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FOR FLUID SURFACE PHENOMENA

by

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1. Introduction

The purpose of this thesis is to provide a continuum theory for fluid surface phenomena that accounts for the interaction of the surface with the surrounding materials. Of primary interest is the transport of mass into and out of the surface. The proposed theory was constructed by considering the surface or interface between two materials to be a geometrical surface but possessing finite physical properties different from those of the surrounding media. Constitutive equations for a fluid surface are studied and a linear theory is obtained.

There exists an extensive literature dealing with surface phenomena from the classical and statistical thermodynamic viewpoint. All of this work has been profoundly influenced by GIBBS [1]. He postulates the use of a geometrical "dividing surface" located in or near the physical surface of discontinuity. The exact location of the dividing surface for other than planar interfaces was chosen by Gibbs so that the sum of the principal radii of curvature is zero. For the planar case he stated: "It is generally possible to place the dividing surface so that the total quantity of any desired component in the vicinity of the surface of discontinuity shall be the same as if the density of the component were uniform on each side quite up to the dividing surface." The location of the dividing surface has been a subject of controversy and various authors have
proposed different methods of determining it. Another problem associated with the use of the dividing surface is that several parameters, such as the volume of the bulk phases and the mass occupying the physical surface, become functions of the location of the dividing surface.

The theory employed by GUGGENHEIM [2 - 3] is based on a three layer model for the interface. The dividing surface of Gibbs and parallel surfaces on either side of the dividing surface are used in studying variation in physical properties in the physical interface. Even though the properties of a physical system are not homogeneous up to the interface but are characterized by large gradients in these properties, the thickness of such a layer is extremely small. For example, direct measurement of the thickness of entrained water due to the flow of a monolayer of oleic acid moving at between 1 and 5 cm/sec on the water surface is 3 x 10^{-3} cm - independent of film velocity [4]. Another problem in employing Guggenheim's theory is that the location of the parallel surfaces is not rigorously specified by the theory. They are usually chosen to be equidistant from the dividing surfaces for convenience but it is not difficult to envision systems for which it would be desirable to specify unequal spacing. Additional difficulties in locating the surfaces are encountered when nonplanar surfaces are studied.

Although there are many physical systems for which an exact location of an interface is a difficult, if not impossible task, the approach utilized in this thesis presumes the existence of a well delineated physical interface. This requirement
allows the exact location of the interface to be specified and thus avoids the difficulties inherent in the theories of Gibbs and Guggenheim. Also, these theories define the properties of the surface as the excess quantities which are left over after all the other quantities in the system have been specified. Because, as previously mentioned, some of the surface quantities depend on the location of the dividing surface, it is often possible to locate the dividing surface such that a particular surface quantity is zero. A fundamentally different approach is employed in this thesis. The surface is endowed with physical properties inherently its own and is considered to interact with the surrounding bulk material in much the same way as if it were the tightly stretched membrane originally proposed by Young in 1805 [5]. The simple experiment of floating a needle or razor blade on a liquid surface provides a very persuasive argument for the present viewpoint. The needle will float on the surface but once it passes below the surface it immediately begins to sink. A conclusion that can be reached is that the molecules that constitute the surface exhibit different physical properties from those of the bulk material. The surface molecules are able to support the weight of the needle while the bulk material cannot. Thus, it appears reasonable to treat the interface as a separate entity possessing physical properties different from those of the bulk material even though from a molecular viewpoint they are the same, differing only because the surface molecules are acted on by different forces.

Of particular interest are the comments of Tolman [6]
concerning the relevance and meaning of applying macroscopic thermodynamic variables to the microscopic interfacial region. He discusses the problem in detail with regard to the pressure, density, free energy, and potential of the surface and outlines a statistical-mechanical interpretation of these quantities. He thus rests the ultimate justification of the problem on statistical mechanics but also admits that significant results have been obtained by using the macroscopic approach. Tolman also extended the classical theory by making a detailed study of a transition layer of spherical form. The various thermodynamic quantities were considered to be functions of the distance normal to the dividing surface and the results obtained were in terms of definite integrals evaluated on either side of the surface.

A recent series of articles by ERIKSSON [7 - 11] provide an excellent review of the classical thermodynamic literature as well as some extensions of this theory. Some of his comments will be of use later when the problem of the equilibrium state is discussed. The ideas of Gibbs have been extensively developed by the workers in the general area of irreversible thermodynamics [12]. Their efforts have been closely tied to classical thermodynamics and to experimental results; thus, providing an excellent source of both useful information which aided in the formulation of the continuum theory and material with which to compare the results of the proposed theory.

A few comments are in order at this point regarding the classical theories. The most important fact to remember
is that they deal almost exclusively with the equilibrium state or, at best, small excursion from equilibrium. These considerations have so dominated thermodynamics that it would seem there are no non-equilibrium problems while, obviously, the states other than equilibrium are the most interesting and demanding of close attention. Related to this problem is the lack of temporal consideration. It will be recalled that time does not enter the consideration of classical thermodynamics. Therefore, it is very difficult to compare the results of a continuum theory, where the velocity is a quantity of fundamental importance, with a theory that does not involve changes with time. The great majority of the theoretical work that has been done is limited to either plane or spherical interfaces. Nearly all of the experimental work involves planar surfaces only, with some measurements being made with spherical drops or bubbles. The only restrictions on the surface geometry in this thesis are those that will ensure the persistence of the surface in time and space.

There exist several excellent review articles dealing more directly with the engineering aspects of liquid-liquid and liquid-gas interfaces. The articles by URSELL [13], WEHAUSEN [14] and WEHAUSEN & LAITONE [15] provide a starting place for this literature and describe several interesting experiments. One of the oldest wave propagation problems is the water wave problem. The ancient Greeks were aware of the calming effect of pouring oil on turbulent seas [4]. More recent interest has centered around descriptions of
wind generated waves and the study of sea states. STOKER [16] points out that until 1957 the analytical solutions of the water wave problem were based almost exclusively on the two approximate theories which result when either the amplitude of the surface wave is considered small with respect to the wave length or the depth of water is small compared to the wave length. Both, however, neglect the effect of surface tension. The classical method of treating surface tension is to employ Young's hypothesis of a membrane stretched to a uniform constant tension, placed on the surface. Using this model the following expression for the speed of propagation of the wave may be derived [17]:

\[ C^2 = \frac{g\lambda}{\rho} + \frac{2\pi T}{\lambda^2} \]  \hspace{1cm} (1.1)

where \( g \) is the acceleration due to gravity, \( \lambda \) the wave length, \( \rho \) the fluid density and \( T \) the surface tension. If \( \lambda \) is large gravity effects dominate (gravity waves) and if \( \lambda \) is small the surface tension effects are most important (capillary waves). Unfortunately, ocean waves are characterized by long swells upon which are superimposed short wave length waves. The damping of these short capillary waves by oil spread on the sea is responsible for the calming effect [4]. Also, the wind drag on the large waves is reduced, thus reducing their tendency to break.

A problem related to water waves is that of hydrodynamic stability, which has been systematically treated by Chandrasekhar [18]. The following three problems are of
primary interest: the Benard problem - the thermal instability of a layer of fluid heated from below; the Rayleigh-Taylor problem - the instability of the plane interface between two fluids of different densities; and the Kelvin-Helmholtz problem - the instability of a plane interface between superposed fluids flowing one over the other with relative horizontal velocity. The Bernard cells are a familiar example of free convection heat transfer [19]. However, the currently accepted explanation of the observed hexagonal patterns is that the surface tension varies from point to point due to variations in the surface temperature and thus causes the cellular patterns to develop [20]. When surface tension is considered in the other two stability problems the interface is treated as a membrane subject to uniform tension.

The present theory has been primarily directed toward these general types of problems; i.e., the interface between two fluids. The related problems of surface phenomena at solid surfaces and absorption of gases at solid surfaces have received less attention. The proposed theory, based on the principles of continuum mechanics, provides a mathematically rigorous theory which will account for the interaction of the surface with the bulk material on either side of the surface.

Turning to previous research that has a more direct influence on the present work, SCRIVEN'S paper [21] is the earliest that approaches the desired level of generality. He assumes that the interface can be represented as a geometrical surface and the material in the surface is an isotropic fluid
continuum. Equations of balance of mass and momentum are written for the surface and, by direct analogy with the three dimensional fluid, a constitutive equation relating surface stress to rate of strain in the surface is postulated. The balance of momentum equation does not include momentum exchange with the surroundings. SCRIVEN does not postulate a balance of moment of momentum or a balance of energy. There is no reference to the second law of thermodynamics. Thus, the theory, though correct, cannot be considered complete.

SLATTERY [22, 23] attempted to extend SCRIVEN's theory by proposing a momentum balance which includes the interaction with the surroundings and a moment of momentum balance. He is unsuccessful in his first paper and tries to correct the error by proposing a mixture theory for the surface. He does not develop this theory to any extent and does not consider the balance of energy or the entropy inequality.

The most complete work to date is that of GHEZ [24]. Although set in the forces and fluxes language of non-equilibrium thermodynamics, the balance laws that he obtains are identical with those proposed in this thesis. However, his treatment of the entropy inequality is somewhat less than desirable because he assumes: the surface internal energy is a function of the surface entropy and density; the surface temperature is equal to the rate of change of the internal energy with respect to the entropy; and the isentropic part of the surface stress tensor is equal to the rate of change of the internal energy with respect to the inverse of the density. Proper handling of the entropy inequality would have allowed GHEZ to prove
these statements, or ones similar to them, as will be demonstrated.

Obviously, the results of workers in the general area of shell theory should be very beneficial in any attempt at formulating a surface theory. Unfortunately, there is still considerable disagreement as to the proper definition of strain in a shell. The problem is concisely summarized in a comment by BUDIANSKY & SANDERS [25], "On the 'Best' First-Order Linear Shell Theory." "In marked contrast to the theories of bending and stretching of flat plates, the general linear theory of thin elastic shells has not yet received a universally accepted formulation; it is only a slight exaggeration to say that each investigator favors a different theory." By first order the authors mean that the middle surface with displacement of material points off the middle surface rendered determinate by the Kirchhoff assumption: material normals to the undeformed middle surface do not change length and remain normal to the deformed middle surface after deformation of the shell. Various stress and strain measures are discussed and a choice among them is made by considering features thought most desirable by the authors. These discussions are restricted to the static case and no mention is made of the approach accepted by the proponents of continuum mechanics, except for the requirement that the equations be written in general tensor form for arbitrary shells.

The remarks of TRUESDELL & TOUPIN [26, Sections 60, 212, and 213] are particularly appropriate. These authors
favor the theory of oriented bodies first suggested by Duhem [27] and later developed by E. & F. Cosserat [28]. The physical body is represented as an assembly of points to each of which is associated a direction. This theory of Cosserat's materials is proposed to overcome the highly singular nature of rod and shell theory that occurs when the diameter of the rod or the thickness of the shell is allowed to approach zero. The more recent developments of these ideas by Ericksen & Truesdell [29] and Green, Naghdi & Wainwright [30] have unfortunately not settled the controversy. In fact, the introduction of a deformable vector associated with every material point in the body creates considerable confusion. Also, no method of measuring the physical constants associated with the director has been proposed. Therefore, the present theory has not utilized this concept even though there may be some conceptual advantage gained by its use.

