Chapter 16: Elastic Solids

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16.1 INTRODUCTION

As most of us were taught in grade school, solids and liquids represent distinct states of matter that are most clearly differentiated by their response to gravity (that is, by their mechanical properties). A liquid that is placed in a container conforms to the shape of the container while a solid does not. The liquid behaves as it does because its mechanical energy depends only on its volume. Its shape is irrelevant. The solid behaves very differently because its energy depends on shape as well as volume. The solid resists forces that act to change its shape. If the force is not too great, it deforms only slightly, and reverts to its original shape as soon as the force is removed. This behavior is called elastic, and the materials that exhibit it are called elastic solids.

A solid responds elastically to forces that are less than its yield strength. When the applied force exceeds the yield strength the solid deforms plastically, and permanently changes its shape. The transition from elastic to plastic behavior is difficult to treat exactly because the effective yield strength depends on the exact starting state of the material, the nature of the loading, the temperature and the time over which the load is applied. Plastic deformation is fluid-like in the sense that after the load is removed the plastically deformed solid is left in a new configuration that has nearly the same energy as the original one; the only change is the relatively small energy associated with the defects and residual stresses that may be introduced by the mechanism of plasticity. Plastic deformation differs from fluid flow in that it almost always has an elastic deformation associated with it. When the deforming load is removed a solid does not retain the shape it had under load, but undergoes a small, spontaneous elastic relaxation that recovers some of the shape change.

This behavior suggests that the equilibrium states of a deformable solid should be described in terms of two simultaneous configurations: a reference configuration that describes the size and shape of the body in the absence of mechanical load, and a deformation that describes the difference between the reference configuration and the actual configuration that is in equilibrium with the applied mechanical forces. Plastic deformation changes the reference state; elastic deformation changes the equilibrium configuration for a fixed reference state. Plastic deformation is an inherently non-equilibrium phenomenon. If we neglect the energy associated with residual defects, which are themselves non-equilibrium features, states that are connected by plastic deformation have the same thermodynamic content; the solid retains the configuration in which it is left after plastic deformation. Elastic deformation, on the other hand, is the natural equilibrium response of a solid to the imposition of a mechanical load, and is uniquely determined by the temperature, composition and mechanical forces.

The need to utilize two distinct configurations to specify the state of a solid adds considerable formal complexity to the theory of deformation, as one can readily verify by opening any modern text on continuum mechanics. Fortunately, a great many of the important problems in materials science (and the vast majority of the problems that have
been solved) can be treated in a model in which the reference state is well-defined and the deformation from the reference state is small. In this case we can use the much simpler formalism of infinitesimal or linear elasticity. There are, of course, important engineering materials, such as rubber elastomers, that are capable of very large elastic strains. A well-developed theory of finite strain exists to treat these materials, but we shall not consider it here.

16.2 THE ELASTIC STRAIN

To describe the difference between the actual configuration of a solid and its reference state, we define a second-order tensor, the elastic strain, in the following way.

16.2.1 The displacement vector

Let the reference state of a solid fill the volume \( V^0 \). Each elementary volume of the reference state can be designated by its vector position, \( \mathbf{R} \), in a Cartesian coordinate frame. A reconfiguration of the body is accomplished by giving each elementary volume a vector displacement, \( \mathbf{u}(\mathbf{R}) \), that carries it to the position

\[
\mathbf{r} = \mathbf{R} + \mathbf{u}(\mathbf{R})
\]

We assume that the displacement is continuous in the sense that two volumes that are neighbors in the reference configuration remain neighbors in the deformed state. For this to be true the displacement, \( \mathbf{u}(\mathbf{R}) \), must be continuous vector field over \( V^0 \), and, as can be shown from the conditions of compatibility that are established in the theory of elasticity, must be three times differentiable.

The displacement, \( \mathbf{u} \), is separable into three parts: a rigid translation that causes the same displacement of every point, \( \mathbf{R} \), in \( V^0 \); a rigid rotation that simply rotates every \( \mathbf{R} \) in \( V^0 \) about some axis; and a displacement that displaces adjacent parts of the material with respect to one another. Only the deformation affects the thermodynamic state of the body.

16.2.2 The deformation gradient

To define the deformation consider two elementary volumes in \( V^0 \) that are neighbors in the sense that they occupy the positions \( \mathbf{R} \) and \( \mathbf{R} + \mathbf{dR} \). Their separation after the displacement is

\[
\mathbf{dR} = \mathbf{dR} + \mathbf{u}((\mathbf{R} + \mathbf{dR}) - \mathbf{u}(\mathbf{R})) = \mathbf{dR} + \nabla \mathbf{u} \cdot \mathbf{dR}
\]

or, in Cartesian tensor notation,

\[
\mathbf{dR}_i = (\delta_{ij} + u_{ij}) \mathbf{dR}_j
\]
where the deformation gradient, $\nabla \mathbf{u}$, is a second order tensor whose components are the partial derivatives of the components of $\mathbf{u}$ taken with respect to the coordinates of the reference configuration,

$$u_{ij} = \frac{\partial u_i}{\partial R_j}$$  

16.4

It is useful to separate the tensor $\nabla \mathbf{u} = u_{ij}$ into its symmetric and antisymmetric parts:

$$u_{ij} = \varepsilon_{ij} + \omega_{ij}$$  

16.5

where

$$\varepsilon_{ij} = \frac{1}{2} \left[ u_{ij} + u_{ji} \right] = \varepsilon_{ji}$$  

16.6

$$\omega_{ij} = \frac{1}{2} \left[ u_{ij} - u_{ji} \right] = -\omega_{ji}$$  

16.7

### 16.2.3 The Lagrangian strain tensor

The relative vector displacement of neighboring points in $V^0$ depends on both the rotation, which changes only the angle of the vector, and the deformation, which changes its magnitude. We isolate the deformation by considering the change in the squared element of length, $|d\mathbf{R}|^2$, between neighboring points, and use it to define the Lagrangian strain tensor, $\mathbf{E}$, by the relation

$$|d\mathbf{r}|^2 - |d\mathbf{R}|^2 = 2\mathbf{E} : d\mathbf{R} d\mathbf{R} = 2E_{ij} dR_i dR_j$$  

16.8

The elements, $E_{ij}$, of the strain tensor are related to the deformation gradients by the equation

$$E_{ij} = \frac{1}{2} \left[ u_{ij} + u_{ji} + u_{ik}u_{kj} \right]$$  

16.9

The Lagrangian strain is a second-order tensor field over $V^0$ that specifies the deformation of the neighborhood of any point, $\mathbf{R}$. The Lagrangian strain is a symmetric tensor, but depends on both the symmetric and antisymmetric parts of the deformation gradient, $\nabla \mathbf{u}$.

### 16.2.4 The infinitesimal strain

If the components of the deformation gradient are small their products can be neglected and the strain is, by equation 16.9,

$$E_{ij} = \varepsilon_{ij}$$  

16.10
The symmetric second-order tensor, \( \varepsilon_{ij} \), is called the *infinitesimal* or *linear strain*, or, more often, is simply called the *strain*, since it is the measure of the strain that is actually used in most applications. Like the Lagrangian strain, the infinitesimal strain, \( \varepsilon(\mathbf{R}) \), is a tensor field that is defined on the reference configuration.

The infinitesimal strain has several useful properties. First, *infinitesimal strains are additive*. If a solid is given successive displacements, \( \mathbf{u}_1, \mathbf{u}_2, \ldots \) the total displacement is

\[
\mathbf{u} = \mathbf{u}_1 + \mathbf{u}_2 + \mathbf{u}_3 + \ldots
\]

the deformation gradient is

\[
\nabla \mathbf{u} = \nabla \mathbf{u}_1 + \nabla \mathbf{u}_2 + \nabla \mathbf{u}_3 + \ldots
\]

and the strain is

\[
\varepsilon = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \ldots
\]

and is equal to the Lagrangian strain provided that the magnitude of the net deformation gradient, \( \nabla \mathbf{u} \), is small.

Second, since the strain tensor is symmetric it can be diagonalized. Its diagonal form is

\[
\varepsilon = \varepsilon_1 \mathbf{e}_1 \mathbf{e}_1^0 + \varepsilon_2 \mathbf{e}_2 \mathbf{e}_2^0 + \varepsilon_3 \mathbf{e}_3 \mathbf{e}_3^0
\]

where the \( \varepsilon_i \) are the three *principle strains* and the \( \mathbf{e}_i^0 \) are the three orthogonal *principle axes* of the strain. It follows from equation 16.14 that an arbitrary infinitesimal strain is equivalent to a stretch along each of three orthogonal directions, the principle axes of the strain.

Third, *the trace of the strain tensor is the fractional volume change due to the strain*. To prove this note that the volume element in the reference configuration of the solid is

\[
dV^0 = d\mathbf{R}_1 \cdot (d\mathbf{R}_2 \times d\mathbf{R}_3) = d\mathbf{R}_1 d\mathbf{R}_2 d\mathbf{R}_3
\]

where \( d\mathbf{R}_i \) is a differential vector along the \( i \)th axis of the reference configuration and we have used the fact that the coordinates of the reference configuration are Cartesian. The volume element in the deformed state is

\[
dV = d\mathbf{r}_1 \cdot (d\mathbf{r}_2 \times d\mathbf{r}_3)
\]
\[\delta V = \int_{S^0} (u \cdot n) \, dS = \int_{S^0} u_{i} n_{i} \, dS \]  

where \( n \) is the unit outward normal to the surface element \( dS \) and the integral is taken over the boundary, \( S^0 \), of \( V^0 \). Using the divergence theorem,

\[\delta V = \int_{S^0} u_{i} n_{i} \, dS = \int_{V^0} u_{i|i} dV \]

\[= \int_{V^0} \varepsilon_{ii} \, dV \]  

Equation 16.18 follows from 16.20 if we recognize that the latter holds for any arbitrary subvolume of \( V^0 \). The subvolume may be chosen small enough that \( \varepsilon_{ii} \) is constant within it.

### 16.2.5 The infinitesimal rotation

When the displacement gradient, \( \nabla u(R) \), is infinitesimal its antisymmetric part, \( \omega \), can be shown to be an infinitesimal rotation of the material in the neighborhood of \( R \). Let a rigid body be rotated through a differential angle, \( d\theta \), about an axis, \( a \), that can be taken to pass through the origin of coordinates without loss of generality. The resulting vector displacement of the material at the vector position, \( R' \), is

\[u(R') = (a \times R') \, d\theta \]  

where \( a \) is a unit vector along the axis of rotation. In component form this equation reads
\[ u_i = e_{ijk} a_j R_k \theta \]  
\[ \text{16.22} \]

where \( e_{ijk} \) is the permutation tensor (= 1 if \( ijk \) are an even permutation of 123, -1 if \( ijk \) are an odd permutation of 123, 0 if any two of the \( ijk \) are the same). The displacement gradients at \( R^t \) are, then

\[ u_{ijk} = e_{ijk} a_j d\theta = \omega_{ijk} \]  
\[ \text{16.23} \]
since the symmetry of the permutation tensor with respect to an interchange of \( i \) and \( k \) has the consequence that the components \( u_{ijk} \) are antisymmetric. 

Hence an infinitesimal rigid body rotation is represented by the antisymmetric tensor, \( \omega \). The converse is also true. Given any set of three small numbers that are the components of an antisymmetric tensor equation 16.23 can be inverted to determine an axis and angle of rotation.

It follows that when the deformation gradients are small the change in the differential vector, \( dR \), that connects neighboring points in the solid is

\[ dr - dR = (\epsilon + \omega)\cdot dR \]  
\[ \text{16.24} \]

which is the sum of a strain and a rotation. Note, however, that this decomposition is only possible when the strain tensor is infinitesimal; otherwise the strain is given by the Lagrangian tensor, 16.9, whose value depends on both the symmetric and antisymmetric parts of \( \nabla u \).

