MONTANA
STATE UNIVERSITY

A continuum approach to sintering kinetics

by Carl Ricklef Reid

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Engineering Mechanics
Montana State University
© Copyright by Carl Ricklef Reid (1984)

Abstract:
Sintering is the process by which an initially unconnected collection of particles form bonds at their points of contact resulting in a single, solid framework. As this process proceeds, the relative density increases from that of the initial loose particle stack to a density which may approach that of the solid material. The material rearrangement which is necessary for densification is driven by a surplus of energy associated with the excess of free surface area in the material and also by the particular arrangement of this free surface.

A continuum theory for granular (or porous) materials is proposed to describe the kinetics of sintering. The stresses which promote densification of the material are quantified in terms of two microstructural parameters associated with a granular material: the specific surface area and the mean curvature of the void-solid interface.

' The theory was applied to two materials which can be sintered: copper and snow. In the case of copper, the microstructural data were available and the stresses induced in the material as it sintered could be evaluated. In the case of snow, the microstructural data were not available so only an estimate of the stresses induced in snow as it sinters was found.

The application of the theory to copper gave very good results. This indicates that the proposed theory is an accurate representation of the processes that occur in a material as it sinters. The result of applying the theory to snow indicates that the stresses produced by sintering are of comparable magnitude to other stresses found in a natural snowpack.

A CONTINUUM APPROACH TO SINTERING KINETICS

by

Carl Ricklef Reid

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Master of Science

in

Engineering Mechanics

MONTANA STATE UNIVERSITY
Bozeman, Montana

April 1984

MAIN LIB
N378
R2715
cop 2

APPROVAL

of a thesis submitted by

Carl Ricklef Reid

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citation, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

April 3, 1984
Date

Robert G. Oakberg
Chairperson, Graduate Committee

Approved for the Major Department

April 3, 1984
Date

Fred F [illegible]
Head, Major Department

Approved for the College of Graduate Studies

April 20, 1984
Date

Henry L Parsons
Graduate Dean

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a master's degree at Montana State University, I agree that the Library shall make it available to borrowers under rules of the Library. Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of source is made.

Permission for extensive quotation from or reproduction of this thesis may be granted by my major professor, or in his absence, by the Dean of Libraries when, in the opinion of either, the proposed use of the material is for scholarly purposes. Any copying or use of the material in this thesis for financial gain shall not be allowed without my permission.

Signature Carl R. Reid

Date April 4, 1984

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. R. G. Oakberg for his guidance and constructive input during the preparation of this thesis. The author also wishes to thank Dr. R. L. Brown and Dr. J. R. Lund for their help.

The author would like to thank Mrs. Jean Julian for her expert typing. A special thanks is extended to the author's wife, Judy, for her encouragement and perseverance.

The financial support of the Engineering Experiment Station at Montana State University and the National Science Foundation EPSCoR grant No. ISP-8011449 was also appreciated.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figures Page

ABSTRACT

Sintering is the process by which an initially unconnected collection of particles form bonds at their points of contact resulting in a single, solid framework. As this process proceeds, the relative density increases from that of the initial loose particle stack to a density which may approach that of the solid material. The material rearrangement which is necessary for densification is driven by a surplus of energy associated with the excess of free surface area in the material and also by the particular arrangement of this free surface.

A continuum theory for granular (or porous) materials is proposed to describe the kinetics of sintering. The stresses which promote densification of the material are quantified in terms of two microstructural parameters associated with a granular material: the specific surface area and the mean curvature of the void-solid interface.

The theory was applied to two materials which can be sintered: copper and snow. In the case of copper, the microstructural data were available and the stresses induced in the material as it sintered could be evaluated. In the case of snow, the microstructural data were not available so only an estimate of the stresses induced in snow as it sinters was found.

The application of the theory to copper gave very good results. This indicates that the proposed theory is an accurate representation of the processes that occur in a material as it sinters. The result of applying the theory to snow indicates that the stresses produced by sintering are of comparable magnitude to other stresses found in a natural snowpack.

CHAPTER 1

INTRODUCTION

Sintering is the process by which a collection of loose particles, under the proper conditions, form permanent bonds at their points of contact. The result of this process is a single, solid framework. This adherence between particles is driven by an excess of energy in the system due to the abundance of free surface. Since molecules on the surface of a material are at a higher energy than those in the interior, it is thermodynamically more stable if material rearrangement reduces the amount of free surface. Rearrangement occurs more readily at temperatures near to, but still below, the melting point of the given material. Materials in which sintering occurs include metals, ceramics, and snow.

Previous Investigations

There are numerous articles in the powder metallurgy and snow literature concerning sintering. Although much debate exists on particular aspects of sintering, two general statements can be made regarding this process. The first, as indicated in the previous paragraph, is that the primary driving force for sintering is the excess of surface energy [1]. The second is that only certain mechanisms of material transport can provide densification of the material [2].

In reference to the problem of material transport, there are four main processes to be considered: viscous or plastic flow, volume diffusion, surface diffusion, and evaporation-condensation. Many articles have appeared in an effort to resolve this problem (e.g., [3, 4, 5]). Kuczynski [3] used the simplified geometry of a sphere being brought into contact with a flat plate in order to decide which mechanism was responsible for material transport.

On the basis of his results, he inferred that material was transported by volume diffusion. Hobbs and Mason [4] sintered two spheres of ice together and deduced that the main mechanism of material transport was that of evaporation-condensation. These results indicate that the same mechanism may not be responsible for material transport in all cases and also that several mechanisms may be operative in any single case.

No matter what the primary mechanism of material transport is, densification of a collection of particles can only be accomplished by those mechanisms which are not related to surface phenomena. The following argument (as given in [2]) supports this statement. Consider a branched network composed of points at the centers of each particle connected by lines through the contacts between particles. Surface diffusion and evaporation-condensation can change the contours surrounding this network but they cannot change the network itself. Viscous or plastic flow and volume diffusion can change this network by lengthening or shortening the branches between points. Densification of the material is accomplished by shortening the branches. Therefore, only volume related phenomena can promote densification of a mass of particles.

As pointed out by Exner, Petzow, and Wellner [6], results such as those obtained by Kuczynski [3] and Hobbs and Mason [4] are not easily applied to large collections of particles. The main reason for this difficulty is the highly complex geometry that exists in real systems. An example of an attempt to describe the densification of a large collection of particles is that done by Kuczynski [7]. However, his approach was of a phenomenological nature and did not describe the nature of the forces which promote densification.

Purpose

The purpose of this study is to describe the kinetics of sintering of large collections of particles in terms of the forces which drive this process and the response of the material to these forces. It is not intended that the question be resolved as to what mechanism of material transport is responsible for densification nor is it necessary to know this fact in order to develop this theory.

In developing a theory to describe the sintering kinetics of a large collection of particles, two things must be considered. The first is that the material must be described in a rational manner and the second is that the forces which promote densification of the material must be characterized.

Two possible approaches can be taken to describe a collection of particles. One would be to maintain the discrete nature of the particles and describe the material in terms of the characteristics of each particle and the relationships between particles. A second way to describe the material is to assign continuous functions of position to the properties of the material and define the material in terms of these functions. In doing so, the concept of discrete particles is lost and it is assumed that the material can be subdivided indefinitely without losing any of its defining properties. It is the latter approach which is used here. The theory which is used to characterize the material is Goodman's [8] continuum theory of granular (or porous) materials. Slight modifications of the original theory are used to include the effects necessary to describe the sintering phenomena.

The forces which promote densification of a material as it sinters are also considered in this study. Since densification implies material rearrangement, it follows that some stress must be applied to the material. This stress is related to the excess surface energy and the related concept of surface tension. Expressions are developed which relate the stress in the material to the thermodynamics of the free surface in the material and the specific microstructural arrangement of this surface.

The theory proposed in this study is applied to two materials: copper and snow. In the case of copper, all the necessary data on the microstructure are available which allows a quantitative evaluation of the stress in the material. In the case of snow, the microstructural

data are not known but an estimation of the stress due to sintering is found. The results and possible implications of this theory are discussed.

CHAPTER 2

THEORETICAL CONSIDERATIONS

In this chapter, a continuum theory for granular materials is developed. Continuity is imposed upon the system of discrete particles and the equations governing the dynamics of this system are postulated. Some general constitutive assumptions are made and restrictions upon constitutive forms are derived by considering the second law of thermodynamics. The discussion in this chapter follows that of Goodman [8] and Goodman and Cowin [9].

The Distributed Body

The purpose of this section is to develop a generalized concept of continuity which will make the problem of dealing with a granular material amenable to the procedures used in continuum mechanics. In light of this, it can be noted that a granular material such as snow, sand, or a sintered compact has the distinguishing property that most of the mass is contained in discrete (although connected) particles surrounded by a void. This is the feature which separates granular materials from those materials which are classically considered as solids or fluids. Therefore, a complete description of a granular material must in some way describe the relationship that exists between the solid matrix material and the void. Furthermore, in order to develop a continuum approach, some notion of continuity must be imposed on an otherwise discrete system.

To begin with, the idea of a *distributed body* will be introduced. First, heuristic motivation will be presented and then a more precise mathematical definition will be developed.

Consider, for instance, a block of snow. The majority of mass in the system is due to the ice phase. If the mass of the material in the voids is neglected, the total mass of the system is related directly to the amount of ice contained in the system. Consequently, if the volume of ice in the system is reduced, then so is the mass of the system. Symbolically, the above can be expressed as follows by letting

B_t be the body of snow at time t,

$\mathrm{M}_t(\mathrm{B}_t)$ = mass of snow,

$\mathrm{V}_t(\mathrm{B}_t)$ = total volume of snow,

$\mathit{V}_t(\mathrm{B}_t)$ = volume of ice phase only.

Intuitively, if the total volume of snow is reduced to zero, then the mass should also reduce to zero:

$$\mathrm{V}_t(\mathrm{B}_t) \rightarrow 0 \Rightarrow \mathrm{M}_t(\mathrm{B}_t) \rightarrow 0 \tag{1}$$

Similarly, if the mass in the voids is neglected, then when the volume of ice is reduced to zero, then so is the mass:

$$\mathit{V}_t(\mathrm{B}_t) \rightarrow 0 \Rightarrow \mathrm{M}_t(\mathrm{B}_t) \rightarrow 0 \tag{2}$$

Also, it is obvious that the volume of the ice in the system can be no greater than the total volume of the system:

$$\mathit{V}_t(\mathrm{B}_t) \leqslant \mathrm{V}_t(\mathrm{B}_t) \tag{3}$$

These conditions are also valid for any part, P_t, of B_t.

The preceding expressions form the basis for a more precise mathematical definition of a distributed body. From Goodman and Cowin [9], the definition is:

> A distributed body is a one parameter family B_t, $-\infty < t < \infty$, of regions of Euclidean three space such that
> (a) for any t and t′, the region B_t is homeomorphic to the region $\mathrm{B}_{t'}$, and
> (b) for each t, the region B_t is endowed with a structure given by two real valued set functions M_t and V_t subject to the following axioms:
> (b1) M_t and V_t are non-negative measures defined for all Borel subsets $\mathrm{P}_t \subset \mathrm{B}_t$,
> (b2) $\mathit{V}_t(\mathrm{P}_t) \leqslant \mathrm{V}_t(\mathrm{P}_t)$, for all $\mathrm{P}_t \subset \mathrm{B}_t$,
> (b3) M_t is absolutely continuous with respect to V_t.

In the above, B_t is the *configuration* of the distributed body at time t, M_t is the *distributed mass* of the body at time t, and V_t is the *distributed volume* of the body at time t.

The above definition of a distributed body conforms to the intuitive description of a granular material. Axiom (a), in simple terms, merely states that the distinct configurations of a granular body can be obtained by a continuous, one-to-one deformation. This allows such continuum concepts as the deformation gradient to be defined. Axiom (b1) is obvious since mass and volume are always considered to be nonnegative quantities. Axiom (b2) is a restatement of Equation (3) and also implies that $\mathcal{V}_t \ll V_t$ (read, $\mathcal{V}_t$ is absolutely continuous with respect to V_t) where V_t is a Lebesque volume measure.* Axiom (b3) is the precise statement of the idea expressed in Equation (2). Further, since absolute continuity is transitive, and since $M_t \ll \mathcal{V}_t$ and $\mathcal{V}_t \ll V_t$, it is true that $M_t \ll V_t$ which is equivalent to the idea expressed in Equation (1).

Axiom (b3) supplies the central concept necessary to formulate a continuum theory of granular materials. Since $\mathcal{V}_t$ has the property of being continuous (in this generalized context), M_t must also be continuous by this axiom. Hence, the mass has become a continuous property of the material and the discrete nature of the material has been lost. This necessarily rules out the possibility of point, line, or surface concentrations of mass. Also, any mass in the voids must be disregarded by this axiom.**

Since Axiom (b2) implies that $\mathcal{V}_t \ll V_t$, the Radon-Nikodym representation theorem of measure theory [10] implies that there exists a (unique) real valued Lebesque integrable function $\nu(\underline{x}, t)$ defined on B_t such that for any part $P_t \subset B_t$,

---

*If when some measure (V_t) defined on a set B_t goes to zero implies another measure ($\mathcal{V}_t$) also defined on B_t goes to zero for all subsets, P_t, of B_t, then $\mathcal{V}_t$ is said to be absolutely continuous with respect to V_t.

**This implies that the solid constituent is the determining factor for all material properties. If this is not the case (as in a multi-phase sinter body), then a different theory (possibly a mixture theory [11]) would have to be developed.

$$V_t(\mathrm{P}_t) = \int_{\mathrm{P}_t} \nu(\underline{x}, t)\, d\mathrm{V}_t \qquad (4)$$

$\nu(\underline{x}, t)$ is called the *volume distribution function.* The arguments denote that it is a function of position and time. By Axiom (b2), it has the obvious property that

$$0 \leqslant \nu(\underline{x}, t) \leqslant 1 \qquad (5)$$

Similarly, it follows from Axiom (b3) that there exists another function, $\gamma(\underline{x}, t)$, such that

$$\mathrm{M}_t(\mathrm{P}_t) = \int_{\mathrm{P}_t} \gamma(\underline{x}, t)\, dV_t \qquad (6)$$

$\gamma(\underline{x}, t)$ is called the *distributed mass density*. Finally, since $\mathrm{M}_t \ll \mathrm{V}_t$, it also follows that

$$\mathrm{M}_t(\mathrm{P}_t) = \int_{\mathrm{P}_t} f(\underline{x}, t)\, d\mathrm{V}_t \qquad (7)$$

Differentiation of Equation (4) yields $dV_t = \nu(\underline{x}, t)\, d\mathrm{V}_t$, so Equation (6) implies that

$$\mathrm{M}_t(\mathrm{P}_t) = \int_{\mathrm{P}_t} \gamma(\underline{x}, t)\, \nu(\underline{x}, t)\, d\mathrm{V}_t \qquad (8)$$

and hence $f(\underline{x}, t) = \gamma(\underline{x}, t)\, \nu(\underline{x}, t)$. Comparison of Equations (7) and (8) with the classical continuum expression for mass shows that $f(\underline{x}, t) = \rho(\underline{x}, t) = \gamma(\underline{x}, t)\ \nu(\underline{x}, t)$ = bulk density. In this case, $\gamma(\underline{x}, t)$ corresponds to the mass density of the particles themselves and $\nu(\underline{x}, t)$ corresponds to the particle volume distribution. Hence, the mass of a granular material is uncoupled from that of the individual particles allowing the mass density of the system to change either through a change in the density of the matrix material or through a change in the distribution of the matrix material.

Kinematics

In the previous section, a generalized concept of continuity was developed which enables the use of the usual procedures of continuum mechanics to describe the kinematics of granular materials. As a result of this, a new independent kinematic field variable has been introduced; namely the volume distribution function. In this section, some of the usual kinematic relations will be developed and also a useful relation specific to the volume distribution function will be derived.

Let the motion of a granular material be described relative to some reference configuration defined at some time t_o. The position of a given material point at any time t is given by the mapping

$$\underline{x} = \underline{\chi}_{t_o}(\underline{X}, t) \tag{9}$$

In the above, $\underline{x}$ is the position of the particle at time t which occupied the position $\underline{X}$ at time t_o. The subscript on the mapping function $\underline{\chi}$ merely indicates the reference configuration is taken at time t_o. It is assumed that this mapping is (at least) twice differentiable with respect to time. Also, by Axiom (a), The Distributed Body, this mapping is spatially continuous.

Using Equation (9), some of the traditional kinematic quantities can now be written down. Denoting the velocity of a material point by $\underline{v}$,

$$\underline{v}(\underline{x}, t) = \frac{\partial}{\partial t} \underline{\chi}_{t_o}(\underline{X}, t) \tag{10}$$

Similarly, the acceleration, $\underline{a}$, is

$$\underline{a}(\underline{x}, t) = \frac{\partial^2}{\partial t^2} \underline{\chi}_{t_o}(\underline{X}, t) \tag{11}$$

The deformation gradient, $\underset{\sim}{F}$, is

$$\underset{\sim}{F}(\underline{x}, t) = (\underline{\chi}_{t_o}(\underline{X}, t)\overleftarrow{\underline{\nabla}}_x)^* \tag{12}$$

and the velocity gradient, $\underset{\sim}{L}$, at the spatial point $\underline{x}$ is

$$\underset{\sim}{L}(\underline{x}, t) = (\underline{v}(\underline{\chi}^{-1}_{t_o}(\underline{x}, t), t)\overleftarrow{\underline{\nabla}}) \tag{13}$$

---

*The gradient operator with a subscript X denotes differentiation with respect to the material coordinates $\underline{X}$. If the subscript is not present, it denotes differentiation with respect to the spatial coordinates $\underline{x}$. The direction arrow over the gradient operator denotes the order of the operation, e.g., in Cartesian index notation,

$$(\underline{v}\overleftarrow{\underline{\nabla}})_{ij} = \frac{\partial v_i}{\partial x_j} \quad \text{and} \quad (\overrightarrow{\underline{\nabla}}\underline{v})_{ij} = \frac{\partial v_j}{\partial x_i}\ .$$

where $\underline{\chi}_{t_o}^{-1}$ is the inverse mapping of Equation (9). The rate of deformation tensor, $\underset{\sim}{D}$, and the spin tensor, $\underset{\sim}{W}$, are the symmetric and antisymmetric parts of the velocity gradient, respectively:

$$\underset{\sim}{D} = \frac{1}{2}\,(\underset{\sim}{L} + \underset{\sim}{L}^{T}) \tag{14}$$

$$\underset{\sim}{W} = \frac{1}{2}\,(\underset{\sim}{L} - \underset{\sim}{L}^{T}) \tag{15}$$

Now a kinematic constraint on the volume distribution function will be derived. As a starting point, the following familiar result will be used:

$$d\mathrm{V}_t = J\,d\mathrm{V}_{t_o} \tag{16}$$

where $J = |\det \underset{\sim}{F}|$ and the subscript t_o refers to the reference configuration.

Differentiation of Equation (4) yields, for any time t,

$$dV_t = \nu\,d\mathrm{V}_t \tag{17}$$

and in the reference configuration,

$$dV_{t_o} = \nu_o\,d\mathrm{V}_{t_o} \tag{18}$$

Combining Equations (16-18) produces

$$dV_t = \frac{\nu}{\nu_o}\,J\,dV_{t_o} \tag{19}$$

For the purpose of the paper, it will be assumed that the solid constituent is incompressible. To express this concept, it can be noted that for this case, the distributed volume is invariant with respect to time. Hence, $\dot{\overline{dV_t}} = 0$ or $\dot{\nu}J + \nu\dot{J} = 0$. It is known from mechanics that $J = \rho_o/\rho$, so the following can be easily arrived at by using the continuity equation:

$$\dot{J} = J\,(\vec{\underline{\nabla}}\cdot\,\underline{v}) \tag{20}$$

Therefore, the following equation defines the notion of incompressible granules:

$$\dot{\nu} + \nu(\vec{\underline{\nabla}}\cdot\,\underline{v}) = 0 \tag{21}$$

Although the above appears similar to the continuity equation, it is not an expression of any conservation principle. It is merely the kinematic constraint imposed on the deformation if the idea of incompressible granules is assumed. Through this equation, the motion and the volume distribution function become coupled.

Balance Equations

During any thermo-mechanical process involving granular materials (or any other material), certain conservation principles are postulated to be satisfied. These include, for instance, mass conservation and energy conservation (first law of thermodynamics). Additionally, the direction of any process is further restricted by the second law of thermodynamics. It is the purpose of this section to enunciate these conservation principles and to express the second law of thermodynamics in the form of the Clasius-Duhem inequality.

In order to accomplish the above objectives, the necessary thermal and mechanical field variables will be introduced as primitive quantities. The familiar ones which require no discussion are: the (Cauchy) stress tensor, $\underset{\sim}{t}$; the body force, $\underline{b}$; the specific internal energy, ϵ; the heat flux vector, $\underline{q}$; the heat supply, r; the specific entropy, η ; and the temperature, θ. In addition to these, the following quantities are introduced which are specific to this theory: the equilibrated inertia, k; the equilibrated stress vector, $\underline{h}$; the extrinsic equilibrated body force, l; and the intrinsic equilibrated body force, g.

The first three balance equations are familiar ones from continuum mechanics. Therefore, they will not be derived. They are (in local form)

$$\dot{\overline{\gamma\nu}} + \gamma\nu(\underline{\vec{\nabla}} \cdot \underline{v}) = 0 \qquad (22)$$

$$\gamma\nu\underline{a} = \underline{\vec{\nabla}} \cdot \underset{\sim}{t} + \gamma\nu\underline{b} \qquad (23)$$

$$\underset{\sim}{t} = \underset{\sim}{t}^{T} \qquad (24)$$

Equation (22) is the principle of conservation of mass (continuity equation). This form is obtained by substituting $\gamma\nu$ for ρ in the usual continuity equation. Equations (23) and (24) are the principles of conservation of linear and angular momentum, respectively.