In Section 2 the balance laws and the entropy inequality are systematically developed. In order to investigate the significance of these laws, constitutive equations for a fluid surface are proposed in Section 3. The principle of equipresence and the entropy inequality are used to restrict the form of the constitutive equation and equilibrium conditions are specified. Section 4 contains a discussion of material frame indifference as applied to the surface. Polynomial constitutive equations are derived and compared with appropriate related theories in Section 5.
NOTATION

In the component notation employed, Greek indices denote quantities which refer to the surface and Latin indices denote quantities which refer to the Euclidean 3-space. The Greek indices take values 1, 2 and are summed diagonally. Latin indices have values 1, 2, 3 and are likewise summed. Occasionally direct notation will be employed with vectors and tensors denoted by Latin and Greek boldface letters: $\mathbf{A}, \mathbf{\Gamma}, \mathbf{Z}$. A colon denotes total covariant differentiation, a semicolon indicates partial covariant differentiation, and a comma implies a partial derivative. A superposed dot, $\dot{A}$, denotes the material derivative. Since it will be clear from the context, no distinction will be made between differentiation following the motion of the $\mathbf{\mathcal{Y}}$ surface particle and differentiation following the $\mathbf{\mathcal{X}}$ bulk material particle. Occasionally a superposed caret, $\hat{A}$, will be used to denote the partial derivative of $A$, a two-point tensor quantity, with respect to time holding the space and surface coordinates fixed. If the meaning is clear the caret notation will be used for various other partial derivatives with respect to time. The symbols $\otimes$ and $\langle, \rangle$ denote, respectively the tensor and scalar products [31]. The base vectors in the surface will be denoted by $\mathbf{e}^\alpha, a^\alpha$, and the corresponding quantities in the 3-dimensional Euclidean space are symbolized by $e^\alpha, e^\iota$. Although in Cartesian coordinates covariant and contravariant vectors are identical the distinction is maintained here as a notational convenience.
2. Balance Equations

In this section the entropy inequality and the balance of mass, momentum, moment of momentum and energy equations for an arbitrary surface media which interacts with its surrounds are systematically developed. The form of a general balance law is assumed and the desired conservation laws are obtained by selecting the appropriate thermodynamic variables using the general equation as a guide. The various terms and symbols needed throughout the thesis are defined. Also included, in the form of lemmas, are the derivation of the material derivative following the motion of a surface particle, and the necessary and sufficient conditions that the surface stress tensor be symmetric with the normal component equal to zero.

The configuration to be considered is that of two material media separated by a surface $\mathcal{J}$ of zero thickness but having finite physical properties. The unit surface normal $n$, will be chosen to point in the direction of propagation of the surface; thus, the velocity of the surface through space will always be positive. If the surface is stationary in space or oscillating about an equilibrium position, this restriction is no longer necessary.

The material bodies $\mathcal{B}$ and $\mathcal{B}$ may be different but each consists of only a single component. Motion of the particles of the bulk materials into the surface is accounted for by considering that upon entering the surface, the particles
lose their original identity and become surface particles subject to the constitutive equations defining the surface. By neglecting the individual motion of the bulk materials upon entering or leaving the surface it is possible to avoid the complexity of a mixture theory and to maintain a viewpoint that is consistent with the physical problems previously discussed. Therefore, fluxes of mass into and out of the surface will be accounted for by changes in the surface density $\gamma$. The material particles that constitute the bodies $\mathcal{B}, \mathcal{B}$ and the surface $\gamma$ will be denoted by $\bar{X}, \bar{X}$, and $\gamma$ respectively. The bodies $\mathcal{B}$ and $\mathcal{B}$ are considered to be specified materials and obey the usual laws and assumptions of continuum mechanics [26, 32, 33, 34, 35].

**Definition.** The motion of the surface in the 3-dimensional Euclidean space is given by

$$\bar{X}^k = \phi^k(y^\alpha, t)$$

(2.1)

where the $y^\alpha$ are Gaussian coordinates in the surface and $t$ is time. The function $\phi^k$ is assumed to be an allowable representation as defined by KREYSZIG [36].

**Definition.** The velocity of the surface through space is given by

$$u^k = \frac{\partial \phi^k}{\partial t} \bigg|_{y^\alpha}$$

(2.2)

**Definition.** The motion of $\gamma$ in the surface is given by

$$\gamma^\alpha = \gamma^\alpha(y^\gamma, t) \quad \gamma^\gamma = \gamma^\gamma(y^\gamma, t)$$

(2.3)

where $\gamma^\gamma$ refer to a fixed reference configuration.
Definition: The velocity of \( y \) in space is

\[
\dot{y} = \dot{\alpha} \xi^a + \alpha^a \tag{2.5}
\]

where \( \dot{\alpha} = \frac{\partial \alpha}{\partial y^a} \).

Definition: The \( \lambda \)-velocity difference is defined as

\[
\begin{align*}
\dot{x}_\lambda &= \dot{x} - \dot{x}_\lambda \\
\end{align*}
\]

where \( \dot{x}_\lambda \) is the velocity of the \( \lambda \) material particle. \( \lambda = \alpha, \alpha' \).

Lemma 1. Given an arbitrary two-point tensor field

\[
A = A^\kappa_{\mu\nu}(x, y, t) \epsilon^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f
\]

the material derivative \( \dot{A} \) is given by

\[
\begin{align*}
\dot{A} &= (A^\kappa_{\mu\nu}(x, y, t) \dot{\epsilon}^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f + A^\kappa_{\mu\nu}(x, y, t) \dot{\epsilon}^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f) \epsilon^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f + \\
&\quad (A^\kappa_{\mu\nu}(x, y, t) \epsilon^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f + A^\kappa_{\mu\nu}(x, y, t) \dot{\epsilon}^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f) \dot{\epsilon}^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f + \\
&\quad A^\kappa_{\mu\nu}(x, y, t) \dot{\epsilon}^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f + A^\kappa_{\mu\nu}(x, y, t) \epsilon^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f)
\end{align*}
\]

\[
(\epsilon^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f = -\alpha^{\mu\nu} a^\alpha \epsilon^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f + \epsilon^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f)
\]

\[
(\epsilon^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f = \epsilon^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f + \epsilon^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f)
\]

where \( a_{\mu\nu} \) and \( a_{\alpha\beta} \) are the first and second fundamental forms of the surface.

Proof:

\[
\begin{align*}
\dot{A} &= \frac{\partial A}{\partial x^m} \dot{\epsilon}^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f + \frac{\partial A}{\partial y^a} \dot{\epsilon}^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f + \frac{\partial A}{\partial t} \dot{\epsilon}^a \epsilon^b \epsilon^c \epsilon^d \epsilon^e \epsilon^f
\end{align*}
\]

To obtain (2.7) the following quantities are required.

\[
\begin{align*}
\frac{\partial a_{\mu\nu}}{\partial x^m} &= 0 \\
\frac{\partial a_{\mu\nu}}{\partial y^a} &= \{a_{\alpha\beta}\} a_{\alpha\beta} + b_{\alpha\beta} \tag{2.5}
\end{align*}
\]

Christoffel symbol based on \( a_{\mu\nu} \)
\[
\frac{\partial a^\mu}{\partial y^\rho} = - \left\{ a^\lambda \right\} a^\lambda + b^\mu \\dot{n}
\]
\[
\frac{\partial \sigma_k}{\partial t} = 0
\]
\[
\frac{\partial a^\mu}{\partial t} = \mathbf{f}_k \cdot \mathbf{e}_R
\]
\[
\frac{\partial a^k}{\partial t} = - a^\alpha \lambda a^\beta \mu \epsilon_{k\ell} \left( \mathbf{f}_\lambda \mathbf{f}_\mu + \mathbf{f}_\lambda \mathbf{f}_\ell \right) a^\beta + a^\alpha \lambda \mathbf{f}_k \cdot \mathbf{e}_R
\]

By inserting these relations in (2.8) and regrouping the proper terms (2.7) is obtained.

The general balance equation for the surface was derived by equating the jump condition for a singular surface [26, Section 193] to the surface analog of the general three dimensional balance equation. [26, Section 157]. GHEZ [24] appears to use a more fundamental approach but points out that his balance equations reduce to the "discontinuity conditions across shocks and phase fronts" when the properties of the surface are neglected. This obviously desirable feature is an integral part of the present theory.

Assumption: The general balance equation for the surface is given by

\[
\frac{d}{dt} \int y \lambda \, dl = - \int \xi(\lambda) \cdot \mathbf{e} \, dl + \int y \xi(\lambda) \, dl
\]
\[
+ \int \left( \left[ \frac{\partial}{\partial x} \lambda \frac{\partial}{\partial x} \lambda \right] - \left[ \frac{\partial}{\partial x} \lambda \lambda \right] + \left[ \lambda \lambda (\lambda) \right] \right) \, dl
\]

(2.9)
\( \Lambda \) - any scalar, vector or tensor quantity

\( \nabla \) - unit surface vector normal to the curve

\( \mathcal{S}(\Lambda) \) - surface source of \( \Lambda \)

\( i(\Lambda) \) - vector flux of \( \Lambda \) in the surface

\( i_n(\Lambda) \) - flux of \( \Lambda \) normal to the surface

\( \left[ \frac{\partial \Lambda}{\partial n} \right] = \frac{\partial \Lambda}{\partial n} - \frac{\partial \Lambda}{\partial n} \) - jump of the corresponding bulk quantities across the surface

\( n_n = n_2 \)

Using the surface form of Green's theorem [35 Section 9.42] and evaluating the left hand side of (2.9), the general balance equation may be written as

\[
\frac{\partial \gamma}{\partial \Lambda} + \gamma \Lambda \left( \frac{i_n^\alpha + \frac{\partial}{\partial n} \frac{\partial \Lambda}{\partial n}}{2} \right) + \text{grads} i(\Lambda) - \gamma \mathcal{S}(\Lambda) + \left[ \frac{\partial \Lambda}{\partial n} \right] \left[ \frac{\partial \Lambda}{\partial n} \right] = 0
\]

where the gradient with respect to the surface coordinates is denoted by grad and \( \alpha = \text{det} \left| a_{\alpha n} \right| \).

Assumption: The balance of mass equation is obtained by choosing

\( \Lambda = 1 \)

\( \mathcal{A} = 1 \)

\( i(\Lambda) = 0 \)

\( i_n(\Lambda) = 0 \)

\( \mathcal{S}(\Lambda) = 0 \)

\[
\gamma \left( \frac{i_n^\alpha + \frac{\partial}{\partial n} \frac{\partial \Lambda}{\partial n}}{2} \right) + \left[ \frac{\partial \Lambda}{\partial n} \right] = 0
\]

Assumption: The balance of momentum equation results from setting
\[ \Lambda = \mathbf{\dot{x}}^i \]

\[ \mathbf{\dot{\Lambda}}(A) = \mathbf{I} \] - surface stress tensor

\[ S(\Lambda) = \mathbf{F} \] - body force/unit surface mass

\[ \Lambda^k = \dot{\mathbf{x}}^k \]

\[ \dot{\mathbf{\dot{\Lambda}}}^k(\Lambda) = \frac{\partial T^{ij}}{\partial x^k} \] - stress tensor

\[ \sum_{\alpha} \mathbf{\dot{x}}^i \dot{\mathbf{\dot{\Lambda}}}^i(\Lambda) = \frac{\partial T^{ij}(x, t)}{\partial x^j} + T_{\alpha}^{i\alpha} - \gamma \mathbf{F}^i \]

\[ + \left[ \mathbf{G}^{\alpha \beta} \prod_{\alpha} \mathbf{\dot{x}}^i \dot{\mathbf{\dot{\Lambda}}}^i(\Lambda) - \left[ \mathbf{G}^{\alpha \beta} \prod_{\alpha} \mathbf{\dot{x}}^i \dot{\mathbf{\dot{\Lambda}}}^i(\Lambda) \right] = 0 \] (2.12)

Assumption: The balance of moment of momentum equation is derived by letting

\[ \Lambda = \mathbf{E}_{\text{rem}} \mathbf{\dot{x}}^m \]

\[ \dot{\mathbf{\dot{\Lambda}}}^k(\Lambda) = \mathbf{E}_{\text{rem}} \frac{\partial \mathbf{\dot{x}}^m}{\partial x^k} \]

\[ S(\Lambda) = \mathbf{E}_{\text{rem}} \mathbf{\dot{F}}^m \]

\[ \dot{\mathbf{\dot{\Lambda}}}^k(\Lambda) = \mathbf{E}_{\text{rem}} \frac{\partial \mathbf{\dot{F}}^m}{\partial x^k} \]

\[ \mathbf{\dot{E}}(\Lambda) = \mathbf{E}_{\text{rem}} \mathbf{\dot{T}}^{mn} \]

\[ \mathbf{E}_{\text{rem}} = \text{alternating tensor} \]

\[ \sum_{\alpha} \mathbf{\dot{x}}^i \dot{\mathbf{\dot{E}}}(\Lambda) = \frac{\partial \mathbf{\dot{x}}^m}{\partial x^j} + \mathbf{\dot{F}}_{\alpha}^{i\alpha} - \gamma \mathbf{F}^i \]

\[ - \gamma \mathbf{E}_{\text{rem}} \mathbf{\dot{F}}^m + \left[ \mathbf{G}^{\alpha \beta} \mathbf{\dot{E}}_{\text{rem}} \mathbf{\dot{\dot{x}}^m} \right] - \left[ \mathbf{G}^{\alpha \beta} \mathbf{\dot{E}}_{\text{rem}} \frac{\partial \mathbf{\dot{x}}^m}{\partial x^k} \right] = 0 \] (2.13)