16.2.6 Physical meaning of the strain components

The diagonal strains are the fractional elongations of the material in the direction of its three coordinate axes. The diagonal strain \( \epsilon_{11} \), for example, changes the differential length in the direction \( e_1 \) by the amount

\[ dr_1 - dR_1 = e_{11} dR_1 \]  
\[ \text{16.25} \]

Hence

\[ \epsilon_{11} = \frac{\delta(dR_1)}{dR_1} \]  
\[ \text{16.26} \]
is the fractional elongation along the axis \( e_1 \) when only this strain is imposed. Since a similar relation holds for each of the other directions, the three diagonal components of \( \epsilon \) have the effect of distorting a unit cube into a rectangular parallelepiped whose \( i \)th face is displaced normal to itself by the fractional amount \( \epsilon_{ii} \).
The *off-diagonal* or *shear strains* determine the change in angle between initially perpendicular lines along the coordinate axes. Let the strain $\varepsilon_{12} = \varepsilon_{21}$ be imposed. Differential vectors $d\mathbf{R}_1$ and $d\mathbf{R}_2$ in the directions $\mathbf{e}_1$ and $\mathbf{e}_2$ are changed into the vectors

$$d\mathbf{r}_i = (1 + \varepsilon) d\mathbf{R}_i \quad (i = 1, 2)$$

16.27

The vectors $d\mathbf{R}_i$ are originally orthogonal; the strain rotates them toward one another by the angle $\gamma_{12}$, where $\gamma_{12}$ is determined by the equation

$$d\mathbf{r}_1 \cdot d\mathbf{r}_2 = |d\mathbf{r}_1||d\mathbf{r}_2| \cos \left[ \frac{\pi}{2} - \gamma_{12} \right] = |d\mathbf{r}_1||d\mathbf{r}_2| \sin(\gamma_{12})$$

$$\approx |d\mathbf{R}_1||d\mathbf{R}_2| \gamma_{12}$$

16.28

where equation 16.28 is accurate to within terms of order $(\varepsilon_{12})^2$. Using equation 16.27,

$$\gamma_{12} = \frac{d\mathbf{r}_1 \cdot d\mathbf{r}_2}{|d\mathbf{r}_1||d\mathbf{r}_2|} = (\varepsilon_{12} + \varepsilon_{21}) = 2\varepsilon_{12}$$

16.29

That is, the imposition of the off-diagonal strain, $\varepsilon_{12} = \varepsilon_{21}$, causes vectors in the directions $\mathbf{e}_1$ and $\mathbf{e}_2$ to rotate toward one another through the angle $\gamma_{12} = 2\varepsilon_{12}$. This strain is called a *shear*. It maintains the length of a vector (to within terms of order $\varepsilon^2$) and, therefore, does not change the volume. But it changes the shape of the body by changing the relative orientations of vectors in the reference state.

It is common in elementary mechanics to use the total angle, $\gamma_{ij}$, rather than the strain component, $\varepsilon_{ij}$, as a measure of the shear. This definition has the advantage that the $\gamma_{ij}$ are easy to visualize physically, but has the greater disadvantage that the $\gamma_{ij}$ do not form a tensor with the diagonal components, $\varepsilon_{ii}$, and obey cumbersome transformation laws when the coordinates are changed.

### 16.2.7 The deviatoric strain

Since the difference between a solid and a fluid is that the former resists changes in shape while the latter does not, it is useful to define a strain tensor that measures the shape change only. This is the *deviatoric strain*, $\varepsilon^d$, whose elements are

$$\frac{d}{d} \varepsilon_{ij} = \varepsilon_{ij} - \frac{\varepsilon_{ii}}{3} \delta_{ij}$$

16.30

that is, its diagonal elements are the diagonal elements of the strain tensor less one-third its trace. The trace of the deviatoric strain is

$$\text{Tr}(\varepsilon^d) = \varepsilon_{ii} = 0$$

16.31
which confirms that the deviatoric strain imposes a shape change at constant volume. Hence the deviatoric strain is a pure shear.

16.3 Stress and Mechanical Work

To define and measure the internal energy of an elastic solid it is necessary to find the mechanical work done on the solid in an arbitrary displacement, \( \mathbf{u}(\mathbf{R}) \). The work is the product of the displacement and its associated mechanical force. From an experimental point of view there are two types of mechanical forces that can be applied to a solid. They are called body forces and contact forces.

16.3.1 The body force

A body force is one that acts directly on the material elements of a body. The body forces that are most often important represent the action of external fields, such as the gravitational field that acts independently on each element of mass and the electric field that acts on each charged particle. We shall ordinarily use the symbol \( \mathbf{b} \) for the body force per unit mass (or per mole if the potential is so defined) where, if the body force is determined by the scalar field, \( \phi(\mathbf{r}) \),

\[
\mathbf{b} = -\nabla\phi \quad 16.32
\]

Since the scalar field, \( \phi(\mathbf{r}) \), is a field over space the body force is a vector field, \( \mathbf{b}(\mathbf{r}) \). Defining the force per unit volume,

\[
\mathbf{f} = \rho \mathbf{b} \quad 16.33
\]

where \( \rho \) is the density, the total force on a body of volume, \( V \), is

\[
\mathbf{F} = \int_V \rho \mathbf{b} \, dV = \int_V \mathbf{f} \, dV \quad 16.34
\]

16.3.2 Contact forces: traction and stress

A contact force is a force that is applied to the surface of the body, and transmitted to the interior because the elements of the body interact with one another. A contact force is usually imposed by attaching the body to a second body that exerts a force on its boundary. Examples include a tensile testing machine, whose grips are attached to the sample and pulled, a fluid whose internal pressure presses on the surface of any body that is immersed in it, and the deformed body itself, since any volume element in the interior of a deformed body experiences a force on its boundary that acts to deform it to conform with the state of the material outside.
The contact force is represented by the vector traction, \( \mathbf{T} \), that acts on the element, \( dS \), of the surface of the body. The traction is a vector field, \( \mathbf{T}(\mathbf{r}) \), over the surface. The total contact force on a body that has surface, \( S \), is

\[
\mathbf{F} = \int_S \mathbf{T} \, dS
\]

In a continuous system the traction, \( T \, dS \), on an element of surface, \( dS \), represents the total force that the material outside the surface exerts on the material inside it. Consequently the traction depends on the orientation of the surface element as well as on its location. To account for the change in the traction with the orientation of the surface element, let \( T_i(\mathbf{r}) \) be the traction on a differential element of surface, \( dS_i \), that is perpendicular to the \( i \)th coordinate at the position \( \mathbf{r} \). Then the total traction on a surface element, \( dS \), at \( \mathbf{r} \) is the sum

\[
T(\mathbf{r}) \, dS = T_i(\mathbf{r}) \, dS_i = T_i(\mathbf{r})n_i \, dS
\]

where \( \mathbf{n} \) is the normal vector to the surface element, \( dS \), and \( dS_i = n_idS \) is the projection of \( dS \) perpendicular to the \( i \)th coordinate. Since \( \mathbf{T} \) is a vector it can be written

\[
T_i = \sigma_{ij} \mathbf{e}_j
\]

where the stress, \( \sigma_{ij} \), is the \( j \)th component of the traction on an element of surface perpendicular to the \( i \)th coordinate. Using equation 16.37, equation 16.36 can be written in the form

\[
T_j \, dS = \sigma_{ji} n_i \, dS
\]

where \( T_j \) is the \( j \)th component of the traction, \( \mathbf{T} \). Since both \( \mathbf{T} \) and \( \mathbf{n} \) are vectors, equation 16.38 shows that the nine stresses, \( \sigma_{ij} \), are the components of a second-order tensor, the stress tensor, \( \sigma \), which is determined by the equation

\[
\mathbf{T} = \sigma \cdot \mathbf{n}
\]

Since a traction (which may be zero) acts on a surface element in any orientation at any location within the material, the stress is a tensor field, \( \sigma(\mathbf{r}) \). If the material is continuous \( \sigma(\mathbf{r}) \) will ordinarily be continuous as well. Since the traction is ordinarily taken to be positive when it does positive work in an expansion of the body (that is, when it acts in the direction of \( \mathbf{n} \)) the stress component is positive when it acts to displace the surface element, \( dS \), in the outward direction.

The vector traction, \( \mathbf{T} \), is the simplest form of the contact force. The second-order stress field that it defines, \( \sigma(\mathbf{r}) \), is sufficient to describe the mechanics of most of the systems of interest in materials science. However, there are materials whose internal constitution or inhomogeneity is such that the contact interaction between the material on the two sides of the surface element, \( dS \), includes moments of the force that do not vanish.
when dS is made small. Examples include materials made of rigid, rod-shaped elements, such as rigid organic molecules, where the contact interaction includes force moments on the molecules, and materials that maintain strong concentration or density gradients, where the contact interaction includes locally inhomogeneous forces that arise form the material gradients. In such cases the contact force cannot be represented by a single vector and the stress field that represents the contact force must include third- and higher-order tensor stresses. Such materials are called multipolar media in continuum mechanics. We shall not treat them here.

16.3.3 Mechanical work

Let a body be subject to a body force, \( \mathbf{f}(\mathbf{r}) \), and a traction, \( \mathbf{T}(\mathbf{r}) \), that acts on its boundary. Let it undergo a small displacement, \( \mathbf{u}(\mathbf{R}) \). The total work done by the system of forces during the displacement is

\[
\delta W = \int_V \mathbf{f} \cdot \mathbf{u} \, dV + \int_S \mathbf{T} \cdot \mathbf{u} \, dS
\]

\[
= \int_V \mathbf{f} \cdot \mathbf{u} \, dV + \int_S (\sigma \cdot \mathbf{n}) \cdot \mathbf{u} \, dS \quad 16.40
\]

By the divergence theorem

\[
\int_S (\sigma \cdot \mathbf{n}) \cdot \mathbf{u} \, dS = \int_V \nabla \cdot (\mathbf{u} \cdot \sigma) \, dV = \int_V [\sigma_{ij} u_{ij}] \, dV
\]

\[
= \int_V \sigma_{ij} u_{ij} \, dV + \int_V \sigma_{ij} u_{ij} \, dV \quad 16.41
\]

From which it follows that

\[
\delta W = \int_V \{ \rho \dot{b}_i + \sigma_{ij} u_{ij} \} \, dV + \int_V \sigma_{ij} u_{ij} \, dV \quad 16.42
\]

The integral in equation 16.42 is taken over the actual configuration of the body, which differs from the reference configuration if the body is already strained. However, if both the initial strain and the subsequent displacement gradients are small then, to the accuracy of small correction terms

\[
\mathbf{u}_{ij} = \frac{\partial u_i}{\partial R_j} = \frac{\partial u_i}{\partial (\delta_{jk} + \varepsilon_{jk}) \partial R_k} \approx \frac{\partial u_i}{\partial R_j} - \varepsilon_{jk} \frac{\partial u_i}{\partial R_k}
\]

\[
\approx \frac{\partial u_i}{\partial R_j} \quad 16.43
\]

and
\[ dV = \begin{bmatrix} \frac{dV}{dV^0} \end{bmatrix} dV^0 = (1 + \epsilon_{ij}) dV^0 \]

\[ \equiv dV^0 \]

from which it follows that the deformation gradient can be taken with respect to the initial state and the integrals taken over the reference configuration of the body. Note that this result only applies when the elastic strain is small.

The conditions of mechanical equilibrium for an elastic medium (Cauchy's First and Second Laws) follow from equation 16.42 on imposing the requirement that the work done be invariant to a rigid translation or rotation of the coordinate frame (Gallilean invariance). However, we shall obtain them in an alternate way that also identifies the constitutive coordinates for the elastic solid.

### 16.4 COORDINATES AND CONDITIONS OF EQUILIBRIUM

An elastic solid was implicitly defined in the preceding sections as a solid whose mechanical interaction with its environment is described by a body force, \( \mathbf{b}(\mathbf{r}) \), that acts on its interior and a traction, \( \mathbf{T}(\mathbf{r}) \), that acts on its boundary, and which undergoes a small, recoverable deformation under the action of these forces. This is a sufficient mechanical definition of an elastic solid. We can use it to frame a thermodynamic definition of an elastic solid by using the conditions of equilibrium to identify the complete set of constitutive variables that leads to the behavior described.

