds**

Consider the situation where a body is subjected to a stress \( \Sigma_{ij} \) and the actual stress field and distribution of interface reaction stresses in the body are \( \sigma_{ij} \) and \( \sigma_r \). Further let \( \varepsilon_{ij} \), \( v_a \) and \( j_s \) form an assumed compatible field which produces a macroscopic strain-rate \( \dot{E}_{ij} \).

The deformation of the grains is described in terms of the potential \( \phi_c \). The convexity condition for this potential can be derived from inequality (A5)

\[
\phi_c \geq (\sigma_{ij} - \sigma_{ij}^*) \frac{\partial \phi_c^*}{\partial \varepsilon_{ij}} + \phi_c^* \quad (22)
\]

where the superscripts 1 and 2 identify two arbitrary stress and strain-rate fields. If we identify 1 with the assumed field and 2 with the actual field we obtain, after noting equations (3) and (4)

\[
\phi_c \geq \sigma_{ij} \dot{\varepsilon}_{ij}^c - \psi_c^c \quad (23)
\]

where \( \psi_c^c \) is the value of \( \psi_c \) in (3a) determined from the assumed field \( \dot{\varepsilon}_{ij}^c \).

Similarly the convexity condition for the potentials \( \phi_b \) and \( \phi_i \) yield

\[
\phi_b \geq s_s j_s^b - \psi_b^c \quad (24)
\]

and

\[
\phi_i \geq \sigma_r v_a^i - \psi_i^c \quad (25)
\]

where again \( \psi_b^c \) and \( \psi_i^c \) are the values of \( \psi_b \) and \( \psi_i \) determined from (11) and (9a) using the assumed field.

Integrating equation (23) over the material volume and equations (24) and (25) over the grain-boundary area, combining these integrals and noting equations (15), (19) and (20) we obtain

\[
\Phi \geq \Sigma_{ij} \dot{E}_{ij}^c - \Psi^c \quad (26)
\]

where \( \Psi^c \) is the value of \( \Psi \) given by (20) using the assumed field.

If instead the strain-rate \( \dot{E}_{ij} \) is prescribed and the assumed field is scaled such that \( \dot{E}_{ij}^c = \dot{E}_{ij} \) equation (26) becomes, on noting equation (21)

\[
\Psi \leq \Psi^c. \quad (27)
\]

**Statical bounds**

Now we consider the situation where an arbitrary stress field, \( \sigma_{ij}^* \), which is in equilibrium with a remote stress \( \Sigma_{ij}^* \) and pore surface tension, \( \gamma, \) and distribution of interface reaction stresses, \( \sigma_r^* \), are assumed. If we now identify state 1 of inequality (22) with the actual field and state 2 with the assumed field inequality (22) becomes, after noting equation (3)

\[
\phi_c \leq (\sigma_{ij} - \sigma_{ij}^*) \dot{\varepsilon}_{ij} + \phi_c^*. \quad (28)
\]

Similarly

\[
\phi_b \leq (s_s - s_s^*) j_s + \phi_b^*. \quad (29)
\]

and

\[
\phi_i \leq (\sigma_r - \sigma_r^*) v_a + \phi_i^*. \quad (30)
\]

where, as earlier, \( \phi_c^*, \phi_b^* \) and \( \phi_i^* \) are the values of \( \phi_c, \phi_b \) and \( \phi_i \) determined from (3a), (10a) and (11) using the assumed field.

Integrating equation (28) over the material volume and equations (29) and (30) over the grain-boundary area and noting equations (19), (15) and (16) we find

\[
\Phi \leq (\Sigma_{ij} - \Sigma_{ij}^*) \dot{E}_{ij} + \Phi^* \quad (31)
\]

where \( \Phi^* \) is the value of \( \Phi \) determined from (19) using the assumed field.

If the stress \( \Sigma_{ij} \) applied to the body is specified and \( \Sigma_{ij}^* = \Sigma_{ij} \), eqn (31) becomes

\[
\Phi \leq \Phi^*. \quad (32)
\]
Alternatively, if the strain-rate \( \dot{E}_{ij} \) is specified we find, after noting eqn (21)
\[
\Psi \geq \sum_n \dot{E}_{ij} - \Phi^*.
\]
(33)

The coupled problem

The bounds presented in the last two sub-sections can accept any assumed fields. In practice it is useful to restrict the class of displacement and stress fields as far as possible and to separate the influence of the individual processes. In this section we examine the possibility of separating the effects of power-law creep from grain-boundary diffusion.

If the body only deforms by power-law creep then the macroscopic potential \( \Phi \) of equation (19) is simply \( \Phi_c = \Phi^c \), where the superscript \( c \) signifies creep alone. Let \( \dot{\epsilon}^c_{ij} \) represent the corresponding strain-rate field within the grains for the actual solution in this limit and \( \sigma^c_{ij} \) the corresponding stress field, which is in equilibrium with a remote stress \( \Sigma_{ij} \).

In the other limit we can assume that grain-boundary diffusion is the only mechanism of densification and deformation with the grains remaining rigid. In this limit
\[
\Phi = \Phi_d + \Phi_r = \Phi^d + \Phi^r
\]
with \( \dot{j}^d \) and \( v^d \) representing the flux pattern and velocity field and \( \sigma^d_{ij} \) and \( \sigma^r_{ij} \) representing the boundary stress gradient and interface reaction stress respectively for an applied stress \( \Sigma_{ij} \), where the superscript \( d \) represents diffusion alone.

Now consider the coupled problem with the body subjected to a stress \( \Sigma_{ij} \), for which the actual fields are \( \sigma_{ij}, \epsilon_{ij}, \dot{\epsilon}_{ij}, v_n \) and \( j_s \) and
\[
\Phi = \Phi_c + \Phi_d + \Phi_r.
\]

If we identify state 1 with the field for power-law creep alone and state 2 with the coupled solution inequality (22) becomes
\[
\left( \sigma^c_{ij} - \sigma_{ij} \right) \dot{\epsilon}^c_{ij} - \left( \dot{\epsilon}^c_{ij} \right) - \Phi_c \geq 0.
\]
(34)

Integrating over the material volume \( V_m \) and noting equation (15) we find
\[
\Phi_c \geq \Phi^c.
\]
(35)

Similarly, the convexity condition for the diffusion and interface reaction potentials yield, after integration over the grain-boundary area \( A_b \)
\[
\Phi_b + \Phi_r \geq \Phi^b + \Phi^r.
\]
(36)

Combining equations (35) and (36) we obtain
\[
\Phi = \Phi_c + \Phi_b + \Phi_r \geq \Phi^c + \Phi^b + \Phi^r
\]
(37)
i.e. the potential for the coupled problem is greater than or equal to the sum of the potentials for the individual mechanisms. This means that in, say, a simple uniaxial test the creep-rate is faster than that for the sum of the individual mechanisms. This bound still holds if we replace the exact results for each mechanism by the kinematic bounds of inequality (26). In the following sections we concentrate on applying the kinematic and statical bounds when a simple mechanism operates and employ inequality (37) to examine the coupling between the different mechanisms.