Assumption: The balance of energy equation arises from letting
\[ \Delta = e^{+\frac{1}{2}x^2} \quad \Delta = e^{+\frac{1}{2}x^2} \]
\[ \dot{\mathcal{L}}(\Lambda) = \mathcal{G}^k + T^k - \dot{x}_k \quad \dot{\mathcal{L}}(\Lambda) = \mathcal{G}^k + T^k - \dot{x}_k \]
\[ \mathcal{S}(\Lambda) = \mathcal{H} + F^k \dot{x}_k \quad \mathcal{S}(\Lambda) = \mathcal{H} + F^k \dot{x}_k \]

\[ c - \text{internal energy/unit surface mass} \]
\[ \mathcal{G}^k - \text{heat flux vector in the surface} \]
\[ \mathcal{A} - \text{internal energy of the } \lambda \text{ material} \]
\[ \mathcal{G}_\lambda^k - \text{heat flux vector in the } \lambda \text{ material} \]
\[ \mathcal{H} - \text{surface heat source} \]

\[ \frac{1}{2} \mathcal{H}^k \dot{x}_k = \gamma \left( e^{+\frac{1}{2}x^2} \right) + \gamma \left( e^{+\frac{1}{2}x^2} \right) \left( \mathcal{G}^k + \mathcal{G}_\lambda^k \right) + \left( \mathcal{G}^k + T^k - \dot{x}_k \right) \cdot \gamma \]

\[ - \gamma \left( \mathcal{H} + F^k \dot{x}_k \right) + [\gamma \left( e^{+\frac{1}{2}x^2} \right) \mathcal{H}] - [\gamma \left( e^{+\frac{1}{2}x^2} \right) \mathcal{G}_\lambda^k] = 0 \]

Assumption: The entropy inequality is obtained by letting

\[ \Lambda = \mathcal{H} \quad \Delta = \mathcal{L} \]
\[ \dot{\mathcal{L}}(\Lambda) = \mathcal{G}^k / \mathcal{L} \quad \dot{\mathcal{L}}(\Lambda) = \mathcal{G}^k / \mathcal{L} \]
\[ \mathcal{S}(\Lambda) = \mathcal{H} / \mathcal{L} \quad \mathcal{H} > 0 \quad \mathcal{L} > 0 \]

and requiring that the equality be replaced by an inequality.

\[ \gamma - \text{surface entropy/unit surface mass} \]
\[ \mathcal{L} - \text{surface temperature} \]
\[ \mathcal{L} - \text{entropy of } \lambda \text{ material} \]
\[ \mathcal{L} - \text{temperature of } \lambda \text{ material} \]
\[
\bar{v}' + y_\eta \left( \bar{\gamma} \alpha + \bar{\beta} \right) + \left( \bar{\gamma} \beta \right) \alpha - \frac{\partial \phi}{\partial \theta}
\]
\[
+ \left[ \bar{\gamma} \beta \eta \right] - \left[ \bar{\gamma} \beta \eta \right] / \theta \]
(2.15)

Lemma 2. For a surface in which (2.12) is satisfied, a necessary and sufficient condition for (2.13) to be satisfied is that the tangential component of the surface stress tensor be symmetric and the normal component be zero.

Proof: The proof is rather straightforward if it is observed that
\[
\Gamma^l_a = \Gamma^l_b = \Gamma^l_c
\]
\[
\text{Exem} \eta^l \chi^m = \text{Exem} \chi^l \chi^m
\]
(2.16)
\[
(\text{Exem} \eta^l) \alpha = \text{Exem} \eta^l_i^\alpha
\]
Inserting (2.12) into (2.13) and noting that \( T^{\alpha \beta} \) may be written as
\[
T^{\alpha \beta} = T^{\alpha \beta} + T_n \eta^k
\]
(2.17)
obtain
\[
\text{Exem} \eta^l \dot{T}^{\alpha \beta} = 0 \Rightarrow \dot{T}^{\alpha \beta} = \dot{T}_n \eta^k
\]
(2.18)
Since \( n \dot{T}_n = 0 \) (2.17) may be combined with (2.18) to yield
\[
T^{\alpha \beta} = T^{\beta \alpha}
\]
\[
T_n \dot{\alpha} = 0
\]
(2.19)
3. Constitutive Theory

In order to study the consequences of the balance equations, which are valid for any continuous media, the type of material which constitutes the surface must be specified. Since the transfer of mass is of primary interest a fluid surface is considered.

The definitions of a thermodynamic process and an admissible thermodynamic process for the surface are stated and the existence of a unique admissible thermodynamic process is established in order to use the entropy inequality to restrict the functional form of the constitutive equations. These concepts were developed by COLEMAN & MIZEL [37] and COLEMAN & NOLL [38] but are applied here for the first time to surface phenomena. The remainder of the section is devoted to a systematic study of the equilibrium condition for the surface and a comparison of the present results with those of other authors.

Definition: A thermodynamic process for the surface is the set of 27 functions whose values are

\[ x = x(x, t) \quad \phi = \phi(x, t) \]

\[ \rho = \rho(x, t) \quad \kappa = \kappa(x, t) \]

\[ \varepsilon = \varepsilon(x, t) \quad \gamma = \gamma(x, t) \]

\[ (3.1) \]
\[ t = \frac{t}{\lambda} (\dot{\chi}, t) \]
\[ \dot{\gamma} = \gamma (\dot{\chi}, t) \]
\[ \dot{\chi} = \chi (\dot{\chi}, t) \]
\[ \mathcal{I} = \mathcal{I} (\dot{\chi}, t) \]
\[ \mathcal{F} = \mathcal{F} (\dot{\chi}, t) \]
\[ \Theta = \Theta (\dot{\chi}, t) \]

\[ \lambda = \lambda (\dot{\chi}, \alpha) \]
\[ \sigma = \sigma (\dot{\chi}, t) \]
\[ \varphi^\infty = \varphi^\infty (\dot{\chi}, t) \]
\[ \h = \h (\dot{\chi}, t) \]
\[ \zeta = \zeta (\dot{\chi}, t) \]

and the specification of the surface (2.1) which satisfy (2.11), (2.12), (2.13), (2.14) and

\[ \frac{\partial \mathcal{I}}{\partial t} + \text{div} (\mathcal{H} \dot{\chi}) = 0 \]

\[ \mathcal{H} \dot{\chi} = \text{div} \dot{\chi} + \mathcal{K} \dot{\chi} \]
\[ \mathcal{F} = \mathcal{F} \]

\[ \mathcal{R} (\mathcal{H} + \mathcal{K} \dot{\chi}) = \text{div} (\mathcal{H} \dot{\chi}) - \text{div} \dot{\chi} + \mathcal{K} \dot{\chi} \cdot \dot{\chi} + \mathcal{K} \dot{\chi} \]

A close review of the balance equations, the entropy inequality, and the background of experience with 3-dimensional theories suggests that constitutive equations should be written for the surface stress \( \mathcal{I} \), the heat flux in the surface \( \varphi \), the surface Helmholtz free energy \( \varphi = e - \sigma \sigma \) and the surface entropy \( \zeta \). The free energy is introduced as a matter of convenience.
Definition. A fluid surface is defined by the constitutive equations

\[ T^k\alpha = \tilde{T}^k\alpha(\mathbf{A}) \quad \varphi = \tilde{\varphi}(\mathbf{A}) \]

\[ g^{\alpha} = \tilde{g}^{\alpha}(\mathbf{A}) \quad \eta = \tilde{\eta}(\mathbf{A}) \]

\[ \mathbf{A} = \{ \Theta, \varphi, \eta, f, \lambda, \lambda', \lambda'', \gamma, \Omega, \lambda_{\kappa} \} \]  \hspace{1cm} (3.3)

\[ g = \Theta, \alpha = \gamma \]

\[ f = \lambda_{\kappa}, \alpha = \gamma \]

\[ \Omega = \lambda_{\kappa}, \kappa = \gamma \]

The determination of which variables to include in the constitutive equations, though seemingly arbitrary, is by no means trivial. The process involves picking a set of variables, working through the equations—as will be demonstrated—and looking at the results to ensure that they are meaningful. Usually they are not and several variables must be added or replaced and the process repeated. Though time consuming the procedure is not random; the variables \( \Theta \), \( \Theta_{\alpha} \), \( \lambda_{\kappa} \) and \( \gamma \) were included in the constitutive equations because of experience with 3-dimensional fluid mixtures [39, 40]. Since mass is being exchanged between the surface and the surrounding bulk media, the densities \( \lambda \) and velocities \( \lambda' \) should affect the stress, for example, in the surface. The quantities \( \lambda^k_\alpha \) and \( \lambda'^k_{\alpha, \beta} \) require a little more explanation. The first and second fundamental forms of the surface are related to these
quantities through
\[ a_{\alpha \beta} = \delta_{\alpha \beta} \, \gamma^{\kappa} \gamma_{\kappa} \quad \quad \quad b_{\alpha \beta} = \gamma^{\kappa} \, \gamma_{\kappa} \, \gamma_{\mu} \] (3.4)

\[ \gamma_{\kappa} = \frac{1}{2} \, \varepsilon_{\kappa \mu} \varepsilon_{\kappa \lambda} \, \frac{\partial x^\mu}{\partial x^\lambda} \]

Thus \( a_{\alpha \beta} \) and \( b_{\alpha \beta} \) contain the same information as \( a_{\alpha \beta} \) and \( b_{\alpha \beta} \) but have the advantage of being easier to manipulate. Length changes in the surface are given by
\[ a_{\alpha \beta} \, dy^\alpha \, dy^\beta \] (3.5)

Also the Gaussian curvature \( K \), the mean curvature \( H \), and the principal curvatures \( K_1, K_2 \) are related by
\[ K = K_1 K_2 = b/a \quad \quad \quad b = \text{det} / |b_{\mu \nu}| \] (3.6)

\[ H = \frac{1}{2} (K_1 + K_2) = \frac{1}{2} \, a_{\alpha \beta} \, b_{\alpha \beta} \]

Therefore any geometric property of the surface can be calculated if \( a_{\alpha \beta} \) and \( b_{\alpha \beta} \) are known; both classical theory and intuition suggest that the properties of the surface depend on its geometrical shape.

Definition. An admissible thermodynamic process is one that is consistent with the constitutive equations (3.3).

Theorem 1. Given that an admissible thermodynamic process can be defined for the bulk materials, for every choice of the deformation function \( \gamma \), the temperature distribution \( \Theta \), and specification of the surface \( E \), there exists a unique admissible thermodynamic process for the surface.

Proof. From the given information the properties on
either side of the surface may be evaluated at \( \mathcal{Z} = \mathcal{A}(y, t) \) and thus enter the balance and constitutive equations for the surface as known quantities. Knowledge of \( \Theta = \Theta(y, t) \) determines \( \theta, \alpha \). The specification of the surface allows the calculation of \( f^k \), \( \mathcal{F} \), \( \mathcal{N} \) and \( u^k \). The density can then be computed from the mass balance equation and the constitutive equations may now be used to determine the body force \( \mathcal{F} \) and the heat source \( \mathcal{H} \) in the balance of momentum and energy equations. By these calculations an admissible thermodynamic process is obtained.