The following additional balance equations for granular materials are now postulated (in global form):

Balance of Energy

$$\frac{d}{dt}\int_{P_t}\gamma\nu\left(\epsilon+\frac{1}{2}\,\underline{v}\cdot\underline{v}+\frac{1}{2}\,k\,\dot{\nu}^2\right)dV=\int_{\partial P_t}\left[\underline{t}_n\cdot\underline{v}+(\underline{h}\dot{\nu})\cdot\underline{n}-\underline{q}\cdot\underline{n}\right]ds$$

$$+\int_{P_t}\gamma\nu(\underline{b}\cdot\underline{v}+l\dot{\nu}+r)\,dV \qquad (25)$$

Balance of Equilibrated Force

$$\frac{d}{dt}\int_{P_t}\gamma\nu k\dot{\nu}\,dV=\int_{\partial P_t}(\underline{h}\cdot\underline{n})\,ds+\int_{P_t}\gamma\nu(l+g)\,dV \qquad (26)$$

Entropy Inequality

$$\frac{d}{dt}\int_{P_t}\gamma\nu\eta\,dV\geqslant-\int_{\partial P_t}\frac{\underline{q}}{\theta}\cdot\underline{n}\,ds+\int_{P_t}\gamma\nu\,\frac{r}{\theta}\,dV \qquad (27)$$

In the above, $\underline{t}_n$ is the stress vector which is related to the stress tensor by $\underline{t}_n = \underline{n}\cdot\underset{\sim}{t} = \underset{\sim}{t}\cdot\underline{n}$ (since $\underset{\sim}{t}$ is symmetric) and $\underline{n}$ is the unit normal to a given surface.

Equations (25-27) are common to most articles concerning this particular theory of granular materials [9,12,13]. The entropy mequality varies slightly from that given by Goodman and Cowin [9] in that what they call the entropy flux, $\underline{\phi}$, is written here in the more conventional form, $\underline{q}/\theta$. No difficulty arises from this, however, since these authors show that for the linear case, $\underline{\phi} = \underline{q}/\theta$. They also include a relation called the *balance of equilibrated inertia* which leads to $\dot{k} = 0$. This is probably an invalid expression as will be discussed shortly.

At this point, the rationale for the introduction of the equilibrated terms is somewhat obscure. In order to justify their inclusion into the balance equations, the equations will be discussed in more detail.

Consider first the balance of energy equation (25). Except for the equilibrated terms, it is identical to the classic energy equation. The additional terms arise due to the introduction of the kinematically independent volume distribution function. Hence, there are now three independent energy absorbing or storing aspects of the model: the motion $\underline{\chi}_{t_o}$, the temperature θ, and the volume distribution function ν. The approach usually taken in continuum mechanics only involves considering the motion and the temperature.

As is apparent in Equation (25), each of these independent variables is accounted for in each term of the equation. The temperature presents itself in the first term through the internal energy, in the second term through the heat flux vector, and in the third term through the heat supply. Similarly, the motion supplies kinetic energy in the first term, produces power via the surface tractions in the second term, and also produces power in the third term by acting in concert with the body forces. In light of this, the power derived from the time derivative of the volume distribution function must also be incorporated into each term. The obvious way to do this is to include it by using a parallel construct with the other terms under each of the integral signs. The factors k, $\underline{h}$, and l are included to make these terms dimensionally homogenous with the rest of the terms. In the first integral, the $1/2\ k\dot{\nu}^2$ is similar to the kinetic energy and the equilibrated inertia, k, imparts an inertial character to this term. In the second integral which deals with the surface of the volume in question, $\dot{\nu}$ must somehow have the character of a flux which is why its coefficient is the equilibrated stress vector, $\underline{h}$. The last integral deals with volumetric considerations; therefore, a term such as the extrinsic equilibrated body force, l, is included.

It might be noted that the intrinsic equilibrated body force, g, is conspicuously missing from the energy equation. This is not surprising, however, if a closer look is taken at the first law of thermodynamics. According to Langhaar [14], the first law can be symbolically stated as

$$W_e + Q = \Delta T + \Delta U \tag{28}$$

W_e is the work performed by external source, Q is the heat supply, ΔT is the change in kinetic energy, and ΔU is the change in internal energy. According to this, only external sources can supply work. Therefore, l (the extrinsic equilibrated body force) appears, but g (the intrinsic equilibrated body force) does not.

At this point, it may be instructive to elaborate on why the adjective equilibrated is applied to these new terms. In Goodman's original work [8], the equilibrated stress vector, $\underline{h}$, was a derived rather than a postulated quantity (k, g, and l did not appear in that work).* Goodman showed that $\underline{h}$ was equivalent to terms found in higher order stress theories (for instance, see Mindlin [15]). These higher order theories allow for double forces, which may or may not produce a couple, to act at a point. If these forces do produce a couple, then a couple stress theory is arrived at and the symmetry of the stress tensor is broken. However, Goodman showed that the equilibrated stress vector corresponds to those terms in the higher order theory which do not produce a couple at a point. In other words, it is related to a force pair which results in either a center of compression or a center of dilitation. Hence, it represents a quantity which is self-equilibrating. Also, Goodman states that most experimental evidence concerning granular materials indicates that the stress tensor is symmetric. Therefore, there is no reason to expect that these new terms are anything other than self-equilibrating quantities.

The origin of Equation (26) is motivated by a variational analysis done by Goodman [8]. The underlying concept behind this equation is very similar to the expressions of the conservation of linear and angular momentum. As such, Equation (26) could be considered

---

*It turns out that $\underline{h}$ is the same quantity in Goodman's work [8] and in the present work; see Equation (43).

as the mathematical statement of the following idea: The time rate of change of the generalized momentum due to the volume distribution function is equal to the action of the related (equilibrated) forces. The equilibrated stress vector is similar to a surface traction and l and g are the body forces related to the volume distribution. To compliment the extrinsic equilibrated body force, l, the intrinsic equilibrated body force, g, is included here.

Equation (27), the entropy inequality, is not modified in this theory. This is because it is a temperature related phenomena and therefore does not include the volume distribution function (except to quantify the amount of mass present).

Up to this point, the equilibrated terms have been included merely as abstract quantities. In order to make this theory applicable to real situations, some physical significance must be attached to these terms. To this end, Nunziato and Cowin [12] are referenced. In their article, they compare this theory of granular materials as applied to an elastic material with voids to another theory developed by Knowles and Jakub [16]. In doing so, they show that the equilibrated inertia is related to the geometrical features of the voids. This is the reason for not including Goodman and Cowin's [9] balance of equilibrated inertia as discussed earlier in this section. Also, they draw the conclusion that the intrinsic equilibrated body force depends upon the geometry of the voids, the stress state in the solid matrix, and the material properties of the matrix. The extrinsic equilibrated body force becomes an externally controllable pore pressure. Finally, the equilibrated stress vector represents the resultant force in the matrix acting upon the void due to the interaction of neighboring voids. This implies that $\underline{h}$ can only be important if the void distribution is non-uniform (see Equation (51)). These ideas will be exploited in Chapter 2.

It is now expedient to put Equations (25-27) in local form. To begin with, consider Equation (26). In dealing with the first integral, it is noted that the indicated volume integral is time dependent. Hence, in order to take the time derivative of the volume integral, the Reynold's Transport Theorem must be used:

$$\frac{d}{dt}\int_{P_t}\gamma\nu k\dot{\nu}\,dV = \int_{P_t}\gamma\nu\,\dot{\overline{(k\nu)}}\,dV \tag{29}$$

To transform the surface integral in Equation (26) into a volume integral, Gauss' Theorem is used:

$$\int_{\partial P_t}(\underline{h}\cdot\underline{n})\,ds = \int_{P_t}(\underline{h}\cdot\underline{\overleftarrow{\nabla}})\,dV \tag{30}$$

Substituting Equations (29) and (30) into Equation (26) and combining terms in a single integral results in (noting that the volume is arbitrary)

$$\gamma\nu\,\dot{\overline{(k\dot{\nu})}} - \underline{h}\cdot\underline{\overleftarrow{\nabla}} - \gamma\nu(l+g) = 0 \tag{31}$$

This is the local form of Equation (26).

Now consider the energy equation (25). Using a process similar to the above, the following expression is found:

$$\begin{aligned}&\frac{d}{dt}\int_{P_t}\gamma\nu\left(\epsilon + \frac{1}{2}\,\underline{v}\cdot\underline{v} + \frac{1}{2}\,k\dot{\nu}^2\right)dV = \\ &\qquad\int_{P_t}\gamma\nu\left[\dot{\epsilon} + \underline{v}\cdot\underline{a} + \frac{1}{2}\,(\dot{k}\dot{\nu}^2 + 2k\dot{\nu}\ddot{\nu})\right]dV\end{aligned} \tag{32}$$

The surface integral is transformed as follows:

$$\begin{aligned}&\int_{\partial P_t}[\underline{t}_n\cdot\underline{v} + (\underline{h}\dot{\nu})\cdot\underline{n} - \underline{q}\cdot\underline{n}]\,ds = \int_{\partial P_t}[(\underline{v}\cdot\underset{\sim}{t})\cdot\underline{n} + (\underline{h}\dot{\nu})\cdot\underline{n} - \underline{q}\cdot\underline{n}]\,ds = \\ &\qquad\int_{P_t}[(\underset{\sim}{t}\cdot\underline{v}) + \underline{h}\dot{\nu} - \underline{q}]\cdot\underline{\overleftarrow{\nabla}}\,dV\end{aligned} \tag{33}$$

Combining terms results in

$$\begin{aligned}&\gamma\nu\left[\dot{\epsilon} + \underline{v}\cdot\underline{a} + \frac{1}{2}\,(\dot{k}\dot{\nu}^2 + 2k\dot{\nu}\ddot{\nu})\right] - (\underset{\sim}{t}\cdot\underline{v})\cdot\underline{\overleftarrow{\nabla}} \\ &\qquad - (\underline{h}\dot{\nu})\cdot\underline{\overleftarrow{\nabla}} + \underline{q}\cdot\underline{\overleftarrow{\nabla}} - \gamma\nu(\underline{b}\cdot\underline{v} + l\dot{\nu} + r) = 0\end{aligned} \tag{34}$$

Using Equations (23), (24), and (32) and noting that

$$(\underset{\sim}{t}\cdot\underline{v})\cdot\overleftarrow{\underline{\nabla}} = (\underline{v}\cdot\underset{\sim}{t})\cdot\overleftarrow{\underline{\nabla}} = \underline{v}\cdot(\underset{\sim}{t}\cdot\overleftarrow{\underline{\nabla}}) + \underset{\sim}{t}:(\underline{v}\,\overleftarrow{\underline{\nabla}})$$

$$= \underline{v}\cdot(\overrightarrow{\underline{\nabla}}\cdot\underset{\sim}{t}) + \underset{\sim}{t}:\underset{\sim}{L} \qquad (35)$$

yields

$$\gamma\nu\dot{\epsilon} - \underset{\sim}{t}:\underset{\sim}{L} - \underline{h}\cdot(\overrightarrow{\underline{\nabla}}\,\dot{\nu}) + \overrightarrow{\underline{\nabla}}\cdot\underline{q} + \gamma\nu\dot{\nu}(g - \frac{1}{2}\,\dot{k}\,\dot{\nu}) - \gamma\nu r = 0 \qquad (36)$$

This is the local form of the energy equation.

The entropy inequality, Equation (27), simply reduces to

$$\gamma\nu\dot{\eta} + \overrightarrow{\underline{\nabla}}\cdot(\underline{q}/\theta) - \gamma\nu r/\theta \geqslant 0 \qquad (37)$$

After solving for r in Equation (36) and introducing the free energy, $\psi = \epsilon - \eta\theta$, the entropy inequality becomes

$$-\gamma\nu(\dot{\psi} + \eta\dot{\theta}) + \underset{\sim}{t}:\underset{\sim}{L} + \underline{h}\cdot(\overrightarrow{\underline{\nabla}}\,\dot{\nu}) - \gamma\nu\dot{\nu}(g - \frac{1}{2}\,\dot{k}\dot{\nu}) - \frac{1}{\theta}\,\underline{q}\cdot(\overrightarrow{\underline{\nabla}}\,\theta) \geqslant 0 \qquad (38)$$

This is the form of the entropy inequality which will be used to develop restrictions on the constitutive equations and which will also be used to define equilibrium.

General Constitutive Assumptions

The equations of the previous section are applicable to any granular material. The explicit forms of the conservation principles are given in Equations (22), (23), (24), (31), and (36). A further restriction given by the second law of thermodynamics is given in Equation (38). In order to predict the actual thermo-mechanical response of a given material, however, constitutive equations for the assumed variables must be postulated. It is the purpose of this section to enumerate these constitutive assumptions and also to deduce some restrictions imposed by the entropy inequality on the functional forms that the constitutive equations may take. In doing so, the general case of compressible granules will be considered first and then a modified version will be given which will account for the case of incompressible granules.

To begin with, some assumptions will be made with regard to constitutive equations. Generally, the stress at a point is a function of the history of the motion in a neighborhood of the point. This will be accounted for by assuming that the materials to be dealt with behave as viscoelastic materials. Also, it will be assumed that the stress at a point is determined by the motion in an arbitrarily small neighborhood of the point. As a result of this, the independent variables and, at most, their first time and spatial derivatives will be considered in the constitutive equations. Finally, the principle of equipresence will be assumed. This means that an independent variable assumed to be present in one constitutive equation of the material must be assumed to be present in all constitutive equations of the material unless its presence contradicts some fundamental principle such as material objectivity or the entropy inequality.

In view of the above, the independent variables will be considered to be the following group:

$$\gamma, \nu_o, \nu, \dot{\nu}, \underline{\vec{\nabla}}\, \nu, \theta, \underline{\vec{\nabla}}\, \theta, \underset{\sim}{E}, \dot{\underset{\sim}{E}}, \underline{a}, \dot{\underline{a}}, \underline{\vec{\nabla}}\, \underline{a} \tag{39}$$

$\underset{\sim}{E}$ is the Lagrangian strain tensor. $\underline{a}$ is what will be called the *internal state vector* (similar to but not exactly the same as the internal state vector described in [17,18]). It should be noted that it is not a vector in the sense of the velocity or temperature gradient; it is a listing of some set of scalars ($\lambda_1, \lambda_2, \ldots, \lambda_n$), which are considered to be pertinent in describing the internal state of the material. Some examples of these scalars which might be relevant to granular materials are the average curvature of the system, the average number of bonds per grain in the system, the average size of the particles in the system, or any other quantity which is deemed important to the analysis. It therefore follows that $\underline{\vec{\nabla}}\, \underline{a}$ is not a tensor but is a list of the gradients of the internal state variables. Hence, all the quantities in Equation (39) are objective variables.

The constitutive equations can now be written in the following form:

$$\xi = \hat{\xi}(\gamma, \nu_o, \nu, \dot{\nu}, \underline{\vec{\nabla}}\, \nu, \theta, \underline{\vec{\nabla}}\, \theta, \underset{\sim}{E}, \dot{\underset{\sim}{E}}, \underline{a}, \dot{\underline{a}}, \underline{\vec{\nabla}}\, \underline{a}) \tag{40}$$

ξ is a scalar, vector, or tensor valued function of the indicated parameters and denotes any of the primitive variables listed in the beginning of the section entitled Balance Equations.

Assuming the free energy has the above form, the time derivative becomes

$$\dot{\psi} = \frac{\partial\psi}{\partial\gamma}\,\dot{\gamma} + \frac{\partial\psi}{\partial\nu}\,\dot{\nu} + \frac{\partial\psi}{\partial\dot{\nu}}\,\ddot{\nu} + \frac{\partial\psi}{\partial\underline{\vec{\nabla}}\nu}\cdot\dot{\overline{(\underline{\vec{\nabla}}\nu)}}$$

$$+ \frac{\partial\psi}{\partial\theta}\,\dot{\theta} + \frac{\partial\psi}{\partial\underline{\vec{\nabla}}\theta}\cdot\dot{\overline{(\underline{\vec{\nabla}}\theta)}} + \frac{\partial\psi}{\partial\underset{\sim}{E}} : \dot{\underset{\sim}{E}} + \frac{\partial\psi}{\partial\dot{\underset{\sim}{E}}} : \ddot{\underset{\sim}{E}}$$

$$+ \frac{\partial\psi}{\partial\underline{a}}\cdot\dot{\underline{a}} + \frac{\partial\psi}{\partial\dot{\underline{a}}}\cdot\ddot{\underline{a}} + \frac{\partial\psi}{\partial\underline{\vec{\nabla}}\underline{a}}\cdot\dot{\overline{\underline{\vec{\nabla}}\underline{a}}} \tag{41}$$

Substituting this into the entropy inequality, Equation (38), and making use of the continuity equation as well as the identity $\dot{\overline{\underline{\vec{\nabla}}f}} = \underline{\vec{\nabla}}\dot{f} - \underline{\vec{\nabla}}f\cdot\underset{\sim}{L}$ (where f denotes a scalar, vector, or tensor valued quantity) results in the following:

$$-\gamma\nu\left(\frac{\partial\psi}{\partial\theta} + \dot{\eta}\right) - \gamma\nu\dot{\nu}\left(g - \frac{1}{2}\,\dot{k}\dot{\nu} + \frac{\partial\psi}{\partial\nu} - \frac{\gamma}{\nu}\frac{\partial\psi}{\partial\gamma}\right)$$

$$-\gamma\nu\left(\frac{\partial\psi}{\partial\underline{\vec{\nabla}}\nu} - \frac{1}{\gamma\nu}\,\underline{h}\right)\cdot(\underline{\vec{\nabla}}\dot{\nu}) - \gamma\nu\ddot{\nu}\,\frac{\partial\psi}{\partial\dot{\nu}} - \gamma\nu\,\frac{\partial\psi}{\partial\underline{\vec{\nabla}}\theta}\cdot\dot{\overline{(\underline{\vec{\nabla}}\theta)}}$$

$$-\gamma\nu\,\frac{\partial\psi}{\partial\underline{a}}\cdot\dot{\underline{a}} - \gamma\nu\,\frac{\partial\psi}{\partial\dot{\underline{a}}}\cdot\ddot{\underline{a}} - \gamma\nu\,\frac{\partial\psi}{\partial\underline{\vec{\nabla}}\underline{a}}\cdot\underline{\vec{\nabla}}\dot{\underline{a}} - \gamma\nu\,\frac{\partial\psi}{\partial\underset{\sim}{E}} : \dot{\underset{\sim}{E}}$$

$$-\gamma\nu\,\frac{\partial\psi}{\partial\dot{\underset{\sim}{E}}} : \ddot{\underset{\sim}{E}} + \Big[\underset{\sim}{t} + \gamma^2\nu\,\frac{\partial\psi}{\partial\gamma}\,\underset{\sim}{1} + \gamma\nu\left(\frac{\partial\psi}{\partial\underline{\vec{\nabla}}\nu}\;\underline{\vec{\nabla}}\nu\right)$$

$$+ \gamma\nu\left(\frac{\partial\psi}{\partial\underline{\vec{\nabla}}\underline{a}}\;\underline{\vec{\nabla}}\,\underline{a}\right)\Big] : \underset{\sim}{L} - \frac{1}{\theta}\,\underline{q}\cdot\underline{\vec{\nabla}}\theta \geqslant 0 \tag{42}$$

The quantities $\dot{\theta}$, $\underline{\vec{\nabla}}\dot{\nu}$, $\ddot{\nu}$, $\dot{\overline{\underline{\vec{\nabla}}\theta}}$, $\ddot{\underline{a}}$, $\ddot{\underset{\sim}{E}}$, and $\underline{\vec{\nabla}}\dot{\underline{a}}$ are not in the list of independent variables, Equation (39). Hence, there exists at least one theromodynamic process where these quantities can be prescribed independently of any other term in the inequality. Since they are independent and since they only appear once in the inequality, their choice could conceivably violate the second law of thermodynamics. In order to guarantee the integrity of the inequality, the coefficients preceding these terms must be zero. This gives the following restrictions:

$$\begin{aligned} &\frac{\partial\psi}{\partial\theta} = -\eta && \frac{\partial\psi}{\partial\dot{\underline{a}}} = \underline{0} \\ &\underline{h} = \gamma\nu\,\frac{\partial\psi}{\partial\underline{\vec{\nabla}}\,\nu} && \frac{\partial\psi}{\partial\dot{\underset{\sim}{E}}} = \underset{\sim}{0} \\ &\frac{\partial\psi}{\partial\dot{\nu}} = 0 && \frac{\partial\psi}{\partial\underline{\vec{\nabla}}\,\underline{a}} = \underline{0} \\ &\frac{\partial\psi}{\partial\underline{\vec{\nabla}}\,\theta} = \underline{0} \end{aligned} \tag{43}$$

Considering the above restrictions, the entropy inequality reduces to

$$\begin{aligned} &-\gamma\nu\dot{\nu}\,(g - \frac{1}{2}\,\dot{k}\dot{\nu} + \frac{\partial\psi}{\partial\nu} - \frac{\gamma}{\nu}\,\frac{\partial\psi}{\partial\gamma}) - \gamma\nu\,\frac{\partial\psi}{\partial\underline{a}}\cdot\dot{\underline{a}} \\ &-\gamma\nu\,\frac{\partial\psi}{\partial\underset{\sim}{E}} : \dot{\underset{\sim}{E}} + [\,\underset{\sim}{t} + \gamma^2\nu\,\frac{\partial\psi}{\partial\gamma}\,\underset{\sim}{1} + (\underline{h}\,\underline{\vec{\nabla}}\,\nu)] : \underset{\sim}{L} \\ &-\frac{1}{\theta}\,\underline{q}\cdot\underline{\vec{\nabla}}\,\theta \geqslant 0 \end{aligned} \tag{44}$$

and the functional form of the free energy is required to be

$$\psi = \hat{\psi}\,(\gamma, \nu_0, \nu, \underline{\vec{\nabla}}\,\nu, \theta, \underset{\sim}{E}, \underline{a}) \tag{45}$$

It should be noted that the above derivation applies to the general case of compressible granules. However, since the case of incompressible granules will be dealt with here, the derivation of the entropy inequality can be modified accordingly.