#### 16.4.1 The condition of local equilibrium for an elastic solid

Consider an n-component elastic solid that has an impermeable, adiabatic boundary. Let the system be in contact with a mechanical reservoir that imposes a traction, \( \mathbf{T}(\mathbf{r}) \), on its boundary, and assume it is subject to an external field that causes the \( \alpha \)th component to have the potential, \( \phi^\alpha(\mathbf{r}) \), per mole. The condition of equilibrium for the whole system (solid plus reservoir) is that its total energy (internal plus potential energy) have a minimum value for all variations of the state that leave its entropy, chemical content, and overall boundaries fixed. Since the reservoir is relevant only insofar as it does mechanical work on the system, the general condition of equilibrium for the system can be written

\[ \delta(H - W)_{s(N)} \geq 0 \]

where \( H \) is the total energy of the system

\[ H = E + \Phi \]

and \( W \) is the work done on the system by the reservoir.
The total potential energy of the system is

\[
\Phi = \int_V \left\{ \sum_\alpha n_\alpha(r)\phi^\alpha(r) \right\} \, dV = \int_{V^0} \left\{ \sum_\alpha n_\alpha(R)\phi^\alpha(R) \right\} \, dV \quad 16.47
\]

where \( \phi^\alpha(R) \) is the potential of the particle of \( \alpha \) that occupies position, \( R \), in the reference configuration, \( n_\alpha(R) \) is the molar density of the \( \alpha \)th component per unit volume of the reference configuration, the sum is taken over the independent chemical components, and the integral is taken over the volume, \( V^0 \). Using equation 16.47,

\[
H = \int_{V^0} \left\{ E_V + \sum_\alpha n_\alpha(R)\phi^\alpha(R) \right\} \, dV \quad 16.48
\]

where \( E_V \) is the energy per unit volume in the reference configuration.

The condition of equilibrium, 16.45, can be simplified by introducing Lagrange multipliers to incorporate the constraints on the total entropy and chemical content. The result is

\[
\delta H - \theta \delta S - \sum_\alpha \gamma_\alpha \delta n_\alpha - \delta W \geq 0 \quad 16.49
\]

where \( \theta \) and the \( \{\gamma\} \) are Lagrange multipliers. The possible equilibrium states differ from one another through infinitesimal variations in the entropy density, \( \delta S_V(R) \), the chemical densities, \( \delta n_\alpha(R) \), and the displacement field, \( \delta u(R) \). The variation of the total energy is

\[
\delta H = \int_{V^0} \left\{ \delta E_V + \sum_\alpha \phi^\alpha(R)\delta n_\alpha(R) + \sum_\alpha n_\alpha(R)\delta\phi^\alpha(R) \right\} \, dV
\]

\[
= \int_{V^0} \left\{ \delta E_V + \sum_\alpha \phi^\alpha(R)\delta n_\alpha(R) - f \cdot \delta u \right\} \, dV \quad 16.50
\]

where we have used the relation

\[
\delta\phi^\alpha = \nabla\phi^\alpha \cdot \delta u = - b^{\alpha \cdot \delta u} \quad 16.51
\]

which follows from the fact that the change in the potential of the element of \( \alpha \) component located at \( R \) is due to its displacement in the potential field by the vector, \( u \), and have defined the net body force, \( f \), as
\[ f = \sum_{\alpha} n_{\alpha} b^\alpha \]  

which is the molar analog of equation 16.33.

The fourth term in the inequality 16.49 is the work done by the surface traction, \( \mathbf{T} \), which induces the stress field, \( \mathbf{\sigma}(\mathbf{R}) \). Using the methods of the previous section

\[
\delta W = \int_S \mathbf{T} \cdot \delta \mathbf{u} \, dS = \int_S \sigma_{ij} \delta u_i n_j \, dS
\]

\[
= \int_{V^0} \left[ \sigma_{ijij} \delta u_i + \sigma_{ij} \delta u_{ijj} \right] \, dV
\]

16.53

With the substitution of equations 16.50 and 16.53 the general condition of equilibrium becomes

\[
\int_{V^0} \left\{ \delta E_V - \theta \delta S_V + \sum_{\alpha} \left[ \phi^{\alpha} - \gamma_{\alpha} \right] \delta n_{\alpha} - \left[ f_i + \sigma_{ijij} \delta u_i - \sigma_{ij} \delta u_{ijj} \right] \right\} \, dV \geq 0
\]

16.54

which must hold for arbitrary values of the independent variations \( \delta S_V(\mathbf{R}) \), \( \delta n_{\alpha}(\mathbf{R}) \) and \( \delta u_i(\mathbf{R}) \).

### 16.4.2 Thermal and chemical equilibrium

First consider a change of state that involves only a redistribution of the entropy. The condition of equilibrium is

\[
\int_{V^0} \left\{ \delta E_V - \theta \delta S_V \right\} \, dV \geq 0
\]

16.55

where \( \delta E_V \) is the associated change in the energy density. This condition can only hold if the kernel of the integral vanishes everywhere. It follows that the energy density must depend on the entropy density according to the relation

\[
\delta E_V = \left[ \frac{\partial \tilde{E}_V}{\partial S_V} \right] \delta S_V = T \delta S_V
\]

16.56

where

\[
T = \left[ \frac{\partial \tilde{E}_V}{\partial S_V} \right] = \theta = \text{constant}
\]

16.57
Equation 16.57 is the condition of thermal equilibrium. It shows that the temperature of the elastic solid is defined from the fundamental equation just as it is in a fluid, and is constant when the solid is in equilibrium.

Now let the distribution of the \( \alpha \)th component be changed without changing the entropy, the displacement, or the distribution of any other component. To satisfy the condition of equilibrium it is necessary that

\[
\int_V \left\{ \delta E_V + \sum_\alpha \left[ \phi^{\alpha} - \gamma_\alpha \right] \delta n_\alpha \right\} \, dV \geq 0 \tag{16.58}
\]

where \( \delta E_V \) is the associated change in the energy density. Again, the kernel of the integral must vanish everywhere. The simplest dependence of the energy function that yields this behavior is

\[
\delta E_V = \left[ \frac{\partial E_V}{\partial n_\alpha} \right] \delta n_\alpha = \left[ \gamma_\alpha - \phi^{\alpha} \right] \delta n_\alpha \tag{16.59}
\]

If we define the chemical potential of the \( \alpha \)th component in the usual way

\[
\left[ \frac{\partial E_V}{\partial n_\alpha} \right] = \mu_\alpha \tag{16.60}
\]

then equation 16.59 regenerates the usual condition of chemical equilibrium for a component in an external field:

\[
\mu_\alpha + \phi^{\alpha} = \gamma_\alpha = \text{constant} \tag{16.61}
\]

Equation 16.61 holds independently for each component.

16.4.3 The conditions of mechanical equilibrium

Finally, let the displacement of the solid be varied by imposing the variation \( \delta u(R) \). The condition of equilibrium is

\[
\int_V \left\{ \delta E_V - \left[ f_i + \sigma_{ijj} \right] \delta u_i - \sigma_{ij} \delta u_{ij} \right\} \, dV \geq 0 \tag{16.62}
\]

where \( \delta E_V \) is the variation of the energy density.

The inequality 16.62 contains three separate conditions of mechanical equilibrium. First, since \( \delta u(R) \) is arbitrary, consider the case in which
\[ \delta u(R) = \delta a \]

and the displacement is constant. In this case \( \delta E_V = 0 \), since the internal energy is not changed by a rigid displacement, and the displacement gradients, \( u_{ij} = 0 \), also vanish. the condition of equilibrium reduces to

\[ \int_{V^0} \left[ f_i + \sigma_{ijj} \right] \delta a_i \, dV \geq 0 \]

But equation 16.64 must be constant for any subvolume, \( V^0' \), of \( V^0 \), since we can redefine the system by assigning the part of \( V^0 \) that is external to \( V^0' \) to the reservoir and re-deriving the equation. It follows that the kernel of the integral in 16.64 must vanish everywhere, and

\[ \sigma_{ijj} + f_i = 0 \]

The condition of mechanical equilibrium that is given in equation 16.65 can be derived in many different ways, and is known as Cauchy’s First Law.

The second condition of mechanical equilibrium follows from the fact that \( E_V \) is also unchanged by a rigid rotation of the body. Given Cauchy’s First Law the condition of mechanical equilibrium reduces to

\[ \int_{V^0} \{ \delta E_V - \sigma_{ij} \delta u_{ij} \} \, dV \geq 0 \]

An infinitesimal rigid rotation yields the displacement gradient

\[ \delta u_{ij} = \delta \omega_{ij} \]

where \( \delta \omega \) is a constant, antisymmetric tensor. Since \( \delta E_V = 0 \) in a rigid rotation and equation 16.66 must hold irrespective of the choice of the volume, \( V^0 \), we must have

\[ \sigma_{ij} \delta \omega_{ij} = 0 \]

Any second-order tensor can be written as the sum of its symmetric and antisymmetric parts:

\[ \sigma_{ij} = \frac{1}{2} \left[ \sigma_{ij} + \sigma_{ji} \right] + \frac{1}{2} \left[ \sigma_{ij} - \sigma_{ji} \right] = \sigma_{ij}^s + \sigma_{ij}^a \]

Since the scalar product of a symmetric and an antisymmetric tensor is zero,

\[ \sigma_{ij} \delta \omega_{ij} = \sigma_{ij}^s \delta \omega_{ij} + \sigma_{ij}^a \delta \omega_{ij} = \sigma_{ij}^a \delta \omega_{ij} \]
which can hold for arbitrary $\delta\omega$ only if the antisymmetric part of $\sigma$ vanishes. It follows that the stress, $\sigma$, is symmetric:

$$\sigma_{ij} = \sigma_{ji}$$  \hspace{1cm} (16.71)

The condition of mechanical equilibrium that is expressed by equation 16.71 can also be derived in many ways, and is known as Cauchy's Second Law.

The third condition of mechanical equilibrium sets the dependence of $E_V$ on the deformation gradient in an elastic material. Since $\sigma$ is symmetric,

$$\sigma_{ij} \delta u_{ij} = \sigma_{ij} \delta \epsilon_{ij}$$  \hspace{1cm} (16.72)

where $\epsilon_{ij}$, the elastic strain, is the symmetric part of the deformation gradient. The condition of equilibrium reduces to

$$\int \left\{ \delta E_V - \sigma_{ij} \delta \epsilon_{ij} \right\} \, dV \geq 0$$  \hspace{1cm} (16.73)

where $\delta E_V$ is the change in the energy density due to a variation in the strain. The condition, 16.73, can be true for arbitrary variations of the strain only if the kernel of the integral vanishes. Hence the energy density must vary with the strain. The simplest dependence is

$$\left[ \frac{\partial \tilde{E}_V}{\partial \epsilon_{ij}} \right] = \sigma_{ij}$$  \hspace{1cm} (16.74)

Since the term $\sigma_{ij} \delta \epsilon_{ij}$ is the mechanical work done per unit volume when the strain is changed by the infinitesimal amount $\delta \epsilon$, equation 16.74 has a natural meaning. If we take the deformation coordinates to be the strains, $\epsilon_{ij}$, then the stress, $\sigma_{ij}$, is the force conjugate to the strain in the differential work. The partial derivative of the energy function with respect to the deformation coordinate yields the force conjugate to that coordinate.

Equation 16.74 is a useful relation because it is physically transparent. However, it is important to recognize that the set of variables $\{\epsilon_{ij}\}$ is redundant. Since $\epsilon_{ij} = \epsilon_{ji}$ only six of the nine strain components are independent. The energy density function can be written in a form that is formally simpler by using the symmetry to write

$$E_V = \tilde{E}_V(\{\epsilon_{ij}\}) = \tilde{E}_V(\epsilon_{11}, \epsilon_{22}, \epsilon_{33}, \epsilon_{12}, \epsilon_{13}, \epsilon_{23})$$  \hspace{1cm} (16.75)

which expresses the energy density as a function of independent coordinates. In this case, however, the value of the partial derivatives of $E_V$ differs between the diagonal and off-diagonal components.
\[
\begin{bmatrix}
\frac{\partial \tilde{E}_V}{\partial \varepsilon_{ij}}
\end{bmatrix}
= \begin{cases}
\sigma_{ij} & (i = j) \\
2\sigma_{ij} & (i \neq j)
\end{cases}
\]  
16.76

These equations are awkward. It is somewhat simpler to replace the off-diagonal strains by the associated shears,

\[\gamma_{ij} = 2\varepsilon_{ij} \quad (i \neq j)\]  
16.77

since

\[
\begin{bmatrix}
\frac{\partial \tilde{E}_V}{\partial \gamma_{ij}}
\end{bmatrix}
= \sigma_{ij}
\]  
16.78

and this is often done. However, the replacement of the nine strain components by the three diagonal strains and three shears produces a simplification at the considerable cost of using strain measures that are not the components of a tensor, and obey complex transformation laws on a change of coordinates. It is, therefore, often convenient for theoretical work to retain the complete set of the nine \(\varepsilon_{ij}\) as constitutive variables and simply recognize that the set is redundant because of the symmetry of the tensors \(\varepsilon\) and \(\sigma\).