If the entropy inequality is required to hold for all admissible thermodynamic processes, it must be valid for every choice of \( \mathcal{Z}, \varphi, \mathcal{F}, \Theta, \) and \( \mathcal{Q} \) by Theorem 1. Thus, in particular, it must be valid for the following:

\[
\begin{align*}
\mathcal{X} &= \phi^\alpha(y^\alpha, t) = \alpha(t) + \lambda^\alpha \frac{\partial}{\partial t} y^\alpha + \sum_{\beta} \lambda^\alpha \eta^{\alpha\beta} y^\beta + \sum_{\alpha} \lambda^\alpha \eta^{\alpha\gamma} y^\gamma \\
\eta^\alpha &= \eta^\alpha(y^\alpha, t) = \dot{\eta}^\alpha(t) + \epsilon^\alpha(t) y^\alpha \\
\dot{y} &= \dot{y}^\alpha \left( y^\alpha - \mathcal{Z} \right) \\
\Theta &= \Theta(t) + \eta^\alpha(t) y^\alpha + \beta dt \cdot y^\alpha y^\beta \\
\mathcal{X} &= \mathcal{X}^\alpha(y^\alpha, t) = \mathcal{F}(t) + \mathcal{H}(t) \mathcal{X} \\
\mathcal{X}^\alpha &= \frac{\partial}{\partial t} \left( \mathcal{X} - \dot{H} \right) \\
\varphi &= \varphi(t) + \sum_{\alpha} \mathcal{M}_{\alpha} \mathcal{X}^\alpha \\
\mathcal{Q} &= \mathcal{Q}^\alpha = \mathcal{D}_{\alpha} \mathcal{X}^\alpha = \mathcal{D}_{\alpha} \mathcal{Q} = \mathcal{D}_{\alpha} \mathcal{Q} = \mathcal{D}_{\alpha} \mathcal{Q}
\end{align*}
\]

By requiring the entropy inequality (2.15) to be satisfied for all admissible thermodynamic processes, it is possible to
derive necessary and sufficient conditions that the constitutive equations must satisfy.

To ensure that a process is admissible, $\mathbf{A}$, $\mathbf{F}$, $\dot{\mathbf{Y}}$, and $\dot{\mathbf{H}}$ must be eliminated from the entropy inequality. The balance of energy equation (2.14) is solved for $\mathbf{A}$ and substituted into (2.15). Since (2.14) contains $\mathbf{F}$ the balance of momentum equation (2.12) is solved for the body force and used to remove this term from (2.15). Finally, the balance of mass equations (2.11) and (3.12), are solved for $\dot{\mathbf{Y}}$ and $\dot{\mathbf{H}}$. Therefore a combined inequality

$$-\gamma \left( \dot{\mathbf{Y}} + \Theta \dot{\mathbf{Q}} \right) = \frac{\mathbf{F}^T \Theta}{\Theta} - \int^k \mathbf{J} dx_\alpha - \left[ \int^l \frac{\mathbf{J}^T}{2} dx_\alpha \right]$$

$$- \left[ \frac{f^k}{\alpha} \mathbf{y} \right] + \left[ \frac{\mathbf{F}^T}{\mathbf{J}^T} \right] (\mathbf{Y} - \mathbf{Q}) + \left[ \frac{\mathbf{F}^T}{\mathbf{J}^T} \right] \mathbf{Q} + \left[ \frac{\mathbf{F}^T}{\mathbf{J}^T} \right] \mathbf{Q}$$

$$- \left[ \frac{\mathbf{F}^T}{\mathbf{J}^T} \right] \mathbf{Q} \left( \frac{\delta}{\Theta - \delta} \right) \geq 0$$

is obtained that can be used to restrict the constitutive equations. To do this $\mathbf{Y}$ must be evaluated.

**Definition.** The material derivative of $\mathbf{Y}$ is

$$\dot{\mathbf{Y}} = \frac{\partial \mathbf{Y}}{\partial \Theta} \dot{\Theta} + \frac{\partial \mathbf{Y}}{\partial \mathbf{Y}} \dot{\mathbf{Y}} + \left( \frac{\partial \mathbf{Y}}{\partial \mathbf{F}} \right) \dot{\mathbf{F}} + \left( \frac{\partial \mathbf{Y}}{\partial \mathbf{A}} \right) \dot{\mathbf{A}} + \left( \frac{\partial \mathbf{Y}}{\partial \mathbf{Q}} \right) \dot{\mathbf{Q}}$$

$$+ \left( \frac{\partial \mathbf{Y}}{\partial \mathbf{H}} \right) \dot{\mathbf{H}} + \left( \frac{\partial \mathbf{Y}}{\partial \mathbf{Q}} \right) \dot{\mathbf{Q}} + \left( \frac{\partial \mathbf{Y}}{\partial \mathbf{H}} \right) \dot{\mathbf{H}}.$$

**Definition.**

$$\frac{\partial \mathbf{Y}}{\partial \mathbf{H}} = \mathbf{Y}^k \mathbf{e}_k \mathbf{e}_l \mathbf{e}_\alpha \mathbf{e}_\beta \mathbf{e}_\gamma \mathbf{e}_\delta \mathbf{e}_\epsilon$$

(3.10)
\[ \psi = \psi (\Theta, \gamma, \omega, \omega_\alpha, \dot{x}^\mu, \dot{w}, \gamma^k, \omega^k, \Omega_\alpha) \]

Using (2.7), (3.9), (3.10) and the various properties of the scalar and tensor products, \( \psi \) may be calculated and (3.8) becomes

\[
- \gamma \left\{ \frac{\partial \psi}{\partial \Theta} + \frac{\partial \psi}{\partial \Theta_\alpha} \left[ (\Theta_\alpha)_{,\beta} \gamma^\beta + \Theta^{\alpha}_{,\beta} + \Theta_\alpha \Theta_{\beta} \right] \right\} + \\
- \frac{\partial \psi}{\partial \gamma} \left( \gamma (\gamma_{,\alpha} + \frac{\partial \gamma}{\partial \gamma_\alpha}) \right) + \frac{\partial \psi}{\partial \omega_\mu} \left( \omega_\mu (\omega_\mu - \omega^2) \right) + \\
\frac{\partial \psi}{\partial \dot{x}^\mu} \left( \dot{x}^{\mu} (\dot{x}^{\mu} - \dot{x}^2) \right) + \frac{\partial \psi}{\partial \dot{w}} \left( \dot{w} (\dot{w} - \dot{w}^2) \right) + \\
\frac{\partial \psi}{\partial \gamma^k} \left( \gamma^k (\gamma^k - \gamma^2) \right) + \frac{\partial \psi}{\partial \omega^k} \left( \omega^k (\omega^k - \omega^2) \right) + \\
\frac{\partial \psi}{\partial \Omega_\alpha} \left( \Omega_\alpha (\Omega_\alpha - \Omega^2) \right) - \frac{\partial \gamma}{\partial \gamma_{,\alpha}} \left( \gamma_{,\alpha} \gamma + \gamma_{,\alpha} \gamma + \gamma_{,\alpha} \gamma \right) + \\
+ \frac{\partial \psi}{\partial \omega^k} \left( \omega^k (\omega^k - \omega^2) \right) + \frac{\partial \psi}{\partial \Omega_\alpha} \left( \Omega_\alpha (\Omega_\alpha - \Omega^2) \right) - \frac{\partial \psi}{\partial \dot{x}^\mu} \left( \dot{x}^{\mu} (\dot{x}^{\mu} - \dot{x}^2) \right) + \\
- \frac{\partial \psi}{\partial \Theta_\alpha} \left[ \Theta_\alpha (\Theta_\alpha - \Theta^2) \right] - \left[ \frac{\partial \psi}{\partial \omega^k} \right] - \left[ \frac{\partial \psi}{\partial \dot{x}^\mu} \right] - \left[ \frac{\partial \psi}{\partial \Theta_\alpha} \left( \Theta_\alpha - \Theta^2 \right) \right] \geq 0
\]

By close inspection of (3.11) and the constitutive equations (3.3), it can be seen that the term \( \Theta \) may be varied independent of the other terms in (3.11) i.e., the
equation may be written in the form

\[(\gamma^* + \frac{\partial \gamma}{\partial \Theta}) \dot{\Theta} + B \geq 0\]  

(3.12)

where \(B\) represents the terms in (3.11) which are independent of \(\dot{\Theta}\). The only way that (3.12) can be satisfied for all values of \(\dot{\Theta}\) is for its coefficient \(\gamma^* + \frac{\partial \gamma}{\partial \Theta}\) to be identically zero and \(B \geq 0\).

\[\gamma = -\frac{\partial \gamma}{\partial \Theta}\]  

(3.13)

Thus starting with (3.1), (3.2), (3.3), the definition of an admissible thermodynamic process and Theorem 1, it has been possible to prove mathematically that (3.13), a result usually assumed to be true in classical thermodynamic theory and one which was assumed by Ghez [24] in a slightly different form, is true for the surface regardless of any restrictions concerning equilibrium.

Similarly, it can be noted that \(\dot{\Theta}_x\) may be varied independently. Therefore

\[\frac{\partial \gamma}{\partial \Theta_x} \geq 0\]  

(3.14)

Unfortunately the remaining restrictions are not so easily obtained but the procedure of isolating quantities that may be varied independently and equating their coefficients to zero remains the same. In order to establish the desired independence (3.7) is introduced into (3.11) and evaluated at the time \(z\) and the point on the surface \(\gamma = 0\). To avoid some of the writing involved, evaluate \(\gamma\) for the choice (3.7) and realize that any terms that appear in the constitutive equation cannot be varied independently of the other terms.
in (3.11).

\[ \psi^{\mu}_{r=0} = \psi(f, g_{\alpha}, \gamma, \lambda, \rho_{\alpha}, \sigma_{\alpha}, \xi, a_{\alpha}, \beta, \epsilon, \gamma, b_{\alpha}, b'_{\alpha}, \tilde{a}_{\alpha}, \tilde{b}_{\alpha}, \tilde{h}_{\alpha}, \tilde{h}'_{\alpha}, \tilde{h}^{\mu}_{\alpha}, \tilde{h}^{\mu}_{\alpha}, \tilde{h}^{\mu}_{\alpha}, \tilde{h}^{\mu}_{\alpha}) \tag{3.15} \]

\[ \tilde{\epsilon}^{\alpha}_{\beta} = \tilde{e}^{\alpha}_{\beta}, \tilde{A}^{\mu}_{\alpha} = \tilde{A}^{\mu}_{\alpha}, \tilde{H}^{\mu}_{\alpha} = \tilde{H}^{\mu}_{\alpha}, \tilde{H}^{\mu}_{\alpha} = \tilde{H}^{\mu}_{\alpha} \]

Therefore, only those quantities which involve terms other than those appearing in (3.14) will be written out when (3.7) is introduced into (3.11).

\[-\gamma \left\{ -\frac{\partial \psi^{\mu}_{\alpha}}{\partial \gamma} \left[ \gamma \left( \psi^{\mu}_{\alpha} + \frac{\partial \psi^{\mu}_{\alpha}}{\partial \gamma} \right) + \sum k_{\mu} \psi_{\alpha}^{\mu} \right] \right\} + \frac{\partial}{\partial x^{\alpha}} \left( \gamma \left( \psi^{\mu}_{\alpha} + \frac{\partial \psi^{\mu}_{\alpha}}{\partial \gamma} \right) + \sum k_{\mu} \psi_{\alpha}^{\mu} \right) \]

\[ + \frac{\partial}{\partial x^{\alpha}} \left( \gamma \left( \psi^{\mu}_{\alpha} + \frac{\partial \psi^{\mu}_{\alpha}}{\partial \gamma} \right) + \sum k_{\mu} \psi_{\alpha}^{\mu} \right) + \frac{\partial}{\partial x^{\alpha}} \left( \gamma \left( \psi^{\mu}_{\alpha} + \frac{\partial \psi^{\mu}_{\alpha}}{\partial \gamma} \right) + \sum k_{\mu} \psi_{\alpha}^{\mu} \right) \]

\[ - \frac{\partial}{\partial x^{\alpha}} \left( \gamma \left( \psi^{\mu}_{\alpha} + \frac{\partial \psi^{\mu}_{\alpha}}{\partial \gamma} \right) + \sum k_{\mu} \psi_{\alpha}^{\mu} \right) \]

\[ + \frac{\partial}{\partial x^{\alpha}} \left( \gamma \left( \psi^{\mu}_{\alpha} + \frac{\partial \psi^{\mu}_{\alpha}}{\partial \gamma} \right) + \sum k_{\mu} \psi_{\alpha}^{\mu} \right) \]

\[ + \frac{\partial}{\partial x^{\alpha}} \left( \gamma \left( \psi^{\mu}_{\alpha} + \frac{\partial \psi^{\mu}_{\alpha}}{\partial \gamma} \right) + \sum k_{\mu} \psi_{\alpha}^{\mu} \right) \]

\[ + \frac{\partial}{\partial x^{\alpha}} \left( \gamma \left( \psi^{\mu}_{\alpha} + \frac{\partial \psi^{\mu}_{\alpha}}{\partial \gamma} \right) + \sum k_{\mu} \psi_{\alpha}^{\mu} \right) \]