To begin with, the assumption of incompressible granules implies that γ is a constant and the first terms on the right hand side of Equation (41) is zero. Also, the kinematic constraint implied by incompressible granules, as expressed by Equation (21), can be incorporated by the method of Lagrange multipliers. This is accomplished by adding the term

$$p[\dot{\nu} + \nu(\vec{\underline{\nabla}} \cdot \underline{v})] \tag{46}$$

to the left hand side of Equation (42), where the coefficient p can be interpreted as a pressure. Following the previous procedure, precisely the same restrictions as those in Equation (43) are arrived at, but the entropy inequality now has the form

$$- \gamma\nu\dot{\nu}\,(g - \frac{1}{2}\,\dot{k}\dot{\nu} + \frac{\partial\psi}{\partial\nu} - \frac{1}{\gamma\nu}\,p) - \gamma\nu\,\frac{\partial\psi}{\partial\underline{a}} \cdot \dot{\underline{a}}$$

$$- \gamma\nu\,\frac{\partial\psi}{\partial\underset{\sim}{E}} : \dot{\underset{\sim}{E}} + [\,\underset{\sim}{t} + (\underline{h}\,\vec{\underline{\nabla}}\,\nu) + p\nu\underset{\sim}{1}\,] : \underset{\sim}{L} - \frac{1}{\theta}\,\underline{q} \cdot \vec{\underline{\nabla}}\,\theta \geqslant 0 \tag{47}$$

The notation in the above inequality is somewhat inconsistent in that both $\underset{\sim}{L}$ and $\dot{\underset{\sim}{E}}$ appear. In order to alleviate this problem, it will be assumed that the materials to be dealt with here are isotropic. Hence, the free energy must be an isotropic function of its arguments and must take the following form:

$$\psi = \hat{\psi}\,(\gamma, \nu_O, \nu, \vec{\underline{\nabla}}\nu \cdot \vec{\underline{\nabla}}\nu, \theta, \underset{\sim}{E}, \underline{a}) \tag{45a}$$

This form arises since $\vec{\underline{\nabla}}\nu$ is not isotropic and $\vec{\underline{\nabla}}\nu \cdot \vec{\underline{\nabla}}\nu$ is the only isotropic representation of a first order tensor (vector). From this, it follows that

$$(\frac{\partial\psi}{\partial\vec{\underline{\nabla}}\nu}\;\vec{\underline{\nabla}}\,\nu) = (\vec{\underline{\nabla}}\nu\;\frac{\partial\psi}{\partial\vec{\underline{\nabla}}\nu}) \tag{48}$$

and, hence,

$$(\underline{h}\,\vec{\underline{\nabla}}\,\nu) = (\underline{h}\,\vec{\underline{\nabla}}\,\nu)^{T} \tag{49}$$

Therefore, all the terms contained in the square brackets in Equation (47) are symmetric.

If $\underset{\sim}{L}$ is now decomposed into $\underset{\sim}{D}$ and $\underset{\sim}{W}$, there occurs the scalar product of the term in square brackets and with both $\underset{\sim}{D}$ and $\underset{\sim}{W}$. Since the term in brackets is symmetric and $\underset{\sim}{W}$ is antisymmetric, this scalar product vanishes identically. This leaves

$$- \gamma\nu\dot{\nu}\,(g - \frac{1}{2}\,\dot{k}\,\dot{\nu} + \frac{\partial\psi}{\partial\nu} - \frac{1}{\gamma\nu}\,p) - \gamma\nu\,\frac{\partial\psi}{\partial\underline{a}}\cdot\dot{\underline{a}}$$

$$- \gamma\nu\,\frac{\partial\psi}{\partial\underset{\sim}{E}} : \dot{\underset{\sim}{E}} + [\underset{\sim}{t} + (\underline{h}\,\underline{\vec{\nabla}}\,\nu) + p\nu\,\underset{\sim}{1}] : \underset{\sim}{D} - \frac{1}{\theta}\,\underline{q}\cdot\underline{\vec{\nabla}}\theta \geqslant 0 \qquad (50)$$

Substituting $\underset{\sim}{D} = \underset{\sim}{F}^{T-1}\,\dot{\underset{\sim}{E}}\,\underset{\sim}{F}^{-1}$ into the inequality, the final form is obtained:

$$- \gamma\nu\dot{\nu}\,(g - \frac{1}{2}\,\dot{k}\,\dot{\nu} + \frac{\partial\psi}{\partial\nu} - \frac{1}{\gamma\nu}\,p) - \gamma\nu\,\frac{\partial\psi}{\partial\underline{a}}\cdot\dot{\underline{a}}$$

$$+ [\frac{\nu}{\nu_o}\,\tilde{\underset{\sim}{T}} + \underset{\sim}{F}^{-1}(\underline{h}\,\underline{\vec{\nabla}}\,\nu)\,\underset{\sim}{F}^{-1} + p\nu\,\underset{\sim}{F}^{-1}\,\underset{\sim}{F}^{T-1}$$

$$- \gamma\nu\,\frac{\partial\psi}{\partial\underset{\sim}{E}}] : \dot{\underset{\sim}{E}} - \frac{1}{\theta}\,\underline{q}\cdot\underline{\vec{\nabla}}\,\theta \geqslant 0 \qquad (51)$$

In the above, $\tilde{\underset{\sim}{T}}$ is the second Piola-Kirchhoff stress tensor which is related to the Cauchy stress tensor by $\rho_o/\rho\;\underset{\sim}{F}^{-1}\,\underset{\sim}{t}\,\underset{\sim}{F}^{T-1}$.

Equation (51) is the form of the entropy inequality which will be used in the next section to investigate equilibrium.

Equilibrium

In this section, the conditions which exist at equilibrium will be derived. These will be useful in writing specific constitutive equations since the constitutive equations must reduce to the forms developed in this section at equilibrium.

First, equilibrium will be defined. For the purpose of this paper, equilibrium will be the state in which all time derivatives of the variables are zero and additionally, the state in which there exist no temperature gradients.

If Equation (51) is written as

$$\Phi \geqslant 0 \qquad (52)$$

where the functional Φ denotes the left hand side of the inequality, the following equality holds at equilibrium:

$$\Phi = 0 \tag{53}$$

Also, since the functional Φ is positive semi-definite, Φ must obtain a (local) minimum at equilibrium. A necessary condition for a minimum in Φ is that

$$\left[\frac{d}{d\lambda}\,\Phi\,(\xi_e + \lambda\,\xi^P)\right]\Big|_{\lambda=0} = 0^{*} \tag{54}$$

where ξ denotes the primitive variables (see Equation (40)), the subscript e denotes the equilibrium values of the variables, and the superscript P indicates an arbitrary perturbation away from the equilibrium value.

Performing the operation indicated in Equation (54) results in

$$\begin{aligned} &-\gamma\nu_e\dot{\nu}^P\left(g_e + \frac{\partial\psi}{\partial\nu_e} - \frac{1}{\gamma\nu_e}\,p_e\right) - \gamma\nu_e\,\frac{\partial\psi}{\partial\underline{a}_e}\cdot\dot{\underline{a}}^P \\ &+\Big[\frac{\nu_e}{\nu_o}\,\underset{\sim}{\tilde{T}}_e + \underset{\sim}{F}{}_e^{-1}\,(\underline{h}_e\,\underline{\vec{\nabla}}\,\nu_e)\,\underset{\sim}{F}{}_e^{T-1} + p_e\,\nu_e\,\underset{\sim}{F}{}_e^{-1}\,\underset{\sim}{F}{}_e^{T-1} \\ &\quad -\gamma\nu_e\,\frac{\partial\psi}{\partial\underset{\sim}{E}_e}\Big] : \dot{\underset{\sim}{E}}{}^P - \frac{1}{\theta_e}\,\underline{q}_e\cdot\underline{\vec{\nabla}}\,\theta^P = 0 \end{aligned} \tag{55}$$

Since the perturbations are assumed arbitrary, the conditions that exist at equilibrium are

$$\begin{aligned} &\underline{q} = \underline{0} \\ &\frac{\partial\psi}{\partial\underline{a}} = \underline{0} \\ &p = \gamma\nu\left(g + \frac{\partial\psi}{\partial\nu}\right) \\ &\underset{\sim}{\tilde{T}} = \frac{\nu_o}{\nu}\left[\gamma\nu\,\frac{\partial\psi}{\partial\underset{\sim}{E}} - p\nu\,\underset{\sim}{F}{}^{-1}\,\underset{\sim}{F}{}^{T-1} - \underset{\sim}{F}{}^{-1}\,(\underline{h}\,\underline{\vec{\nabla}}\,\nu)\,\underset{\sim}{F}{}^{T-1}\right] \end{aligned} \tag{56}$$

where the subscript e has been dropped.

---

*This is, however, not a sufficient condition for a minimum to exist. A zero slope in the surface of the functional Φ could indicate a minimum, a maximum, or a saddle point. To check for these possibilities, higher order derivatives would have to be evaluated. It will be assumed that Equation (54) does indeed indicate a minimum.

The implications of the expression in Equation (56) are fairly straightforward. First, it can be noted that there is no heat flux at equilibrium which can obviously be attributed to the fact that there are no temperature gradients. Also, there is the somewhat surprising result that the free energy at equilibrium is not a function of the internal state variables. This indicates that a change in any of the internal state variable represents some form of non-recoverable energy under isothermal conditions. Another result of equilibrium is that an expression for the Lagrange multiplier used in the section entitled General Constitutive Assumptions has been derived. Finally, an expression for the stress necessary to maintain equilibrium is found. This stress is a function of the strain energy in the system (as indicated by the term $\partial\psi/\partial\underset{\sim}{E}$), a hydrostatic pressure (as denoted by p), and the gradient of the volume distribution function (as expressed by $(\underline{h}\,\underline{\vec{\nabla}}\,\nu)$).

The quantity p is a hydrostatic stress state at equilibrium. This is intuitively appealing since during sintering, a granular material tends to densify and therefore contract. To maintain equilibrium (i.e., no motion), some form of stress state must be applied. This stress (in the absence of strain energy and gradients in the volume distribution function) is determined by p which is in turn dependent upon the microstructure as follows. At equilibrium, the stress in the material depends on two quantities: the intrinsic equilibrated body force, g, and the free energy, ψ. As indicated in the section entitled Balance Equations, the intrinsic equilibrated body force is related to the geometry and the material properties of the matrix. For the purpose of this paper, it is assumed to be due to surface tension effects. The other component of the equilibrium stress is due to the free energy and the volume distribution function. A granular material has an excess of energy due to the abundance of free surface in the system. The component of stress attributable to this term may represent the attempt by the material to lower its energy state by minimizing its surface area.

These two components might not represent all the important factors. However, it is assumed that these are the dominant ones. A more detailed explanation of these two components of the equilibrium stress and the derivation of explicit forms for their application will be carried out in the next section.

CHAPTER 3

APPLICATIONS

This chapter applies the theory developed in the previous chapter to copper and snow. Explicit constitutive equations are derived for the equilibrium stress in terms of the thermodynamics and microstructure of the material.

Explicit Constitutive Equations

In order to apply this theory of granular materials to specific situations, explicit forms for the constitutive equations are required. It is the purpose of this section to develop these forms with the intent of describing the sintering phenomenon. To accomplish this, an expression for the equilibrium stress is formulated in terms of the microstructure and a stress-strain relationship is postulated to describe the behavior of materials that undergo the sintering process.

As a first step, three simplications of the general theory will be made. First, it is assumed that the materials to be considered do not have any spatial variations in the volume distribution function. This implies that the last term in the expression for the equilibrium stress in Equation (56) is zero and hence this term is not considered in any future equations. Second, only isothermal conditions are considered. Finally, even though the expression for the stress in Equation (56) is correct if large deformations occur, the resulting differential equations are non-linear and hence difficult to treat analytically. To alleviate this problem, small strain approximations are used. In this case, the second Piola-Kirchhoff stress tensor, $\underset{\sim}{\tilde{T}}$, is approximately the Cauchy stress tensor, $\underset{\sim}{t}$; the Lagrangian strain tensor, $\underset{\sim}{E}$, is approximately the Eulerian (small) strain tensor, $\underset{\sim}{\epsilon}$; the deformation gradient, $\underset{\sim}{F}$, is approximately the identity tensor, $\underset{\sim}{1}$; and ν_o is approximately ν. These simplifications result in the following linearized form of Equation (56):

$$\underset{\sim}{t} = \gamma\nu \frac{\partial\psi}{\partial \underset{\sim}{\epsilon}} - \gamma\nu^2 \left(g + \frac{\partial\psi}{\partial\nu}\right) \underset{\sim}{1} \tag{57}$$

The first constitutive equations considered are the stress-strain equations. In reality, such equations would undoubtedly be non-linear and would have to reflect many types of deformation mechanisms–elastic, viscous, and plastic [19,20,21,22]. However, it is assumed that a linear, viscoelastic model gives an adequate first approximation to the stress-strain relationship. The following equations are assumed:

$$\begin{gathered} \operatorname{tr} \underset{\sim}{t} + A_1 \operatorname{tr} \dot{\underset{\sim}{t}} = \nu A_2 \operatorname{tr} \underset{\sim}{\epsilon} + \nu A_3 \operatorname{tr} \dot{\underset{\sim}{\epsilon}} - 3\theta \\ \underset{\sim}{t}' + A_4 \dot{\underset{\sim}{t}}' = \nu A_6 \dot{\underset{\sim}{\epsilon}}' + \underset{\sim}{\kappa} \end{gathered} \tag{58}$$

The $\operatorname{tr} \underset{\sim}{t}$ is the first invariant of the given tensor (t_{kk} in index notation) and the primes denote the deviatoric components of the given tensor ($t_{ij'} = t_{ij} - 1/3\ t_{kk}\,\delta_{ij}$ in index notation).

The above equations warrant some discussion. To begin with, it should be noted that, in general, the material coefficients could be functions of any or all of the variables listed in Equation (39). Here, however, they are considered constants. The inclusion of the factor ν on the right side of the equations reflects the idea that given the same stress state, a porous material with a lower density will probably strain more and at a higher rate than a material with a higher density. The above equations are simple forms which reflect the density dependence of the strain and strain rate. The first of Equations (58) describes the volumetric response of the material. It has the form of a three-parameter solid and indicates that the material will not compress or expand indefinitely under a given stress state. The second of Equations (58) describes the deviatoric, or shape-changing, behavior of the material. A two parameter fluid is chosen since, for instance, snow can be made to flow indefinitely under the influence of a shear stress. Finally, the terms 3θ and $\underset{\sim}{\kappa}$ are included to make Equations (58) compatible with the equilibrium conditions. Explicit forms for these two additional terms are derived later in this section.

It should be noted that the basis for Equations (58) is empirical and not theoretical. No attempt was made to find an optimal stress-strain relationship. Although the equations represent some of the known response of a porous material, they obviously do not take into account all of the responses.

In order to find complete forms for Equations (57) and (58), constitutive equations must be postulated for the free energy, ψ, and the intrinsic equilibrated body force, g. Since these two quantities provide the driving force for the sintering process, they must be related in some manner to the surface tension. Therefore, as a preliminary step, it is instructive to discuss the concepts of surface tension and, conjointly, surface energy.

Surface energy is defined as the amount of energy required to increase the surface of a material by one unit of area. It has dimensions of energy per unit area and will be denoted by σ. Surface tension is the force which resists stretching of the surface: it has dimensions of force per unit length and will be denoted by ϕ. The following argument which relates the two was given by Shuttleworth [23]. Consider a planar element of the surface of some material as shown in Figure 1. Assume a deformation of the surface element caused by forces opposing the surface tension in the element. The work done by these forces is equal to the increase in energy due to the increase in surface area:

$$\phi_1 \, dA_1 + \phi_2 \, dA_2 = d(A\sigma) \tag{59}$$

If the surface is anisotropic, ϕ_1 and ϕ_2 will depend upon the orientation of the surface. However, in a fluid which is isotropic or a solid at elevated temperatures (near the melting point) where the atomic mobility is high, this effect can be neglected and ϕ_1 will be equal to ϕ_2. In this case, Equation (59) will reduce to

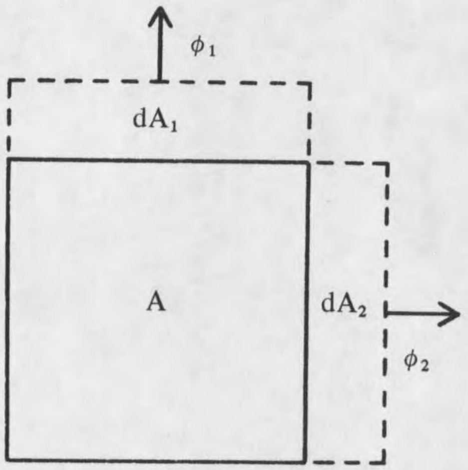

Figure 1. Diagram of the deformation of a surface.

$$\phi = \sigma + A \frac{d\sigma}{dA} \tag{60}$$

To simplify this even further, it can be noted that since it has been assumed that the atomic mobility is high, the surface density of atoms will remain essentially constant during the deformation. Hence, the change in surface energy with respect to the change in surface area will be zero. Therefore, under these conditions, the surface energy and the surface tension can be considered equivalent quantities. During sintering, it is assumed that the above conditions are approximately satisfied and, hence, the common value of the surface energy and the surface tension will be denoted by σ throughout the remainder of this work.

It is now possible to derive explicit forms for the free energy and the intrinsic equilibrated body force. Consider first the intrinsic equilibrated body force. As was noted in the section entitled Balance Equations, this term depends upon the geometry of the microstructure and the material properties of the matrix material. Also, in the derivation of the equilibrium stress, it was found that the constitutive equation for the intrinsic equilibrated body force could include quantities associated with the internal state vector. For the purpose of this work, it is assumed that the pertinent quantities are the mean curvature of the void-solid interface and the surface tension. The importance of these quantities was indicated in the work done by Gregg [19] and the explicit dependence can be derived as follows.

Consider a square, curved surface as shown in Figure 2. The discussion at the beginning of this section shows that the surface tension in a flat surface of zero curvature can be balanced by applying a force parallel to the surface at its periphery. However, for a curved surface, a pressure normal to the surface must be imposed in order to counteract the effect of surface tension. As shown in Figure 2, the components of the force due to the surface tension acting perpendicular to the surface normal are self-equilibrating. However, parallel to the surface normal, the surface tension produces a net force. If θ is small, then $\sin \theta/2 \cong \theta/2$ and the net force (relative to one of the principle radii of curvature) is $\sigma s^2/r$. The total force acting upon the surface is

$$\frac{\sigma s^2}{r_1} + \frac{\sigma s^2}{r_2} = \sigma s^2 \overline{H} \tag{61}$$

where $\overline{H}$ is two times the mean curvature of the surface at the point in question. To maintain equilibrium, a force is required which arises from a pressure differential which exists across the interface. If this differential is denoted by ΔP, the force is $\Delta P s^2$ and

$$\Delta P = \sigma \overline{H} \tag{62}$$

At this point, a little care must be exercised in order to translate the above into a form compatible with this theory. The main point to be considered is the use of the correct sign. The sign convention that will be used is as follows. If the radii of curvature extend into the solid, then the surface will be considered convex and the curvature will be positive ($\overline{H} > 0$). Alternatively, if the radii of curvature extend into the void, then the surface will be considered concave and the curvature will be negative ($\overline{H} < 0$).

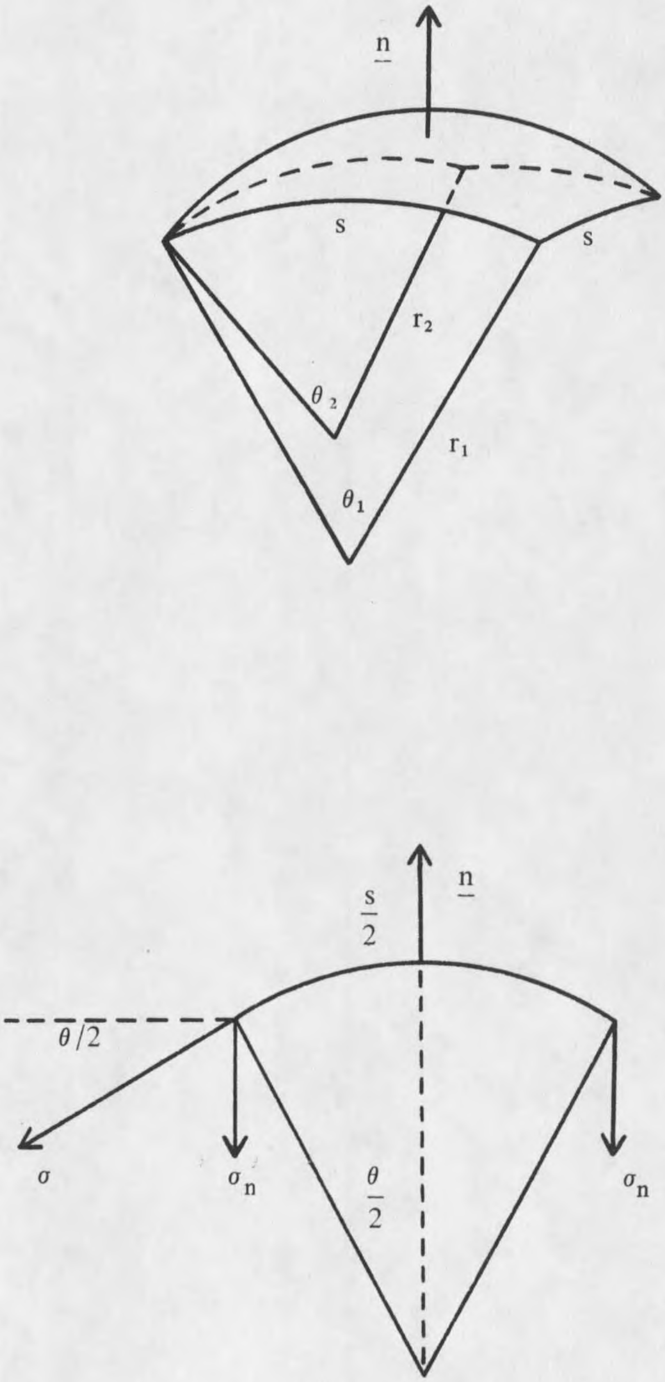

Figure 2. Resolution of surface tension into a pressure differential acting across a curved surface.

Now consider the effect of the pressure differential on the sign of the curvature. For a convex surface to exist, a negative pressure (tension) must be maintained in the region external to the solid matrix. Similarly, a positive pressure (compression) must be maintained in order to induce a negative curvature. Therefore, if the externally applied pressure is measured with respect to some reference pressure in the matrix material, the pressure must have the opposite sign to that of the curvature. Thus, the correct form of Equation (62) is

$$P = -\sigma \bar{H} \tag{63}$$

where the Δ has been dropped.