### 16.5 The Fundamental Equation of an Elastic Solid

To formulate the fundamental equation of the linear elastic solid we set two constraints:

1. The fundamental equation must produce a behavior that is consistent with the results derived in the previous section.

2. The fundamental equation must reduce to the fundamental equation of an \(n\)-component fluid when the energy does not depend on the shape, or when the shear stress vanishes.

Surprisingly (at least to me) the second of these constraints is rarely used in developments of the thermodynamics of elastic media. Even Landau and Lifshitz (Theory of Elasticity, 3rd edition) don't use it, and produce a fundamental equation that is inconsistent with the thermodynamics of fluids. They are not, really, in error. So long as one makes a clean separation of material classes, that is, so long as one applies the thermodynamics of elastic media to systems that contain only elastic solids, applies the thermodynamics of fluids to systems that contain only fluids, and never mixes the two, there is no problem. This is the case, or can be made to be the case, in most of the problems that are addressed in the mechanics of elastic solids. But in Materials Science we are often interested in the equilibrium of systems that contain both elastic solids and
fluids (as Gibbs was in his original development of the subject), and, when shear stresses are not important, we are in the habit of treating elastic solids as fluids, as is done, for example, in virtually all discussions of phase diagrams. It is inconvenient to depend on a theory that has a step discontinuity whenever a shear stress appears. As we shall see, it is unnecessary to write such a theory.

First, consider the constraints imposed by the results of the previous section. The conditions of equilibrium require that the energy density depend on the entropy density, the molar densities of the independent components, and the tensor elastic strain. Given our assumptions regarding the mechanical work, which were adopted from the continuum mechanics of elastic solids, the energy density cannot depend explicitly on any quantities that are independent of these since the general condition of equilibrium would be violated if any such quantity were varied in a direction that decreased the energy. It follows that the volumetric form of the fundamental equation for the simple elastic solid is

$$E_V = \tilde{E}_V(S_V, \{n\}, \varepsilon)$$  \hspace{1cm} 16.79

where the densities are defined with respect to the volume of the reference state, $V^0$. The energy density has the differential form

$$dE_V = TdS_V + \sum_{\alpha} \mu_{\alpha} dn_{\alpha} + \sigma_{ij} d\varepsilon_{ij}$$  \hspace{1cm} 16.80

Equations 16.79 and 16.80 define a class of materials that we shall call linear elastic solids.

It is convenient to use the elements of the deviatoric strain as constitutive variables, since these give the shape change at constant volume. Writing the fractional volume change as

$$\varepsilon = \frac{\delta V}{V^0}$$  \hspace{1cm} 16.81

the set of variables $\{\varepsilon_{ij}\}$ can be replaced by the set $\{\varepsilon_{ij}^d, \varepsilon\}$, since the six independent components of the strain are related to the five independent deviatoric strain components and the fractional change in the volume by the relations

$$\varepsilon_{ij} = \varepsilon_{ij}^d + \frac{\varepsilon}{3} \delta_{ij}$$  \hspace{1cm} 16.82

We define the deviatoric stress tensor, $\sigma^d$, by the relations

$$\sigma_{ij}^d = \sigma_{ij} + P\delta_{ij}$$  \hspace{1cm} 16.83

Since the stress tensor that corresponds to a hydrostatic pressure is
\[ \sigma_{ij} = -P \delta_{ij} \]  

16.84

the variable \( P \) in equation 16.83 is the \textit{hydrostatic pressure},

\[ P = -\frac{\sigma_{ii}}{3} \]  

16.85

The deviatoric stress is equivalent to a shear stress just as the deviatoric strain is equivalent to a shear strain. Since

\[
\sigma_{ij} d\varepsilon_{ij} = \left[ \sigma_{ij}^d - P \delta_{ij} \right] \left[ d\varepsilon_{ij}^d + \frac{d\varepsilon}{3} \delta_{ij} \right] 
\]

\[
= \sigma_{ij}^d d\varepsilon_{ij}^d - P d\varepsilon 
\]  

16.86

the volumetric form of the fundamental equation can be written

\[
E_V = \tilde{E}_V(S_V, \{ \eta \}, \mathbf{e}^d, \varepsilon) 
\]  

16.87

where

\[
dE_V = TdS_V + \sum_{\alpha} \mu_{\alpha} \rho_{\alpha} + \sigma_{ij}^d d\varepsilon_{ij}^d - P d\varepsilon 
\]  

16.88

with

\[
\left[ \frac{\partial \tilde{E}_V}{\partial d\varepsilon_{ij}^d} \right] = \sigma_{ij}^d 
\]

16.89

\[
\left[ \frac{\partial \tilde{E}_V}{\partial \varepsilon} \right] = -P 
\]  

16.90

Only five of the nine partial derivatives 16.89 are independent.

To obtain the fundamental equation, \( E = \tilde{E}(\{ u \}) \) in a form that is compatible with both eq. 16.88 and the fundamental equation of the \( n \)-component fluid recognize that, for a given reference volume, \( V^0 \),

\[
d\varepsilon = \frac{d(V - V^0)}{V^0} = \frac{dV}{V^0} 
\]  

16.91

and
\[ dE = V^0 dE_V \]
\[ = Td(V^0 S_V) + \sum_{\alpha} \mu_{\alpha e}(V^0 n_{\alpha}) + \sigma^{d}_{ij} d(V^0 \varepsilon_{ij}) - PdV \]
\[ = TdS + \sum_{\alpha} \mu_{\alpha e} dN_{\alpha} + \sigma^{d}_{ij} d(V^0 \varepsilon_{ij}) - PdV \quad 16.92 \]

which differs from the corresponding expression for the n-component fluid through the inclusion of the term in \( \varepsilon^d \), the shape strain. The variables that appear in the differentials are geometric; they scale with the reference volume, \( V^0 \). If we take these as the constitutive coordinates, we have

\[ E = \tilde{E}(S, \{N\}, V^0 \varepsilon^d, V) \quad 16.93 \]

where

\[
\begin{bmatrix}
\frac{\partial \tilde{E}}{\partial S} \\
\frac{\partial \tilde{E}}{\partial N_{\alpha}} \\
\frac{\partial \tilde{E}}{\partial (V^0 \varepsilon_{ij})} \\
\frac{\partial \tilde{E}}{\partial V}
\end{bmatrix} = T
\]
\[ \quad 16.94 \]

\[
\begin{bmatrix}
\frac{\partial \tilde{E}}{\partial N_{\alpha}} \\
\frac{\partial \tilde{E}}{\partial (V^0 \varepsilon_{ij})}
\end{bmatrix} = \mu_{\alpha}
\]
\[ \quad 16.95 \]

\[
\begin{bmatrix}
\frac{\partial \tilde{E}}{\partial (V^0 \varepsilon_{ij})}
\end{bmatrix} = \sigma^{d}_{ij}
\]
\[ \quad 16.96 \]

\[
\begin{bmatrix}
\frac{\partial \tilde{E}}{\partial V}
\end{bmatrix} = -P
\]
\[ \quad 16.97 \]

Since \( \tilde{E} \) is a linear homogeneous function of its variables it can be integrated to the form

\[ E = TS + \sum_{\alpha} \mu_{\alpha e} N_{\alpha} + V^0 \sigma^{d}_{ij} \varepsilon_{ij} - PV \quad 16.98 \]

From which it follows that the Gibbs-Duhem equation takes the form

\[ SdT + \sum_{\alpha} N_{\alpha} d\mu_{\alpha} + V^0 \varepsilon_{ij} d\sigma^{d}_{ij} - VdP = 0 \quad 16.99 \]

which differs from the fluid form only through the inclusion of the shape term.
To show that eq. 16.98 is consistent with 16.88, note that division by $V^0$ gives

$$E_V = TS_V + \sum_{\alpha} \mu_{\alpha} n_{\alpha} + \sigma_{ij}^d \epsilon_{ij}^d - P \frac{V}{V^0} \quad 16.100$$

Given eq. 16.99, the differential of this equation is

$$dE_V = TdS_V + \sum_{\alpha} \mu_{\alpha} dn_{\alpha} + \sigma_{ij}^d d\epsilon_{ij}^d - Pd \left[ \frac{V}{V^0} \right]$$

$$= TdS_V + \sum_{\alpha} \mu_{\alpha} dn_{\alpha} + \sigma_{ij}^d d\epsilon_{ij}^d - Pd\epsilon \quad 16.101$$

which is identical to 16.88.

### 16.6 ALTERNATE POTENTIALS FOR THE ELASTIC SOLID

Alternate forms of the fundamental equation and conditions of equilibrium for the elastic solid are obtained by taking Legendre transforms in the usual way. It is convenient to use definitions and names for the thermodynamic potentials that parallel those defined for the simple fluid. There is some ambiguity in doing this, however. When the Legendre transform includes mechanical variables the single mechanical variable of the fluid is replaced by seven independent mechanical variables of the elastic solid. This ambiguity affects the definitions of the enthalpy and the Gibbs free energy, which can, and have been given different definitions in the literature that are not identical to one another.

#### 16.6.1 The Helmholtz free energy

When the controllable variables are $T$, $\{N\}$, plus the volume and the shape the system is governed by the potential

$$F = \tilde{F}(T, \{N\}, V, \epsilon^d) = E - TS$$

$$= \sum_{\alpha} \mu_{\alpha} N_{\alpha} - PV + V^0 \sigma_{ij}^d \epsilon_{ij}^d \quad 16.102$$

which can be taken to be the Helmholtz free energy without ambiguity. The Helmholtz free energy has the differential form

$$dF = SdT + \sum_{\alpha} \mu_{\alpha} dN_{\alpha} - PdV + \sigma_{ij}^d d(V^0 \epsilon_{ij}^d) \quad 16.103$$
or, since
\[ dV = d(V^0\varepsilon_{ii}) \]
\[ dF = SdT + \sum_{\alpha} \mu_\alpha dN_\alpha + \sigma_{ij} d(V^0\varepsilon_{ij}) \]

The Helmholtz free energy per unit volume, \( F_V \), is essentially the same as the *elastic energy function* that is defined in texts on linear elasticity.

### 16.6.2 The work function

When the elastic body is an open system the controllable variables are \( T, \{\mu\} \) and \( \varepsilon \), where the \( \{\mu\} \) are the chemical potentials of the independent components, and the pertinent thermodynamic potential is the work function, defined by the Legendre transform

\[ \Omega = \tilde{\Omega}(T,\{\mu\},V,\varepsilon^d) = E - TS - \sum_{\alpha} \mu_\alpha N_\alpha \]
\[ = -PV + V^0\sigma_{ij}^d \varepsilon_{ij} \]

The differential of the work function is
\[ d\Omega = -SdT - \sum_{\alpha} N_\alpha d\mu_\alpha - PdV + \sigma_{ij}^d d(V^0\varepsilon_{ij}) \]
\[ = -SdT - \sum_{\alpha} N_\alpha d\mu_\alpha + \sigma_{ij} d(V^0\varepsilon_{ij}) \]

### 16.6.3 The Gibbs free energy

If the controllable variables can be taken to be the set \( \{T,\{N\},P,\sigma^d\} \), the governing potential is the *Gibbs free energy*

\[ G = \tilde{G}(T,\{N\},P,\sigma^d) = E - TS + PV - V^0\sigma_{ij}^d \varepsilon_{ij} \]
\[ = \sum_{\alpha} \mu_\alpha N_\alpha \]

which has the differential
\[ dG = SdT + \sum_{\alpha} \mu_\alpha dN_\alpha + VdP - V^0 e_{ij}^d d\sigma_{ij}^d \]

\[ = SdT + \sum_{\alpha} \mu_\alpha dN_\alpha + V^0 dP - V^0 e_{ij} d\sigma_{ij} \quad 16.109 \]

While equation 16.108 has an immediate parallel to the definition of the Gibbs free energy of an n-component fluid, some authors use the alternate definition,

\[ G' = \tilde{G}'(T,\{N\},\sigma) = E - TS - V^0 \sigma_{ij} e_{ij} = F - V^0 \sigma_{ij} e_{ij} \]

\[ = \sum_{\alpha} \mu_\alpha N_\alpha - PV^0 \quad 16.110 \]

which has the differential

\[ dG' = SdT + \sum_{\alpha} \mu_\alpha dN_\alpha - V^0 e_{ij} d\sigma_{ij} \quad 16.111 \]

The function defined in equation 16.110 is also called the complementary energy function in the theory of elasticity. When it is useful to use this function, I prefer the latter name, and would reserve the term Gibbs free energy for the function that parallels the definition of this function for the fluid.