\[ + \frac{\partial}{\partial x^{\alpha}} \left( \gamma \left( \psi^{\mu}_{\alpha} + \frac{\partial \psi^{\mu}_{\alpha}}{\partial \gamma} \right) + \sum k_{\mu} \psi_{\alpha}^{\mu} \right) \]

\[ + \frac{\partial}{\partial x^{\alpha}} \left( \gamma \left( \psi^{\mu}_{\alpha} + \frac{\partial \psi^{\mu}_{\alpha}}{\partial \gamma} \right) + \sum k_{\mu} \psi_{\alpha}^{\mu} \right) \]

\[ + \frac{\partial}{\partial x^{\alpha}} \left( \gamma \left( \psi^{\mu}_{\alpha} + \frac{\partial \psi^{\mu}_{\alpha}}{\partial \gamma} \right) + \sum k_{\mu} \psi_{\alpha}^{\mu} \right) \]

\[ + \frac{\partial}{\partial x^{\alpha}} \left( \gamma \left( \psi^{\mu}_{\alpha} + \frac{\partial \psi^{\mu}_{\alpha}}{\partial \gamma} \right) + \sum k_{\mu} \psi_{\alpha}^{\mu} \right) \]

\[ + \frac{\partial}{\partial x^{\alpha}} \left( \gamma \left( \psi^{\mu}_{\alpha} + \frac{\partial \psi^{\mu}_{\alpha}}{\partial \gamma} \right) + \sum k_{\mu} \psi_{\alpha}^{\mu} \right) \]

\[ + \frac{\partial}{\partial x^{\alpha}} \left( \gamma \left( \psi^{\mu}_{\alpha} + \frac{\partial \psi^{\mu}_{\alpha}}{\partial \gamma} \right) + \sum k_{\mu} \psi_{\alpha}^{\mu} \right) \]

\[ + \frac{\partial}{\partial x^{\alpha}} \left( \gamma \left( \psi^{\mu}_{\alpha} + \frac{\partial \psi^{\mu}_{\alpha}}{\partial \gamma} \right) + \sum k_{\mu} \psi_{\alpha}^{\mu} \right) \]
\[ + a^{m} \delta_{mn} R_{\lambda}^{m} \nabla_{\alpha} R_{\lambda}^{m} + a^{m} \delta_{mn} R_{\lambda}^{m} \nabla_{\alpha} R_{\lambda}^{m} \]

\[- a^{m} \delta_{mn} R_{\lambda}^{m} \nabla_{\alpha} R_{\lambda}^{m} - a^{m} \delta_{mn} R_{\lambda}^{m} \nabla_{\alpha} R_{\lambda}^{m} - \left\{ \xi \gamma \frac{\partial}{\partial t_{\alpha}} \right\} \]

\[- \frac{\partial}{\partial t_{\alpha}} R_{\lambda}^{m} \nabla_{\lambda} R_{\lambda}^{m} - \frac{\partial}{\partial t_{\alpha}} R_{\lambda}^{m} \nabla_{\lambda} R_{\lambda}^{m} - \frac{\partial}{\partial t_{\alpha}} R_{\lambda}^{m} \nabla_{\lambda} R_{\lambda}^{m} - \frac{\partial}{\partial t_{\alpha}} R_{\lambda}^{m} \nabla_{\lambda} R_{\lambda}^{m} \]

\[- \int R_{\lambda}^{m} \nabla_{\lambda} R_{\lambda}^{m} - \int R_{\lambda}^{m} \nabla_{\lambda} R_{\lambda}^{m} - \int R_{\lambda}^{m} \nabla_{\lambda} R_{\lambda}^{m} \]

\[+ \left\{ \frac{\partial}{\partial t_{\alpha}} R_{\lambda}^{m} \nabla_{\lambda} R_{\lambda}^{m} \right\} - \left\{ \frac{\partial}{\partial t_{\alpha}} R_{\lambda}^{m} \nabla_{\lambda} R_{\lambda}^{m} \right\} = 0 \]  \( (3.16) \)

A close inspection of (3.15) and (3.16) reveals that the terms \( H_{\lambda}^{m}, b^{\alpha}, C^{m}_{\alpha}, \) and \( d^{m}_{\lambda \alpha} \) may be varied independently. The desired results are obtained as follows: The independence of \( H_{\lambda}^{m} \) and \( b^{\alpha} \) implies respectively that

\[ \frac{\partial}{\partial a^{m}} = 0 \quad \frac{\partial}{\partial a^{\alpha}} = 0 \]  \( (3.17) \)

Grouping the terms containing \( C^{m}_{\alpha \beta} \) and remembering that \( C^{m}_{\alpha \beta} = C^{m}_{\beta \alpha} \), gives

\[ n^{k} \delta_{nm} \frac{\partial}{\partial t_{\alpha}} = 0 \]  \( (3.18) \)

Taking the scalar product of (3.18) with \( n_{m} \) yields

\[ n^{k} \frac{\partial}{\partial a^{m}} = 0 \]  \( (3.19) \)

The variation of \( d^{m}_{\lambda \alpha} \) provides no new information since the only term containing this quantity is zero by (3.19).
Finally the independence of \( a^m \) implies

\[
\sum_{\lambda} \frac{\partial \psi}{\partial a_{\lambda}^{m}} = 0 \tag{3.20}
\]

Taking the partial derivative of (3.20) with respect to \( a^m \) and utilizing (3.17), results in

\[
\frac{\partial \psi}{\partial a_{\lambda}^{m}} = 0 \tag{3.21}
\]

Using these results (3.11) is reduced to

\[
-\gamma \left\{ -\frac{\partial \psi}{\partial \theta} \left( \xi (\dot{y}^m_{\lambda} + \frac{\dot{\xi}}{\dot{\theta}} a_{\lambda}^m) + \left[ K_{\lambda} \dot{a}_{\lambda}^{m} \right] \right) + \frac{\partial \psi}{\partial \xi_{\lambda}} \left( \dot{a}_{\lambda}^{m} \dot{y}^m_{\lambda} + n_{\lambda}^m \dot{y}_{\lambda}^{m t} \right) \\
+ \frac{\partial \psi}{\partial \xi_{\lambda}} \left[ n_{\lambda}^{m t} \dot{y}^m_{\lambda} + n_{\lambda}^{m t} \right] - \frac{\partial \psi}{\partial \theta} \theta_{\lambda} - \tau_{\lambda}^{m t} + \zeta_{\lambda}^{m t} \right\}
- \left[ \sum_{\lambda} \xi_{\lambda}^{m t} \dot{y}^m_{\lambda} \right] + \left[ K_{\lambda} \dot{a}_{\lambda}^{m t} \right] + \left[ \sum_{\lambda} \xi_{\lambda}^{m t} \dot{y}^m_{\lambda} \right] - \\
\left[ \sum_{\lambda} \xi_{\lambda}^{m t} \dot{y}^m_{\lambda} \left( \frac{\xi_{\lambda}^{m t}}{\theta - \zeta_{\lambda}^{m t}} \right) \right] = D \left( \dot{y}^m_{\lambda}, \theta_{\lambda}, \dot{\zeta}_{\lambda}^{m t}, \zeta_{\lambda}^{m t} \right) \geq 0 \tag{3.22}
\]

Further information may be extracted from (3.22) by considering the equilibrium conditions.

**Definition.** The surface is in equilibrium when the entropy production \( D \) is a minimum.

**Lemma 3.** The entropy production is a minimum, i.e. \( D = 0 \), when the independent variables \( \dot{y}^m, \theta_{\lambda}, \dot{\zeta}_{\lambda}^{m t}, \) and \( \zeta_{\lambda}^{m t} \) are all zero.

**Proof.** By inspection (3.22) becomes
\[- \gamma \left\{ - \frac{\partial \psi}{\partial \chi} \left( \dot{\chi}^\rho + \frac{\alpha}{2a} \right) + \frac{\partial \psi}{\partial \dot{\chi}^\alpha} \left( f_{\alpha}^\beta \dot{\chi}^\beta + n^k \chi^\alpha \right) \right\} + \frac{\partial \psi}{\partial \dot{\chi}^\alpha} \right\} \geq 0 \]

(3.23)

The first term can be shown to be zero by noting that

$$\delta_{kk} \dot{\chi}^\alpha \chi^\beta = 0 \Rightarrow \dot{\chi}^\alpha + a^\beta \delta_{kk} \chi^\beta = 0$$

(3.24)

$$\dot{\chi}^\alpha + \frac{\alpha}{2a} = \dot{\chi}^\alpha + a^\beta \delta_{kk} \chi^\beta$$

The second term requires the following:

$$n_k \dot{\chi}^\alpha \Rightarrow b_{\alpha \beta} \dot{\chi}^\alpha + n_k \chi^\beta = 0$$

(3.25)

$$f_{\alpha \beta} \dot{\chi}^\alpha + n^k \chi^\alpha \Rightarrow n_k \left( b_{\alpha \beta} \dot{\chi}^\alpha + n_k \chi^\alpha \right)$$

Finally, it may not very easily be shown that the last term can be expressed as

$$\frac{\partial \psi}{\partial \dot{\chi}^\alpha} \left( b_{\alpha \beta} \delta_{kk} \chi^\beta \right)$$

(3.26)

By Lemma 3 and (3.22),

$$D(\dot{\chi}, \chi, \dot{\chi}^\alpha, \chi^k) = 0$$

$$D(0, 0, 0, 0) = 0$$
Definition. Let

\[ D(\Theta_1, \Theta_2, \xi_1, \xi_2, \ddot{x}_1, \ddot{x}_2, \ldots, \ddot{x}_z, \gamma_1, \gamma_2, \gamma_3, \ldots, \gamma_z) = \]

\[ D(k_i, k_2, \ldots, k_{i,c}) \]

Necessary condition for \( D \) to have a relative minimum value at \( k_i = 0 \) i.e. at equilibrium are

\[ \frac{\partial^2 D}{\partial k_i^2} \bigg|_{k_i=0} = 0 \quad i, j = 1, 2, \ldots, n \quad (3.29) \]

\[ \begin{vmatrix} \frac{\partial^2 D}{\partial k_i^2} \bigg|_{k_i=0} \end{vmatrix} \]

be a positive-definite matrix \( (3.30) \)

Necessary and sufficient conditions for a real symmetric matrix to be positive definite is that each of its discriminants be positive [41, 42].

Although this is the usual mathematical statement of the requirements for \( D \) to be a minimum at equilibrium, it does not exclude the possibility that \( 3.30 \) be positive semi-definite. It is important from the physical standpoint to allow the possibility of the discriminants of \( 3.30 \) to be greater than or equal to zero. Therefore, the requirement \( 3.30 \) will be relaxed to allow the matrix to be positive semi-definite with the realization that there is no loss in generality or mathematical preciseness but a great gain in the physical understanding of the results.