The above is the pressure which is associated with the intrinsic equilibrated body force. Since the material is considered continuous, each point in the material has a curvature associated with it and hence must have some applied stress acting at that point in order to maintain the given curvature. Comparison of Equation (63) with the term in Equation (57) associated with the intrinsic equilibrated body force shows that an equivalence is established if

$$g = -\frac{1}{\gamma \nu^2} \sigma \bar{H} \tag{64}$$

The above will be taken as the constitutive equation for the intrinsic equilibrated body force.

To complete the formulation of the stress-strain equation, a constitutive equation for the free energy must be postulated. The form that will be used is (see [24], pg. 271)

$$\gamma \nu \psi = \nu[C_1 \operatorname{tr}(\underset{\sim}{\epsilon}\, \underset{\sim}{\epsilon}) + \frac{1}{2} C_2 (\operatorname{tr} \underset{\sim}{\epsilon})^2 + \sigma S_V] \tag{65}$$

where $\gamma \nu \psi$ gives the energy per unit volume and S_V is the specific surface area of the material in units of area per unit volume. The first two terms on the right side of the equality give the free energy of a linear, isotropic, elastic material. To account for the increase in energy due to the excess of free surface in the material, the third term on the right is added. The coefficient ν on the right side renders this equation consistent with the postulated forms for Equations (58).

The evaluation of the two added terms in Equations (58) can now be accomplished. In order to do this, the equilibrium stress given by Equation (57) must be evaluated using the constitutive equations for the free energy and the intrinsic equilibrated body force. The equilibrium stress involves the following two quantities: $\partial\psi/\partial\nu$ and $\partial\psi/\partial\underset{\sim}{\epsilon}$. In calculating these two quantities, it must be remembered that the volume distribution function and the deformation are not independent due to the kinematic constraint imposed by the assumption of incompressible granules. This constraint gives a relationship between ν and $\underset{\sim}{\epsilon}$ which can be derived by rewriting Equation (21) as

$$\frac{d\nu}{dt} = -\nu\,\frac{d(\mathrm{tr}\,\underset{\sim}{\epsilon})}{dt} \tag{66}$$

Solving this differential equation and assuming that $\nu = \nu_0$ when $\underset{\sim}{\epsilon} = \underset{\sim}{0}$ yields

$$\nu = \nu_0 \exp(-\,\mathrm{tr}\,\underset{\sim}{\epsilon}) \tag{67}$$

Using the above, the following expressions are obtained for the required derivatives:

$$\frac{\partial\psi}{\partial\underset{\sim}{\epsilon}} = \frac{1}{\gamma}\,[2C_1\,\underset{\sim}{\epsilon} + C_2\,(\mathrm{tr}\,\underset{\sim}{\epsilon})\,\underset{\sim}{1} - \sigma\nu\,\frac{\partial S_V}{\partial\nu}\,\underset{\sim}{1}\,] \tag{68}$$

and

$$\frac{\partial\psi}{\partial\nu} = \frac{1}{\gamma}\,[-\frac{1}{\nu}\,(2C_1 + 3C_2)\,\mathrm{tr}\,\underset{\sim}{\epsilon} + \sigma\,\frac{\partial S_V}{\partial\nu}\,] \tag{69}$$

Substituting Equations (68) and (69) into Equation (57) results in the following expression for the stress at equilibrium:

$$\underset{\sim}{t} = \nu(2C_1)\,\underset{\sim}{\epsilon} + \nu(2C_1 + 4C_2)(\mathrm{tr}\,\underset{\sim}{\epsilon})\,\underset{\sim}{1} - \gamma\nu^2 g\,\underset{\sim}{1} - 2\nu^2\sigma\,\frac{\partial S_V}{\partial \nu}\,\underset{\sim}{1} \tag{70}$$

The final forms for Equations (58) can now be obtained. If the equilibrium forms for Equations (58) are used in conjunction with Equation (70), the two forms will be equivalent if

$$\begin{aligned} A_2 &= 8C_1 + 12C_2\,, \\ \theta &= 2p_1 + p_2\,, \\ \underset{\sim}{\kappa} &= \nu A_5\,\underset{\sim}{\epsilon}' \end{aligned} \tag{71}$$

where

$$\begin{aligned} p_1 &= \nu^2\sigma\,\frac{\partial S_V}{\partial \nu}\,, \\ p_2 &= \gamma\nu^2 g = -\sigma\,\overline{H}\,, \\ A_5 &= 2C_1 \end{aligned} \tag{72}$$

Thus, the final forms for the stress-strain equations are

$$\begin{aligned} &\mathrm{tr}\,\underset{\sim}{t} + A_1\,\mathrm{tr}\,\dot{\underset{\sim}{t}} = \nu A_2\,\mathrm{tr}\,\underset{\sim}{\epsilon} + \nu A_3\,\mathrm{tr}\,\dot{\underset{\sim}{\epsilon}} - 3(2p_1 + p_2) \\ &\underset{\sim}{t}' + A_4\,\dot{\underset{\sim}{t}}' = \nu A_5\,\underset{\sim}{\epsilon}' + \nu A_6\,\dot{\underset{\sim}{\epsilon}}' \end{aligned} \tag{73}$$

Equations (73) illustrate the driving mechanism for the densification of a sintering material. Even with zero strain, a non-zero stress is required to prohibit spontaneous straining of the material. This stress is directly related to the microstructure by the term $3(2p_1 + p_2)$. If no external stress is applied to counteract the effect of this last term, the material will have non-zero strains and strain rates. Thus, the microstructure of the porous material promotes, in some fashion, the densification of a sintering material.

It should be noted that the derivatoric part of Equations (73) has lost its fluid character and now has the form of a three parameter solid. This is a result of using a form for the free energy which is indicative of a solid. Even though this contradicts the experimental evidence of snow flowing continually under a sustained shear stress, Equations (73) will be used in the following sections to apply this theory to specific situations.

An Application to Copper

In this section, the theory is applied to sintered copper. To do so, it is necessary to have quantitative data on the microstructure of porous copper as well as data on the stresses induced in the material during sintering. Suitable data were collected by Gregg [19]. The following is a brief description of Gregg's test procedure.

Gregg began with copper powders having spherical grains of three different diameters: 12 μm, 30 μm, and 48 μm. The powder was placed in a cylindrical mold and presintered for a short time in order to provide cohesion between the particles. The presintered specimen was then introduced into a load column which would place the material in uniaxial tension. A furnace surrounded the specimen in order to provide the temperatures necessary to promote sintering (950°C to 1050°C). Initially, an axial load sufficient to produce extensional creep was applied to the specimen. After this initial load was applied, the load was continually adjusted by the amount necessary to insure no further extension or contraction of the specimen occurred in the axial direction. As a result of this procedure, the axial force relaxed for some time after which it began to grow due to the influence of the stresses induced by the microstructure in the material. At this point, the test was terminated. The axial force was recorded and the specimen was removed from the furnace to preserve the internal state of the material. The relative density was determined and the microstructural properties (the mean curvature of the interface and the specific surface area) were evaluated using the methods of quantitative microscopy [25]. This procedure was repeated for each of the initial particle sizes and for various initial densities. The three tests covered a range of relative densities from about 0.65 to about 0.95.

In order to apply the proposed theory to the results obtained by Gregg, three things must be considered. First, the microstructural data must be put in a form which can be used in determining a value for the equilibrium stress (Equations (71 and (72)). Second, the material coefficients in Equations (73) must be evaluated in order to get numerical results which can be compared to the actual data. Finally, solutions for Equations (73) must be found which will approximate the test conditions.

The microstructural data are used in the two terms which represent the equilibrium stress in the material. The intrinsic equilibrated body force is related to the mean curvature of the interface by the second of Equations (72). Since the mean curvature is reported by Gregg for the various densities a direct substitution is all that is required. The term associated with the free energy is given by the first of Equations (72). To evaluate this term, the change in the specific surface area with respect to a change in the volume distribution function (the relative density) must be known. As indicated by Gregg's data, the dependence of the specific surface area upon the relative density is approximately linear for each particle size; hence, the quantity $\partial S_V/\partial \nu$ is constant. The numerical values for the mean curvature and $\partial S_V/\partial \nu$ are given in Tables 1, 2, and 3 for the three different particles sizes. A value of 1.65 Pa•m* was used for the surface tension for copper.

The determination of the material coefficients presents some difficulty. Ideally, these quantities should be obtained from an independent investigation into the stress-strain relationship for porous copper at elevated temperatures. However, such an investigation under the prescribed conditions would include the effects of the stresses due to the microstructural components of the porous material. Unless these effects are accounted for, they would be absorbed into the determination of the material coefficients and hence make these coefficients inapplicable to the present situation. To circumvent this problem, the

---

*There is some discrepancy in the reported values for the surface tension of copper. This value is given by Udin [26].

Table 1. Data and Results for 48 μm Copper Particles.

Volume Fraction	$\bar{H}$ ($\times 10^4$ m^{-1})	S_V ($\times 10^4$ m^{-1})	Actual Stress ($\times 10^4$ Pa)	Calculated Stress ($\times 10^4$ Pa)
0.658	-4.660	4.58	1.724	1.724
0.667	-2.720	5.20	1.926	1.930
0.733	-6.420	4.60	2.529	2.524
0.770	-9.460	3.62	2.771	2.760
0.783	-10.10	3.56	2.463	2.455
0.799	-10.11	3.30	2.150	2.147
0.843	-11.89	2.50	2.868	2.858
0.848	-12.30	2.35	3.951	3.929
0.863	-12.97	2.18	4.023	4.000
0.913	-14.68	1.37	6.235	6.190

$$\partial S_V/\partial \nu = -1.432 \times 10^5 \text{ m}^{-1}$$

Table 2. Data and Results for 30 μm Copper Particles.

Volume Fraction	$\overline{H}$ ($\times 10^4$ m^{-1})	S_V ($\times 10^4$ m^{-1})	Actual Stress ($\times 10^4$ Pa)	Calculated Stress ($\times 10^4$ Pa)
0.723	−16.71	9.40	5.049	5.051
0.748	−16.31	8.60	4.158	4.177
0.775	−26.43	6.64	6.006	5.989
0.778	−17.26	8.30	6.629	6.628
0.821	−27.63	6.14	6.972	6.955
0.885	−23.73	3.66	6.714	6.729
0.893	−31.30	3.22	7.713	7.702
0.904	−24.13	3.14	8.194	8.199
0.915	−41.48	2.30	8.854	8.814
0.919	−55.07	1.36	9.925	9.841
0.934	−45.82	1.64	10.16	10.10
0.938	−34.16	1.26	9.810	9.785

$$\partial S_V/\partial \nu = -3.786 \times 10^5 \text{ m}^{-1}$$

Table 3. Data and Results for 12 μm Copper Particles.

Volume Fraction	$\bar{H}$ ($\times 10^4$ m^{-1})	S_V ($\times 10^4$ m^{-1})	Actual Stress ($\times 10^4$ Pa)	Calculated Stress ($\times 10^4$ Pa)
0.688	-9.05	17.78	5.935	5.989
0.735	-25.42	16.24	8.848	8.852
0.796	-34.73	11.20	10.93	10.92
0.810	-32.41	12.10	11.49	11.48
0.857	-32.34	7.44	12.84	12.84
0.873	-40.08	7.40	12.78	12.77
0.912	-39.57	4.70	15.39	15.38
0.917	-37.26	4.30	16.12	16.11
0.951	-75.76	2.14	16.83	16.73
0.959	-42.49	2.10	19.00	18.97
0.969	-47.90	1.22	18.23	18.20

$\partial S_V/\partial \nu = -6.105 \times 10^5$ m^{-1}

coefficients were determined by using a least squares fit to Gregg's data for the 30 μm particles. The numerical values for the coefficients were then used to predict the results of the tests on the 12 μm and 48 μm particles.

As indicated above, a solution must be found before a least squares fit can be applied to the data for the 30 μm particles. Two major problems arise. The first is that Equations (73) will be solved in terms of the independent variable time and no quantitative reference to time is given by Gregg. All of the data is presented in terms of density. Hence a suitable time at which to evaluate the time-dependent stress must be found. Another problem is that Gregg never precisely elaborates as to what the actual loading history was up to the point at which the axial load was measured. Since sufficient data concerning the loading history is not available, it is difficult to devise a solution which accurately reflects the test conditions. Therefore, the results of Gregg's tests will be analyzed using the following solution.

Initially, an axial load of one and a half times the reported axial stress is applied to an unstressed, unstrained specimen. The ends of the specimen are then fixed so that no additional axial strain occurs beyond the initial elastic response of the material. The values for the equilibrium stress are assumed to be those values determined by the final relative density and are further assumed to be constant throughout the duration of the test. This results in time-dependent expressions for the axial stress and the radial and tangential strains. Since times are not reported by Gregg, a time must be determined which reflects the transition from a state in which the axial stress is relaxing to a state in which the axial stress is increasing due to stresses induced by sintering. This indicates that the appropriate time at which to measure the stress is the point at which the stress rate is zero. The stress evaluated at this time is then compared to the stress measured by Gregg. The specifics of this derivation and the appropriate solutions are given in Appendix A.

Using the solution obtained by the above procedure, a least squares fit* to Gregg's data for the 30 μm particles resulted in the following numerical values for the material coefficients:

$$\begin{aligned} A_1 &= 6.071 \cdot 10^6 \text{ sec} \\ A_2 &= 6.551 \cdot 10^6 \text{ Pa} \\ A_3 &= 1.595 \cdot 10^{11} \text{ Pa} \cdot \text{sec} \\ A_4 &= 4.957 \cdot 10^3 \text{ sec} \\ A_5 &= 9.926 \cdot 10^3 \text{ Pa} \\ A_6 &= 9.956 \cdot 10^7 \text{ Pa} \cdot \text{sec} \end{aligned} \tag{74}$$

The above material coefficients were used to produce the results in Tables 1, 2, and 3.

Some remarks regarding the numerical solution which lead to Equations (74) are appropriate. The algorithm to find the values for the constants takes an initial guess and iterates towards a set of values where the sum of the squares of the residuals is a minimum. As a result of this iterative process, the solution seems to be very sensitive to the initial guess. In many cases, the step size used puts the constants into a domain from which a run-time error occurs either due to an overflow condition or due to a set of constants which result in a square root being taken of a negative number (see Equations (A.12) in Appendix A). In other cases, since the algorithm is designed to find a local minimum from a given initial guess, a solution is obtained which is physically unreasonable. An unreasonable solution would be one where either some of the material coefficients are negative or the values were such that the small strain assumptions were violated. The particular solution given in Equations (74) represents the most physically reasonable set of values obtained.

---

*International Math and Statistics Library (IMSL) routines were used to produce the coefficients necessary to fit the data and to find the times at which the stress rates were zero. The routine which found the coefficients minimized the sum of the squares of the residuals using a Levenberg-Marquardt algorithm [27]. The routine used to find the times at which the stress rate was zero used the Brent algorithm [28].

In terms of the computed stresses, the results given in Tables 1, 2, and 3 are remarkably accurate. This accuracy is even more striking in the light of the fact that Gregg never actually measures the axial stress on the specimen. Gregg measured the force at a given relative density and estimated the area with respect to relative density. Hence, what are termed the actual stresses in Tables 1, 2, and 3 are inferred from Gregg's data. Furthermore, the insufficient data on the loading history must raise some question as to the validity of the solution used to approximate the test conditions. Nonetheless, the accuracy of the theoretical solutions leads to the following conclusions.

The most important result is that the theory of granular materials can be successfully applied to the sintering phenomena. Specifically, the physics used in deriving the constitutive equations for the intrinsic equilibrated body force and the free energy (Equations (64) and (65)) seem to be essentially correct. Other factors related to the internal state vector (Equation (39)) such as particle size may have some influence upon sintering; however, the results indicate that such terms may be of secondary importance. Another conclusion which may be drawn is that the stress-strain relationships given in Equations (73) are valid approximations to the material response of a porous material subjected to this range of stress and stress rates. Also, these equations seem to be relatively insensitive to temperature since Gregg's data was taken at temperatures from 950°C to 1050°C. Finally, it appears as though the solution used to approximate Gregg's test conditions is valid.

An Application to Snow

In the previous section, the stresses induced in porous copper as it sintered could be directly calculated since the values for the microstructural parameters were known. In applying this theory to snow, the evaluation of these stresses cannot be done since the necessary microstructural data were not obtained. Therefore, an indirect approach was taken by assuming that stresses due to the microstructure do exist and then determining the magnitude of these stresses by fitting the theory to a given set of data. The data used was obtained by Brown, Lang, and St. Lawrence [29].

As a starting point, consider the effect of loading a snow sample. Since the stresses induced by the microstructure tend to densify the material, it would seem to require a smaller magnitude of compression to achieve a given deformation than would be required in tension to achieve the same (although opposite) deformation. To test this hypothesis, a single sample should be alternatively tested in tension and compression. This was not done in [29]. Separate samples were tested in either compression or tension but not both. The effect of the stresses due to the sintering process could be accounted for in any single test by appropriate adjustment of the material coefficients. It was therefore deemed necessary to consider several tension and compression tests in order to alleviate this problem. Since the tests in [29] were done on different samples, a variability in the stresses due to the microstructure was undoubtedly present. However, since the objective was to obtain an estimate of these stresses (specifically, the quantity θ in Equations (71)), the scatter in the actual values between samples should result in an approximate value representative of all samples.

In order to analyze the material response of the snow, the same constitutive equations that were used for copper (Equations (73)) were used in this case. The solution was derived by assuming an axial load was applied to an initially unstressed, unstrained specimen. The axial load remained constant throughout the duration of the test and the time dependent axial and lateral strains are solved for. Since the data in [29] presents the strains as functions of time, a least squares fit can be used to match the measured and calculated strains. The specific functional forms used to fit the data are derived in Appendix B.

The least squares fit to the data gives the following numerical values for the material coefficients and the equilibrium stress:

$$\begin{aligned} A_1 &= 5.088 \cdot 10^3 \text{ sec} \\ A_2 &= 2.238 \cdot 10^6 \text{ Pa} \\ A_3 &= 9.408 \cdot 10^{10} \text{ Pa-sec} \\ A_4 &= 1.244 \cdot 10^3 \text{ sec} \\ A_5 &= 9.814 \cdot 10^5 \text{ Pa} \\ A_6 &= 2.672 \cdot 10^{10} \text{ Pa-sec} \\ \theta &= -5.641 \cdot 10^2 \text{ Pa} \end{aligned} \tag{75}$$

The results are presented graphically in Figures 3 through 18*. In these figures, the volumetric strain, ϵ_V, is the quantity

$$\epsilon_V = \epsilon_a + 2\epsilon_L \tag{76}$$

where the ϵ_a denotes the axial strain and ϵ_L denotes the lateral strain. Similarly, the deviatoric strain, ϵ_d, is the quantity

$$\epsilon_d = \epsilon_a - \epsilon_L \tag{77}$$

It is possible to make some observations regarding the results shown in Figures 3 through 18. First, it is apparent that the calculated results are sometimes quantitatively quite different than the actual results. This can be partially attributed to the fact that, owing to the use of different samples with different internal structure, the equilibrium stress most likely varied from test to test. The result of this variation would be to raise or lower the calculated curves for the volumetric strain by some amount (this variation would not affect the deviatoric results). However, qualitatively, the actual and calculated curves appear to have approximately the same shape. This indicates that the postulated stress-strain relationships (Equations (73)), while not being exactly correct, seem to be a reasonable approximation to the mechanical behavior of snow.

---

*The test identification numbers are those used in [29].

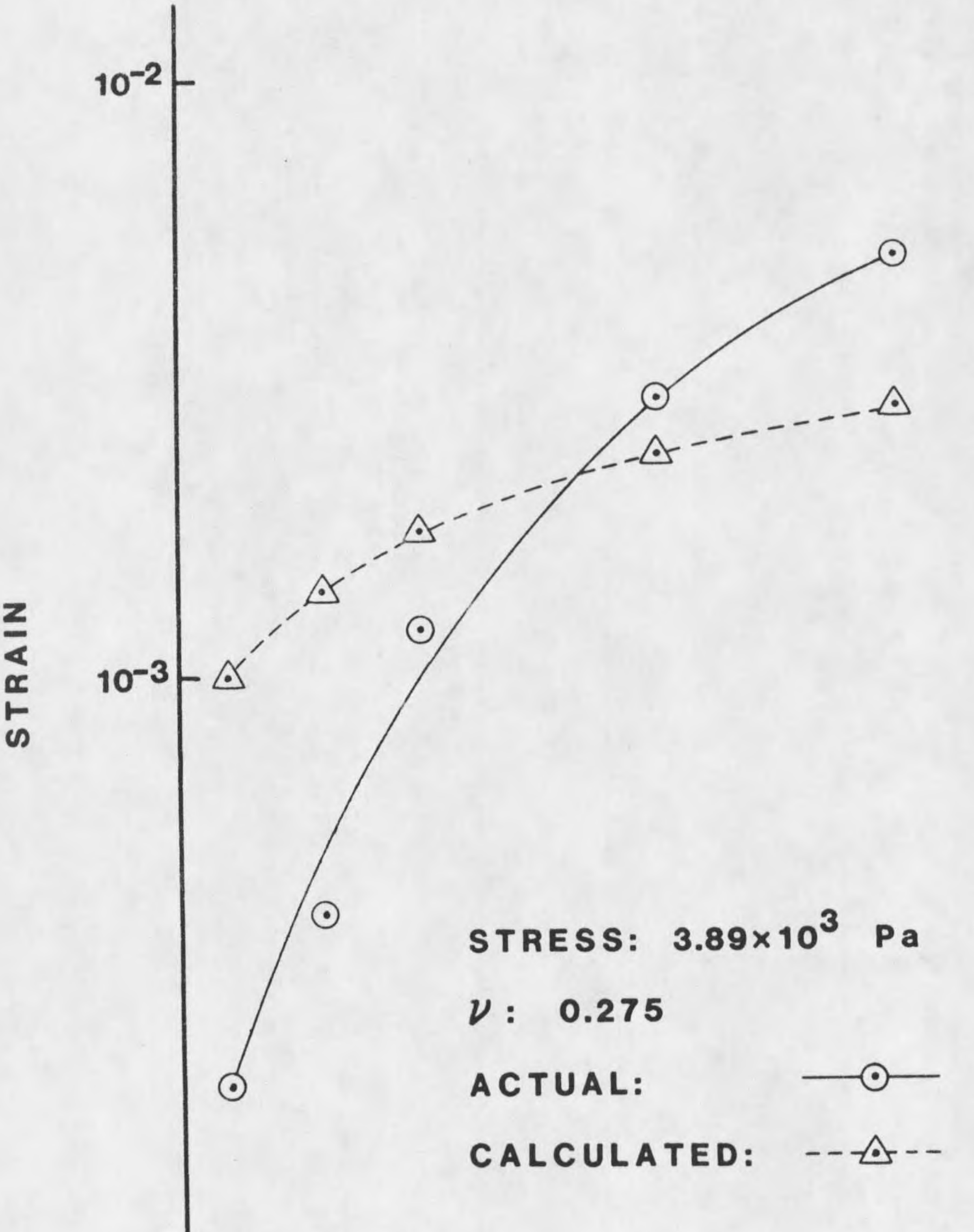

Figure 3. Creep tension test CT - 16 - .01.17.73 - 10; volumetric strain.