### 16.6.4 The enthalpy

When the controllable variables are S, \( \{N\} \), P and \( \sigma^d \) the thermodynamic potential is the elastic analog of the enthalpy. The definition of the enthalpy involves the same ambiguity as was encountered in the definition of the Gibbs free energy. Keeping the parallel with the thermodynamics of fluids, I shall define the enthalpy by the Legendre transform

\[ H = \tilde{H}(S,\{N\},V,\sigma^d) = E + PV - V^0 \sigma_{ij}^d \epsilon_{ij}^d \]

\[ = TS + \sum_{\alpha} \mu_\alpha N_\alpha \quad 16.112 \]

which has the differential form

\[ dH = TdS + \sum_{\alpha} \mu_\alpha dN_\alpha + VdP - V^0 \epsilon_{ij}^d d\sigma_{ij}^d \]
\[ = TdS + \sum_{\alpha} \mu_{\alpha} dN_{\alpha} + V^0 dP - V^0 \epsilon_{ij} \sigma_{ij} \]

The enthalpy of the elastic solid reduces to the entropy of a simple fluid when the stress is hydrostatic or the material is incapable of supporting a deviatoric stress.

### 16.7 Hooke's Law: The Isothermal Elastic Constants

Since many of the important applications of elasticity to materials science occur in situations where the composition, temperature and strain are controlled, we shall use the Helmholtz free energy to phrase Hooke's Law and define the elastic constants, which are the thermodynamic properties of the linear elastic solid.

#### 16.7.1 Hooke's Law

The components of the stress tensor can be obtained from the Helmholtz free energy by the differential equations

\[ \sigma_{ij} = \frac{\partial \tilde{F}_V}{\partial \epsilon_{ij}} = \sigma_{ij}^\dagger(T, \{n\}, \varepsilon) \]

Since the strain is small the function \( \sigma_{ij}^\dagger \) can be evaluated by Taylor expansion about the state \( \varepsilon = 0 \). To first order in the strain

\[ \sigma_{ij} = \sigma_{ij}^0 + \lambda_{ijkl} \varepsilon_{kl} \]

where \( \sigma^0 \) is the stress at zero strain and

\[ \lambda_{ijkl} = \left[ \frac{\partial \sigma_{ij}^\dagger}{\partial \varepsilon_{kl}} \right]_{\varepsilon = 0} = \left[ \frac{\partial^2 \tilde{F}_V}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \right]_{\varepsilon = 0} = \lambda_{ijkl}^\dagger(T, \{n\}) \]

is the fourth-order tensor of isothermal elastic constants. Equation 16.115 is Hooke's Law, and is the basic constitutive equation of linear elasticity.

#### 16.7.2 The stress at zero strain

The stress, \( \sigma^0 \), that appears in the general statement of Hooke's Law is the stress at zero strain, or the residual stress on the material when it is in its reference state. Since the reference state is arbitrary, it is always possible to choose it so that it is stress-free. However, it is often convenient to choose a reference state in which the stress has a non-zero value. At least four such cases are common. First, plastic deformation is equivalent to a stress-free strain since it changes the state in which the stress is zero. If an elastic solid with a given reference state is given an infinitesimal plastic deformation, then it
must be stressed elastically to return it to the reference state. Second, a change in temperature introduces a stress-free strain. Let the reference state have temperature, \( T_0 \). If the solid is then brought to any other temperature the strain is the sum of the elastic strain induced by mechanical stress and a stress-free strain, \( \varepsilon^0 \), due to thermal expansion. Third, a change in composition almost always introduces a stress-free strain since the atoms that make up the solid differ in their effective size and shape. Hence when a solid is stress-free in the reference composition, \( \{n_0\} \), it is strained with respect to the reference state when it has some other composition, \( \{n\} \), and must be stressed to return it to the reference configuration. Fourth, structural phase transformations almost always involve a stress-free strain that provides the connection between the original and final crystal lattices.

When the stress-free strain, \( \varepsilon^0 \), is non-zero it is necessary to impose a stress

\[
\sigma_{ij} = -\lambda_{ijkl}\varepsilon_{ij}^0
\]

16.117
to reverse the stress-free strain and re-establish the reference state. If we define the elastic strain by the relation

\[
\varepsilon_{ij}^e = \varepsilon_{ij} - \varepsilon_{ij}^0
\]

16.118
Hooke's Law reads

\[
\sigma_{ij} = \lambda_{ijkl}\varepsilon_{kl}^e
\]

16.119
which is the form in which it is often written.

16.7.3 The isothermal elastic constants

The isothermal elastic constants are thermodynamic properties that are given by the second partial derivatives:

\[
\lambda_{ijkl} = \left[ \frac{\partial^2 F_V}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \right]_{\varepsilon = 0} = \lambda_{ijkl}^\dagger(T,\{n\})
\]

16.120
It follows that there are 81 elastic constants. However, the number of independent values is reduced to 36 by the symmetry relations

\[
\lambda_{ijkl} = \lambda_{jikl} = \lambda_{ijlk}
\]

16.121
which follow from the fact that \( \sigma_{ij} \) and \( \varepsilon_{ij} \) are symmetric tensors, and is decreased to 21 by the symmetry relations

\[
\lambda_{ijkl} = \lambda_{klji}
\]

16.122
that follow from the symmetry of 16.120 to a change in the order of differentiation.

Almost all solids of interest have symmetry elements that reduce the number of independent elastic constants still further. The results are tabulated for all point groups in a number of references, for example, Nye's text on the physical properties of crystals. The elastic constants are usually tabulated as the 6 x 6 matrix of Voigt constants, \(c_{ij}\), where the subscripts \(i\) and \(j\) each represent a pair of indices according to the convention

\[
egin{align*}
11 &\to 123 \text{ or } 32 \to 4 \\
22 &\to 213 \text{ or } 31 \to 5 \\
33 &\to 312 \text{ or } 21 \to 6 \quad 16.123
\end{align*}
\]

With this notation, for example,

\[
\begin{align*}
c_{11} &= \lambda_{1111} \\
c_{12} &= \lambda_{1122} = \lambda_{2211} \\
c_{44} &= \lambda_{1313} = \lambda_{3113} = \lambda_{3131} = \lambda_{1331} \\
c_{14} &= \lambda_{1113} = \lambda_{1311} = \lambda_{3111} = \lambda_{1131} \quad 16.124
\end{align*}
\]

where we have used the symmetry relations \(c_{ij} = c_{ji}\). Since the matrix is symmetric the maximum possible number of independent elastic moduli is 21.

The two symmetries that are most often encountered are the cubic and isotropic types. In the case of cubic symmetry

\[
\begin{align*}
c_{11} &= c_{22} = c_{33} \quad 16.125 \\
c_{44} &= c_{55} = c_{66} \quad 16.126 \\
c_{12} &= c_{21} = c_{23} = c_{32} = c_{31} = c_{13} \quad 16.127
\end{align*}
\]

and all other \(c_{ij}\) are zero. Hence the cubic solid has three independent elastic constants. It is often most convenient to choose these to be the two Lame' constants, \(c_{12}\) and \(c_{44}\), and the anisotropy ratio,

\[
\Delta = c_{11} - c_{12} - 2c_{44} \quad 16.128
\]

With this choice the fourth-order tensor of elastic constants can be written

\[
\lambda_{ijkl} = c_{44}[\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}] + c_{12}\delta_{ij}\delta_{kl} + \Delta\delta_{ijkl} \quad 16.129
\]
where $\delta_{ijkl}$ is the fourth-order Kronecker delta, which is unity if $i = j = k = l$ and zero otherwise.

When the solid is isotropic the anisotropy factor vanishes:

$$2c_{44} = c_{11} - c_{12} \quad 16.130$$

and there are only two independent elastic constants. In the theory of elasticity it is common to write the Lame' constants as

$$\lambda = c_{12} \quad 16.131$$
$$\mu = c_{44} \quad 16.132$$

The matrix of elastic constants is then

$$\lambda_{ijkl} = \mu [\delta_{ik}\delta_{jl} + \delta_{ij}\delta_{kl}] + \lambda \delta_{ij}\delta_{kl} \quad 16.133$$

In materials science it is common to use four isotropic elastic constants, which relate to the four common loading situations. The Young's modulus, $E$, relates stress to strain in a uniaxial tension test,

$$\sigma = E\varepsilon \quad 16.134$$

where $\sigma$ is the applied stress along the axis of tension and $\varepsilon$ is the uniaxial strain in that direction. In terms of the Lame' constants,

$$E = \frac{\mu(2\mu + 3\lambda)}{\lambda + \mu} \quad 15.135$$

Poisson's ratio, $\nu$, governs the lateral contraction of an isotropic material that is stretched in tension, for example, if $x$ is the axis of tension in a uniaxial tension test,

$$\varepsilon_{yy} = \varepsilon_{zz} = -\nu\varepsilon_{xx} \quad 15.136$$

where

$$\nu = \frac{\lambda}{2(\lambda + \mu)} \quad 15.137$$

The bulk modulus, $\beta$, relates the change in pressure to the change in volume during hydrostatic compression,

$$P = -\beta \begin{bmatrix} \Delta V \\ \sqrt{V} \end{bmatrix} \quad 16.138$$
where

\[ \beta = (\kappa T)^{-1} = \frac{3\lambda + 2\mu}{3} \] 16.139

and \( \kappa_T \) is the compressibility. The shear modulus, \( \mu \), relates the shear stress (which is conventionally symbolized by \( \tau \)) to the shear strain, \( \gamma \):

\[ \tau = G\gamma \] 16.140

where

\[ G = \mu \] 16.141

The elastic constants that are usually tabulated in handbooks of mechanical properties are Young's modulus, \( E \), and Poisson's ratio, \( \nu \), since these are usually the most useful for stress analysis in mechanical design. In fact, it is often only necessary to know \( E \), since the value of Poisson's ratio is confined to a narrow range \( (0 < \nu < 1/2) \), and since its value is approximately 1/3 for most structural metals and alloys.

However, from the point of view of thermodynamics the most meaningful elastic constants are the compressibility, which relates pressure to volume (fluid behavior) and the shear modulus, which relates the deviatoric stress to the strain (elastic behavior). The same viewpoint is suggested by the theory of cohesive bonding in solid state physics, in which it is convenient to write the cohesive energy as the sum of a dominant term that depends only on the atomic volume, without respect to the arrangement of atoms, and a correction term that depends on the configuration of atoms (crystal structure) at given volume. The constants \( E \) and \( \nu \) are, then, given by the relations

\[ E = \frac{9\beta G}{(G+3\beta)} = 2G(1+\nu) = 3\beta(1-2\nu) \] 16.142

\[ \nu = \frac{3\beta - 2G}{2(G+3\beta)} \] 16.143

To develop a physical feel for the relative values of the elastic constants, it is useful to consider three classes of materials. The first class includes materials that resist changes in volume much more strongly than changes in shape. This class includes many polymeric solids, such as rubber. Then \( \beta \gg G \), and

\[ \nu \approx 0.5, \ E \approx 3G \] 16.144

The second class includes most metals, for which \( \beta \approx 3G \), and

\[ \nu \approx 0.35, \ E \approx 2.7G \approx 0.9\beta \] 16.145
The third class includes relatively rigid materials, like diamond and most semiconductors, for which $\beta \approx G$, and

$$\nu \approx 0.125, \ E \approx 2.25G \approx 2.25\beta$$  \hspace{1cm} 16.146

These three examples span the range of real materials, and show that in all cases $\nu > 0$, and $E$ is of the order of $G$. However, it is relevant to note that these restrictions come from the physical principle that $\beta$ should be at least as great as $G$, and not from thermodynamics itself. It is possible to imagine a material that has extreme rigidity, so that $G \gg \beta$. In this case Poisson’s ratio is negative, and

$$\nu \approx -1, \ E \approx 9\beta$$  \hspace{1cm} 16.147

so that $E$ is governed by the relatively small bulk modulus. In fact, structured foams have been constructed in the laboratory that are more rigid than compressible, and do have $\nu < 0$.