POWER-LAW CREEP ALONE

In this section we examine stages 1 and 2 of sintering when power-law creep is the dominant mechanism. We start by examining some general results for the relationship between the potentials for different values of the creep exponent \( n \). We then present results from the literature for situations were power-law creep is the dominant mechanism. Cocks [9] demonstrates that a convenient way of expressing the constitutive law is in terms of a macroscopic effective stress, \( \Sigma \), (not to be confused with the von Mises effective stress, \( \Sigma^e \)) where
\[
\Phi = \frac{1}{n+1} \dot{\epsilon} \sigma_0 \left( \frac{\Sigma}{\sigma_0} \right)^{n+1}
\]
(38)

and
\[
\Sigma = \left\{ V^{-1} \int_{V_m} \left( \dot{\epsilon}^{n+1} \right) dV \right\}^{\frac{1}{n+1}}.
\]
(38a)

Surfaces of constant \( \Sigma \) in stress space are convex with the strain-rate vector, \( \dot{E}_{ij} \), normal to the surface. In the limit as \( n \rightarrow \infty \) \( \Sigma \) is equivalent to the macroscopic yield surface for the material [9].

Nesting surfaces

In this sub-section we follow Calladine and Drucker [19] and demonstrate that surfaces of constant \( \Sigma \) in stress space for different values of \( n \) nest inside each other, with the surface for \( n = 1 \) forming the outer surface.

Consider two surfaces of constant \( \Sigma = \sigma_0 \) in stress space for two different values of \( n \), \( n_1 \) and \( n_2 \), where \( n_1 < n_2 \). Let \( \sigma_{ij}^1 \) represent the micro-stress field for any point on the surface for \( n = n_1 \) and, similarly, let \( \sigma_{ij}^2 \) represent the stress field for any point on the surface for \( n = n_2 \). Employing the convexity condition of inequality (22) for \( n = n_1 \) identifying states 1 and 2 with the stress field of \( n = n_1 \) and \( n = n_2 \) respectively, integrating over the volume and noting equation (15) we find
\[
\left( \Sigma_{ij}^1 - \Sigma_{ij}^2 \right) \dot{E}_{ij}^1 - \frac{V^{-1}}{n_1 + 1} \sigma_0 \left\{ \int_{V_m} \left( \dot{\epsilon}^1 \right)^{n_1 + 1} dV \right\} \geq 0.
\]
(39)

Now, according to equation (38a)
\[
V^{-1} \int_{V_m} \left( \dot{\epsilon}^1 \right)^{n_1 + 1} dV = \Sigma^{n_1 + 1}
\]
Fig. 4. Surfaces of constant $\bar{\Sigma}$ in stress space for two different values of $n$, $n_1$ and $n_2$, where $n_2 > n_1$. The surface for $n_2$ nests inside that for $n_1$.

and

$$\int_{\Omega_n} (\bar{\sigma})^{n+1} \, dV = \int_{\Omega_n} \left\{ (\bar{\sigma})^{n_1} + 1 \right\}^{(n_2+1)} \, dV$$

where the inequality arises from Hardy, Littlewood and Polya’s “general properties of means” [20] and equation (38a) has been used again to relate the microscopic field $\delta_{ij}^n$ for $n_2$ to the macroscopic stress $\bar{\Sigma}$. Inequality (39) then becomes

$$(\Sigma_{ii}^1 - \Sigma_{ii}^2) \bar{E}_{ii} \geq 0.$$  

This inequality is shown diagrammatically in Fig. 4, and is simply a statement of the fact that all stress states $\Sigma_{ii}^2$ corresponding to the surface of constant $\bar{\Sigma}$ for $n = n_2$ lie inside the corresponding surface for $n = n_1$.

It can similarly be demonstrated that surfaces of constant $\bar{\Sigma}$, where

$$\bar{E}_{ij} = \frac{\partial \bar{\Sigma}_{ij}}{\partial \bar{\Sigma}_{ii} \partial \bar{\Sigma}_{jj}}$$

in strain-rate space nest inside each other with the surface for $n = 1$ again forming the outer surface. In practice it is more straightforward to obtain results for $n = 1$ and $n \to \infty$ than for intermediate values of $n$. If the resulting surfaces of constant $\bar{\Sigma}$ and $\bar{E}$ in stress and strain-rate space are close together then surfaces for all values of $n$ will lie close to each other and these solutions will provide a reasonable approximation for all values of $n$. We consider this point further when examining detailed solutions for stages 1 and 2 of sintering.

Variation of creep exponent with stress

We have assumed so far that the creep exponent $n$ is a material constant. In practice $n$ increases with increasing stress for many materials. We evaluate this type of problem in this sub-section in terms of a strain-rate potential $\phi$ which is the sum of two potentials

$$\phi_c = \phi_1 + \phi_2$$

$$\epsilon_{ij} = \frac{\partial \phi_1}{\partial \sigma_{ij}} + \frac{\partial \phi_2}{\partial \sigma_{ij}}$$  \hspace{1cm} (41)

where $\phi_1$ and $\phi_2$ are potentials with the form of equation (3) with $n = n_1$ and $n_2$, $\epsilon_b = \epsilon_b^1$ and $\epsilon_b^2$ and $\sigma_b = \sigma_b^1$ and $\sigma_b^2$.

Consider a body which is subjected to a stress $\Sigma_{ij}$. Let $\sigma_{ij}$ represent the equilibrium stress field for a body which deforms according to equation (41) and $\sigma_{ij}^1$ and $\sigma_{ij}^2$ the stress fields for $\phi_1$ and $\phi_2$ acting alone. First consider the convexity condition of inequality (22) for $\phi_1$, identifying state 1 with $\sigma_{ij}^1$ and state 2 with $\sigma_{ij}^2$. Integrating over the volume, making use of the virtual power expression of equation (15) and noting that both $\sigma_{ij}$ and $\sigma_{ij}^1$ are in equilibrium with the same remote stress, we find

$$\int_{\Omega_n} \phi_1 (\sigma_{ij}) \, dV \geq \int_{\Omega_n} \phi_2 (\sigma_{ij}^1) \, dV.$$  \hspace{1cm} (42)

Similarly

$$\int_{\Omega_n} \phi_2 (\sigma_{ij}) \, dV \geq \int_{\Omega_n} \phi_2 (\sigma_{ij}^2) \, dV.$$  \hspace{1cm} (43)

Combining these two results we find

$$\Phi_c = V^{-1} \left\{ \int_{\Omega_n} \phi_1 (\sigma_{ij}) \, dV + \int_{\Omega_n} \phi_2 (\sigma_{ij}^1) \, dV \right\}$$

$$\geq V^{-1} \left\{ \int_{\Omega_n} \phi_1 (\sigma_{ij}^2) \, dV + \int_{\Omega_n} \phi_2 (\sigma_{ij}) \, dV \right\}$$

$$= \phi_1 + \phi_2$$  \hspace{1cm} (44)

i.e. the macroscopic potential for the combined microscopic potential of equation (41) is bounded from below by the sum of the macroscopic potentials derived from each microscopic potential. The bounding character of this result is retained if $\phi_1$ and $\phi_2$ are replaced by kinematic bounds for the individual potentials derived from inequality (23). This result can readily be generalised to more than two potentials.