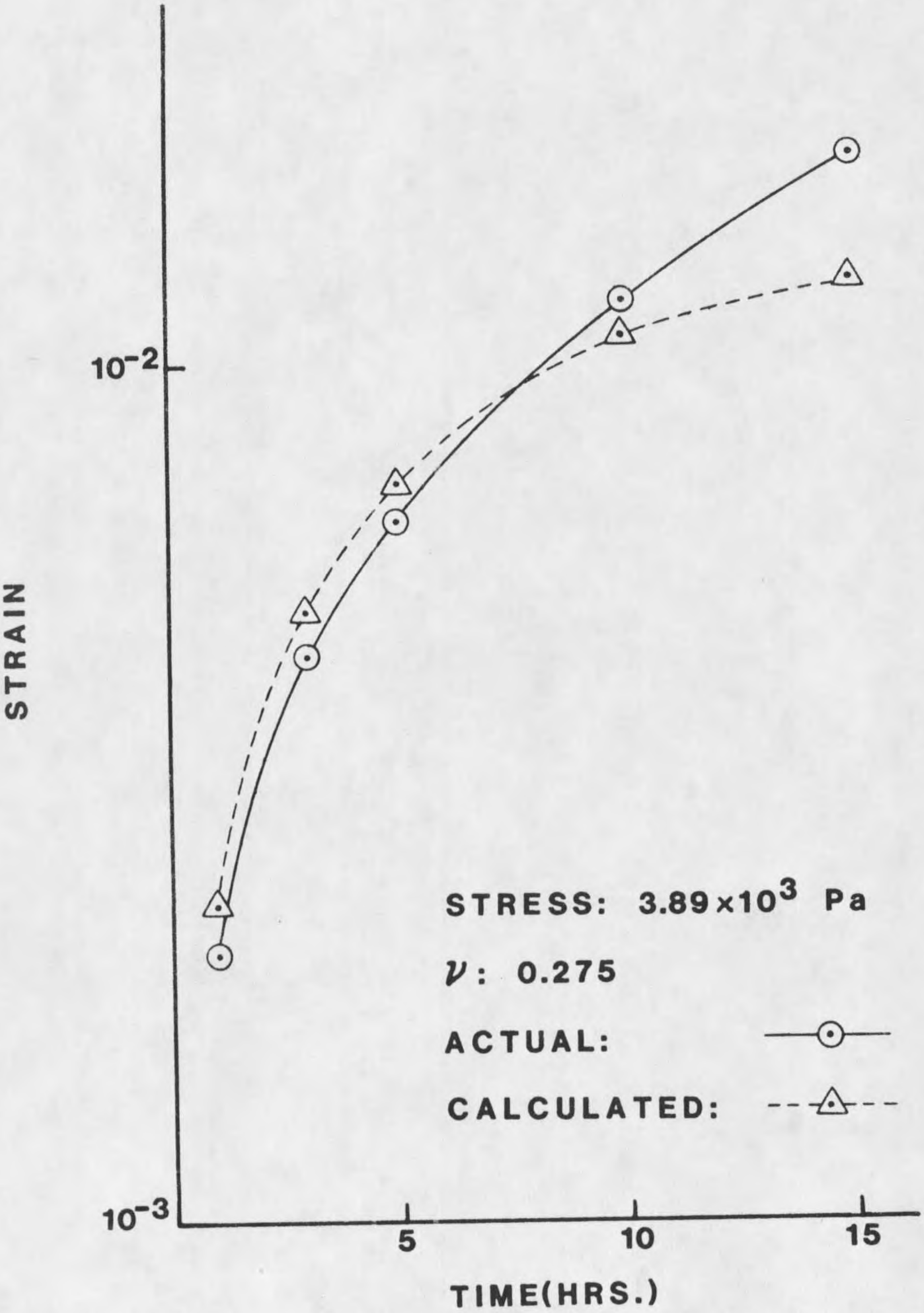

Figure 4. Creep tension test CT - 16 - .01.17.73 - 10; deviatoric strain.

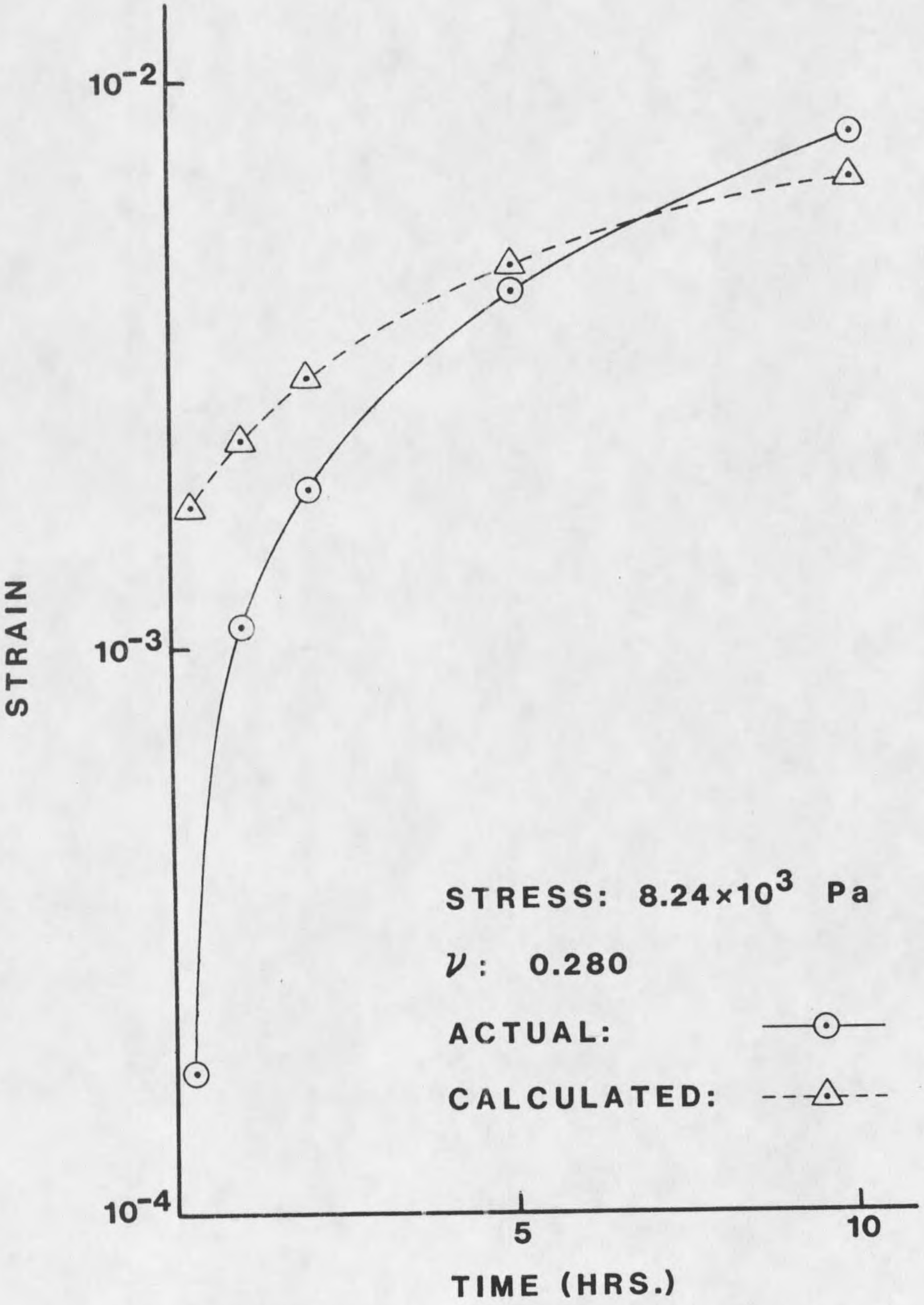

Figure 5. Creep tension test CT - 17 - .01.19.73 - 10; volumetric strain.

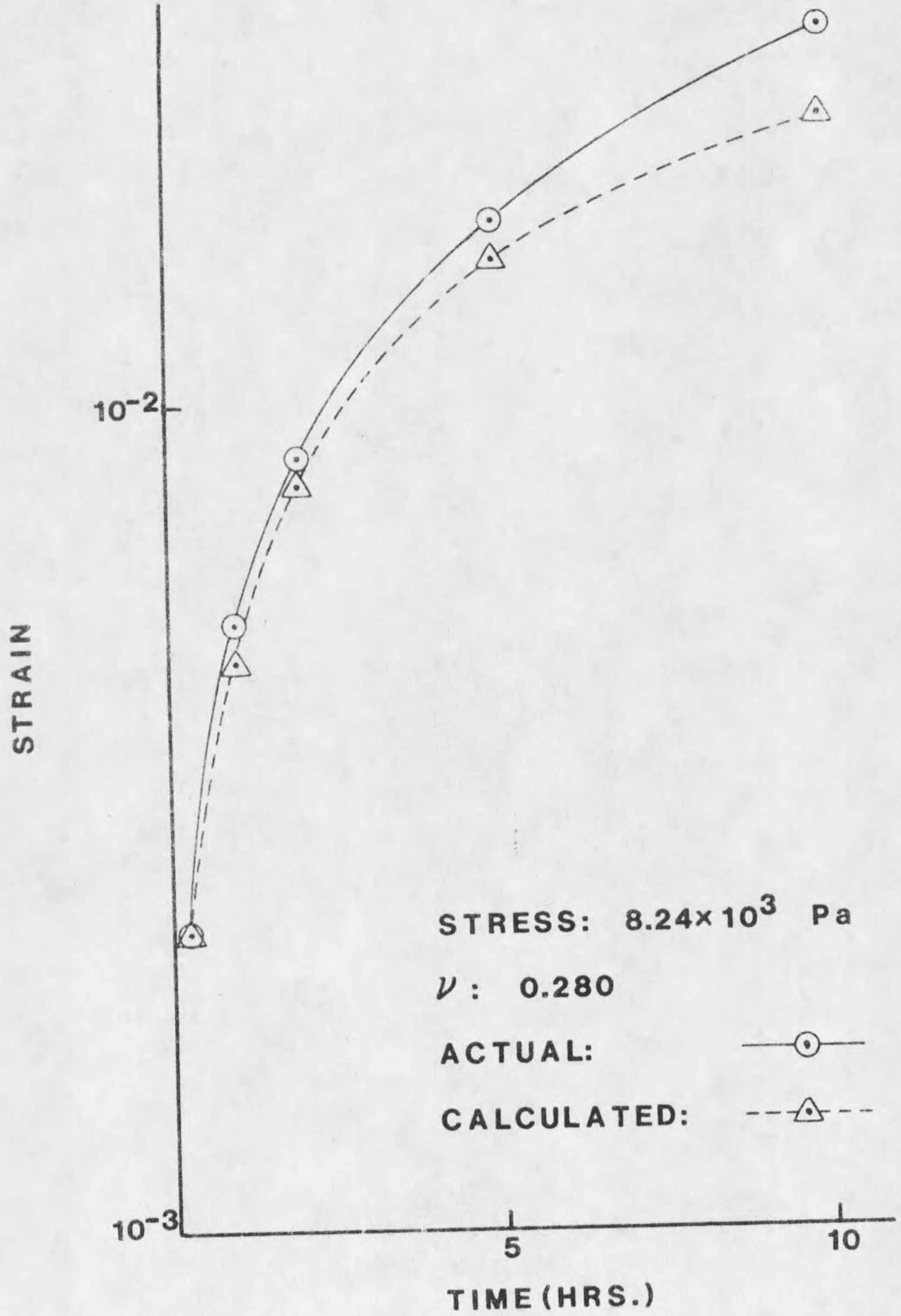

Figure 6. Creep tension test CT - 17 - .01.19.73 - 10; deviatoric strain.

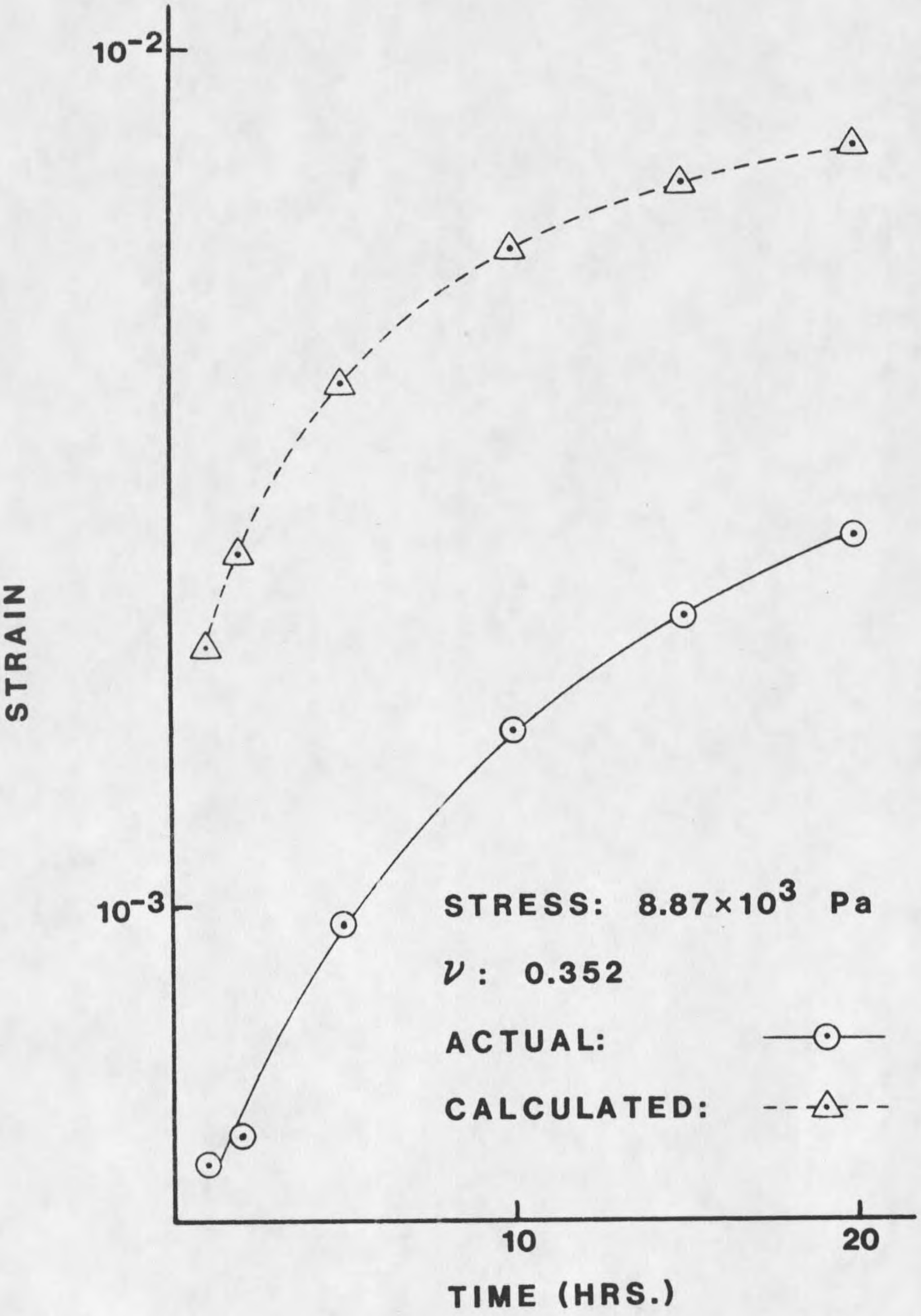

Figure 7. Creep tension test CT - 2 - 05 - 31 - 73 - 10; volumetric strain.

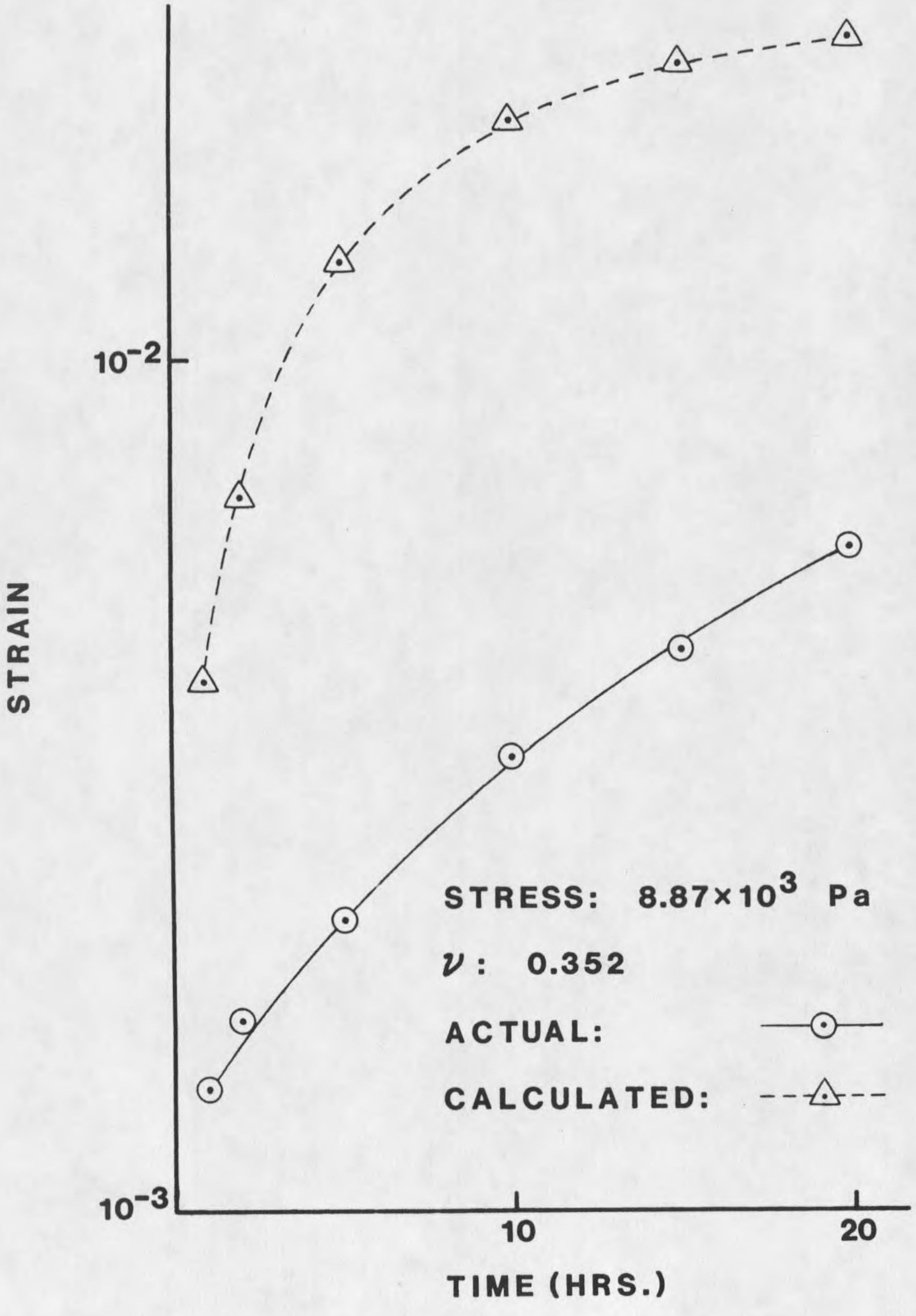

Figure 8. Creep tension test CT – 2 – 05 – 31 – 73 – 10; deviatoric strain.