### 16.8 Elastic Properties for Other Sets of Constraints

The isothermal elastic constants that are given by the fourth-order tensor, $\lambda$, are functions of the temperature and composition, and govern the behavior of the elastic solid when these are the controllable variables in the unstrained state. While the most common problems in elasticity involve strain at constant $T$ and $\{n\}$, there are situations in which the strain is done isentropically (constant $S_V$, $\{n\}$), for example, when the temperature is very low or the rate of strain is very fast, and other situations in which at least one of the chemical potentials remains constant during strain (constant $T$, $\mu$, $\{n'\}$), usually because the rate of strain is slow compared to the rate of chemical diffusion of that specie. In the former case the system is governed by the internal energy, $E$, and the elastic constants are called the isentropic elastic constants. In the latter the system is governed by a mixed thermodynamic potential, and the elastic constants are called the open system elastic constants. Since the elastic constants are first-order thermodynamic properties of the solid, the elastic constants that relate to different choices of the independent variables can be derived from one another by the appropriate Jacobian transformations.

#### 16.8.1 The isentropic elastic constants

When the entropy and composition are held constant during strain the system is governed by its internal energy and the pertinent elastic constants are the isentropic elastic constants. The fourth-order tensor of isentropic elastic constants, $\lambda^S$, is defined from the internal energy by the relations

$$\lambda^S = \left[ \frac{\partial^2 E^V}{\partial \varepsilon \partial \varepsilon} \right]_{\varepsilon = 0} = \left[ \frac{\partial \sigma}{\partial \varepsilon} \right]_{\varepsilon = 0} = \lambda^S(S_V, \{n\})$$  \hspace{1cm} 16.148
To relate the isentropic elastic constants to the isothermal set, $\lambda$, we use the properties of the Jacobian to transform the independent variables from the set $\{S_V, \{n\}\}$ to the set $\{T, \{n\}\}$. Since the composition, $\{n\}$, is a constitutive variable for both cases, we need only replace the entropy, $S_V$, by the temperature, $T$. At constant $\{n\}$,

$$\lambda S = \frac{\partial (\sigma S_V)}{\partial (\varepsilon S_V)} = \frac{\partial (\sigma S_V)}{\partial (\varepsilon T)} \left[ \frac{\partial (\varepsilon S_V)}{\partial (\varepsilon T)} \right]^{-1}$$

$$= \left[ \frac{\partial \sigma}{\partial \varepsilon} \right]_T - \left[ \frac{\partial S_V}{\partial T} \right]_T \frac{\partial S_V}{\partial \varepsilon}$$

16.149

To simplify this equation we define some of the other properties of the elastic system. The second derivative of the free energy density with respect to the temperature,

$$\left[ \frac{\partial^2 F_V}{\partial T^2} \right] = - \left[ \frac{\partial S_V}{\partial T} \right]_T = \frac{c_\varepsilon}{T}$$

16.150

defines the isometric specific heat of the system, $c_\varepsilon$. The second derivative of the free energy density with respect to temperature and strain,

$$\left[ \frac{\partial^2 F_V}{\partial T \partial \varepsilon} \right] = - \left[ \frac{\partial S_V}{\partial T} \right]_T = \left[ \frac{\partial \sigma}{\partial T} \right]_T = \pi$$

16.151

where $\pi$ is the symmetric second-order tensor of thermal stress coefficients. The thermal stress coefficient, $\pi_i$, is the stress that would have to be imposed to reverse the thermal expansion caused by a unit increase in temperature. It is simply related to the tensor coefficient of thermal expansion. Since

$$d\sigma_{ij} = \lambda_{ijkl}d\varepsilon_{kl} + \pi_{ij}dT$$

16.152

then if the temperature is changed at constant stress

$$\pi_{ij} = - \lambda_{ijkl}\left[ \frac{\partial \varepsilon_{kl}}{\partial T} \right]_\sigma = - \lambda_{ijkl}\alpha_{kl}$$

16.153

where

$$\alpha = \left[ \frac{\partial \varepsilon}{\partial T} \right]_\sigma$$

16.154
is the second-order tensor coefficient of thermal expansion, which is the analog of the coefficient of thermal expansion of a fluid. The tensor $\alpha$ is symmetric since $\epsilon$ is.

It follows from equations 16.149-151 that the isentropic elastic constants are related to the isothermal set by the relations

$$\lambda_{ijkl}^S = \lambda_{ijkl} + \frac{T}{c_\epsilon} \pi_{ij} \pi_{kl}$$  \hspace{1cm} 16.155

Hence when an elastic solid is strained at constant entropy Hooke's Law reads

$$\sigma_{ij} = \lambda_{ijkl}^S \epsilon_{kl} = \lambda_{ijkl} \epsilon_{kl} + \frac{T}{c_\epsilon} \left[ \pi_{kl} \epsilon_{kl} \right] \pi_{ij}$$  \hspace{1cm} 16.156

The isentropic elastic constants must, of course, obey the same symmetry relations as the isothermal ones. In particular, when the solid has cubic or isotropic symmetry,

$$\pi_{ij} = \pi \delta_{ij} = \frac{\alpha}{\kappa_T} \delta_{ij}$$  \hspace{1cm} 16.157

where $\alpha$ is the coefficient of thermal expansion

$$\alpha = \frac{1}{V^0} \left[ \frac{\partial V}{\partial T} \right]_\sigma = \alpha_{ii}$$  \hspace{1cm} 16.158

and $\kappa_T$ is the isothermal compressibility

$$\kappa_T = \frac{3}{c_{11} + 2c_{12}}$$  \hspace{1cm} 16.159

which is the reciprocal of the bulk modulus. It follows that the stress developed during an adiabatic strain of a cubic or isotropic solid is governed by the equations

$$\sigma_{ij} = \lambda_{ijkl} \epsilon_{kl}^e + \frac{T \alpha^2 \epsilon^e}{c_\epsilon \kappa_T^2} \delta_{ij} = \lambda_{ijkl} \epsilon_{kl}^e - \Delta P S \delta_{ij}$$  \hspace{1cm} 16.160

where $\epsilon^e$ is the fractional increase in volume due to the elastic part of the strain. It follows from equation 16.160 that the effect of the entropic constraint is to add a term that has the form of a hydrostatic pressure, $\Delta P S$, to the isothermal stress, where the isentropic pressure increment is

$$\Delta P = - \frac{T \alpha^2 \epsilon^e}{c_\epsilon \kappa_T^2}$$  \hspace{1cm} 16.161
16.8.2 The "open-system" elastic constants

Suppose that there is a mobile component in the elastic solid. When the solid is strained this component adjusts its distribution so that its chemical potential (or relative chemical potential) retains the value that is fixed by the reservoir. According to LeChatelier's Principle the additional strain caused by diffusion is a deformation that relaxes the stress generated by the original strain. The effect of the chemical relaxation can be incorporated into the elastic constants. The result is to replace the isothermal elastic constants by the open-system elastic constants.

For simplicity assume that the temperature is constant and that there is only one mobile component. The operational variables are then T, µ, \{n'\}, and \(\varepsilon\), where \(\mu\) is the chemical potential of the mobile component and \{n'\} is the set of all other components. The equilibrium of the system is governed by the thermodynamic potential whose volume density is

\[
\Phi_V = F_V - \mu n = \tilde{\Phi}_V(T, \mu, \{n'\}, \varepsilon)
\]

and the elastic constants are

\[
\lambda^\mu = \left[ \frac{\partial^2 \tilde{\Phi}_V}{\partial \varepsilon \partial \varepsilon} \right]_{\mu} = \left[ \frac{\partial \sigma}{\partial \varepsilon} \right]_{\mu} = \lambda^\mu(\mu)
\]

where \(n\) is the density of the mobile component, the partial derivatives are taken at \(\varepsilon = 0\), and the dependence on T and \{n'\} is suppressed since their values are constant. Using the Jacobian transform to effect a change of variables from \((\varepsilon, \mu)\) to \((\varepsilon, n)\),

\[
\lambda^\mu = \frac{\partial(\sigma, \mu)}{\partial(\varepsilon, n)} = \left[ \frac{\partial(\sigma, \mu)}{\partial(\varepsilon, n)} \right]^{-1} \cdot \frac{\partial(\varepsilon, \mu)}{\partial(\varepsilon, n)}
\]

\[
= \left[ \frac{\partial \sigma}{\partial \varepsilon} \right]_n - \left[ \frac{\partial \mu}{\partial n} \right]_\varepsilon \cdot \left[ \frac{\partial \varepsilon}{\partial n} \right]_\mu
\]

16.164

Using the identity

\[
\left[ \frac{\partial \mu}{\partial \varepsilon} \right]_n = \frac{\partial^2 \tilde{\Phi}_V}{\partial \varepsilon \partial n} = \left[ \frac{\partial \sigma}{\partial n} \right]_\varepsilon
\]

16.165

we have
\[ \lambda_{ijkl}^u = \lambda_{ijkl} - \frac{\partial \mu}{\partial n}_{\varepsilon} \]

16.166

The second term on the right in equation 16.166 is positive, so the open-system elastic constants are less than the corresponding isothermal elastic constants. This result ensures the satisfaction of LeChatelier's Principle, which, in this case, asserts that any chemical relaxation that accompanies an elastic strain in an open system acts to decrease the applied stress; hence the net contribution of diffusion to the isothermal elastic constants is negative. For the same reason, the isothermal elastic constants are, in their net effect, less than or equal to the isentropic ones; the thermal interaction provides an additional degree of freedom that acts to decrease the stress.

Equation 16.166 simplifies considerably when the concentration dependence of the isothermal elastic constants can be ignored and the stress-free strain is linear in the solute density, \( n \). Then

\[
\left[ \frac{\partial \sigma_{ij}}{\partial n} \right]_{\varepsilon} = \left[ \frac{\partial}{\partial n} \lambda_{ijkl} \varepsilon_{kl}^e \right]_{\varepsilon} = - \lambda_{ijkl} \left[ \frac{\partial \varepsilon_{kl}}{\partial n} \right]_{\varepsilon} \varepsilon_{kl}^e
gives
\]

16.167

where the partial derivative in the last form is the partial molar strain of the solute. If the solution is cubic or isotropic then

\[
\left[ \frac{\partial \varepsilon_{kl}}{\partial n} \right]_{\varepsilon} = \frac{1}{3} \left[ \frac{\partial \varepsilon_{kl}}{\partial n} \right]_{\varepsilon} \delta_{kl}
gives
\]

16.168

where \([\partial V, \partial N] \) is the partial molar volume of the solute. Using this result in equation 16.167,

\[
\left[ \frac{\partial \sigma_{ij}}{\partial n} \right]_{\varepsilon} = - \left[ \frac{\partial P}{\partial n} \right]_{\varepsilon} \delta_{ij} = - \frac{1}{kT} \left[ \frac{\partial \varepsilon_{kl}}{\partial n} \right]_{\varepsilon} \varepsilon_{ij}
gives
\]

16.169

Moreover, since

\[
\mu = \frac{\partial F_V}{\partial n} = \mu(T, \{n\}, \varepsilon)
\]

\[
\approx \mu(T, \{n\}) + \left[ \frac{\partial \mu}{\partial \varepsilon_{ij}} \right]_{T \{n\}} \varepsilon_{ij}
\]
\[ \mu(T, \{ n \}) + \left[ \frac{\partial \sigma_{ij}}{\partial n} \right]_{\varepsilon} \varepsilon_{ij} \quad 16.170 \]

where we have used the fact that the strains are small, then

\[ \left[ \frac{\partial \mu}{\partial n} \right]_{\varepsilon} = \left[ \frac{\partial \mu}{\partial n} \right]_{0} + \left[ \frac{\partial^2 \sigma_{ij}}{\partial n^2} \right]_{\varepsilon} \varepsilon_{ij} \equiv \left[ \frac{\partial \mu}{\partial n} \right]_{0} \quad 16.171 \]

where the partial derivative is taken in the fluid limit at zero strain and the approximation holds unless the elastic constants or the partial molar volume are highly non-linear functions of the composition. Equation 16.166 then becomes

\[ \lambda_{ijkl}^\mu = \lambda_{ijkl} - \frac{\left[ \frac{\partial \varepsilon_{ij}^0}{\partial n} \right]^2_{\varepsilon T}}{(\kappa T)^2 \left[ \frac{\partial \mu}{\partial n} \right]_0} \delta_{ij} \delta_{kl} \quad 16.172 \]

The stress developed during a strain at constant chemical potential of a mobile specie is, hence,

\[ \sigma_{ij} = \lambda_{ijkl}^\mu \varepsilon_{kl}^e = \lambda_{ijkl} \varepsilon_{kl}^e + (\Delta P)_\mu \delta_{ij} \quad 16.173 \]

where the incremental pressure, \((\Delta P)_\mu\), is

\[ (\Delta P)_\mu = - \frac{\varepsilon_{kl} \left[ \frac{\partial \varepsilon_{ij}^0}{\partial n} \right]^2_{\varepsilon T}}{(\kappa T)^2 \left[ \frac{\partial \mu}{\partial n} \right]_0} \quad 16.174 \]

That is, when the partial molar strain is a simple dilation and the elastic constants are insensitive to the composition the effect of the chemical redistribution is to lower the diagonal terms in the stress by the constant, - \(\Delta P\), in agreement with LeChatelier's principle.