Before utilizing conditions \( 3.29 \) & \( 3.30 \), \( 3.24 \), \( 3.25 \), and \( 3.26 \) will be used to recast \( 3.22 \) into a more useful form.
\[ D = -v \left\{ -v \frac{\partial}{\partial v} \alpha \delta \delta_{\mu \nu} f^{\alpha}_{\mu} + \frac{\partial}{\partial v} \alpha \delta_{\mu \nu} f^{\alpha}_{\mu} + \frac{\partial}{\partial v} \alpha \delta_{\mu \nu} f^{\alpha}_{\mu} + \frac{\partial}{\partial v} \alpha \delta_{\mu \nu} f^{\alpha}_{\mu} \right\} + \frac{v}{v} \left[ \frac{\partial}{\partial v} \alpha \delta_{\mu \nu} f^{\alpha}_{\mu} \right] \right\} n \neq 0 \]

\[ + \frac{v}{v} \left[ \frac{\partial}{\partial v} \alpha \delta_{\mu \nu} f^{\alpha}_{\mu} \right] n \neq 0 \]

\[ + \frac{v}{v} \left[ \frac{\partial}{\partial v} \alpha \delta_{\mu \nu} f^{\alpha}_{\mu} \right] n \neq 0 \]

\[ - \frac{v}{v} \left[ \frac{\partial}{\partial v} \alpha \delta_{\mu \nu} f^{\alpha}_{\mu} \right] n \neq 0 \]

\[ = 0 \]  (3.31)

The requirement (3.29) leads to the following equilibrium results.

\[ \delta_{\alpha}^{\alpha} n_{\alpha} = 0 \]  (3.32)

\[ \frac{\partial}{\partial v} \alpha \delta_{\alpha}^{\alpha} = 0 \]  (3.33)

\[ \frac{v}{v} \frac{\partial}{\partial v} \delta_{\alpha}^{\alpha} \alpha + \frac{\partial}{\partial v} \delta(\frac{\alpha}{\alpha} - \frac{\alpha}{\alpha}) - \frac{\partial}{\partial v} \delta_{\alpha}^{\alpha} n_{\alpha} n_{\alpha} = 0 \]  (3.34)

\[ \frac{v}{v} \frac{\partial}{\partial v} \delta_{\alpha}^{\alpha} \alpha + \frac{\partial}{\partial v} \delta(\frac{\alpha}{\alpha} - \frac{\alpha}{\alpha}) - \frac{\partial}{\partial v} \delta_{\alpha}^{\alpha} n_{\alpha} n_{\alpha} = 0 \]  (3.35)

\[ \frac{v}{v} \frac{\partial}{\partial v} \alpha \delta_{\alpha}^{\alpha} = -v \frac{\partial}{\partial v} \alpha \delta_{\alpha}^{\alpha} \]  (3.36)

\[ \frac{\partial}{\partial v} \delta_{\alpha}^{\alpha} n_{\alpha} + \frac{\partial}{\partial v} \delta_{\alpha}^{\alpha} n_{\alpha} = 0 \]  (3.37)

To derive (3.36) and (3.37), (2.17), (3.4) and the relation \( n_{\alpha} \frac{\partial}{\partial v} = 0 \) must be used.
These results are particularly satisfying. The vanishing of the heat fluxes, (3.32) & (3.33), is an expected result. The definition of the surface pressure in (3.35) yields a relation that is a direct analog of the equilibrium stress in a Navier-Stokes fluid [33, (30.50)]. The relations (3.34) and (3.35) require more explanation. ERIKSSON [7-11] makes extensive use of the Butler equation in the form

\[ f_i^\text{s} = f_i^\text{b} + a_i^\text{s} \sigma + \frac{\beta}{\gamma} (\psi_i^\text{s} - \psi_i^\text{b}) \] (3.38)

where \( f_i^\text{s} \) is the Helmholtz free energy of the \( i^{th} \) component in the surface phases, \( \sigma \) is the surface tension, \( \beta \) is the bulk pressure, and \( \psi_i^\text{s} \) & \( a_i^\text{s} \) are respectively the partial molar volume and area [9, III. 24]. The prime refers to a reference state. Even though (3.34) and (3.35) cannot be reduced to (3.38) the similarity of the equations lends validity to all of them. If the equilibrium stress on the \( Z \) material takes the form \( \sigma = k_\text{F} \sigma_k \), then (3.34) may be written as

\[ \sigma = \frac{\beta}{\gamma} \psi_i^\text{s} - \frac{\gamma}{\sigma} \] (3.39)

Although ERIKSSON uses the approach first postulated by GIBBS and treats the surface region as having finite thickness, the results (3.38) and (3.39) are amazingly similar.

In deriving (3.38) ERIKSSON defines the surface chemical potential as

\[ \mu_i^\text{s} = f_i^\text{s} + \beta \psi_i^{\text{s}} \] (3.40)

and discusses extensively "the proper definition and physical interpretation of the chemical potential of a substance in a surface phase" [8, Section 5]. He concludes that the surface
chemical potential does not have the property of being equal to the chemical potentials in different phases at equilibrium. These remarks are included here since the usual concept of equilibrium implies that

$$\Psi = \Phi = \phi$$  \hspace{1cm} (3.41)

However, both ERIKSSON'S discussions and (3.34) & (3.35) indicate that neither (3.41) nor the equality of the chemical potentials are necessary conditions for equilibrium. It should be noted that if \( \frac{b}{a} = \frac{b}{a} = \sqrt{\gamma} \) then (3.41) results.

Unfortunately, the requirement (3.30) does not yield new restriction on the constitutive equations.

The preceding results are summarized in the following theorem.

**Theorem 2.** The necessary and sufficient conditions for the entropy inequality (3.8) to be satisfied for every admissible thermodynamic process of the fluid surface defined by (3.3) are

$$\Psi = \Psi(\Theta, \gamma, T; \tau; \rho)$$  \hspace{1cm} (3.42)

$$\eta = - \frac{\partial \Psi}{\partial t}$$  \hspace{1cm} (3.43)

$$n_k \frac{\partial \Psi}{\partial T_k} = 0$$  \hspace{1cm} (3.44)

and

$$-\gamma \left\{ -\gamma \frac{\partial \Psi}{\partial \delta} \alpha^m \frac{e}{e} \frac{\partial k}{\partial \alpha} + \frac{\partial \Psi}{\partial \mu} n_k \frac{e}{e} \frac{\partial k}{\partial \mu} \frac{\partial k}{\partial \mu} \frac{\partial k}{\partial \mu} \right\}$$

\[ \left\{ \int \int \int \int \frac{e}{e} \left( \frac{\delta \Psi}{\delta \psi} \right) + \left\{ \int \int \int \int \frac{e}{e} \left( \frac{\delta \Psi}{\delta \psi} \right) \right\} + \int \int \int \int \frac{e}{e} \left( \frac{\delta \Psi}{\delta \psi} \right) \right\} \]
\[ - \left[ \sum_{\lambda} t^{k\lambda} n_{\lambda} \right] \geq 0 \]  

(3.45)

where at equilibrium

\[ \frac{\partial}{\partial x^k} n_k = 0 \]  

(3.46)

\[ \frac{\partial}{\partial x^k} \lambda_k = 0 \]  

(3.47)

\[ \gamma \frac{\partial}{\partial x^k} \lambda_k - \lambda_k (\gamma - \mu_k) - \frac{1}{2} t^{mn} n_k n_m = 0 \]  

(3.48)

\[ \gamma \frac{\partial}{\partial x^k} \lambda_k + \lambda_k (\gamma - \mu_k) - \frac{1}{2} t^{mn} n_k n_m = 0 \]  

(3.49)

\[ T^{\alpha\beta} = \gamma \frac{\partial}{\partial x^k} a^{\alpha\beta} = -\sigma a^{\alpha\beta} \]  

(3.50)

\[ \frac{\partial}{\partial t^k} n_k + \frac{\partial}{\partial (x^l, \lambda)} b_{kl} \delta^{k\lambda} \epsilon_{\alpha\beta} \epsilon_{\delta\mu} t^{\muh} n_h = 0 \]  

(3.51)
4. Material Frame-Indifference

The axiom of material frame indifference or objectivity is a mathematical expression of the physical argument that the response of a material should not depend on the motion of the observer recording the response. A brief history of the axiom, which was first stated mathematically by NOLL, and detailed references are given by TRUESDELL & NOLL [32, Section 19].

Definition. A change of frame is defined by

\[ \vec{\xi} = Q(t) \xi + \zeta(t) \quad \vec{t} = t - a \]  \hspace{1cm} (4.1)

where \( Q(t) \) is an arbitrary real-valued nonsingular orthogonal transformation and \( \zeta \) is an arbitrary time dependent vector.

If \( Q^T \) and \( I \) denote respectively the transpose of and the identity transformation, the properties of \( Q \) require that

\[ QQ^T = Q^TQ = I \]  \hspace{1cm} (4.2)

The problem involved in defining a change of frame for the surface is that (4.1) and (4.2) have no simple and unambiguous representation and physical interpretation in curvilinear coordinates. Operations with these equations are usually performed in Cartesian coordinates where they take the form

\[ \xi^\kappa = Q^\kappa_\ell(t) \xi^\ell + \zeta^\kappa(t) \]  \hspace{1cm} (4.3)

\[ Q^\kappa_\mu G^\mu_{\m}\sigma_s^\kappa = S_s^\kappa \]  \hspace{1cm} (4.4)
Although restricting the surface to be planar will not provide sufficient information to retain the level of generality required, a somewhat similar result is obtained by using geodesic coordinates. It can easily be shown that at a given point of an arbitrary surface, a coordinate system can be introduced such that the Christoffel symbols vanish [35, p205; 36, pl51]. This coordinate system is usually called the geodesic coordinate system, and the point at which the Christoffel symbols vanish is called the pole. The desired relations can be proved in this simpler system and if they are valid tensor relations, the results are valid for all coordinate systems in the surface. It should be remembered that at any point of an arbitrary surface mutually orthogonal tangent vectors may be constructed and thus real-valued non-singular orthogonal transformation can be defined at each point of the surface [30, 44].

Definition. In geodesic coordinates at the pole a change of surface frame is given by \( \vec{\gamma}^\alpha \) which satisfies the differential equation

\[
\frac{d\gamma^\alpha}{dt} = \frac{d}{dt}(S^\alpha_{\rho}(\gamma^\nu)\gamma^\rho) + \epsilon^\alpha(t) \tag{4.5}
\]

subject to the condition that

\[
\vec{\gamma}^\alpha(\gamma^\nu, 0) = S^\alpha_{\rho} \gamma^\rho \tag{4.6}
\]

\[
S^\alpha_{\lambda} S_{\rho}^{\lambda} = S^\rho_{\alpha}. \tag{4.7}
\]

Thus

\[
\vec{\gamma}^\alpha = S^\alpha_{\rho}(\gamma^\nu)\gamma^\rho + \int_0^t \epsilon^\alpha(z)dz \tag{4.8}
\]
for all $t$ sufficiently near $t = 0$.

Essentially the definition states that if the surface observer does not move too far from the pole a reasonable surface analog for the axiom of material frame indifference can be made.

**Definition.** An arbitrary scalar $S$, vectors $\nu^k, \nu^\alpha$, tensor $A^\alpha_\beta$ and hybrid tensor $B^k_\alpha$ are said to be objective if under the change of frames (4.3) and (4.8), they transform as follows:

\[
\begin{align*}
\bar{S} &= S, \\
\bar{\nu}^k &= Q^k_\ell \nu^\ell, \\
\bar{\nu}^\alpha &= S_\alpha^\beta \nu^\beta
\end{align*}
\]

\[
\bar{A}^{\alpha\beta} = S_\alpha^\gamma S_\beta^\mu A^{\gamma\mu}
\]

\[
\bar{B}^k_\alpha = Q^k_\ell S_\alpha^\beta B^\ell_\beta
\] (4.9)

**Definition.** The surface deformation rate tensor is

\[
\dot{a}_{\alpha\beta} = \frac{1}{2} \left( \dot{t}^k_\alpha \dot{r}^k_\beta + \dot{t}^k_\beta \dot{r}^k_\alpha \right)
\] (4.10)

**Lemma 4.** All of the independent variables in constitutive equations are objective except $\dot{r}^k_\alpha$. The only objective quantity that may be derived from $\dot{r}^k_\alpha$ is the deformate rate tensor.