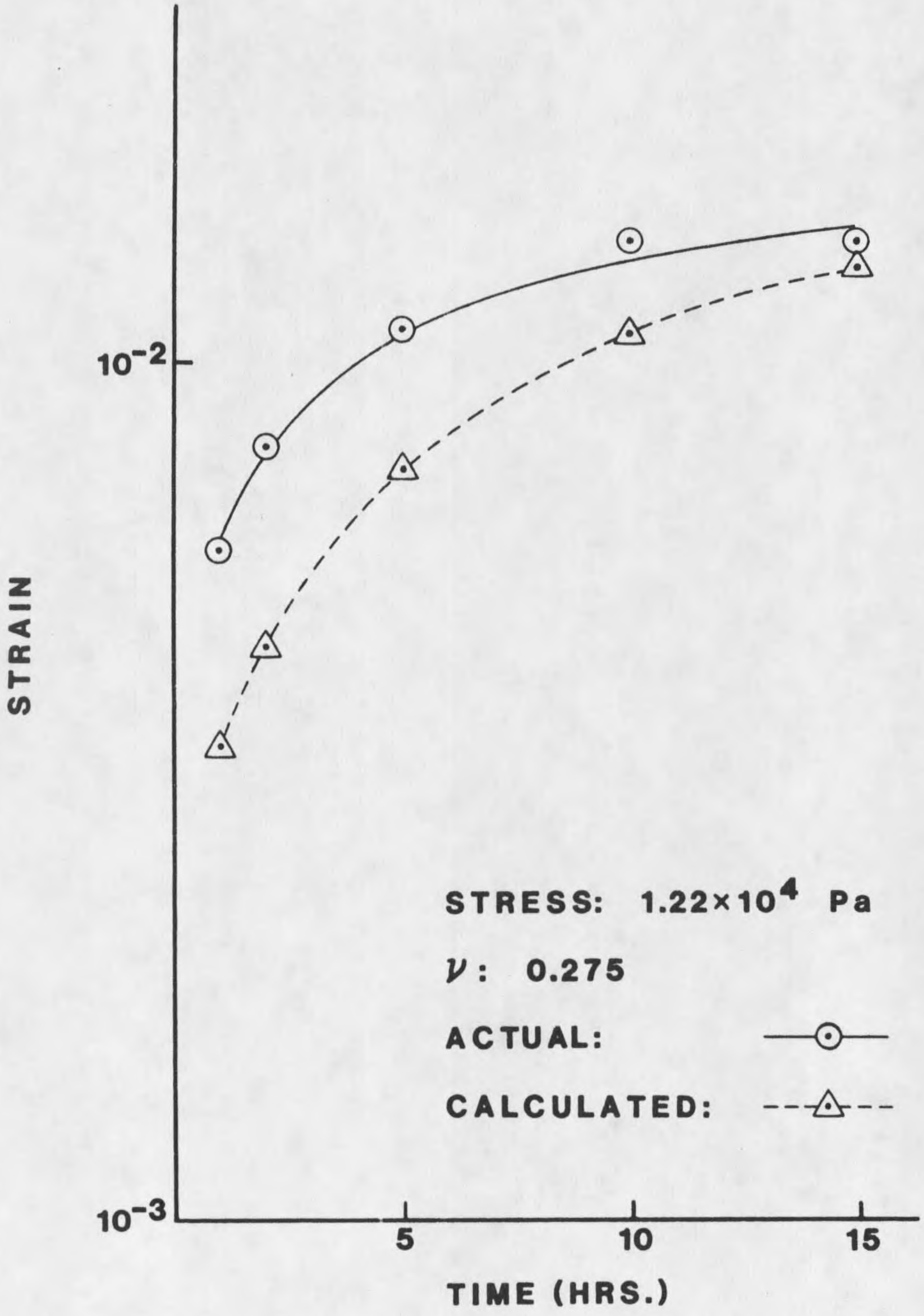

Figure 9. Creep tension test CT - 12 - .01.10.73 - 10; volumetric strain.

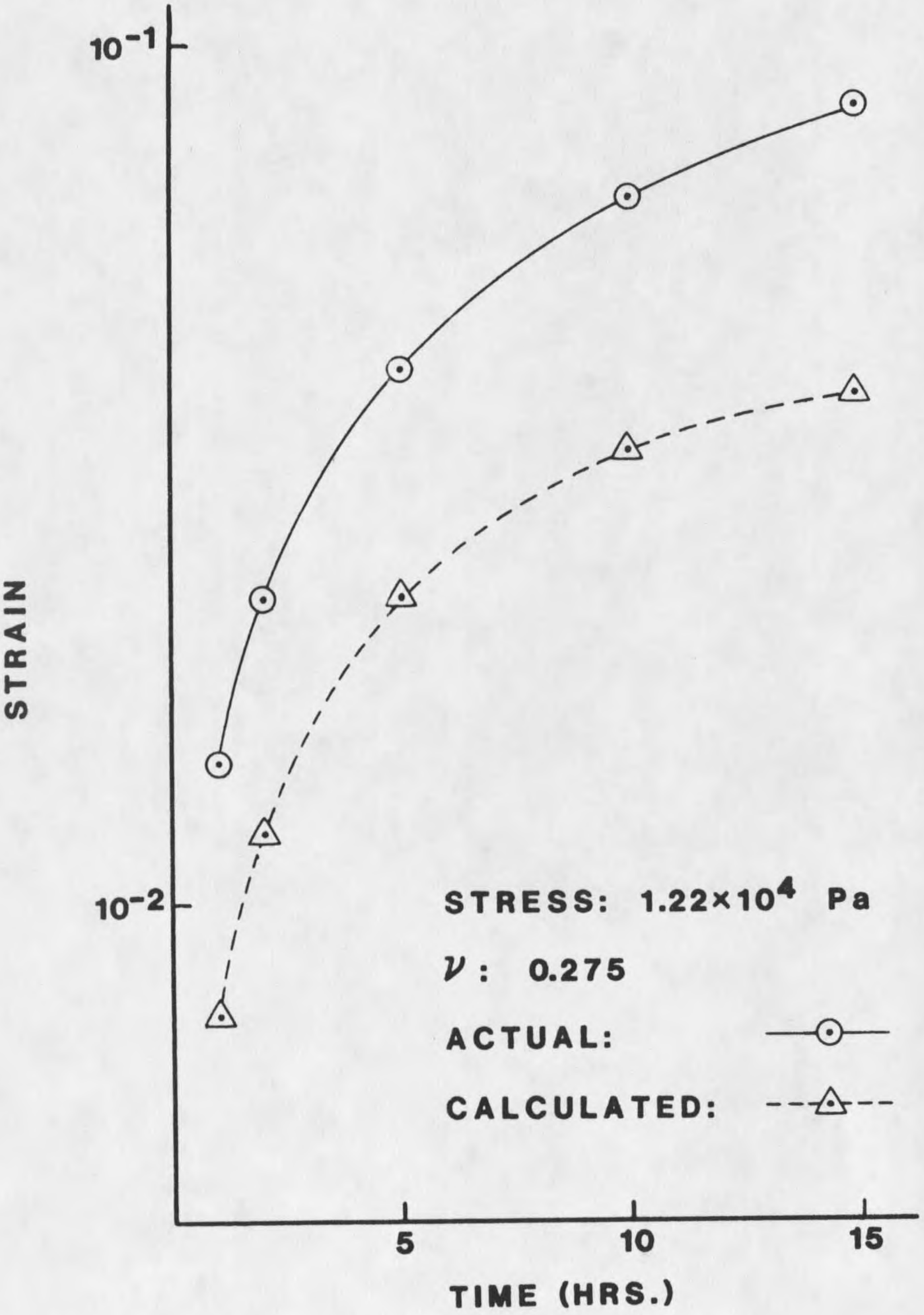

Figure 10. Creep tension test CT - 12 - .01.10.73 - 10; deviatoric strain.

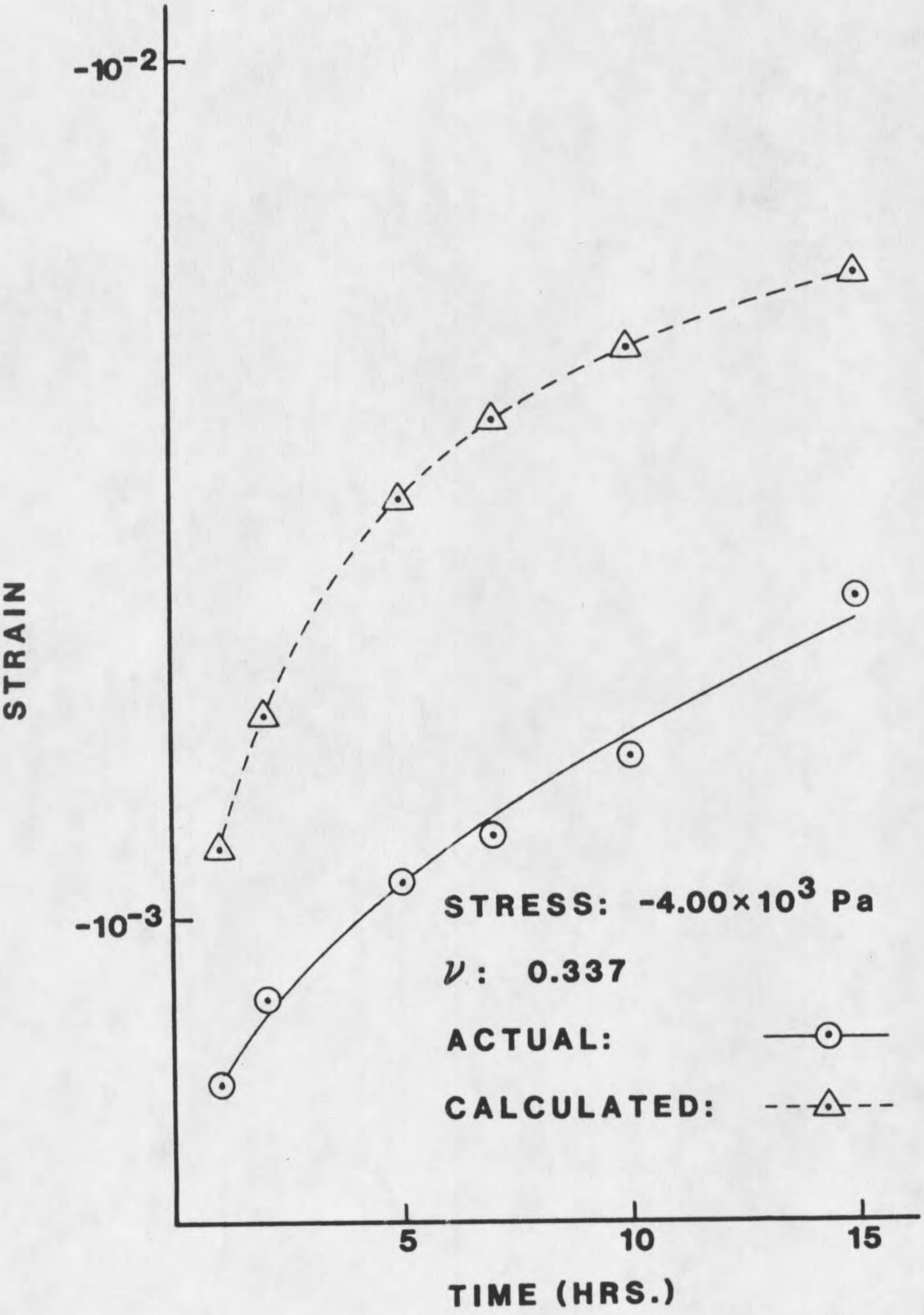

Figure 11. Creep compression test CC - 1 - 2 - 04 - 11 - 73 - 10; volumetric strain.

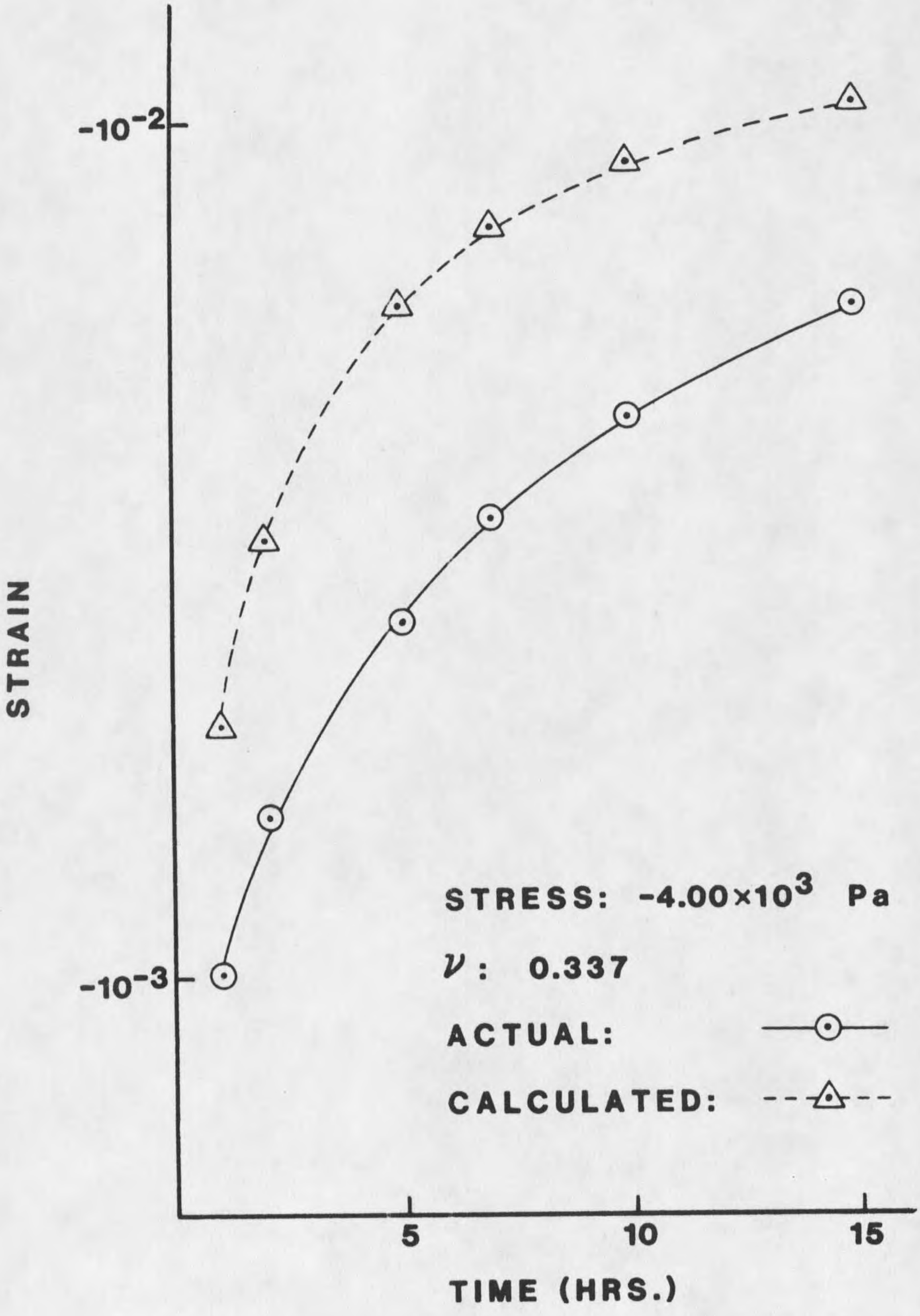

Figure 12. Creep compression test CC – 1 – 2 – 04 – 11 – 73 – 10; deviatoric strain.

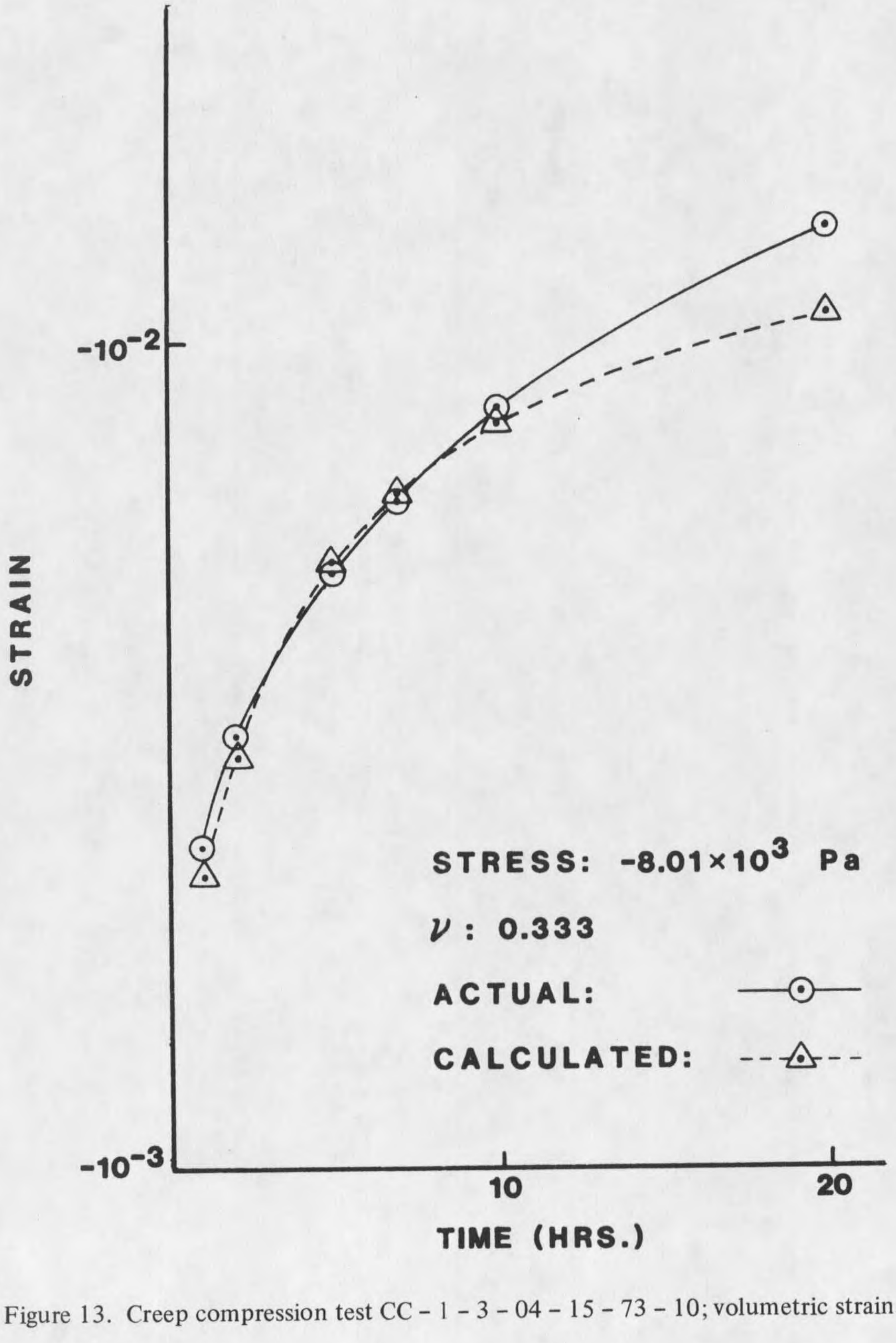

Figure 13. Creep compression test CC – 1 – 3 – 04 – 15 – 73 – 10; volumetric strain.

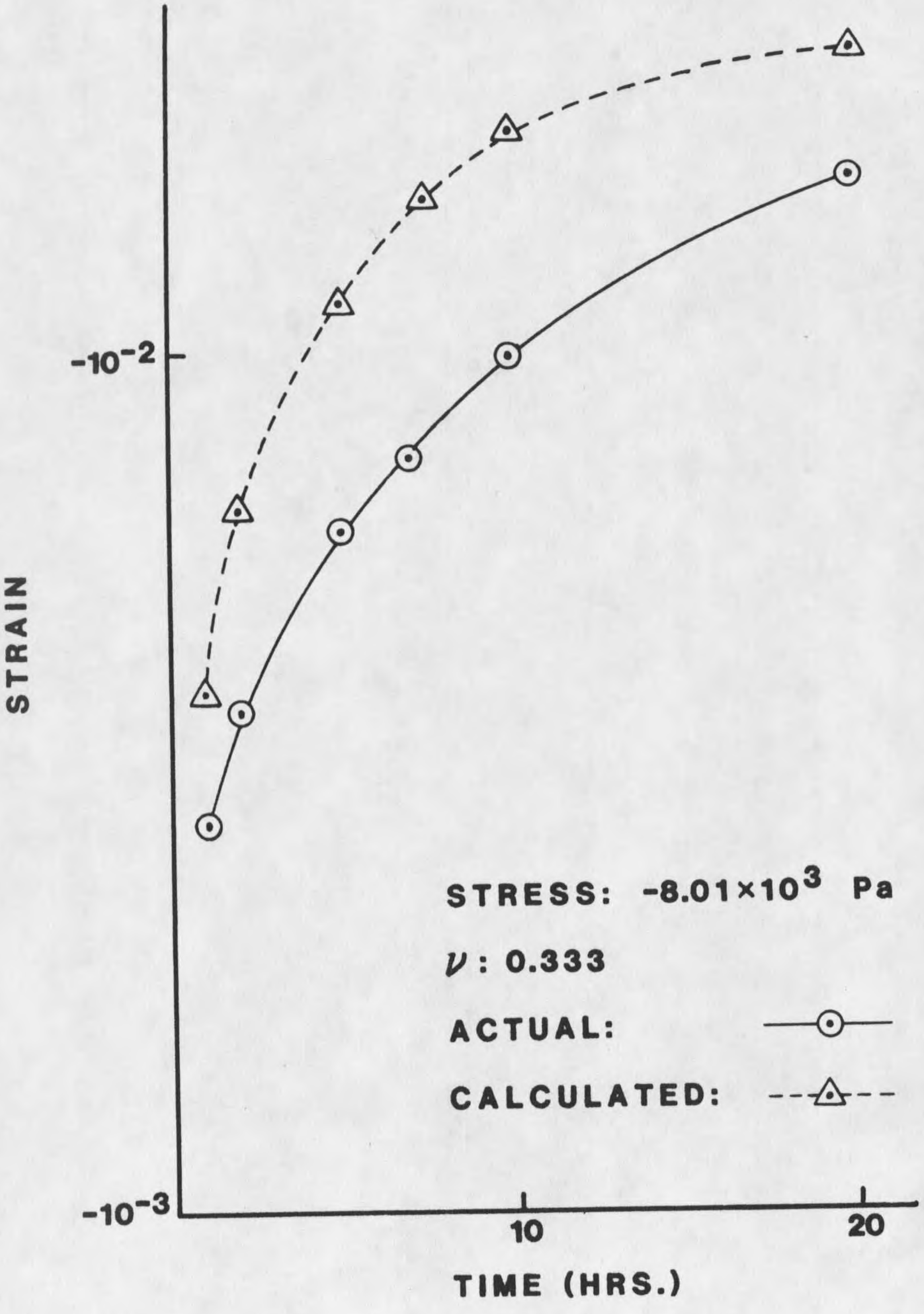

Figure 14. Creep compression test CC – 1 – 3 – 04 – 15 – 73 – 10; deviatoric strain.