### 16.9 The Compliance Tensor

When the stress rather than the strain is the controlled elastic variable Hooke's Law should be inverted. This can be done by inverting Hooke's Law itself or by re-deriving it from the appropriate form of the fundamental equation. We shall take the latter approach.
16.9.1 The isothermal compliance

When only elastic processes are permitted and the controlled variables are $T$, $\{n\}$, $\sigma$ the appropriate thermodynamic potential is the Gibbs free energy, whose volume density is

$$G_V = \frac{G}{V^0} = F_V - \sigma_i \epsilon_{ij} - P = \tilde{G}_V(T, \{n\}, \sigma)$$  \hspace{1cm} 16.175

The strain components can be found by differentiating this function, and are

$$\epsilon_{ij} = - \frac{\partial \tilde{G}_V}{\partial \sigma_{ij}} = \epsilon_{ij}^{\dagger}(T, \{n\}, \sigma)$$  \hspace{1cm} 16.176

Expanding to first order in the stress,

$$\epsilon_{ij} = \epsilon_{ij}^0 + S_{ijkl} \sigma_{kl}$$  \hspace{1cm} 16.177

where $S$ is the fourth-order isothermal compliance tensor, whose elements are the thermodynamic properties

$$S_{ijkl} = \left[ \frac{\partial^2 \tilde{G}_V}{\partial \sigma_{ij} \partial \sigma_{kl}} \right] = \left[ \frac{\partial \epsilon_{ij}}{\partial \sigma_{kl}} \right]_T$$  \hspace{1cm} 16.178

Comparing equation 16.178 with the defining equation for the isothermal elastic constants shows that the compliance tensor is the inverse of the elastic constant tensor,

$$S = \lambda^{-1}$$  \hspace{1cm} 16.179

and hence has the same symmetry properties.

16.9.2 The isentropic compliance

The isentropic compliance tensor governs the change in the strain when the stress is varied at constant entropy. Using the enthalpy density

$$H_V = \tilde{H}_V(S_V, \{n\}, \sigma)$$  \hspace{1cm} 16.180

the strain is

$$\epsilon_{ij} = \left[ \frac{\partial \tilde{H}_V}{\partial \sigma_{ij}} \right]^0 = \epsilon_{ij}^0 + S_{ijkl} \sigma_{kl}$$  \hspace{1cm} 16.181

where the isentropic compliance is
\[ S_{ijkl}^S = \left[ \frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}} \right]_S = - \left[ \frac{\partial^2 \bar{H}_V}{\partial \sigma_{ij} \partial \sigma_{kl}} \right] \tag{16.182} \]

The isentropic and isothermal compliances are related by the equation
\[ S_{ijkl}^S = S_{ijkl} - \frac{T}{c_\sigma} \left[ \frac{\partial \varepsilon_{ij}}{\partial T} \right] \left[ \frac{\partial \varepsilon_{kl}}{\partial T} \right] \sigma \tag{16.183} \]

where the specific heat per unit volume at constant stress (the analog of the isobaric specific heat of a fluid) is
\[ \frac{c_\sigma}{T} = \left[ \frac{\partial S_V}{\partial T} \right] \sigma \tag{16.184} \]

and the temperature derivative of the strain is
\[ \left[ \frac{\partial \varepsilon_{ij}}{\partial T} \right] \sigma = \alpha_{ij} + \left[ \frac{\partial S_{ijkl}}{\partial T} \right] \delta_{ij} \delta_{kl} \tag{16.185} \]

where \( \alpha \) is the tensor coefficient of thermal expansion. When the material is cubic or isotropic and the temperature dependence of the elastic constants is negligible,
\[ S_{ijkl}^S = S_{ijkl} - \frac{T \alpha^2}{9 c_\sigma} \delta_{ij} \delta_{kl} \tag{16.186} \]

16.9.3 The open-system compliance

The open-system compliance applies to a situation in which the temperature and stress are fixed and at least one of the components is free to move (either one of the components must be fixed or the components must substitute for one another on a fixed lattice so that the strain can be defined). If only one component is mobile and only elastic strains are considered the governing potential is
\[ \Phi_V = \tilde{\Phi}_V(T, \sigma, \mu, \{n'\}) = G_V - \mu n \tag{16.187} \]

where \( \mu \) is the chemical potential of the mobile species. The strain at given stress, temperature and chemical potential of the mobile species is given by
\[ \varepsilon_{ij} = - \left[ \frac{\partial}{\partial \sigma_{ij}} \{ \tilde{\Phi}_V(T, \sigma, \mu, \{n'\}) \} \right] \]
\[ 0 = \varepsilon_{ij} + S^u_{ijkl} \sigma_{kl} \]

where

\[
S^u_{ijkl} = - \left[ \frac{\partial^2}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \Phi_{V}(T, \sigma, \mu, \{n\}) \right]
= S_{ijkl} - \left[ \frac{\partial \varepsilon_{ij}}{\partial \mu} \right]_{\sigma} \left[ \frac{\partial \varepsilon_{kl}}{\partial n} \right]_{\sigma} \]

16.189

When the material is isotropic or cubic and the compliance changes negligibly with the composition equation 16.189 simplifies to

\[
S^u_{ijkl} = S_{ijkl} + \left[ \frac{\partial \varepsilon_{ij}}{\partial \mu} \right]_{\sigma} \left[ \frac{\partial \varepsilon_{kl}}{\partial n} \right]_{\sigma} \]

16.190

### 16.10 The Elastic Energy

#### 16.10.1 Definitions of the elastic energy

Let an elastic solid be strained quasi-statically from its reference state. The elastic work done by the applied forces in the infinitesimal displacement, \( \delta u(R) \), is

\[
\delta W = \int_{V} f_i \delta u_i \, dV + \int_{S} T_i \delta u_i \, dS = \int_{V} \left[ f_i + \sigma_{ij} \right] \delta u_i \, dV + \int_{V} \sigma_{ij} \delta u_{ij} \, dV
\]

16.191

If the work is done quasi-statically then the conditions of mechanical equilibrium must be satisfied at all times. Hence the first integral on the right in 16.191 vanishes, and the integrand in the second integral depends only on the symmetric part of the displacement gradient, \( \varepsilon_{ij} \). The **incremental work** done on the solid is

\[
\delta W = \int_{V} \sigma_{ij} \delta \varepsilon_{ij} \, dV
\]

16.192

The total work done to achieve a given total elastic strain, \( \varepsilon \), is
\[ W = \int_V \left( \int_0^\varepsilon \sigma_{ij} d\varepsilon_{ij} \right) dV \]

which is, given Hooke's Law,

\[
W = \int_V \left( \int_0^\varepsilon \left[ \sigma_{ij}^0 + \lambda_{ijkl} \varepsilon_{kl} \right] d\varepsilon_{ij} \right) dV \\
= \int_V \left[ \sigma_{ij}^0 \varepsilon_{ij} + \frac{1}{2} \lambda_{ijkl} \varepsilon_{ij} \varepsilon_{kl} \right] dV \\
= \frac{1}{2} \int_V \left[ \sigma_{ij} + \sigma_{ij}^0 \right] \varepsilon_{ij} dV \]

where the elastic constants, \( \lambda \), are those appropriate to the constraints under which the strain is accomplished.

If the solid is strained at constant temperature \( T \) is the tensor of isothermal elastic constants and the work done adds to the Helmholtz free energy, \( F \), which becomes

\[
F = F^0(T,\{N\},V^0) + \frac{1}{2} \int_V \left[ \sigma_{ij} + \sigma_{ij}^0 \right] \varepsilon_{ij} dV \]

where \( F^0 \) is the free energy of the solid in its reference state. If the final state is homogeneous, that is, if the stress and strain are the same everywhere,

\[
F = F^0 + \frac{V^0}{2} \left[ \sigma_{ij} + \sigma_{ij}^0 \right] \varepsilon_{ij} \]

If the solid is strained adiabatically then \( \lambda \) is the tensor of isentropic elastic constants and the work adds to the internal energy.

Two alternate forms of equation 16.196 are particularly useful. They relate to specific choices of the reference state. First, if the reference state is taken to be the state in which the stress is zero then

\[
\varepsilon_{ij} = \varepsilon_{ij}^e \]

the elastic strain, and the free energy is

\[
F = F_0(T,V_0,\{N\}) + F_{el} \]
where \( F_0 \) is the free energy of the stress-free state and \( V_0 \) is its volume. Second, if the reference state is taken to be the state in which the deviatoric stress, \( \sigma^d \), vanishes, then the deviatoric strain is a pure elastic strain, and

\[
F = F(T,V,\{N\}) + \frac{V_0}{2} \sigma^d \epsilon^d_{ij} \tag{16.199}
\]

This equation has the very useful property that it divides the free energy into two terms: a shape-independent free energy function, \( F(T,V,\{N\}) \), which is the fundamental equation that governs the "fluid-like" behavior of the solid, and a second term that is the shape-dependent part of the elastic energy, which governs the "solid-like" behavior of the solid.

### 16.10.2 The integrated form of the fundamental equation

Equation 16.196 may appear to conflict with the integrated form of the Helmholtz free energy, which can be written

\[
F = \sum_{\alpha} \mu_{\alpha} N_{\alpha} - PV^0 + V^0 \sigma^d \epsilon^d_{ij} \tag{16.200}
\]

The resolution of this apparent conflict comes from the fact that the chemical potentials, \( \{\mu\} \), depend on the stress, and also contribute to the difference between \( F \) and \( F^0 \). From equation 16.200 the Gibbs-Duhem equation for an isothermal transition between equilibrium states can be written

\[
\sum_{\alpha} N_{\alpha} d\mu_{\alpha} = V^0 dP - V^0 \epsilon^d_{ij} d\sigma^d_{ij} \tag{16.201}
\]

Integrating this equation at constant composition yields

\[
\sum_{\alpha} N_{\alpha} (\mu_{\alpha} - \mu^0_{\alpha}) = V^0 (P - P^0) - \frac{V^0}{2} \left[ \sigma^d_{ij} - \sigma^0_{ij} \right] \epsilon^d_{ij} \tag{16.202}
\]

Hence

\[
F^0(T,\{N\},V^0) = \sum_{\alpha} N_{\alpha} \mu^0_{\alpha} - P^0 V^0
\]

\[
= \sum_{\alpha} N_{\alpha} \mu_{\alpha} - PV^0 + \frac{V^0}{2} \left[ \sigma^d_{ij} - \sigma^0_{ij} \right] \epsilon^d_{ij} \tag{16.203}
\]
When equation 16.203 is substituted into equation 16.196 the result is equation 16.200. Hence the two expressions for the Helmholtz free energy are equivalent.

16.11 Stability in Elastic Deformation

To simplify the analysis as much as possible we shall consider stability in the special case that strain remains infinitesimal through the point of instability. When this is not true the stability conditions become more complicated. The more general case is developed in J.W. Morris, Jr. and C.R. Krenn, “Internal Stability of an Elastic Solid”, Phil. Mag. A, 80. 2827-2840 (2000).