A particularly useful utilization of this result is in the description of the combined effects of time independent plasticity and power-law creep. We noted earlier that the solution for $n \to \infty$ is equivalent to that for a perfectly plastic material. If we let $n_2 \to \infty$ and identify $\sigma_b^1$ with the yield stress for the material and let $n_1$ have a value more typical of a power-law creeping material, in the range 3–9, then the material response in uniaxial tension is as indicated in Fig. 5. If the surfaces of constant $\bar{\Sigma}$ in stress space are the same shape for $n_1$ and $n_2$, Fig. 6(a), then for $\bar{\Sigma}^1 < \bar{\sigma}_0^1$ the response can be bounded purely in terms of $\Phi_c$

$$\bar{E}_{ij} \geq \frac{\partial \Phi_c}{\partial \Sigma_{ij}} = \frac{\partial \Phi_1}{\partial \sigma_{ij}} \frac{\partial \bar{\Sigma}_{ij}}{\partial \Sigma_{ij}}$$  \hspace{1cm} (45)
Fig. 5. Response of a creeping/perfectly plastic material in uniaxial tension.

where \( \Sigma^1 \) and \( \Sigma^2 \) represent the values of \( \Sigma \) for surfaces passing through a particular point in stress space for \( n = n_1 \) and \( n_2 \) respectively. When \( \Sigma^2 = \sigma_0^2 \),

\[
\dot{\epsilon}_{ij} = \lambda \frac{\partial \Sigma^2}{\partial \Sigma_{ij}}
\]

(46)

where

\[
\lambda \geq \dot{\epsilon}_0 \frac{\sigma_1}{\sigma_0^2}
\]

The picture is slightly more complex when the shapes of the surfaces of constant \( \Sigma \) are different for different values of \( n \), Fig. 6(b). As before the strain-rate is given by equation (45) when \( \Sigma^2 < \sigma_0^2 \). But when \( \Sigma^2 = \sigma_0^2 \),

\[
\dot{\epsilon}_{ij} \geq \dot{\epsilon}_0 \frac{\Sigma^1}{\sigma_0^2} \frac{\partial \Sigma^1}{\partial \Sigma_{ij}} + \lambda \frac{\partial \Sigma^2}{\partial \Sigma_{ij}}
\]

(47)

where \( \lambda \geq 0 \). This response is shown diagrammatically in Fig. 6(b).

Stage 1 of sintering

The results generated so far apply for any distribution, size and type of pores within the body. In the remainder of this section we concentrate on situations where the distribution of porosity is such that the macroscopic response is isotropic, allowing the material behavior to be described in terms of a single scalar state variable. We examine the predicted material response within the framework described above.

First we consider stage 1 of sintering, where the porosity is open and discrete necks exist between the particles. Kuhn and McMeeking [8] have used the kinematic bound of inequality (26) to evaluate the power-law creep response of an initial dense random packing of spherical particles for situations where plastic flow is limited to the vicinity of the neck formed between adjoining particles and there is no interaction between the necks. They also assumed that the sintering potential, which arises from consideration of changes in total surface and grain-boundary energy, is negligible. They propose that for the situation where \( \theta = \pi/3 \), the von Mises effective stress, in equation (3), that

\[
\Phi \geq \dot{\epsilon}_0 \sigma_0 \frac{1}{n + 1} \left( \frac{G_1(\rho)}{N} \left( \frac{(\Sigma_{m})^{(n+1)/n}}{(\sigma_0)^{n+1\alpha}} + \left( \frac{2\Sigma_v}{3\sigma_0} \right)^{(n+1)/n} \right) \right)
\]

where

\[
G_1(\rho) = \frac{3\rho^2(\rho - \rho_0)}{(1 - \rho_0)} \frac{16\sqrt{3}}{27\pi} \left( \frac{1 - \rho_0}{\rho - \rho_0} \right)^{1/2} \left[ \left( \frac{\Sigma_{m}}{\sigma_0} \right)^{(n+1)/n} + \left( \frac{2\Sigma_v}{3\sigma_0} \right)^{(n+1)/n} \right]^{n(n+1)}
\]

(48)

where \( \Sigma_{m} \) is the macroscopic value of the von Mises effective stress

\[
\Sigma_{m} = \frac{1}{2} \Sigma_{ik} \delta_{ik}
\]

is the mean stress, \( \rho \) is the relative density of the compact (density/density of fully compacted material) and \( \rho_0 \) is the initial relative density, which is equal to 0.64 for a dense random packing of spheres of uniform size.

Surfaces of constant \( \Sigma \) obtained by assuming that the equality of (48) holds are presented in Fig. 7 for \( \rho = 0.7 \) and \( \rho = 0.75 \). The surfaces nest inside each other in accordance with the general theory on nesting surfaces, Fig. 4, with the surfaces lying closest to each other for the higher value of \( \rho \). If \( \rho \), however,
Fig. 7. Surfaces of $\Sigma = \sigma_0$ in stress space for (a) $\rho = 0.7$ and (b) $\rho = 0.75$ demonstrating the nesting character of these surfaces.

When $\rho < 0.81$ the resulting surfaces of constant $\Sigma$ have different shapes for different values of $n$. When considering the coupling between power-law creep and time independent plasticity eqns (45) and (47) then apply.

We now include the influence of the surface and grain-boundary energy terms on the sintering response. For a given deformation mechanism the scale of the mechanism can be chosen to provide the optimum kinematic bound from (26). Following Cocks [9] we find

$$\Sigma \geq \frac{\dot{E}_c}{V} \left( V^{-1} \int_{V_m} \dot{\epsilon} \right)^{\frac{n}{n+1}}$$

where

$$\dot{E}_c = \int_{A_B} \dot{\epsilon}^c dA$$

the superscript $c$ identifies an arbitrary compatible set and $\dot{\epsilon}_c$ is the von Mises effective strain-rate.

For $\rho > 0.76$ we observe that the surfaces for the different values of $n$ intersect each other at almost the same points with the points of intersection moving away from the $\Sigma_m$ and $\Sigma_s$ axes, Fig. 8(a), until $\rho = 0.81$ when the surfaces completely cross over and the surfaces nest inside each other in the reverse order, Fig. 8(b). A better bound can then be obtained by requiring the surfaces to nest inside the surface for $n = 1$, i.e. for a given stress state when $0.76 < \rho < 0.81$ we select the maximum value from $\Sigma_1$ and $\Sigma_s$, the values of $\Sigma$ obtained from (48) for $n = 1$ and the value of $n$ of interest. While for $\rho > 0.81$ the surface for $n = 1$ provides the most appropriate bound for all $n$. 

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We assume that $\tilde{E}_i \Sigma_i$ only exists when there is a volumetric strain-rate. We then identify $\tilde{E}_i$ with the dilatational strain-rate $E_{ik}$, so that

$$z_p > \frac{E_{ik}}{V-1} \int_{V_m} \epsilon^{(n+1)(n+3)} dV$$

and

$$\Sigma_i = \frac{E_{ik}}{V-1} \left( \gamma_s \int_{A_p} \epsilon_i dA + \gamma_b \int_{A_b} \epsilon_i dA \right).$$

If the mechanism is unaltered as a result of the inclusion of these additional terms then

$$z_p (m_2 - m_1) \left( m_2 - m_1 \right)^{n/(n + 1)}$$

A knowledge of the surface and grain-boundary strains are required in order to determine the value of $\Sigma_i$. Kuhn and McMeeking [8], however, employed an approximate analysis due to Matthews [21] in their formalism, which does not provide the required information. Instead we employ an approximate analysis due to Ashby [3] in order to determine an appropriate expression for the sintering potential. Ashby [3] essentially assumed that the sum of the grain-boundary and surface areas around a given grain remains constant, with the loss of surface area as the material densifies matched by an equivalent increase in grain-boundary area. A given grain boundary is shared between two grains so that the total increase in grain-boundary area is half the decrease in surface area. Ashby [3] only considered the contribution to the sintering potential from the surface energy terms. Modifying his result to take into account the increase in grain-boundary area we find

$$\Sigma_i = \frac{2\gamma_s}{r}$$

where $r$ is the radius of a pore. If the pores are all situated at the corners of tetrakaidecahedron shaped grains then $r$ can be directly related to the relative density and grain size [3] giving

$$\Sigma_i = \frac{2\gamma_s}{L} \left( \frac{1 - \rho}{6 \rho} \right)^{1/3}.$$ 

The inclusion of grain-boundary potential effects slightly modifies this result. The pores are now not spherical but consist of a number of spherical segments [23]. Also as the material dilates under hydrostatic loading there is an accompanying increase of grain-boundary area. Inclusion of these effects gives

$$\Sigma_i = \frac{2\gamma_s}{r} + \frac{2\gamma_b}{R}$$

where now $r$ is the radius of a spherical segment to a pore and $R$ is the mean radius of a grain. Now

$$\Sigma_i = \frac{\gamma_s}{L} \left( \frac{1 - \rho}{6 \rho F_i(\theta)} \right)^{1/3} + 8 \cos \theta$$

where the function $F_i(\theta)$ is given by Raj and Ashby [23].