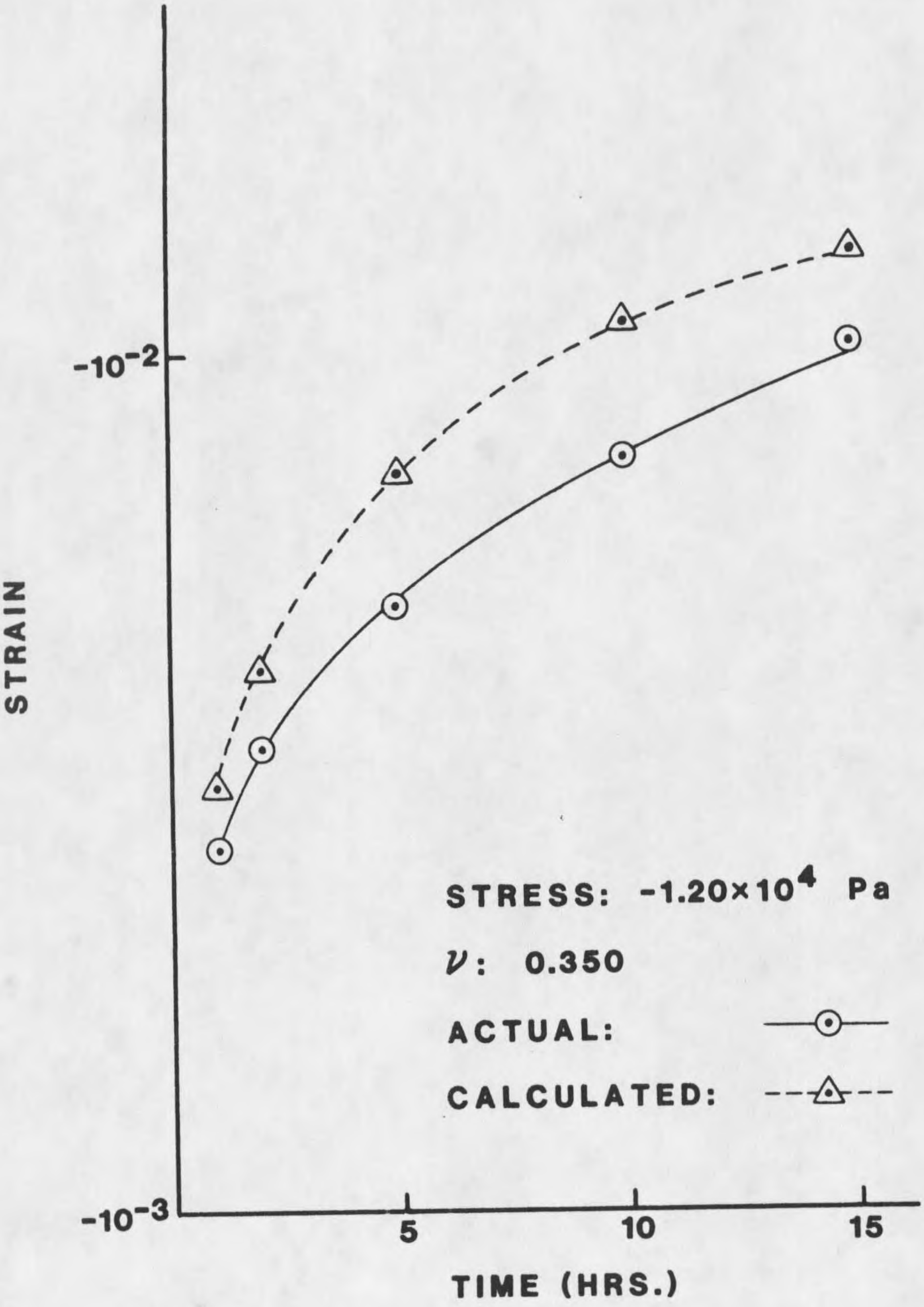

Figure 15. Creep compression test CC – 1 – 4 – 04 – 19 – 73 – 10; volumetric strain.

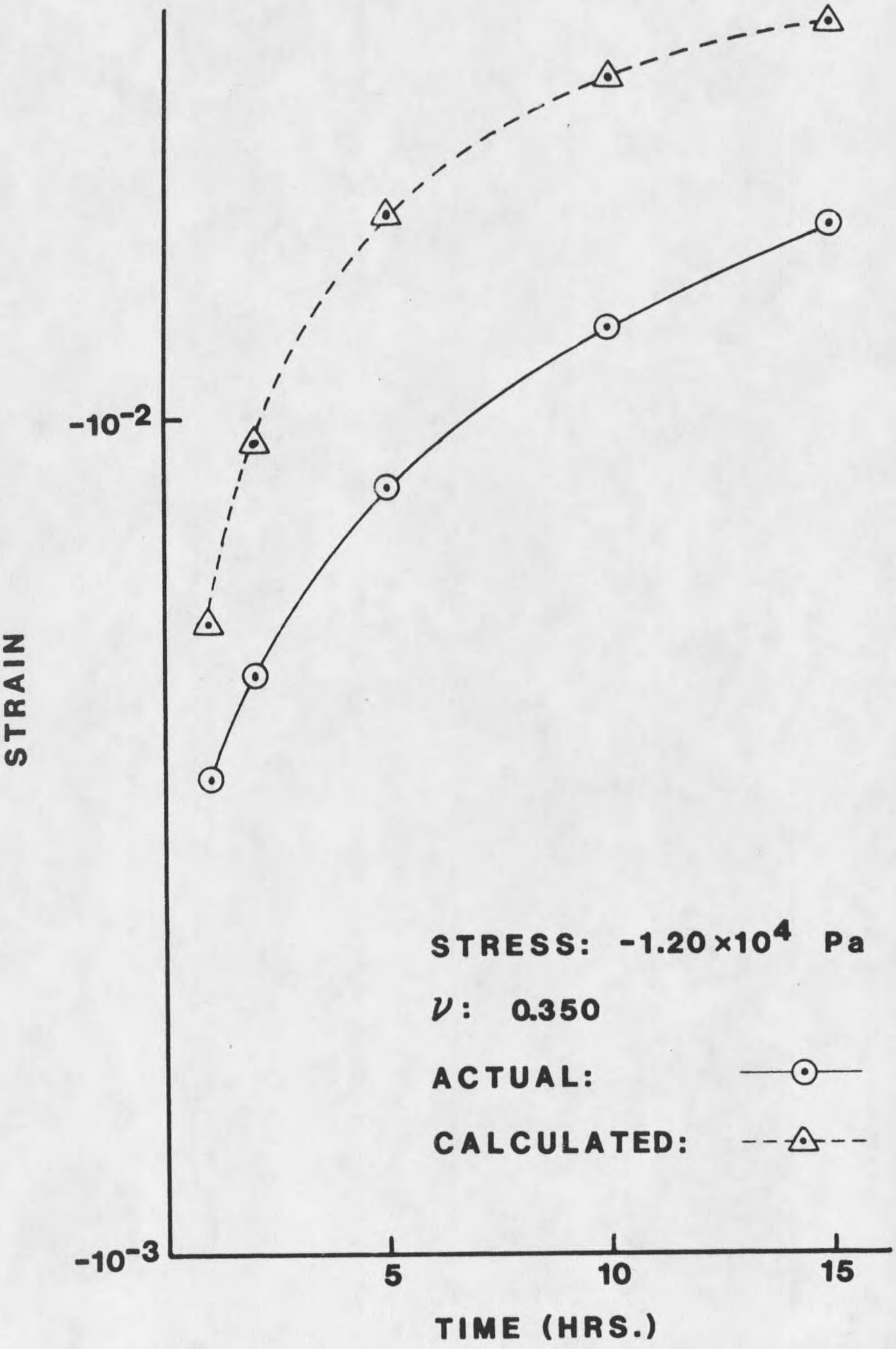

Figure 16. Creep compression test CC – 1 – 4 – 04 – 19 – 73 – 10; deviatoric strain.

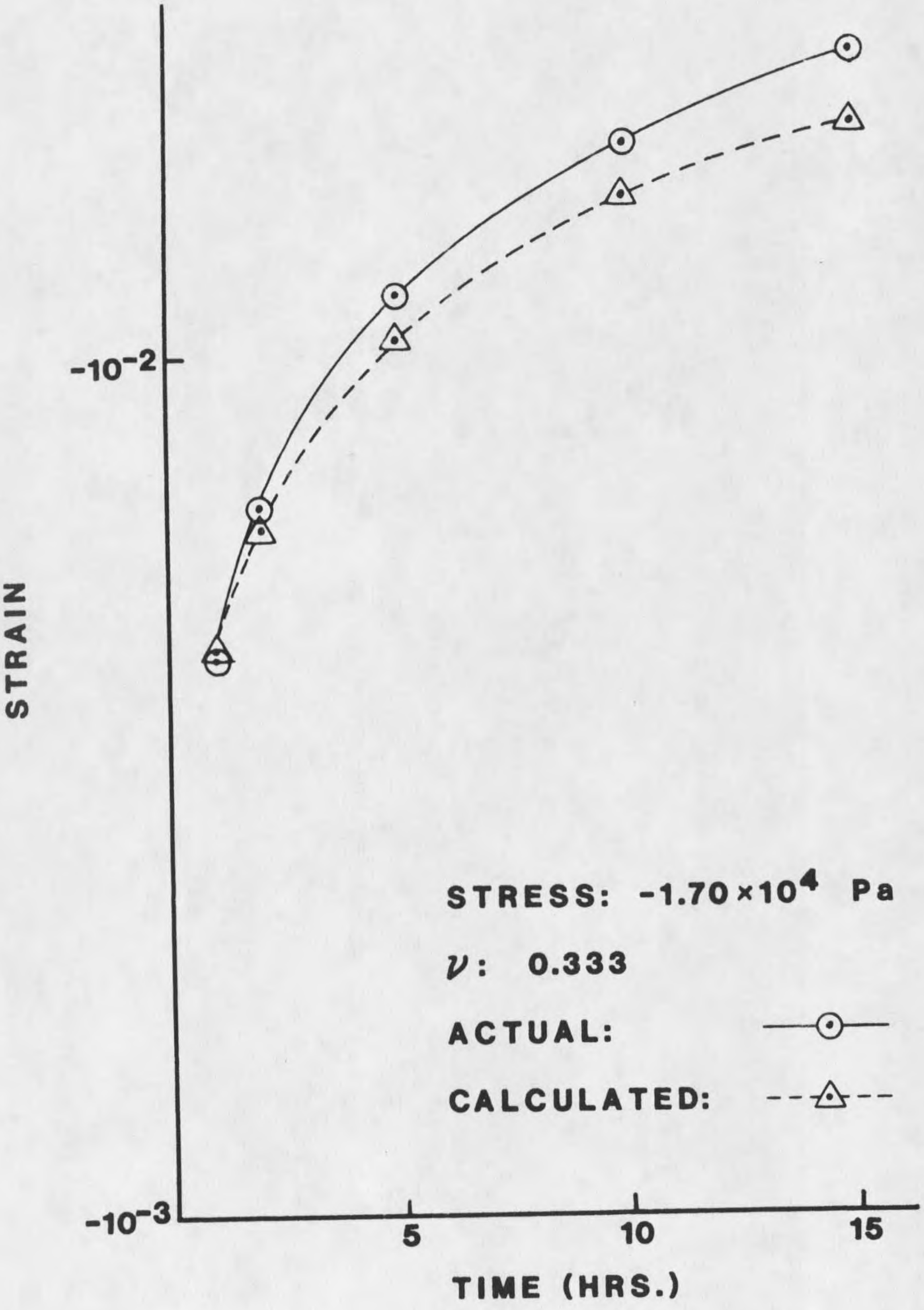

Figure 17. Creep compression test CC – 1 – 5 – 04 – 22 – 73 – 10; volumetric strain.

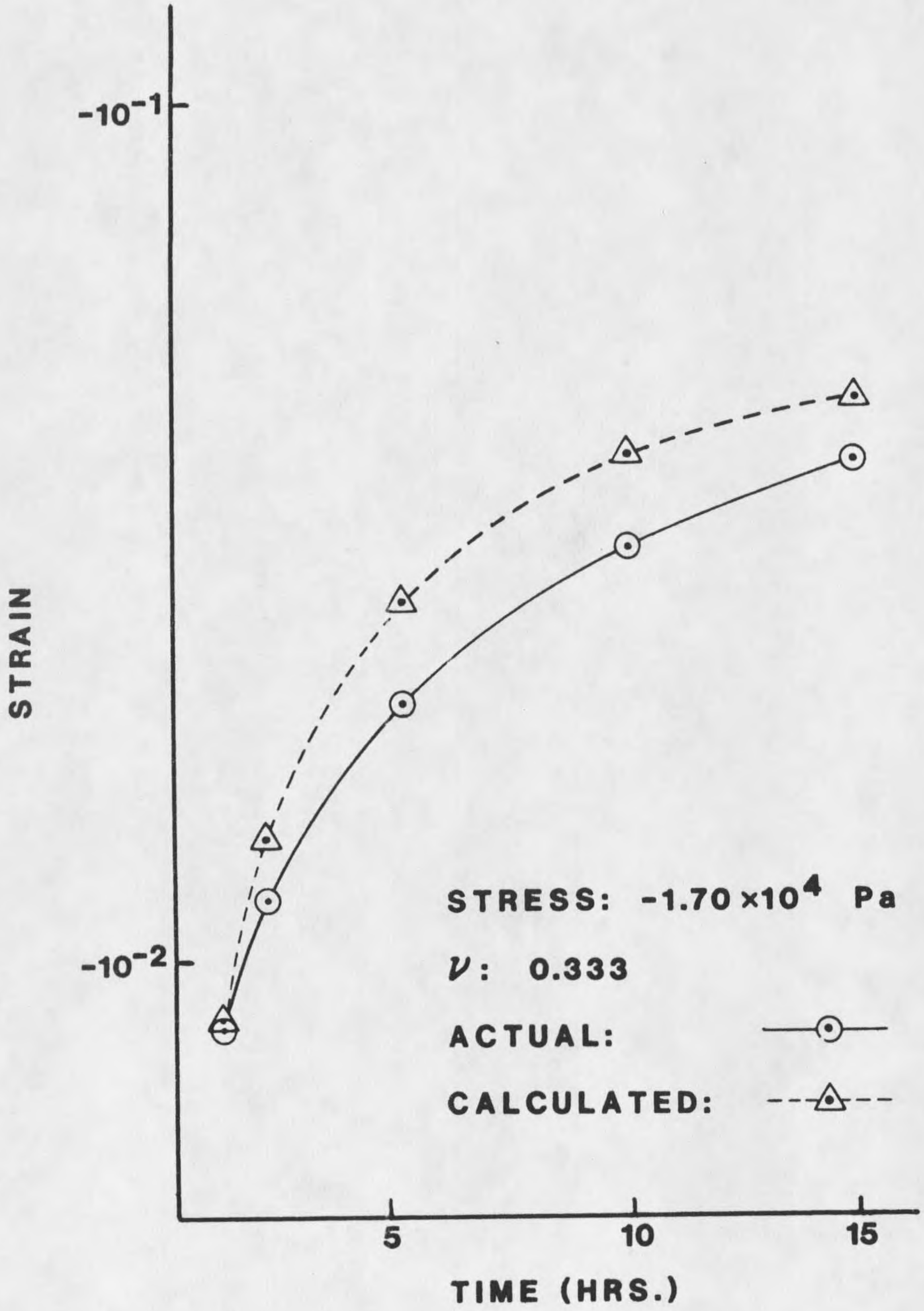

Figure 18. Creep compression test CC – 1 – 5 – 04 – 22 – 73 – 10; deviatoric strain.

The value for the equilibrium stress, θ, seems to be a reasonable quantity. It suggests that snow in the density range considered would require a hydrostatic tension of about 600 Pa (about 0.1 psi) to maintain equilibrium in an unstrained sample. This value is neither excessively high nor so small as to make it insignificant with respect to the stresses found in a normal snowpack. As an example, preliminary estimates of the fracture strength of *in situ* snow puts this value at about 10% of the maximum breaking strength of small samples. The actual value for the equilibrium stress will vary with the values for the microstructural parameters; however, it may be a factor which should be considered in dealing with stress computations for snow.

An interesting question which arises from the idea of the equilibrium stress is that if it does induce a tension in the snowpack, how deep into the snowpack does this tension persist before the compressive effects of the overburden pressure cancel it? One way of considering this is to assume some sort of loading history to simulate the effects of the accumulation of new snow on an old layer which is constrained so that no transverse strains are allowed. Another way to consider this is to use an elastic approximation to the problem by determining the amount of normal stress required to negate transverse strains assuming a transverse stress equal to the equilibrium stress. These two problems are considered below.

First, assume an unstressed, unstrained layer laying on the surface of a horizontal plane. Prescribe a constant loading rate of $-7 \cdot 10^{-3}$ Pa/sec. This rate is equivalent to snow with a density of 200 kg/m^3 falling at a rate of 1.25 cm/hr. The original layer is constrained so that no transverse strains are allowed. The problem is solved to find the time at which the transverse stress changes from tension to compression. This time is used to calculate the depth of snow overlying the original layer. Solution of this problem yields the result that this layer will be about 60 cm below the surface when it is in a state of zero transverse stress. Above this point, the material is in tension; below this point, it is in compression.

The second problem is solved using the equations for a linear isotropic, elastic solid. If a transverse stress is applied which is equivalent to equilibrium stress, a normal stress is required to maintain zero transverse strain. Solving the elastic equations for this case results in the following relationship between the normal and transverse stresses:

$$\sigma_Z = \frac{1 - \nu}{\nu} \sigma_X \tag{78}$$

where ν is Poisson's ratio, σ_Z is the required normal stress, and σ_X is a positive quantity (tensile stress) equal in magnitude to the equilibrium stress. If a representative value for Poisson's ratio of 0.2 is used and it is assumed that the normal stress is provided by snow with a density of 200 kg/m^3, Equation (78) requires a depth of about one meter of snow in order to obtain the required conditions.

The two preceding solutions must be regarded as qualitative approximations to the portion of the snowpack which is under tension. Neither solution reflects the dynamic nature of the snowpack. Variables such as temperature gradients, slope inclination, stratification of the snowpack structure, and a constantly changing microstructure as sintering proceeds must be considered in order to more precisely define the problem. However, the above results indicate that at least *some* of the upper layers of the snowpack are in a state of tension. This fact should be used to modify any stress analyses done on snow.

CHAPTER 4

DISCUSSION AND CONCLUSIONS

The results of the previous chapter indicate that a continuum theory of granular materials may be a valuable aid in describing the sintering kinetics of porous materials. The theory allows the forces which cause sintering to be described in terms of the thermodynamics of the interface which separate the void from the solid matrix. These forces are directly associated with particular features of the microstructure; namely, the average curvature of the void-solid interface and the specific surface area of the material. Stresses induced by these forces promote mechanical deformation of the solid matrix which, in turn, results in densification of the material.

An application of this theory to the data presented by Gregg [19] gave highly accurate results. This indicates two things. First, the relationships between the thermodynamics of the microstructure and the stresses induced in the material must be essentially correct. Second, the constitutive equations used to describe the mechanical response of the material are adequate approximations for the stress levels considered. However, further testing should be done in order to produce additional verification of the theory. The testing may be carried out in the following manner.

Standard creep and relaxation tests could be performed on the material as it sinters. Accurate strain measurements must be taken throughout the test in order to determine the precise time-dependence of these strains. These measurements could be obtained optically. Use of these strain measurements would result in more accurate values for the stresses than could be inferred from Gregg's data. This procedure would result in a more precisely defined problem which could be analyzed in terms of this theory.

In addition to more accurate measurements of the stresses and strains induced during sintering, values for the microstructural parameters must be known for the various densities. These quantities are not measurable during the course of the test. However, as Gregg noted, the application of external stresses in the range he considered did not significantly alter the values of mean curvature or specific surface area. Therefore, a series of unconstrained sintering tests could be conducted and the microstructural parameters could be measured for various densities throughout a given range. This would provide the values necessary to evaluate the equilibrium stress. These values could then be used in conjunction with a creep or relaxation test to fully define the problem.

The results obtained by applying this theory to the tests done on snow were less accurate than the results on copper. Several factors may explain this discrepancy. The most apparent difference between single tests done on snow was the lack of control over the microstructure of each specimen. The specimens were taken from a natural snowpack and stored in a cold room for various times before being tested. Different storage times resulted in different microstructural properties which thereby changes the value of the equilibrium stress from sample to sample. In addition to this dissimilarity between samples, each sample probably had some degree of inhomogeneity due to the inherent layering of a snowpack as it is deposited upon the ground. Both of these factors would have an effect on the mechanical response of snow. Nonetheless, the results show that the equilibrium stress is an intrinsic property of snow as it sinters.

More involved testing procedures are required in order to apply the proposed theory to snow. Microstructural data must be obtained so that the equilibrium stress can be evaluated and the effect of inhomogeneities within the structure of snow should be studied. A more thorough study of the stress-strain relationships should be carried out and the constitutive equations for the mechanical response of snow might be generalized in order to include the effect of things such as particle shape and connectivity of the solid matrix; if necessary. The information gained from expanded research into these aspects of snow could lead to a better understanding of the processes which occur in a natural snowpack. If these processes are better understood, phenomena associated with snow (such as avalanches) might be more accurately predicted or controlled.

One aspect of this theory which was not considered in this thesis was the effect of spatial variations in the volume distribution function. Such variations are the source of the quantity termed the equilibrated stress vector. As indicated in the section entitled Balance Equations, such a quantity results in a center of compression or dilatation. Although an explicit constitutive equation for this quantity was not derived, it may be important in nonhomogeneous materials such as a natural snowpack. Its importance may be suggested by the following discussion.

Figure 19 shows a section of snow through which a skier had passed. The darker portions of the picture indicate a higher relative density due to the mechanical packing of the snow by the skier's weight. Adjacent to these dense regions are regions with a density even lower than the surrounding material. Some of these regions are hollows formed by drifting snow overlaying the ski tracks. However, most of these low density regions seems to be formed in the continuous medium directly adjoining the high density regions (see, for instance, the area labelled A in Figure 19). Close visual examination of the surface which was photographed indicated that the dense region may have contracted faster and pulled away from the unpacked region. If this is indeed the case, it may be argued that small anomalies in a natural snowpack may be enhanced by such a process. Although the above is speculative, investigation into this phenomena may produce some interesting results.