Consider an adiabatic system that is subject to a surface traction, \( \mathbf{T} \), and body force, \( \mathbf{f} \). The general condition of equilibrium with respect to small deviations from the equilibrium state is

\[
\int_{V_0} \left\{ \delta E_V - \theta \delta S_V + \sum_{\alpha} \left[ \phi^\alpha - \gamma^\alpha \right] \delta n_\alpha - \left[ f_i + \sigma_{ijl} \right] \delta u_i - \sigma_{ij} \delta u_{ij} \right\} \, dV \geq 0 \quad 16.204
\]

The fundamental equation is

\[
E_V = \tilde{E}_V(S_V, \{n\}, \varepsilon) = \tilde{E}_V(\{q\}) \quad 16.205
\]

where the set \( \{q\} = \{S_V, \{n\}, \varepsilon\} \). To the second order in the variations of the constitutive variables, \( \{q\} \),

\[
\delta E_V = \sum_{\alpha} \left[ \frac{\partial \tilde{E}_V}{\partial q_\alpha} \right] \delta q_\alpha + \frac{1}{2} \sum_{\alpha} \left[ \frac{\partial^2 \tilde{E}_V}{\partial q_\alpha \partial q_\beta} \right] \delta q_\alpha \delta q_\beta
\]

\[
= \sum_{\alpha} (E_V)_\alpha \delta q_\alpha + \frac{1}{2} \sum_{\alpha} (E_V)_{\alpha\beta} \delta q_\alpha \delta q_\beta \quad 16.206
\]

Substituting equation 16.206 into the condition of equilibrium, 16.204, yields the condition

\[
\int_{V_0} \left[ (E_V)_{\alpha\beta} \delta q_\alpha \delta q_\beta \right] \, dV \geq 0 \quad 16.207
\]

Since 16.207 must be satisfied for arbitrary choices of the volume, the local condition of stability is

\[
(E_V)_{\alpha\beta} \delta q_\alpha \delta q_\beta \geq 0 \quad 16.208
\]
It follows, as expected, that the local condition of stability is that the matrix of thermodynamic properties

\[(E_V)_{\alpha\beta} = \begin{bmatrix} \frac{\partial^2 E}{\partial q_\alpha \partial q_\beta} \end{bmatrix} \]

is positive definite in the sense that all of its eigenvalues are positive.

Among its various consequences the local condition of stability requires that

\[\begin{bmatrix} \frac{\partial^2 E_V}{\partial S_V^2} \end{bmatrix} = \begin{bmatrix} \frac{\partial T}{\partial S_V} \end{bmatrix}_{\{n\} \epsilon} = \begin{bmatrix} T \end{bmatrix} \]  \[c_\epsilon \geq 0 \]

or

\[c_\epsilon \geq 0 \]

where \(c_\epsilon\) is the isometric specific heat,

\[\begin{bmatrix} \frac{\partial^2 E_V}{\partial n_\alpha^2} \end{bmatrix} = \begin{bmatrix} \frac{\partial \mu_\alpha}{\partial n_\alpha} \end{bmatrix}_{S_V\{n\} \epsilon} \geq 0 \]

and

\[\lambda_{ijkl} \delta_{ij} \delta_{kl} \geq 0 \]

The last condition requires that the matrix of isentropic elastic constants be positive semi-definite.

It can be easily shown that the condition 16.213 also applies to the isothermal or open-system elastic constants. Using the Jacobian transformation to relate the isothermal constants to the adiabatic ones,

\[\lambda = \begin{bmatrix} \frac{\partial \sigma}{\partial \epsilon} \end{bmatrix}_T = \frac{\partial(\sigma,T)}{\partial(\epsilon,T)} \]

\[= \begin{bmatrix} \frac{\partial(\sigma,T)}{\partial(\epsilon,S_V)} \end{bmatrix} \begin{bmatrix} \frac{\partial(\epsilon,T)}{\partial(\epsilon,S_V)} \end{bmatrix}^{-1} \]

The denominator of the right-hand side of 16.214 is positive by equation 16.210. The first term is the fourth-order tensor.
\[
\begin{align*}
\left[ \frac{\partial(\sigma,T)}{\partial(\varepsilon,SV)} \right] &= \left[ \frac{\partial \sigma}{\partial \varepsilon} \right]_{SV} \left[ \frac{\partial T}{\partial S_{V}} \right]_{\varepsilon} - \left[ \frac{\partial \sigma}{\partial S_{V}} \right]_{\varepsilon} \left[ \frac{\partial T}{\partial \varepsilon} \right]_{S_{V}} \\
&= (E \varepsilon)_{\varepsilon}(E \varepsilon)_{SS} - [(E \varepsilon)_{\varepsilon}]^2 
\end{align*}
\]

which must be positive semi-definite because it is the determinant of the matrix that governs coupled changes in the strain and the entropy. Similar arguments show that the tensor \( \lambda^\mu \) must be positive semi-definite if the solid is to be stable.

The conditions that must be obeyed by the elastic constants to satisfy the conditions of stability include the following, which we shall phrase in terms of the isothermal elastic constants. First, since the second partial derivative of \( F_V \) with respect to any one of the diagonal strain components must be positive semi-definite, the diagonal components of \( \lambda \) satisfy

\[
\lambda_{1111} = c_{11} \geq 0
\]

and the same condition holds for \( c_{22} \) and \( c_{33} \). When the same condition is applied to the second partial with respect to any one of the off-diagonal strain components the result is, for example,

\[
\lambda_{1212} = \lambda_{1221} = \lambda_{2112} = c_{66} \geq 0
\]

A similar condition holds for the constants \( c_{44} \) and \( c_{55} \). The other elastic constants are obtained from cross-derivatives with respect to the strain components. In this case we have less stringent constraints of the form, for example,

\[
(\lambda_{1122})^2 \leq \lambda_{1111} \lambda_{2222}
\]

or, equivalently,

\[
(c_{12})^2 \leq c_{11} c_{22}
\]

A further useful constraint is obtained from the requirement that the system be stable with respect to a change in the volume at constant shape, that is, that the compressibility be positive definite. This requirement leads to the condition

\[
\lambda_{ijkl} \delta_{ij} \delta_{kl} = \frac{3}{kT} \geq 0
\]

In the case of a cubic solid the conditions of stability are

\[
c_{11} \geq 0 \quad 16.220
\]

\[
c_{44} \geq 0 \quad 16.221
\]
Equation 16.218 then shows that

\[ |c_{12}| < c_{11} \quad 16.222 \]

but a more stringent condition is obtained from 16.219:

\[ c_{11} + 2c_{12} \geq 0 \quad 16.223 \]

Note that equation 16.223 does not require that \( c_{12} \) be positive so long as its magnitude is less than half that of \( c_{11} \). The coefficient \( c_{12} \) is usually positive for a cubic solid, but negative values are known. For example, iron pyrite, FeS\(_2\) (fool's gold), has a negative value of \( c_{12} \).

For an isotropic solid

\[ \mu = c_{44} \geq 0 \quad 16.224 \]

and, since the compressibility is positive,

\[ 3\lambda + 2\mu \geq 0 \quad 16.225 \]

Equation 16.225 admits the possibility that \( \lambda \) can be less than zero, which would cause a negative value of Poisson's ratio. Hence it is not thermodynamically forbidden that \( \nu < 0 \), which would cause a solid to expand laterally when it is pulled longitudinally. As we discussed above, the fact that \( \nu > 0 \) for all common solids has its source in the physical fact that the bulk modulus, \( \beta \), exceeds the shear modulus, \( G \), for all common solids. This is a consequence of the nature of cohesive bonding, and not a consequence of the laws of thermodynamics.

### 16.12 Stability with Respect to Plastic Deformation

It is experimentally observed that if a solid is left under load for a sufficiently long time it will eventually deform so as to relax the load. If the applied load is sufficiently large the relaxation is relatively rapid and occurs through normal plastic deformation. If the load is smaller the relaxation is slow, and occurs through the thermally activated processes that are known as creep or stress relaxation. Since stress relaxation is inevitable, it must be a consequence of a thermodynamic instability.

The plastic deformation of a material has the net effect of imposing a stress-free strain, since it alters the relaxed state of the material without changing the elastic properties in any substantial way. Since plastic deformation conserves volume, the stress-free strain is a deviatoric strain. It is easy to show that a state of a system that includes a non-zero deviatoric stress is unstable with respect to a stress-free strain that
relaxes the stress. Hence a solid that sustains a shear stress is always unstable with respect to plastic deformation if a kinetically possible deformation mechanism exists.

To demonstrate instability with respect to stress-free strain, first consider a solid that is strained and held so that the total strain is fixed, along with the temperature and composition. The Helmholtz free energy controls equilibrium in this case. According to equation 16.199, $F$ can be written

$$F = F(T,V,\{N\}) + F_{el}$$

$$= \tilde{F}(T,V,\{N\}) + \frac{V^0}{2} \lambda_{ijkl} \varepsilon_{ij}^d \varepsilon_{kl}^d$$  

where $\tilde{F}(T,V,\{N\})$ is the Helmholtz free energy of an equivalent fluid in a reference state in which the deviatoric stress is zero ($\sigma^d = 0$) and $\varepsilon^d$ is the deviatoric strain from that state. In the situation described the deviatoric strain is entirely elastic:

$$\varepsilon^e_{ij} = \varepsilon^d_{ij}$$  

and $F_{el}$ is positive. However, the free energy of the equivalent fluid is independent of its shape. Hence the first term in equation 16.213 is unchanged if the solid is given the stress-free strain $\varepsilon^0_{ij}$, which changes the elastic strain to

$$\varepsilon^e_{ij} = \varepsilon^d_{ij} - \varepsilon^0_{ij}$$  

But the elastic contribution to the free energy becomes

$$F_{el} = \frac{V^0}{2} \lambda_{ijkl} \left[ \varepsilon^d_{ij} - \varepsilon^0_{ij} \right] \left[ \varepsilon^d_{kl} - \varepsilon^0_{kl} \right]$$  

which decreases monotonically as $\varepsilon^0$ approaches $\varepsilon^d$. Hence the solid is unstable with respect to plastic deformation, if there is a mechanism that can accomplish it.

Since the deviatoric strain is fixed, equation 16.229 reaches a minimum when $\varepsilon^0 = \varepsilon^d$. If a kinetically possible mechanism exists the solid deforms spontaneously until the elastic stress is fully relaxed and the elastic solid achieves a fluid state.

A similar instability occurs when the stress is fixed at constant temperature and composition. In this case the equilibrium of the solid is governed by the Gibbs free energy, which is, by equation 16.108,

$$G = F + PV - V^0 \sigma^d_{ij} \varepsilon^d_{ij}$$
\[ \tilde{G}(T, P, \{N\}) = \tilde{G}(T, P, \{N\}) - \frac{V^0}{2} \sigma_{ij} d \epsilon_{ij} + \frac{V^0}{2} \left[ \sigma_{ij} d \epsilon_{ij} - \frac{\partial}{\partial \epsilon_{ij}} \right] \]

\[ \tilde{G}(T, P, \{N\}) = \tilde{G}(T, P, \{N\}) - \frac{V^0}{2} \sigma_{ij} d \epsilon_{ij} - \frac{V^0}{2} \sigma_{ij} d \epsilon_{ij} \]

where \( \tilde{G}(T, P, \{N\}) \) is the Gibbs free energy of the equivalent fluid and \( \epsilon^0 \) is the stress-free strain. Since \( G \) is unchanged by a shape change at constant \( P \), the Gibbs free energy decreases monotonically as the deviatoric part of the stress-free strain increases in the direction impelled by the applied stress, that is, the direction for which the product

\[ \sigma_{ij} d \epsilon_{ij} > 0 \]

In this case the work done on the reservoir is negative while the energy of the solid is unchanged. The solid is again unstable with respect to a stress-free deviatoric strain imposed by plastic deformation if a deformation mechanism exists.

The Gibbs free energy continues to decrease so long as the reservoir maintains the deviatoric stress, and the solid deforms at constant elastic strain. Since all real reservoirs are finite, the end point of this process is reached when the deformation relaxes the reservoir so that the applied stress falls to zero. Again, the ultimate equilibrium is a fluid-like state.

The instabilities documented here show that plastic deformation will inevitably occur if it can, and will eventually relax the deviatoric stress. It follows that an elastic solid is only stable when constraints prevent plastic deformation. The applicable constraint is usually a verbal constraint on the system, which is physically realistic when the kinetics of plastic deformation are so slow that stress relaxation can be ignored. The rate of plastic deformation is always finite when \( \sigma^d \) is non-zero, since at least diffusional creep mechanisms (which we shall discuss in the following chapter) are always operative. Hence an elastic solid behaves as a fluid in the limit of long experimental time.

We can also infer from these results that a strained solid is unstable with respect to precipitation of material that is free of deviatoric strain, that is, material that is already in the fluid-like state, provided that a mechanism of precipitation exists. Examples include recrystallization, and the nucleation of stress-free material at an interface, which will be discussed in the following chapter. By the same reasoning a deviatoric stress provides a driving force for the nucleation of a new phase whose structure provides a shear that relaxes the load. This phenomenon is important in structural transformations, particularly transformations of the martensitic type, and will be discussed in some detail below.