Surfaces of constant $\Sigma$ are presented in Fig. 9 for $\rho = 0.9$ and 0.99, with $\Sigma_i$ set equal to zero. In each case we observe the nesting character of these surfaces. The surfaces are close together for low values of $\rho$, but spread out in the $\Sigma_m$ plane as $\rho$ increases.

**DIFFUSION ALONE**

In this section we examine stages 1 and 2 of sintering when diffusion mechanisms dominate the material response. We consider the two extreme situations where most of the work done by the applied load either goes to drive the diffusive flux of material through the body or is required to overcome an interface reaction. First, however, we examine the situation when both processes contribute to the material response and obtain a bound for the stress potential in terms of the potentials obtained for these two extreme conditions.
In the limit where diffusion mechanisms dominate equation (20) for the stress potential becomes

$$\Psi = \Psi_b + \Psi_r.$$  \hspace{1cm} (56)

Let $\Psi_b$ and $\Psi_r$ be the values of the potential when grain-boundary diffusion and the interface reaction dominate the material response respectively. Now consider the situation where the body is subjected to a remote strain-rate $\dot{E}_{ij}$. The potential $\psi_b$ is convex and from equation (21) and inequality (A5) we may write

$$(\dot{E}_{ij} - \dot{E}_{ij}^0) \frac{\partial \psi^b}{\partial \dot{E}_{ij}} - (\psi^b - \psi^a) \geq 0$$  \hspace{1cm} (57)

where $\psi^b$ and $\psi^a$ are determined from flux and displacement patterns that are compatible with $\dot{E}_{ij}^0$ and $\dot{E}_{ij}$ respectively. If we now identify both $\dot{E}_{ij}^0$ and $\dot{E}_{ij}$ with the applied strain-rate $\dot{E}_{ij}$ and let state 1 represent the flux and displacement patterns which determine $\psi^b$ and state 2 the fields for the full problem, then inequality (57) becomes

$$\psi_b \geq \psi^b.$$  

Similarly

$$\Psi_r \geq \Psi_r^f.$$  

Combining these results with equation (56) gives

$$\Psi = \Psi_b + \Psi_r \geq \psi^b + \psi^f$$  \hspace{1cm} (58)

i.e. the stress potential for the full problem is bounded from below by the sum of the potentials for the two extreme problems. The exact meaning of this result can be best visualized by considering a component subjected to a uniaxial strain-rate $\dot{E}$. The stress required to give this strain-rate is greater than or equal to the sum of the stresses required to give the same strain-rate for the situations when the interface reaction is negligible and when it dominates the response. We now examine these two extreme situations in turn.

**Grain-boundary diffusion controlled sintering**

McMeeking and Kuhn [13] originally derived the kinematic bound of inequality (26) for situations where grain-boundary diffusion effects dominate. Cocks and Pan [24] have employed both the kinematic and statical bounds to analyse the classical Hull–Rimmer [25] situation, where a planar grain boundary contains a regular array of lenticular shaped voids. They demonstrate that because of the kinematic constraint imposed by this problem there is only one possible flux pattern in the body, while a large number of possible equilibrium stress fields can be proposed. In many practical problems the range of possible velocity fields is limited and simple reasonable velocity and flux patterns can readily be identified, but it is generally difficult to devise appropriate equilibrium stress fields. In the following sections we therefore concentrate on the kinematic bound. We start by presenting the results obtained by McMeeking and Kuhn [13] for stage 1 of sintering. We then consider the bounds in more detail and apply the kinematic bound to determine the response of simple arrangements of grains and pores and obtain appropriate constitutive relationships for stage 2 of sintering.

**Stage 1 of sintering**

McMeeking and Kuhn [13] considered the situation where the material response is isotropic with contacts of uniform size randomly distributed around each particle. They based their bound on the original variational principle of Needleman and Rice [14] which ignores the contribution of the grain-boundary energy terms to the material response. The inclusion of these terms leads to a slight modification of the sintering potential $\Sigma_r$, but otherwise their results remains unaltered. McMeeking and Kuhn [13] show that

$$\phi_b \geq \frac{1}{2} \frac{153\rho}{E^3F_i(\rho)} \left( \Sigma_r^2 + 1.79(\Sigma_m - \Sigma_i)^2 \right)$$  \hspace{1cm} (59)
where
\[
F_i(\rho) = \frac{0.797 \rho (\rho - \rho_0)^2}{(1 - \rho_0)^2}
\]
where, as in our consideration of power-law creep controlled sintering, it has been assumed that \( \Sigma \) is only related to the dilatational part of the strain-rate such that
\[
\Sigma_i \dot{E}_{hk} = V^{-1} \left\{ \int \sigma_k^e m_j j'_i \, d\Gamma + \int \gamma_k v_k^e \sin \theta \, d\Gamma \\
+ \int \gamma_n v_n^e \frac{1}{2} (\kappa_t^k + \kappa_v^k) \, dA \\
+ \int \gamma_k \Sigma_k v_k^e \frac{\sqrt{3}}{2} \, d\Gamma \right\}
\]
(60)
McMeeking and Kuhn [13] argue that this equation produces the same sintering potential for any assumed compatible velocity and flux field. This is only true if it can be guaranteed that when \( \Sigma_m = \Sigma \) there is zero flux of material at each point of the grain boundaries in the exact solution of the problem. This is a valid assumption for the configuration employed by McMeeking and Kuhn [13], but this does not hold in general. For isolated straight contacts the last two terms of equation (60) are zero. Employing the same displacement-rate and flux pattern used by McMeeking and Kuhn [13] with their expression for \( \sigma_e \) gives
\[
\Sigma = \frac{12 \rho \rho_0}{L \rho_0} \left( \frac{\rho}{\rho_0} \right)^{1/2} \left[ 1 + \left( \frac{\rho - \rho_0}{3(1 - \rho_0)} \right)^{1/2} \sin \theta \right] \]
(61)
The second term within the square brackets is in addition to that proposed by McMeeking and Kuhn [13], which arises directly from inclusion of the second term of equation (60) in the variational principle.

**Stage 2 of sintering**

Before examining stage 2 in detail there are a number of observations that we can make about the underlying diffusion equations and the result of equation (59). The governing equations are linear, producing a potential that is quadratic in stress, and allowing the results from a number of different situations to be superposed. The symmetry of the problem analysed in the previous section means that the potential is the sum of an effective stress term, which gives the shear deformation of the body, and a term involving the mean stress, which gives the volumetric strain-rate. In the present section we analyse another symmetric situation, but one which is not isotropic, and assume that the general quadratic form of equation (59) holds. Wilkinson [26] has analysed the material response under a pure hydrostatic stress state. Helle et al. [2] subsequently simplified Wilkinson’s result and proposed a potential of the form
\[
\Phi_b \approx 1080 \frac{\tau}{L^3} \frac{(1 - \rho)^{1/2}}{\rho} (\Sigma_m - \Sigma)^2.
\]
(62)
If the pores are spherical then \( \Sigma \) is given by equation (54). If grain-boundary energy effects are taken into account it is once more given by equation (55).