**Proof.** Scalars are unaffected by changes of frame.

\[
\dot{\Theta} = \Theta \Rightarrow \frac{\partial \Theta}{\partial y^\alpha} = \frac{\partial \Theta}{\partial y^\beta} \frac{\partial y^\beta}{\partial y^\alpha} = S^\alpha_\beta \frac{\partial \Theta}{\partial y^\beta}
\] (4.11)
Therefore, \( \Theta, \Theta_\lambda, \gamma \) and \( \hat{\rho} \) are objective. Now consider \( \bar{T}^\alpha_{\dot{\alpha}}, \bar{T}^\kappa_{\dot{\alpha} \beta} \) and remember that \( \bar{T}^\kappa_{\dot{\alpha} \beta}, \bar{T}^\kappa_{\dot{\alpha} \beta} \) since the Christoffel symbols all vanish at the pole.

\[
\bar{T}^\kappa_{\dot{\alpha} \beta} = \frac{\partial \tilde{T}^\kappa_{\dot{\alpha} \beta}}{\partial \bar{y}^t} = Q^k_{\dot{\alpha}} S^\lambda_{\dot{\mu}} t^l_{\dot{\lambda}}
\]

The establishment of the objectivity of \( \dot{X}^\kappa \) require a slightly different approach and great care with the notation.

\[
\bar{X}^\kappa = \frac{\partial \tilde{X}^\kappa}{\partial \bar{y}^t} = \dot{Q}^k_{\dot{\alpha}} \dot{X}^l_{\dot{\alpha}} + Q^k_{\dot{\alpha} \beta} \dot{X}^l_{\dot{\alpha} \beta} + \dot{c}^k \\
\bar{X}^\kappa = \frac{\partial \tilde{X}^\kappa_{\dot{\alpha}}}{\partial \bar{y}^t} = \dot{Q}^k_{\dot{\alpha} \beta} \dot{X}^l_{\dot{\alpha} \beta} + Q^k_{\dot{\alpha} \beta} \dot{X}^l_{\dot{\alpha} \beta} + \dot{c}^k
\]

To establish that every tensor is not objective consider \( \dot{X}^\kappa_{\dot{\alpha}} \).

\[
\frac{\partial \tilde{X}^\kappa_{\dot{\alpha}}}{\partial \bar{y}^t} = \dot{Q}^k_{\dot{\alpha}} \frac{\partial \tilde{X}^l_{\dot{\alpha}}}{\partial \bar{y}^t} + Q^k_{\dot{\alpha} \beta} \frac{\partial \tilde{X}^l_{\dot{\alpha} \beta}}{\partial \bar{y}^t}
\]

By comparison with (4.9), \( \dot{X}^\kappa_{\dot{\alpha}} \) is obviously not objective. However \( d_{\dot{\alpha} \beta} \) is objective.

\[
\bar{d}_{\dot{\alpha} \beta} = \bar{\delta}_{\dot{\alpha} \beta} \left( \bar{T}^\kappa_{\dot{\alpha} \beta} \dot{X}^l_{\dot{\alpha} \beta} + \bar{T}^\kappa_{\dot{\alpha} \beta} \dot{X}_{\dot{\alpha} \beta} \right)
\]

\[
= \delta_{\dot{\alpha} \beta} \left( Q^k_{\dot{\alpha}} S^\lambda_{\dot{\mu}} t^l_{\dot{\lambda}} \left( \dot{c}^l_{\dot{\alpha} \beta} + \dot{Q}^l_{\dot{\alpha} \beta} S^\kappa_{\dot{\lambda} \dot{\mu}} \dot{X}^l_{\dot{\lambda} \dot{\mu}} \right) + Q^k_{\dot{\alpha} \beta} S^\lambda_{\dot{\mu}} t^l_{\dot{\lambda}} \left( \dot{c}^l_{\dot{\alpha} \beta} + \dot{Q}^l_{\dot{\alpha} \beta} S^\kappa_{\dot{\lambda} \dot{\mu}} \dot{X}^l_{\dot{\lambda} \dot{\mu}} \right) \right)
\]

\[
= \delta_{\dot{\alpha} \beta} \left( Q^k_{\dot{\alpha}} S^\lambda_{\dot{\mu}} t^l_{\dot{\lambda}} \left( \dot{c}^l_{\dot{\alpha} \beta} + \dot{Q}^l_{\dot{\alpha} \beta} S^\kappa_{\dot{\lambda} \dot{\mu}} \dot{X}^l_{\dot{\lambda} \dot{\mu}} \right) \right)
\]
\[ + \delta_{\alpha \lambda} (Q^k_{\lambda} S^l_{\nu} t^m_{\rho} Q^k_{\mu} S^l_{\rho} \chi^b_{\nu} + Q^k_{\mu} S^l_{\rho} \chi^b_{\nu} Q^l_{\rho} S^k_{\nu} \chi^b_{\nu}) \]

\[ = S^\lambda_{\alpha} S^\rho_{\beta} \delta_{\mu \lambda} (t^m_{\lambda} \chi^b_{\rho} + t^m_{\rho} \chi^b_{\lambda}) \]  

(4.18)

\[ \bar{d}_{\alpha \beta} = S^\lambda_{\alpha} S^\rho_{\beta} d \lambda \rho \]

Equation (4.18) is obtained from (4.17) by recognizing that (4.4) implies

\[ \dot{Q}^k_{\lambda} Q^\lambda_{\mu} + \dot{Q}^k_{\mu} Q^\mu_{\lambda} = 0 \]  

(4.19)

Axiom: The constitutive equations must be invariant under a change of frame and a change of surface frame. If the values of \( \psi, \xi, T^a, \) and \( \phi^\alpha \) are given by the constitutive functions of \( (\theta, \theta_x, \gamma_0, \partial_t, \phi^k, t^a, t^a, \phi^k) \), the values of \( \bar{\psi}, \bar{\xi}, \bar{T}, \) and \( \bar{\phi}^\alpha \) are given by the same functions of \( (\bar{\theta}, \bar{\theta}_x, \bar{\gamma}_0, \partial_t, \bar{\phi}^k, \bar{t}^a, \bar{t}^a, \bar{\phi}^k) \) where

\[ \bar{\psi} = \psi \]

\[ \bar{\xi} = \xi \]

\[ \bar{T}^a = S^\alpha_{\lambda} S^\beta_{\mu} T^\alpha_{\mu} \]  

(4.20)

\[ \bar{\phi}^\alpha = S^\alpha_{\lambda} \phi^\lambda \]

\[ \bar{\phi}^k(\bar{x}, \bar{t}) = Q^k_{\lambda}(t) \bar{\phi}^k(\chi, t) + \bar{C}^k(t) \]

\[ \bar{\theta}^k(\bar{y}, \bar{t}) = Q^k_{\lambda} \phi^k(\gamma_0, t) + C^k(t) \]  

(4.21)

\[ \bar{\phi}^\alpha(\bar{y}, \bar{t}) = S^\alpha_{\beta} \phi^\beta(\bar{y}, t) + \bar{e}^\alpha(t) \]

A consequence of the axiom of material frame indifference is that
\[ \Psi(A) = \Psi(B) \quad \text{and} \quad S^T(I(A)S) = I(B) \tag{4.22} \]

where

\[ A = \left( \theta, \varphi, \gamma, f, \rho, \varphi, t, f \right) \]

\[ B = \left( \theta, S\varphi, \gamma, SF, \rho, OS\varphi, \Omega ST, \Omega S^TST \right) \]

and \( \varphi, \varphi, f, f \) are defined by (3.3) with

\[ L = d_{\mu\nu} a^\mu a^\nu \]

Definition. Scalar, vector and tensor value tensor functions which satisfy (4.22) for all orthogonal transformations \( S \) and \( Q \) are said to be isotropic.

Definition. If (4.22) holds for all \( Q \) and \( S \) in the sub-group \( g \) of orthogonal transformations, the functions are said to be isotropic relative to \( g \).

Definition. If \( g \) is the full orthogonal group \( o \)

\[ (\det S = 1, \det Q = 1) \]

functions isotropic relative to \( o \) are called simply isotropic. If \( g \) is the proper orthogonal group, \( (\det Q = 1, \det S = 1) \) functions isotropic relative to are called hemitropic[32].

The requirement (4.22) places severe restrictions on the form that the constitutive functions may take as will be shown in the next section where polynomial constitutive equations will be discussed.
5. Polynomial Constitutive Equations

The polynomial representation of constitutive equations are very important to applications of the theory and possible discovery of physical phenomena. They are systematically derived by using isotropic tensors.

Assumption: The constitutive function can be approximated by second order polynomials in terms of their vector and tensor quantities with coefficients that are functions of their scalar quantities.

The general form of the polynomials are

\[ \psi = \psi_0 + \psi_1 \tau_1 + \psi_2 \tau_2 \tau_1 + \psi_3 \tau_2 \tau_2 + \psi_4 \tau_2 \tau_1 \tau_1 + \psi_5 \tau_2 \tau_1 \tau_1 \tau_1 \]  \hspace{1cm} (5.1)

\[ \zeta = \zeta_0 + \zeta_1 \kappa_1 + \zeta_2 \kappa_2 \kappa_1 + \zeta_3 \kappa_2 \kappa_2 \kappa_1 \kappa_1 + \zeta_4 \kappa_2 \kappa_2 \kappa_1 \kappa_1 \kappa_1 \kappa_1 \]  \hspace{1cm} (5.2)

\[ \mathbf{T}_{\alpha\beta} = \mathbf{T}_{\alpha\beta}^{(0)} + \left( T_{\alpha\mu} \tau_\mu + \tau_{\alpha\beta} \kappa_\mu + \kappa_{\alpha\beta} \kappa_\mu \kappa_\nu + \kappa_{\alpha\beta} \kappa_\mu \kappa_\nu \kappa_\rho + \kappa_{\alpha\beta} \kappa_\mu \kappa_\nu \kappa_\rho \kappa_\sigma \right) \]
where the same symbol has been used for the function and its coefficient. Advantage has been taken of the thermodynamic restrictions (3.41) & (3.42) in writing (5.1) and (5.2).

Also

\[ \mathcal{F} = i \mathcal{F}(\Theta, \gamma) \]
\[ T = i T(\Theta, \gamma, \beta) \]  
\[ \mathcal{F} = i \mathcal{F}(\Theta, \gamma) \]
\[ \mathcal{F} = i \mathcal{F}(\Theta, \gamma, \beta) \]

these coefficients are restricted by the requirement (4.22) that the polynomials be isotropic functions. This will be true if and only if the coefficients are isotropic tensors [32, 40].

In a Cartesian coordinate system it is relatively
easy to show that the only isotropic and hemitropic tensors can be constructed from the appropriate outer products of the following sets.

Isotropics:

\[ A = \alpha_0 \]
\[ A \varepsilon = 0 \]
\[ A \varepsilon \eta = 0 \]
\[ A_{\varepsilon \varepsilon} = \alpha_0 \varepsilon \varepsilon + \alpha_1 \varepsilon \varepsilon \eta + \alpha_2 \varepsilon \varepsilon \varepsilon \]
\[ A_{\varepsilon \varepsilon \varepsilon} = \alpha_0 \varepsilon \varepsilon \varepsilon \]

Hemitropic:

\[ A = \alpha_0 \]
\[ A \varepsilon = 0 \]
\[ A \varepsilon \varepsilon = \alpha_0 \varepsilon \varepsilon \]
\[ A_{\varepsilon \varepsilon} = \alpha_0 \varepsilon \varepsilon + \alpha_1 \varepsilon \varepsilon \eta + \alpha_2 \varepsilon \varepsilon \varepsilon \]

By direct analog the isotropic and hemitropic surface tensors to the sixth order are as follows:

Isotropic:

\[ \Delta_0 = C_0 \]
\[ \Delta = 0 \]
\[ \Delta_{\varepsilon \varepsilon \varepsilon \varepsilon \varepsilon \varepsilon} = 0 \]
\[ \Delta^{\alpha \beta \gamma \delta} = C_0 a^{\alpha \beta \gamma \delta} + C_1 a^{\alpha \beta \gamma \delta} a^{\varepsilon \varepsilon} + C_2 a^{\alpha \beta \gamma \delta} a^{\varepsilon \varepsilon \varepsilon} \]

\[ \Delta^{\alpha \beta \gamma \delta \varepsilon \varepsilon} = C_0 a^{\alpha \beta \gamma \delta} a^{\varepsilon \varepsilon} + C_1 a^{\alpha \beta \gamma \delta} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} + C_2 a^{\alpha \beta \gamma \delta} a^{\varepsilon \varepsilon \varepsilon} + C_3 a^{\alpha \beta \gamma \delta} a^{\varepsilon \varepsilon \varepsilon} a^{\varepsilon \varepsilon} + C_4 a^{\alpha \beta \gamma \delta} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} + C_5 a^{\alpha \beta \gamma \delta} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} + C_6 a^{\alpha \beta \gamma \delta} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} + C_7 a^{\alpha \beta \gamma \delta} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} + C_8 a^{\alpha \beta \gamma \delta} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} + C_9 a^{\alpha \beta \gamma \delta} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon} a^{\varepsilon \varepsilon}
Hemitropic:
\[ \Delta^\omega = C_0 \]
\[ \Delta^\omega = 0 \]
\[ \Delta^{\alpha\beta} = C_0 \rho^{\alpha\beta} + C_1 \xi^{\alpha\beta} \]
\[ \Delta^{\alpha\beta} = 0 \]
\[ \Delta^{\alpha\beta\mu\nu} = 0 \] (5.9)
\[ \Delta^{\alpha\beta\mu\nu} = C_0 \rho^{\alpha\beta\mu\nu} + C_1 \xi^{\alpha\beta\mu\nu} \]