One other thing worth investigating may be the time-dependence of the microstructural parameters used in this theory. It may be possible to use theories about the mechanism of material transport during sintering [3,4] to develop an evolution equation for the average curvature of the void-solid interface. Likewise, the geometrical evolution of a sin-

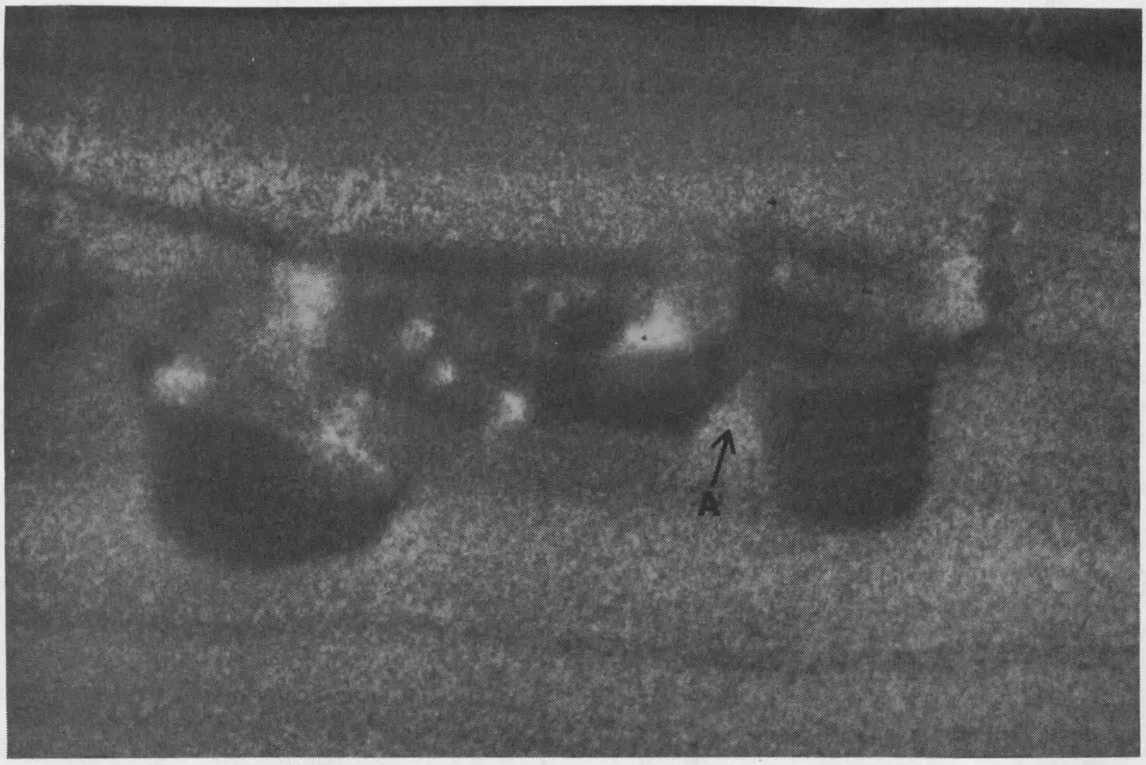

Figure 19. Cross-section of snowpack containing skier tracks.

tering material [1] may indicate how the specific surface area varies with time. If evolution equations could be formulated for these microstructural parameters, the entire history of a sinter body could be given in terms of certain initial conditions. Although formulation of such evolution equations would be a formidable task, it may be worth considering in future investigations into the sintering phenomena.

Based upon the results of this study, several conclusions can be drawn:

1. The continuum theory of granular materials provides a viable approach with which to describe the forces which promote the sintering of a porous material. These forces are a result of the thermodynamics of the free surface associated with a porous material.

2. The equilibrium stress in a sinter body is derived in terms of certain microstructural parameters. Specifically, this stress is given in terms of the surface tension acting upon the curved surfaces of the porous material and also in terms of the excess energy associated with the abundance of free surfaces contained within the material.
3. The stresses induced in copper as it sinters are described very well in terms of the proposed theory.
4. An approximate value for the equilibrium stress in natural snow was found by fitting the proposed theory to creep compression and creep tension tests run on snow. The value of the equilibrium stress appears to be significant relative to the loads normally found in a snowpack.
5. The existence of an equilibrium stress in snow suggests that the upper portions of a snowpack have a tension induced in them by the process of sintering. This tension would be in addition to any stresses generated by gravity.

REFERENCES CITED

REFERENCES CITED

1. Rhines, F. N. and Gregg, R. A. "Surface Tension and the Sintering Force in Copper." *Metallurgical Transactions,* 4 (1973): 1365-1374.

2. Schaler, A. J. "Seminar on the Kinetics of Sintering." *AIME Transactions,* 185 (1949): 796-813.

3. Kuczynski, G. C. "Self-Diffusion in Sintering of Metallic Particles." *AIME Transactions,* 185 (1949): 169-178.

4. Hobbs, P. V. and Mason, B. J. "The Sintering and Adhesion of Ice." *Philosophical Magazine,* 9 (1964): 181-197.

5. Lenel, F. V., Early, J. G. and Ansell, G. S. "The Material Transport Mechanism During Sintering of Copper-Powder Compacts at High Temperatures." *AIME Transactions,* 230 (1964): 1641-1650.

6. Exner, H. E., Petzow, G. and Wellner, P. "Problems in the Extension of Sintering Theories to Real Systems." in *Sintering and Related Phenomena,* pp. 351-362. Edited by G. C. Kuczynski. New York: Plenum Press, 1973.

7. Kuczynski, G. C. "Pore Shrinkage and Ostwald Ripening." in *Sintering and Related Phenomena,* pp. 217-224. Edited by G. C. Kuczynski. New York: Plenum Press, 1973.

8. Goodman, M. A. "A Continuum Theory for the Dynamical Behavior of Granular Materials." Ph.D. dissertation, Tulane University, 1970.

9. Goodman, M. A. and Cowin, S. C. "A Continuum Theory for Granular Materials." *Archive for Rational Mechanics and Analysis,* 44 (1972): 249-266.

10. Rudin, W. *Real and Complex Analysis.* New York: McGraw-Hill, 1966.

11. Nunziato, J. W. and Walsh, E. K. "On Ideal Multiphase Mixtures with Chemical Reactions and Diffusion." *Archive for Rational Mechanics and Analysis,* 73 (1980): 285-311.

12. Nunziato, J. W. and Cowin, S. C. "A Nonlinear Theory of Elastic Materials with Voids." *Archive for Rational Mechanics and Analysis,* 72 (1979): 175-201.

13. Nunziato, J. W., Passman, S. L. and Thomas, J. P. "Gravitational Flows of Granular Materials with Incompressible Grains." *Journal of Rheology,* 24 (1980): 395-420.

14. Langhaar, H. L. *Energy Methods in Applied Mechanics.* New York: John Wiley and and Sons, 1962.

15. Mindlin, R. D. "Micro-structure in Linear Elasticity." *Archive for Rational Mechanics and Analysis,* 16 (1964): 51-78.

16. Knowles, J. K. and Jakub, M. T. "Finite Dynamic Deformations of an Incompressible Elastic Medium Containing a Spherical Cavity." *Archive for Rational Mechanics and Analysis,* 18 (1965): 367-378.

17. Coleman, B. D. and Gurtin, M. E. "Thermodynamics and Internal State Variables." *Journal of Chemical Physics,* 47 (July, 1967): 597-613.

18. Rice, J. R. "Inelastic Constitutive Relations for Solids: An Internal Variable Theory and Its Application to Metal Plasticity." *Journal of the Mechanics and Physics of Solids,* 19 (1971): 433-455.

19. Gregg, R. A. "Analysis of the Sintering Force in Copper." Ph.D. dissertation, University of Florida, 1968.

20. Mellor, M. "Polar Snow—A Summary of Engineering Properties." in *Ice and Snow,* pp. 528-559. Edited by W. D. Kingery. Cambridge: M.I.T. Press, 1963.

21. Narita, H. "Mechanical Behavior and Structure of Snow Under Uniaxial Tensile Stress." *Journal of Glaciology,* 26 (1980): 275-282.

22. Fukue, M. *Mechanical Performance of Snow Under Loading.* Tokyo: Tokai University Press, 1979.

23. Shuttleworth, R. "The Surface Tension in Solids." *Physical Society Proceedings* (London), ser. A, 63 (1950): 444-457.

24. Malvern, L. *Introduction to the Mechanics of a Continuous Medium.* New Jersey: Prentice-Hall, 1969.

25. DeHoff, R. and Rhines, F., eds. *Quantitative Microscopy.* New York: McGraw-Hill, 1968.

26. Udin, H. "Grain Boundary Effect in Surface Tension Measurement." *AIME Transactions,* 191 (1951): 63.

27. Ralston, A. and Rabinowitz, P. *A First Course in Numerical Analysis.* 2nd ed. New York: McGraw-Hill, 1978.

28. Brent, R. P. "An Algorithm with Guaranteed Convergence for Finding a Zero of a Function." *Computer Journal,* 14 (1971): 422-425.

29. Brown, R. L., Lang, T. E. and St. Lawrence, W. Unpublished data, 1973.

APPENDICES

APPENDIX A

APPENDIX A

The solution to the copper sintering problem can be derived as follows. First, since the problem consists of a unaxial stress test on a cylindrical specimen, symmetry arguments require that all shear terms in the stress and strain tensors be zero. The nonzero stress and strain components will be denoted as follows (cylindrical coordinates are used):

$$\begin{aligned} t_{rr} &= t_1 & \epsilon_{rr} &= \partial u/\partial r \\ t_{\theta\theta} &= t_2 & \epsilon_{\theta\theta} &= u/r \\ t_{zz} &= t_3 & \epsilon_{zz} &= w \end{aligned} \tag{A.1}$$

where u is the radial displacement.

Now consider the constitutive equations:

$$\begin{aligned} \operatorname{tr} \underset{\sim}{t} + A_1 \operatorname{tr} \dot{\underset{\sim}{t}} &= \nu A_2 \operatorname{tr} \underset{\sim}{\epsilon} + \nu A_3 \operatorname{tr} \dot{\underset{\sim}{\epsilon}} - 3\theta \\ \underset{\sim}{t}' + A_4 \dot{\underset{\sim}{t}}' &= \nu A_5 \underset{\sim}{\epsilon}' + \nu A_6 \dot{\underset{\sim}{\epsilon}}' \end{aligned} \tag{A.2}$$

Equations (A.1) and (A.2) result in a system of partial differential equations. Assuming the solution is separable, the Laplace Transform can be used to separate out the time dependence so that the spatial dependence can be solved for. The resulting equations can then be inverted to reintroduce the time-dependence.

Before taking the transforms of Equations (A.2), it should be noted that there are four unknowns: the three normal stresses and the radial displacement (the axial strain can be evaluated and is assumed constant throughout the test). Equations (A.2) represent three independent equations since of the three equations represented by the second of Equations (A.2), only two are independent. The fourth equation necessary for a complete set is the only non-trivial equation of motion (neglecting accelerations and body forces):

$$\partial t_1/\partial r + \frac{1}{r}(t_1 - t_2) = 0 \qquad (A.3)$$

In order to take the transforms of Equations (A.2) and (A.3), the initial conditions on the stress and strain must be known. These conditions are the initial elastic deformation and can be derived by assuming that at time $t = 0^-$, the material is in an unstressed, unstrained configuration. By applying some stress state ($\underset{\sim}{t}^\circ$) at $t = 0$ and integrating Equations (A.2) from $t = 0^-$ to $t = 0^+$ (assuming at most finite discontinuities in the stress, the strain, and θ across this interval) results in the following relationships between the initial stress and strain:

$$A_1 \operatorname{tr} \underset{\sim}{t}^\circ = \nu A_3 \operatorname{tr} \underset{\sim}{\epsilon}^\circ$$

$$A_4 \underset{\sim}{t}'^\circ = \nu A_6 \underset{\sim}{\epsilon}'^\circ \qquad (A.4)$$

The transforms of Equations (A.2) and (A.3) can now be evaluated. By using Equations (A.4) and assuming ν and θ are constant for the duration of the test, the following system of equations is produced:

$$\bar{t}_1 + \bar{t}_2 + \bar{t}_3 = f_1(\partial \bar{u}/\partial r + \bar{u}/r + \frac{w^\circ}{s}) - f_2$$

$$2\bar{t}_1 - \bar{t}_2 - \bar{t}_3 = f_3(2\partial \bar{u}/\partial r - \bar{u}/r - \frac{w^\circ}{s})$$

$$2\bar{t}_2 - \bar{t}_1 - \bar{t}_3 = f_3(2\bar{u}/r - \partial \bar{u}/\partial r - \frac{w^\circ}{s})$$

$$\partial \bar{t}_1/\partial r + \frac{1}{r}(\bar{t}_1 - \bar{t}_2) = 0 \qquad (A.5)$$

where the overbars indicate the transforms of the variables, s is the transform variable, w° is the initial axial strain which is assumed fixed, and

$$f_1 = \frac{\nu A_2 + \nu A_3 s}{1 + A_1 s}$$

$$f_2 = \frac{3\theta}{s(1 + A_1 s)} \tag{A.6}$$

$$f_3 = \frac{\nu A_5 + \nu A_6 s}{1 + A_4 s}$$

Manipulation of Equations (A.5) yields the following differential equation for $\bar{u}$:

$$\frac{\partial^2 \bar{u}}{\partial r^2} + \frac{1}{r}\frac{\partial \bar{u}}{\partial r} - \frac{\bar{u}}{r^2} = 0 \tag{A.7}$$

The solution of the above yields

$$\bar{u} = C_1 r + C_2 \frac{1}{r} \tag{A.8}$$

Since the displacement cannot be infinite at $r = 0$, $C_2 = 0$. The constant C_1 is determined by using the boundary condition that the lateral surface is traction free. This condition implies that t_1 and t_2 are zero everywhere and that

$$C_1 = \frac{f_2 + (f_3 - f_1)\frac{w^\circ}{s}}{2f_1 + f_3} \tag{A.9}$$

Using this expression for C_1 results in the following expressions for the transforms of the radial displacement and the axial stress:

$$\frac{\bar{u}}{r} = \frac{f_2 + (f_3 - f_1)\frac{w^\circ}{s}}{2f_1 + f_3}$$

$$\bar{t}_3 = \frac{f_3\,(3f_1 \frac{w^\circ}{s} - f_2)}{2f_1 + f_3} \tag{A.10}$$

The final forms for the radial displacement and the axial stress can now be determined. Inverting Equations (A.10) results in the following:

$$\begin{aligned}
\frac{u(r,t)}{r} &= \frac{\alpha_1}{(\lambda_1 - \lambda_2)}\left(\lambda_1 e^{-\lambda_1 t} - \lambda_2 e^{-\lambda_2 t}\right) \\
&+ \frac{\alpha_2}{(\lambda_1 - \lambda_2)}\left(e^{-\lambda_2 t} - e^{-\lambda_1 t}\right) \\
&+ \frac{\alpha_3}{\lambda_1 \lambda_2 (\lambda_1 - \lambda_2)}\left(\lambda_1 - \lambda_2 + \lambda_2 e^{-\lambda_1 t} - \lambda_1 e^{-\lambda_2 t}\right) \\
t_3 &= \frac{\beta_1}{(\lambda_1 - \lambda_2)}\left(\lambda_1 e^{-\lambda_1 t} - \lambda_2 e^{-\lambda_2 t}\right) \\
&+ \frac{\beta_2}{\lambda_1 - \lambda_2}\left(e^{-\lambda_2 t} - e^{-\lambda_1 t}\right) \\
&+ \frac{\beta_3}{\lambda_1 \lambda_2 (\lambda_1 - \lambda_2)}\left(\lambda_1 - \lambda_2 + \lambda_2 e^{-\lambda_1 t} - \lambda_1 e^{-\lambda_2 t}\right)
\end{aligned} \tag{A.11}$$

where

$$\alpha_1 = \frac{w^\circ (A_1 A_6 - A_3 A_4)}{2A_3 A_4 + A_1 A_6}$$

$$\alpha_2 = \frac{w^\circ (A_6 + A_1 A_5 - A_3 - A_2 A_4) + \dfrac{3\theta A_4}{\nu}}{2A_3 A_4 + A_1 A_6}$$

$$\alpha_3 = \frac{w^\circ (A_5 - A_2) + \dfrac{3\theta}{\nu}}{2A_3 A_4 + A_1 A_6}$$

$$\beta_1 = \frac{3\nu w^\circ A_3 A_6}{2A_3 A_4 + A_1 A_6}$$

$$\beta_2 = \frac{3\nu w^\circ (A_2 A_6 + A_3 A_5) - 3\theta A_6}{2A_3 A_4 + A_1 A_6}$$

$$\beta_3 = \frac{3A_5 (\nu w^\circ A_2 - \theta)}{2A_3 A_4 + A_1 A_6}$$

$$Q_1 = \frac{2A_3 + 2A_2 A_4 + A_6 + A_1 A_5}{2A_3 A_4 + A_1 A_6}$$

$$Q_2 = \frac{2A_2 + A_5}{2A_3 A_4 + A_1 A_6}$$

$$\lambda_1 = \frac{Q_1 + \sqrt{Q_1^2 - 4Q_2}}{2} \tag{A.12}$$

$$\lambda_2 = \frac{Q_1 - \sqrt{Q_1^2 - 4Q_2}}{2}$$

Noting that at $t = 0$, $t_3 = t_3^\circ$, an expression for the initial axial strain can be derived:

$$w^\circ = \frac{t_3^\circ (2A_3 A_4 + A_1 A_6)}{3\nu A_3 A_6} \tag{A.13}$$

Equations (A.11) give the radial displacement and the axial stress as functions of time. As was noted in the section entitled An Application to Copper, the time at which the stress is evaluated is the time at which the stress rate is zero. The equation used to find this time is

$$\begin{aligned} \dot{t}_3 = \frac{1}{\lambda_1 - \lambda_2} [& \beta_1 (\lambda_2^2 e^{-\lambda_2 t} - \lambda_1^2 e^{-\lambda_1 t}) \\ & + \beta_2 (\lambda_1 e^{-\lambda_1 t} - \lambda_2 e^{-\lambda_2 t}) \\ & + \beta_3 (e^{-\lambda_2 t} - e^{-\lambda_1 t})] \end{aligned} \tag{A.14}$$

APPENDIX B

APPENDIX B

The solution of the problem used to analyze the data for snow is found by finding the solution to a unaxial, stress-controlled test. Since the tests were performed on rectangular prisms cut from snow samples and no shears were introduced by the test procedure, the nonzero components of the stress and strain tensors can be denoted by

$$\begin{array}{ll} t_{xx} = t_1 & \epsilon_{xx} = \epsilon_1 \\ t_{yy} = t_2 & \epsilon_{yy} = \epsilon_2 \\ t_{zz} = t_3 & \epsilon_{zz} = \epsilon_3 \end{array} \qquad \text{(B.1)}$$

The postulated constitutive equations are

$$\begin{aligned} \mathrm{tr}\,\underset{\sim}{t} + A_1\,\mathrm{tr}\,\underset{\sim}{\dot{t}} &= \nu A_2\,\mathrm{tr}\,\underset{\sim}{\epsilon} + \nu A_3\,\mathrm{tr}\,\underset{\sim}{\dot{\epsilon}} - 3\theta \\ \underset{\sim}{t}' + A_4\,\underset{\sim}{\dot{t}}' &= \nu A_5\,\underset{\sim}{\epsilon}' + \nu A_6\,\underset{\sim}{\dot{\epsilon}}' \end{aligned} \qquad \text{(B.2)}$$

In this test, an axial load ($t_3°$) was applied to an initially unstressed, unstrained specimen. This load remained constant throughout the duration of the test and the lateral surfaces were kept traction free. The lateral and axial strains were then measured as functions of time.

Using the equations of motion (neglecting accelerations and body forces) in conjunction with the boundary conditions of traction free lateral surface, it can be shown that the stresses t_1 and t_2 must be zero everywhere within the material. Also, the initial elastic response of the material to the applied load is given by Equations (A.4). These two results require the Laplace Transforms of Equations (B.2) to be of the following form:

$$\bar{\epsilon}_1 + \bar{\epsilon}_2 + \bar{\epsilon}_3 = g_1 \, t_3^\circ + g_2$$

$$2\bar{\epsilon}_1 - \bar{\epsilon}_2 - \bar{\epsilon}_3 = g_3 \, t_3^\circ \qquad \text{(B.3)}$$

$$2\bar{\epsilon}_2 - \bar{\epsilon}_1 - \bar{\epsilon}_3 = g_3 \, t_3^\circ$$

where

$$g_1 = \frac{1 + A_1 s}{s(\nu A_2 + \nu A_3 s)}$$

$$g_2 = \frac{3\theta}{s(\nu A_2 + \nu A_3 s)} \qquad \text{(B.4)}$$

$$g_3 = \frac{1 + A_4 s}{s(\nu A_5 + \nu A_6 s)}$$

In the above, the overbars indicate the transforms of the given variables, s is the transform variable, and ν and θ have been assumed constant throughout the test.

Combining the last two of Equations (B.3) yields

$$\bar{\epsilon}_1 = \bar{\epsilon}_2 \qquad \text{(B.5)}$$

Thus, Equations (B.3) can be reduced to the following two equations:

$$\bar{\epsilon}_V = \bar{\epsilon}_3 + 2\bar{\epsilon}_1 = g_1 \, t_3^\circ + g_2$$

$$\bar{\epsilon}_d = \bar{\epsilon}_3 - \bar{\epsilon}_1 = g_3 \, t_3^\circ \qquad \text{(B.6)}$$

where $\bar{\epsilon}_V$ denotes the transform of the volumetric strain and $\bar{\epsilon}_d$ denotes the transform of the deviatoric strain. Inverting Equations (B.6) produces the following results:

$$\epsilon_V = \frac{t_3^\circ + 3\theta}{\nu A_2} \left[1 - \exp\left(- \frac{A_2 t}{A_3}\right)\right]$$

$$+ \frac{t_3^\circ A_1}{\nu A_3} \exp\left(- \frac{A_2 t}{A_3}\right)$$

$$\epsilon_d = \frac{t_3{}^{\circ}}{\nu A_5}\left[1 - \exp\left(-\frac{A_5 t}{A_6}\right)\right] + \frac{t_3{}^{\circ} A_4}{\nu A_6}\exp\left(-\frac{A_5 t}{A_6}\right) \qquad \text{(B.7)}$$

MONTANA STATE UNIVERSITY LIBRARIES
stks N378.R2715@Theses RL
A continuum approach to sintering kineti
3 1762 00150777 9

MAIN LIB.
N378
R2715
cop.2