Here we obtain an expression for the deviatoric part of the potential by analysing the problem shown in Fig. 10, which consists of a regular array of cubic grains with pores at each corner of the grains, and is subjected to the shear loading indicated in the figure. This geometry does not strictly satisfy the requirement that all boundaries intersect at 120° used in the derivation of equation (15). If the overall configuration is initially in equilibrium and the pores do not grow or shrink as the material deforms then the surface and grain-boundary energy terms do not come into play. If we limit the grains to cuboidal shapes then within this limited class of shapes the cube represents the lowest energy state for a given number of grains, and the grain-boundary energy terms do not influence the initial response of the body. The kinematic bound of inequality (26) then becomes
\[
\Phi \geq \Sigma_{ij} \dot{E}_{ij} - \frac{1}{2 \nu} \int \frac{\dot{A}_{ijk}}{A} \dot{\sigma}_{ijk}.
\]
(63)
Following Cocks [9] the magnitude of any proposed mechanism can be chosen so as to minimize the above bound. Doing this gives
\[
\Phi_b \geq 6 \frac{\tau}{L^3} \frac{(1 - \rho)^{1/2}}{\rho} (\Sigma_m - \Sigma)^2.
\]
(64)
and since both the numerator and denominator are quadratic in any parameter chosen to represent the scale of the mechanism, the bound of (63) is independent of the magnitude chosen.

First we analyse the situation where the array does not contain any pores. We consider the mechanism shown in Fig. 10(b), which shows an eighth of one grain. Material is removed uniformly from the two vertical boundaries, and flows along vertical channels to the horizontal boundary. The material then flows along two sets of mutually perpendicular channels parallel to the \( x_1 \) and \( x_2 \) directions indicated in Fig. 10(b), and deposits uniformly on the horizontal boundary. The strain-rate in the \( x_3 \) direction is then twice the rate in each of the transverse directions. Employing this mechanism in the bound of inequality (62) gives
\[
\Phi_b \geq 6 \frac{\tau}{L^3} \frac{(1 - \rho)^{1/2}}{\rho} (\Sigma_m - \Sigma)^2.
\]
(65)
If a series of spherical pores are now introduced at the corners of the grains we obtain
where

\[ F(\rho) = 1 - [5.84 \times (1 - \rho)^{2/3} + 2.80 \times (1 - \rho)^{4/3} - 3.82 \times (1 - \rho)] \]

which is well approximated by

\[ F(\rho) = 1 - 2.5 \times (1 - \rho)^{2/3}. \]  \hspace{1cm} (66)

Du and Cocks [27] employed the structure of equations (62) and (65) with \( F(\rho) \) given by (66) in their mechanistic constitutive laws for alumina. Recently Pan and Cocks [28] have employed the kinematic bound to analyse the response of an array of tetrakaidecahedra shaped grains with pores at each of the apexes as shown in Fig. 11. They show that for a fully dense material

\[ \Phi_\sigma \geq \frac{1}{2} \frac{1153 \sigma_0}{L^3} \Sigma^2 = \frac{1}{2} \frac{E_0}{\sigma_0} \Sigma \left( \frac{\Sigma}{\sigma_0} \right)^2 \]

where \( L \) is taken as the distance between two opposite square faces of a grain. This result is a factor of 12 greater than that for the cubic grains. The reason for this is that for the situation shown in Fig. 11 the body deforms by material diffusing from the vertical square faces to the horizontal square face, with the resulting deformation accommodated by free sliding along the angled hexagonal boundaries. A given increment of axial strain requires a smaller flux of material than for the cubic grain, with grain-boundary sliding making a significant contribution to the overall deformation, which is completely absent with the cubic grains.

By proposing suitable flux and velocity fields Pan and Cocks [28] demonstrate that

\[ \Phi_\sigma \geq \frac{1}{2} E_0 \sigma_0 \left\{ \left[ \Sigma_x / \sigma_0 \right]^2 + \left[ \left( \Sigma_y - \Sigma_z \right) / \sigma_0 \right]^2 \right\} \left( F_2(\rho) / F_3(\rho) \right) \]  \hspace{1cm} (67)

where \( F_2(\rho) \) and \( F_3(\rho) \) are plotted in Fig. 12. \( F_3(\rho) \) is well approximated by an expression of the form proposed by Helle et al. [2]

\[ F_3(\rho) = \frac{0.088 \rho}{\sqrt{1 - \rho}} \]  \hspace{1cm} (67a)

while \( F_2(\rho) \) is well approximated by

\[ F_2(\rho) = \left[ 1 + 39.6 \times (1 - \rho) \right]^{-1} \]  \hspace{1cm} (67b)

over the range \( 0.9 < \rho \leq 1.0 \). These expressions are plotted directly on Fig. 12 where they can be compared with the fuller expressions proposed by Pan and Cocks [28].

**Interface reaction controlled sintering**

In this section we examine the limit where the interface reaction dominates the material response. In the definition of the stress potentials following equation (20) we included all the terms that contribute to the sintering potential either into the power-law creep contribution or the diffusive flux contribution. This was somewhat arbitrary, but it allowed a simple bound on the combined diffusional potential to be developed, inequality (58). We therefore omit consideration of the sintering potential in
this section and reintroduce it when considering the full potential in a later section. In the interface reaction limit the kinematic bound of (26) becomes

\[ \Phi_r \geq \sum_i \frac{E_i}{V - 1} \frac{m + 1}{m + 1} \sigma_0 \int_{A_0} \left( \frac{A}{V_0} \right)^{m+1} dA \]

(68)

where all the interface reaction terms are defined after equation (9).

Following Cocks [9] the magnitude of any proposed mechanism can be chosen so as to optimise the lower bound. Inequality (68) then becomes

\[ \Phi_r \geq \frac{1}{m + 1} \frac{V_0}{V - 1} \left( \frac{\sigma}{\sigma_0} \right)^{m+1} \int_{A_0} \left( \frac{A}{V_0} \right)^{m+1} dA \]

(69)

We employ this form of the lower bound expression when developing constitutive relationships for stages 1 and 2 of sintering in this limit. In most practical situations the interface reaction exponent \( m \) is equal to 2. We therefore limit our attention to this value of \( m \) in all subsequent analyses.