Powers of \( \xi^{\alpha\beta} \) higher than the first are not included since

\[ \xi^{\alpha\beta} \xi^{\mu\nu} = \begin{vmatrix} a^{\alpha\lambda} & a^{\alpha\mu} \\ a^{\beta\lambda} & a^{\beta\mu} \end{vmatrix} \] (5.10)

The coefficients in (5.1)-(5.4) that are hybrid tensors may be expressed as isotropic and hemitropic tensors by taking the appropriate outer products of the tensors listed in (5.6)-(5.9). Thus, for example

\[ \Xi^\alpha_{\mu\nu} = \delta_{\mu\nu} \Delta^{\alpha\beta} = \delta_{\mu\nu} \left( 3C_0 \rho^{\alpha\beta} + 2C_1 \xi^{\alpha\beta} \right) \] (5.11)

By expressing the coefficients of (4.23)-(4.26) in terms of the appropriate combinations of hemitropic and isotropic tensors and making use of the symmetry of the surface stress tensor, the constitutive equations may be expressed as follows:

Hemitropic:
\[ \psi = \sigma + \tau_0 \xi, \quad \omega = \tau_0 \sqrt{K} \]
\[ \chi = \omega + \tau_0 \omega^2 - \tau_0 \sqrt{K} \] (5.12)
\( g^{\alpha} = \left[ (\delta^\alpha + 12 g^\lambda d^\lambda) \Theta, \rho \right] \tau^k + \left[ (12 g + 12 g^\lambda d^\lambda) \Theta, \rho \right] \xi^{\lambda} + \left[ (12 g + 12 g^\lambda d^\lambda) \Theta, \rho \right] \eta^{\lambda} \xi^{\lambda} + (12 g + 12 g^\lambda d^\lambda) \Theta, \rho \eta^{\lambda} \xi^{\lambda} + (12 g + 12 g^\lambda d^\lambda) \Theta, \rho \eta^{\lambda} \xi^{\lambda} + (12 g + 12 g^\lambda d^\lambda) \Theta, \rho \eta^{\lambda} \xi^{\lambda} + (12 g + 12 g^\lambda d^\lambda) \Theta, \rho \eta^{\lambda} \xi^{\lambda} + (12 g + 12 g^\lambda d^\lambda) \Theta, \rho \eta^{\lambda} \xi^{\lambda} + (12 g + 12 g^\lambda d^\lambda) \Theta, \rho \eta^{\lambda} \xi^{\lambda} \) \( (5.14) \)

\( T^{\alpha\beta} = \left[ (-\sigma + \xi_2 T_0 \delta^\alpha + \alpha_0 T_0 H^2 - \alpha_0 T_0 K + \alpha_0 T_0 \Theta, \lambda \Theta, \mu a^{\lambda\mu} + \alpha T_0 \delta^\alpha + \xi_2 T_0 \delta^\alpha + \alpha_0 T_0 H \delta^\alpha + \xi_2 T_0 H \delta^\alpha + \alpha_0 T_0 K \delta^\alpha + \alpha_0 T_0 \Theta, \lambda \Theta, \mu a^{\lambda\mu} + \alpha T_0 \delta^\alpha \right] a^{\alpha\beta} + \left( \xi_2 T_0 + \xi_2 T_0 \delta^\alpha + \alpha T_0 H + \alpha T_0 K \right) a^{\alpha\beta} + \alpha T_0 H a^{\alpha\beta} \) \( (5.15) \)

Isotropic:

\( g^{\alpha} = \left[ (\delta^\alpha + 12 g^\lambda d^\lambda) \Theta, \rho \right] \tau^k + \left[ (12 g + 12 g^\lambda d^\lambda) \Theta, \rho \right] \xi^{\lambda} \) \( (5.16) \)

There is obviously no difference in the hemitropic and isotropic expansion for the functions \( g, \xi, \tau, \) and \( T^{\alpha\beta} \). In the reduction to equations (5.12)-(5.16) use has been made of the geometric relations

\( b^{\alpha} b_{\alpha} = \frac{1}{2} H^2 - 2K \) \( (5.17) \)

\( b^\alpha \gamma b_{\alpha} \gamma = 2H b_{\alpha} \beta - Ka_{\alpha} \beta \)

The various coefficients in the constitutive equations have the form \( i \Delta \) where \( i \) denotes the isotropic tensor in the polynomial expansions (5.1)-(5.4) from which the coefficient
originated and \( j \) simply labels the terms which arise from that tensor.

**LINEAR THEORY**

Since the generality involved in the second order polynomial expressions is either not required or has not been used in the study of many physical surfaces, two linear theories are formulated. The possibility of two linear theories arises because of the interpretation of the linearity of the constitutive equations in the geometric properties of the surface.

If it is assumed that the equations are linear in the quantities

\[
\{ \Theta, \alpha, \lambda_{\alpha}, \lambda_{\alpha}^{\alpha} \} \tag{5.18}
\]

the hemitropic constitutive equations become

\[
\psi = \psi + s \psi H^2 - s \mu K \tag{5.19}
\]

\[
\eta = \eta + s \eta H^2 - s \lambda_{\alpha} K \tag{5.20}
\]

\[
\begin{align*}
\phi_{\alpha} &= \left( \psi, \Theta_{\beta} + \left( 2s \phi_{\alpha} + 2s \phi_{\alpha} \right) \right) \lambda_{\alpha} \lambda_{\alpha}^{k} + \left( \varepsilon_{\alpha} \theta_{\beta} \right) \lambda_{\alpha}^{\alpha} \\
\end{align*}
\]

\[
\begin{align*}
T_{\alpha\beta} &= \left[ -\mu + \left( \lambda_{\alpha} \lambda_{\beta} \right) + \mu \right] \lambda_{\alpha} \lambda_{\beta}^{k} + \left( 2s \psi \varepsilon_{\alpha} \varepsilon_{\beta} \right) \lambda_{\alpha}^{\alpha} + \left( 2s \psi \varepsilon_{\alpha} \varepsilon_{\beta} \right) \lambda_{\alpha}^{\alpha} \tag{5.22}
\end{align*}
\]

Again, the isotropic case is obtained by eliminating the term in (4.44) containing \( \varepsilon_{\alpha}^{\alpha} \). Since the differences between the two cases do not lead to any significant results, only the isotropic case will be discussed from this point.

Consider the restrictions obtained from the entropy inequality. Introducing (5.19) into (3.44) yields
\[ 2 \frac{\mu}{\alpha} H^{\alpha \beta} - \frac{\varepsilon}{\alpha} \varepsilon^{\alpha \mu} e_{\alpha \mu} = 0 \]  
(5.23)

Taking the scalar product of (4.46) with reduces the equation to

\[ 2 \varepsilon \cdot H = 0 \]  
(5.24)

If the surface is a plane, (5.24) is an identity, \((H=0, K=0)\).
If the surface is flat \((K=0, \text{for example, a cylindrical surface})\), then

\[ 2 \varepsilon \cdot H = 0 \]  
(5.25)

If the surface is minimal \((H=0)\), (4.47) reduces to

\[ \varepsilon \cdot K = 0 \]  
(5.26)

Since \(\varepsilon, K\) are functions of \(\Theta, \rho, \gamma\), they do not change with the shape of the surface. Therefore, the only solution for (4.47) valid for all surface shape is

\[ \varepsilon \cdot K = 0 \]  
(5.27)

The restriction (3.43) now implies that

\[ \varepsilon \cdot \rho = - \frac{\partial \rho}{\partial \Theta} \quad \varepsilon \cdot \gamma = 0 \]  
(5.28)

Turning to the equilibrium restrictions it is easily seen that (3.48) and (3.52) are satisfied. Equation (3.51) requires that at equilibrium

\[ \tau_{r} (\Theta, \gamma, \rho) = 0 \quad \tau_{r} (\Theta, \Theta, \rho) = 0 \]  
(5.29)

The other possible linear case involves restricting constitutive equations to be linear in the geometric properties of the surface. Obviously \(\tau_{r}, \tau_{r}^{\rho}\) could not be included in (5.18) since

\[ \alpha \beta = \delta_{\alpha \beta} \frac{\tau^{\rho}}{\rho} \quad \zeta_{\alpha \beta} = \tau_{r}^{\rho} \frac{\tau^{\rho}}{\rho} \]
and requiring that the polynomial be linear in \( \xi, \eta \), would have eliminated all of the equations. However, it seems reasonable to require that the constitutive relations be linear in the principal curvatures \( \kappa_1, \kappa_2 \). This requirement along with (5.18) allows the polynomials to be reduced to

\[
\phi = \phi(\Theta, \gamma) \tag{5.30}
\]

\[
\theta = \phi(\Theta, \gamma) = -\frac{3\nu}{\Theta} \tag{5.31}
\]

\[
\phi^\alpha = \left( \phi_\rho \Theta, \rho + (2s\phi_\rho \gamma + 2s\phi_\gamma \rho) \xi_1 \right) \delta^{\alpha}_\rho \tag{5.32}
\]

\[
\tau^{\alpha\beta} = \left[ -\phi + \alpha T^\lambda d^\lambda + (2s T^\lambda \xi_1 \rho + e T^\lambda \xi_1 \rho) \right] \delta^{\alpha \beta} \tag{5.33}
\]

\[
- \tau^\lambda \xi_1 \rho + (2s T^\lambda \xi_1 \rho + e T^\lambda \xi_1 \rho) \delta^{\alpha \beta}
\]

In this form the linear equation obviously satisfies (3.43), (3.44), (3.48), (3.51) and (3.52). Therefore no additional information can be obtained from the results of entropy inequality.

The dependence of the surface stress and the surface heat flux on the difference of the velocity of material on the surface and the velocity of material on either side of the surface is derived here for the first time. Equation (5.33) shows that if \( \nu^k \) the stress in the surface becomes a direct two dimensional analog of the usual Navier-Stokes theory of viscous flow and is identical with SCRIVEN'S results [21, 35]. It is entirely appropriate that the surface stress be independent of the curvature for a planar surface. However, it may appear at first unreasonable that the velocity difference
terms drop from (5.33) when the surface is planar. The following physical argument indicates that everything is as it should be. When water is placed in a container and heated, the surface remains planar until the water at the bottom becomes hot enough to be convected to the surface. As the warmer liquid enters the surface, the interface develops a pattern of peaks and valleys, thus losing its planar shape. According to (5.33) the stress is then affected by the fluid entering and leaving the surface. A similar phenomena may be observed when a flowing water hose is held under water and directed upward toward the surface.

The dependence of the heat flux on the velocity differences between various components of a mixture is a familiar feature of mixture theories [39, 40]. Its presence here requires a somewhat different explanation. Since \( f \) depends only on the tangential component of \( \gamma^{k} \), (5.32) implies that a mechanism of viscous friction is contributing to the heat flux in the surface. In other words, if the surface is sliding past the bulk material, this motion affects the heat flux in the surface. If a no slip condition is applied at the surface (\( \gamma^{k} \rho S = 0 \)), (5.32) reduces to the usual heat flux expression.

It seems appropriate to conclude this work by deriving at least one rather simple result, which dates back to Kelvin [45], in order to show that this maze of tensor notation can be reduced to a classical theory.

If the balance of mass equation is introduced into the balance of momentum equation the latter becomes
\( \gamma \chi^i + \varphi^i : \Gamma^a_{\alpha} + \varphi^i_\beta \Gamma^a_{\alpha} - \gamma F^i - \left( \sum_{\alpha}^n \chi^i - \sum_{\alpha}^n k^i \right) = 0 \) \hspace{1cm} (5.34)

By taking the dot product of (4.52) with \( \eta_i \), and assuming that the surface is stationary, the body forces can be neglected and the stress in the surrounding material is the pressure \( F^{k_i} = \delta^{k_i} \) (5.34) becomes at equilibrium

\[ \sigma H = \bar{p} - \bar{p} \] \hspace{1cm} (5.35)

If the surface is a sphere of radius \( r \), \( \bar{p} \) is the pressure inside the sphere, and \( \bar{p} \) is the outside pressure, (5.35) becomes the familiar Kelvin relation

\[ \frac{\partial \sigma}{\partial r} = \bar{p} - \bar{p} \] \hspace{1cm} (5.36)

since \( H = \frac{1}{r} \) for a sphere.
REFERENCES


5. Young, T., Phil. Trans. Roy Soc. Lond, 95, 65 (1805).


References (cont'd.)