**Stage 1 of sintering**

A constitutive model is developed in Appendix B for an aggregate of monosize spherical particles using the same axisymmetric remote loading and velocity fields as in the studies of Fleck et al. [6], McMeeking and Kuhn [13] and Kuhn and McMeeking [8]. It is possible to obtain analytical expressions for the potentials under pure hydrostatic and pure shear loading conditions, but numerical procedures are required for more complex loading situations. A surface of constant \( \Phi_r \), normalised such that \( \Sigma_e = 1 \) in the pure shear limit, is plotted in Fig. 13. The numerical results are well approximated by

\[ \Phi_r \approx \frac{5.49}{3} \frac{\sigma_0}{H_1(\rho)^2} \left[ \left( \frac{4 \Sigma_e}{5 \sigma_0} \right)^{3/2} + \left( \frac{\Sigma_m}{\sigma_0} \right)^{3/2} \right] \]

(70)

where

\[ H_1(\rho) = 1.35 \left[ \rho^{2/3}(\rho - \rho_0) \left( \frac{\rho}{(1 - \rho_0)^{1/2}} \right) \right] \]

which agrees with the analytical result in the two limits. It is instructive to compare this result with that proposed by Kuhn and McMeeking [8] for stage 1 sintering by power-law creep, inequality (51)

\[ \Phi_r \geq \frac{\rho_0^2}{16} \frac{1}{\rho} \left( \frac{1 - \rho_0}{\rho} \right)^{3/2} \]

(71)

The procedures adopted in Appendix B are similar to those adopted by Kuhn and McMeeking [8] for power-law creep; each requires the solution of a local contact problem and summing the contributions of each contact to form the global macroscopic potential. In the interface reaction limit the relative velocity of two grains either side of a boundary is only a function of the mean contact pressure, whilst when power-law creep dominates the material response it is also a function of the contact area, which can be expressed in terms of the relative density of the material. This difference accounts for the different functional dependence of the potential on the relative density in the above two expressions. The subsequent integration schemes used in the two models, to sum over all possible contacts, are exactly the same and this should produce the same functional dependence of the potential on \( \Sigma_e \) and \( \Sigma_m \), and indeed the computed shape of the potential curves are the same.
Kuhn and McMeeking [8] chose to give more emphasis to stress states close to the hydrostatic limit in their fitting procedure, while here we have given equal emphasis to all possible stress states. Kuhn and McMeeking's expression, therefore better reflects the shape of the curve for small deviations from the hydrostatic limit, but the potential of (70) provides a more accurate description of the overall shape of the curve.

**Stage 2 of sintering**

When considering the diffusion limit we evaluated a material model that consisted of an array of cubic grains, Fig. 10, with the principal stresses acting normal to the faces of the grains. Adopting the same model in this limit gives a strain-rate potential that is a function of the three principal stresses, with the strain-rate normal to a given grain-boundary only a function of the principal stress acting in that direction. This structure arises from the simple kinematic nature of this model: under a uniaxial stress state material flowing from the boundaries normal to the direction of loading and into the pores forms an appropriate kinematic field. This is perhaps an oversimplified and inappropriate model. A more suitable geometric description is provided by the array of tetrakaidecahedra shaped grains shown in Fig. 11; now, the deformation resulting from the removal of material from a given boundary must be accomodated by a combination of sliding and diffusional rearrangement of material on less favourably oriented grain boundaries. Pan and Cocks [29] have analysed this situation in detail, employing the kinematic bound of (71), and propose that

\[
\psi_a = \frac{1}{2} \dot{E}_0^2 \sigma_0 F_i(\rho) \left( \frac{E_i}{E_0} \right)^2 + \frac{1}{2} \dot{E}_0^2 \sigma_0 \left( \frac{H_5(\rho)}{E_0} \right)^2 + \Sigma_i \dot{E}_{ik} \tag{75}
\]

where

\[
\dot{E}_0 = 5.49 \frac{v_0}{L} \tag{74}
\]

is the uniaxial strain rate of a fully dense material at a uniaxial stress \( \sigma_0 \),

\[
H_5(\rho) = 1 - 1.85 \times (1 - \rho)^{2/3}
\]

and

\[
H_5(\rho) = 1.13 - 0.78 \times (1 - \rho)^{2/3}
\]

**Coupling effect of diffusion and an interface reaction**

Inequality (58) provides a means of evaluating the interaction between diffusion and an interface reaction. This requires evaluation of the dual potentials to those considered so far in this section. We could do this by employing the equivalent kinematic bounds to those employed above and defined in (27). But we adopt a different more direct procedure here which provides a consistent set of constitutive relationships. We assume that the potentials described above provide an accurate description of the material response and use equation (22) to determine the associated dual potentials. Similarly, we do not utilize the bounding character of (58), but use this relationship to obtain an appropriate structure for the constitutive relationships when energy is dissipated due to the diffusive flux of material and as a result of the interface reactions, i.e. we assume that the stress potential is the sum of the stress potentials for the two independent processes. Cocks and Pan [30] demonstrate that this result is exact if the kinematic fields are the same in the two limits. As before we examine stages 1 and 2 of sintering in turn.

**Stage 1 of sintering**

The dual potential in the diffusion limit is obtained by combining (59) and (22). After noting the definition of the uniaxial strain rate for a fully dense material in (66) we obtain

\[
\psi_d = \frac{1}{2} \dot{E}_0^2 \sigma_0 F_i(\rho) \left( \frac{E_i}{E_0} \right)^2 + \frac{1}{2} \dot{E}_0^2 \sigma_0 \left( \frac{H_5(\rho)}{E_0} \right)^2 + \Sigma_i \dot{E}_{ik} \tag{75}
\]

Similarly, the potential in the interface reaction limit can be obtained from (71) and (22), with the uniaxial reference strain-rate given by (74)

\[
\psi_r = \frac{2}{3} \dot{E}_0^2 \sigma_0 H_i(\rho) \left[ \frac{5}{4} \frac{E_i}{E_0} \right] + \left[ \frac{E_i}{E_0} \right]^{3/2} \tag{76}
\]

The material response can then be determined from

\[
\psi = \psi_d + \psi_r, \tag{77}
\]

The strain-rate potential \( \Phi \) for the coupled problem can be obtained from equations (77) and (22). This is not a trivial task, however, and in general numerical schemes are required to perform this inversion. Du and Cocks [31] and Pan and Cocks [29] have described how this can be achieved using a Newton–Raphson procedure.

**Stage 2 of sintering**

Stage 2 can be analysed in exactly the same way as stage 1 above. The stress potential in the diffusion limit obtained from (67) and (22) is

\[
\psi_d = \frac{1}{2} \dot{E}_0^2 \sigma_0 \left( \frac{E_i}{E_0} \right)^2 + F_i(\rho) \left( \frac{E_i}{E_0} \right) + \Sigma_i \dot{E}_{ik} \tag{78}
\]

and that in the interface reaction limit obtained from (73) and (22) is

\[
\psi_r = \frac{2}{3} \dot{E}_0^2 \sigma_0 H_i(\rho) \left[ \frac{5}{4} \frac{E_i}{E_0} \right] + \left[ \frac{E_i}{E_0} \right]^{3/2} \tag{79}
\]

The full potential is once more given by equation (77).

When developing the bounding procedures which led to the above results we arbitrarily collected all the
Table 1. Strain-rate potentials for the three mechanisms examined in this paper. $\dot{\varepsilon}_0$, $E^*_0$ and $E^*_h$ are the uniaxial strain-rates for the fully dense material for each mechanism.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Power-law creep</th>
<th>Grain boundary diffusion</th>
<th>Interface reaction controlled</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\dot{\varepsilon}_0$</td>
<td>$i G_1(\rho) = \frac{\rho (\rho - \rho_s)}{1 - \rho_s} \left[ 16 \left( \frac{3(1 - \rho_s)}{27 \pi} \right)^{5/3} \right]^{1/3}$</td>
<td>$i F_1(\rho) = \frac{0.797 \rho (\rho - \rho_s)^2}{(1 - \rho_s)^2}$</td>
<td>$i H_1(\rho) = 1.35 \left( \frac{\rho (\rho - \rho_s)}{1 - \rho_s} \right)^{1/3}$</td>
</tr>
<tr>
<td>$E^*_0$</td>
<td>$\left( \frac{4 \Sigma_n - \Sigma_m}{\Sigma_m} \right)^{3/2} + \left( \frac{\Sigma_n - \Sigma_m}{\Sigma_m} \right)^{1/2}$</td>
<td>$\left[ \left( \frac{\Sigma_n - \Sigma_m}{\Sigma_m} \right)^{1/2} + \left( \frac{\Sigma_n - \Sigma_m}{\Sigma_m} \right)^{1/2} \right]^{3/2}$</td>
<td>$\left[ \left( \frac{\Sigma_n - \Sigma_m}{\Sigma_m} \right)^{1/2} + \left( \frac{\Sigma_n - \Sigma_m}{\Sigma_m} \right)^{1/2} \right]^{3/2}$</td>
</tr>
<tr>
<td>$E^*_h$</td>
<td>$\frac{1}{\sqrt{2}} \left[ \frac{\rho_s}{\rho} \right]^{1/3} \left[ 1 + \frac{(\rho - \rho_s)}{3(1 - \rho_s)} \right]^{3/2} \sin \theta$</td>
<td>$\frac{1}{\sqrt{2}} \left[ \frac{\rho_s}{\rho} \right]^{1/3} \left[ 1 + \frac{(\rho - \rho_s)}{3(1 - \rho_s)} \right]^{3/2} \sin \theta$</td>
<td>$\frac{1}{\sqrt{2}} \left[ \frac{\rho_s}{\rho} \right]^{1/3} \left[ 1 + \frac{(\rho - \rho_s)}{3(1 - \rho_s)} \right]^{3/2} \sin \theta$</td>
</tr>
</tbody>
</table>

The sintering potential terms are added to the equations of motion, giving an expression for $\Phi$, that is independent of $\Sigma_n$. We note from the above equations that in the interface reaction limit, i.e. when $E^*_h < E^*_0$, the stress potential $\Psi$, and thus the strain-rate potential $\dot{\varepsilon}$, is a function of $\Sigma_n$. Inversion of (77) using (22) gives the same expressions for $\phi$, as given in (71) and (73), but with $\Sigma_m$ replaced by $\Sigma_m - \Sigma_n$, where $\Sigma_n$ is given by (61) in stage 1 and (55) in stage 2.

**SUMMARY**

In this paper we have examined the general structure of constitutive laws for the sintering of fine grained materials. For each of the mechanisms of deformation considered here it has been demonstrated that two potential functions exist: a strain-rate potential $\dot{\varepsilon}$, which is a function of the applied stress and the structure of the material; and a dual potential, $\Psi$, which is a function of strain-rate and material structure. Kinematic and statical bounds have been developed for these potentials, which provide a systematic method of developing constitutive laws for the sintering process. In the present paper we concentrated on use of the kinematic bound and adopted microstructural configurations of grains and pores that allowed a single state variable (the relative density $\rho$) to be used to describe the structure of the material.

Three mechanisms of deformation have been analysed in detail: power-law creep; grain-boundary diffusion; and interface controlled diffusion. The strain-rate potentials for each of these mechanisms are given in Table 1 and the corresponding dual potentials are given in Table 2. When grain-boundary diffusion and the interface reaction contribute to the material response the coupled response can be added together to give the coupled response and when power-law creep and one of the

Table 2. Stress potentials for the three mechanisms examined in this paper. The quantities $F_1(\rho)$, $G_1(\rho)$, $H_1(\rho)$ and $\Sigma_n$ are defined in Table 1.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Power-law creep</th>
<th>Grain boundary diffusion</th>
<th>Interface reaction controlled</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_1(\rho)$</td>
<td>$\frac{\rho (\rho - \rho_s)}{1 - \rho_s} \left[ 16 \left( \frac{3(1 - \rho_s)}{27 \pi} \right)^{5/3} \right]^{1/3}$</td>
<td>$\frac{0.797 \rho (\rho - \rho_s)^2}{(1 - \rho_s)^2}$</td>
<td>$1.35 \left( \frac{\rho (\rho - \rho_s)}{1 - \rho_s} \right)^{1/3}$</td>
</tr>
<tr>
<td>$G_1(\rho)$</td>
<td>$\left( \frac{4 \Sigma_n - \Sigma_m}{\Sigma_m} \right)^{3/2} + \left( \frac{\Sigma_n - \Sigma_m}{\Sigma_m} \right)^{1/2}$</td>
<td>$\left[ \left( \frac{\Sigma_n - \Sigma_m}{\Sigma_m} \right)^{1/2} + \left( \frac{\Sigma_n - \Sigma_m}{\Sigma_m} \right)^{1/2} \right]^{3/2}$</td>
<td>$\left[ \left( \frac{\Sigma_n - \Sigma_m}{\Sigma_m} \right)^{1/2} + \left( \frac{\Sigma_n - \Sigma_m}{\Sigma_m} \right)^{1/2} \right]^{3/2}$</td>
</tr>
<tr>
<td>$H_1(\rho)$</td>
<td>$\frac{1}{\sqrt{2}} \left[ \frac{\rho_s}{\rho} \right]^{1/3} \left[ 1 + \frac{(\rho - \rho_s)}{3(1 - \rho_s)} \right]^{3/2} \sin \theta$</td>
<td>$\frac{1}{\sqrt{2}} \left[ \frac{\rho_s}{\rho} \right]^{1/3} \left[ 1 + \frac{(\rho - \rho_s)}{3(1 - \rho_s)} \right]^{3/2} \sin \theta$</td>
<td>$\frac{1}{\sqrt{2}} \left[ \frac{\rho_s}{\rho} \right]^{1/3} \left[ 1 + \frac{(\rho - \rho_s)}{3(1 - \rho_s)} \right]^{3/2} \sin \theta$</td>
</tr>
</tbody>
</table>
diffusion mechanisms operate the strain-rate potentials can be added to give the material response. When all three mechanisms operate, the dual potentials for the two diffusion mechanisms must first be added, and the combined potential inverted to provide the strain-rate potential for diffusion. This is then added to the strain-rate potential for power-law creep to provide the full material constitutive law.

In Tables 1 and 2 we have identified two stages of sintering: stage 1, when the porosity is open and distinct necks exist between the particles; and stage 2, when the porosity is closed. In practice the transition from stage 1 to stage 2 does not occur at a single value of the relative density but occurs gradually over a range of densities. The simplest way to describe the response in this transition region is to take appropriate proportions of the potentials for stages 1 and 2 and add them. Depending on how one views the physical significance of this averaging process either the strain-rate or its dual potential can be used. Since constitutive laws are more commonly expressed in terms of the strain-rate potential we describe the strain-rate potential in this transition region in the same way as Fleck et al. [6]

\[ \Phi = [(\rho_1 - \rho)\Phi_1 + (\rho - \rho_1)\Phi_2]/(\rho_2 - \rho_1) \]  

(80)

where \( \Phi_1 \) and \( \Phi_2 \) are the strain-rate potentials for stages 1 and 2 respectively, \( \rho_1 \) is the relative density at the start of the transition period, which we take as 0.75, and \( \rho_2 \) is the value at the end of the transition, which is typically 0.95.

The models developed here can be thought of as first generation models, i.e. they represent an initial attempt to develop micromechanical constitutive laws for the sintering process. There are a number of deficiencies in these models that need addressing. The stage 1 models ignore any interactions between the necks. This effect is likely to be most important when plasticity and power-law creep mechanisms dominate. The nesting surface analysis of the power-law creep section suggests that interaction between deformation zones occurs early in the densification process; at relative densities at the order of 0.75. The choice of \( \rho_1 = 0.75 \) in equation (80) provides one method of taking into account, at least approximately, the effect of neck/neck interactions. In the single state variable models considered here it has been assumed that the structure remains isotropic throughout the deformation process. This assumption is likely to be appropriate for the stage 2 diffusion models, but not in the other situations considered here; an anisotropic distribution of neck sizes will develop under non-hydrostatic stress states during stage 1 and pores will become elliptical during stage 2 for the plasticity mechanisms. Also, the expressions for the sintering potential presented here are first order approximations. They do not fully consider the changing shape of the pores as they shrink. A full evaluation requires consideration of the influence of surface diffusion on the pore profile.

In the models presented above for the diffusion mechanisms the rate of deformation is very sensitive to the grain size (it is proportional to \( L^{-3} \) when grain-boundary diffusion dominates and \( L^{-1} \) when an interface reaction is controlling). In material systems where these mechanisms are controlling, principally ceramic materials, densification of the compact is invariably accompanied by significant grain growth. Consideration of this effect is beyond the scope of this paper. Appropriate models for grain growth have been described by Du and Cocks [27] who have also evaluated its influence on the sintering process [31, 32].

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APPENDIX A

Convex Potentials

Limit load theorems for perfectly plastic structures follow directly from the normality and convexity conditions for the yield surface. These conditions are shown diagrammatically in Fig. A1(a). For the yield condition of equation (1) the convexity requirement states that a vector joining a stress state \( \sigma_0 \), which lies on or inside the yield surface, with \( \sigma_0 \) on the yield surface makes an acute angle with the outward normal to the yield surface at this location, i.e.

\[
(a_i^1 - a_i^2) \frac{\partial f}{\partial a_i} + (\Omega^1 - \Omega^2) \frac{\partial f}{\partial \Omega} > 0 \quad (A1)
\]

where the superscripts 1 and 2 refer to quantities evaluated at states 1 and 2 respectively.

![Yield surface in stress space.](image)

**Fig. A1.** (a) Yield surface in stress space. (b) Surface of constant \( \Omega \) in \( a_i \) space. (c) Surface in \( \Omega, a_i \) space containing all states determined from equation (A2).

A similar graphical interpretation can be given for the convexity condition of any convex function. Consider the convex function

\[
\Omega = g(a_i) \quad (A2)
\]

which is a function of \( n \) arguments \( a_i = a_1, \ldots, a_n \). The outward normal to a surface of constant \( \Omega \) in \( a_i \) space is in the direction

\[
\frac{\partial \Omega}{\partial a_i} = \frac{\partial g}{\partial a_i} \quad (A3)
\]

Fig. A1(b). All possible states lie on the surface

\[
f = g(a_i) - \Omega = 0 \quad (A4)
\]

in \( a_i, \Omega \) space, Fig. A1(c). By employing the same arguments that led to the convexity statement of equation (A1) it can be shown that the surface of equation (A4) is convex if

\[
(a_i^1 - a_i^2) \frac{\partial f_i}{\partial a_i} + (\Omega^1 - \Omega^2) \frac{\partial f_i}{\partial \Omega} > 0
\]

i.e. if

\[
(a_i^1 - a_i^2) \frac{\partial \Omega}{\partial a_i} - (\Omega^1 - \Omega^2) > 0. \quad (A5)
\]

The convexity condition of inequality (A5) forms the basis of the bounds developed in the main text.

APPENDIX B

Interface Reaction Controlled Stage 1 Sintering

In this section we follow the procedures described by Fleck et al. [6], Kuhn and McMeeking [8] and McMeeking and Kuhn [13] to determine a lower bound to the strain rate potential for stage I sintering when an interface reaction dominates the material response. The analysis presented here is based on the bound of inequality (69). We consider a random array of monosize spherical particles which is macroscopically isotropic. Fig. B1. The initial density of the compact is \( \rho_i \), which we take as 0.64. The volume of the body associated with a given particle is

\[
V = \frac{4\pi R_0^3}{3\rho} \quad (B1)
\]

where \( R_0 \) is the initial radius of a particle.

![Irregular array of spherical grains subjected to an axisymmetric macroscopic stress state.](image)

**Fig. B1.** An irregular array of spherical grains subjected to an axisymmetric macroscopic stress state.
Fig. B2. Two contacting particles of radius $R_0$, with the normal $n$ to the contact patch making an angle $\theta$ with the $z$-axis.

Following Helle et al. [2] the above authors assumed that the average area of a contact is

$$A = \frac{\pi}{3} \left( \rho - \rho_0 \right) R_0^2.$$  \hfill (B2)

Consider a circular contact patch on a grain of area $A$ whose outward normal $n$ points towards the centre of the contacting grain. Let $v$ represent the relative velocity of the centre of this second grain with respect to the first grain. The rate of separation of the grains $v_n$ is then given by

$$v_n = v n.$$  \hfill (B3)

The contribution of this boundary to the denominator of (69) is

$$A^{-1} \int_A \sigma^{(m+1/n)} \, dA = \frac{3}{2} |v_n|^{1/2}$$  \hfill (B4)

for $m = 2$.

We consider the simple velocity field which is related to the assumed macroscopic strain-rate $\dot{E}_{ij}$ according to the relationship

$$v_n = 2 R_0 \dot{E}_{ij} n_j.$$  \hfill (B5)

We further restrict our attention to the situation where the body is subjected to the axisymmetric macroscopic stress state shown in Fig. B1 and assume an axisymmetric strain-rate which we can represent in terms of the effective and volumetric components $\dot{E}_t$ and $\dot{E}_{kk}$. If $\theta$ is the angle that the outward normal $n$ makes with the $z$-axis, Fig. B2, equations (B3) and (B5) give

$$v_n^* = \left( \frac{\rho_0}{\rho} \right)^{1/2} R_0 [\dot{E}_t (3 \cos^2 \theta - 1) + 2 \dot{E}_{kk} / 3].$$  \hfill (B6)

Combining equations (B2), (B4) and (B6) and averaging over all possible orientations of the contacts gives

$$V^{-1} \int_{4\pi} \sigma^{(m+1/n)} \, dA = \frac{3 \rho^2 (\rho - \rho_0) \left( \frac{\rho_0}{\rho} \right)^{1/2} R_0^{1/2}}{2(1-\rho_0)} \times \int_0^1 \left[ \dot{E}_t (3 y^2 - 1) + 2 \dot{E}_{kk} / 3 \right]^{1/2} \, dy.$$  \hfill (B7)

Equation (B7) can be substituted into (69) to provide a bound on the strain-rate potential $\Phi$. The value of $\dot{E}_t / \dot{E}_{kk}$ can be chosen so as to optimize the bound. In general this optimization must be performed numerically, but analytical solutions can be obtained under pure hydrostatic and pure shear loading conditions. When $\Sigma_m = 0$, $\dot{E}_{kk} = 0$ and (69) becomes

$$\Phi_1 \geq \frac{1}{3} \frac{5.49 \rho_0 \sigma_0}{L} \left( \frac{4 \Sigma_m}{5 \sigma_0} \right)^3.$$  \hfill (B8)

where $H_t (\rho)$ is given following (70). Similarly, when $\Sigma_m = 0$, $\dot{E}_t = 0$, and (69) becomes

$$\Phi_1 \geq \frac{1}{3} \frac{5.49 \rho_0 \sigma_0}{L} \left( \frac{\Sigma_m}{\sigma_0} \right)^3.$$  \hfill (B9)

The full optimized solution to (69) is given as a surface of constant $\Phi$ in Fig. 13 and a suitable fit to this curve is provided by (70) which reduces to (B8) and (B9) in the appropriate limits.