

On the Thermostatistics of Continuous Media

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Introduction

In this article we regard thermostatistics as being that branch of thermodynamics which deals with bodies which are at rest at the present time and which, for all practical purposes, may be regarded as having been at rest at all times in the past.

We attempt to develop here a rigorous theory of thermostatistics for continuous bodies in arbitrary states of strain. The thermodynamics of chemical reactions, phase transitions, and capillarity is not discussed. Our aim is to derive some of the fundamental laws of hydrostatics and elastostatics from thermodynamic principles. Among these laws are the existence of elastic potentials for stress-strain relations, the known inequalities of hydrostatics, and some new inequalities for hydrostatics and elastostatics.

In his classic work, "On the Equilibrium of Heterogeneous Substances", J. W. GIBBS [1] laid down criteria for determining whether a given (global) state of a body is thermodynamically stable. He used these criteria to derive particular equations and inequalities which represent conditions (in some cases necessary

and other cases sufficient) for various special states to be stable. The equations GIBBS obtained as necessary conditions for thermodynamic stability are now recognized as fundamental laws in physical chemistry. GIBBS also derived inequalities which, apparently because they are in obvious accord with everyday experience and thus might be mistakenly called trivial, have attracted relatively little attention and are sometimes not even mentioned in modern thermodynamics courses. For example, in his treatment of homogeneous systems at rest under uniform hydrostatic pressure, GIBBS showed that a necessary condition for such a system to be in a stable state is that both its heat capacity at constant volume and its adiabatic modulus of compression be non-negative. It is inequalities of this type which are emphasized in the present paper. We take, however, a point of view different from that of GIBBS.

In the classical treatments of thermostatics (*e.g.*, [1], [2]) the adjective *stable* is used in two senses. It is sometimes used as a modifier for the word *equilibrium*; *i.e.* one refers to "states of stable equilibrium"; or it is used as a modifier for the word *state*; *i.e.* one refers to "stable states". In this paper we never use the word *stable* in the former sense. The theory which we develop here makes a careful distinction between *local* states, referring to a material point in a body, and *global* states, referring to the body as a whole. A local thermomechanic state is specified by giving the entropy density and the local configuration at a material point. A global thermomechanic state, on the other hand, is specified only when the entropy field and the complete configuration are specified for the entire body. We regard *thermal equilibrium* to be a property of *local states*. We consider just one type of thermal equilibrium. We define a state of thermal equilibrium as a local thermomechanic state which minimizes an appropriate potential rather than as a state at which a first variation vanishes. We regard *stability* as a property of only *global states*. We consider several types of stable states, defined as global thermomechanic states which minimize certain energy integrals subject to different constraints.

Our theory is based on two physical postulates. The first asserts that, at a material point, any local thermomechanic state can be an equilibrium state provided the local temperature and local forces have appropriate values. The second postulate is essentially the assumption that, at least in continuum mechanics, absolute temperatures are never negative. We believe that these physical postulates, which are stated in terms of our definition of equilibrium, contain the physical content for the statics of continuous media of the First and Second Laws of Thermodynamics. From our postulates we prove relationships between the stress-strain equation and the caloric equation of state, and we derive various inequalities restricting the form of the caloric equation of state. We should like to propose that the inequalities which we obtain for the finite theory of elasticity answer some of the questions raised by C. TRUESDELL [3] in his recent article, "Das ungelöste Hauptproblem der endlichen Elastizitätstheorie".

Although our definition of thermal equilibrium is new, some of the definitions of the stability of global states which we propose for study are similar to stability definitions considered by GIBBS [1] and J. HADAMARD [4]. In particular, our concepts of isothermal and adiabatic stability at *fixed boundary* are closely related

to, but not identical to, *Hadamard stability**. We briefly discuss GIBBS' theory of the stability of fluid phases in § 16. In a future article we hope to give a discussion of GIBBS' theory of the stability of fluid mixtures.

We regard the main tasks of the science of thermostatistics to be, first, the exploration of the consequences for the caloric equation of state of the existence of local states of thermal equilibrium and, second, the derivation of useful necessary and sufficient criteria for global states to be stable. In the present paper, § 6—§ 13 are devoted to the first task and § 14—§ 16 deal briefly with the second. From our present point of view, we should say that the great classical thermodynamicists, GIBBS and DUHÉM, devoted their main efforts to the second task.

It will be noticed that in this paper we never mention such notions as "reversible processes" and "quasi-static processes"; in fact, our theory of thermostatistics, being a truly statical theory, has no need of "processes" at all.

In writing the present paper we have striven for a level of mathematical rigor comparable to that of works in pure mathematics rather than to that customary in physics.

Notation and basic mathematical concepts. We often find it convenient to distinguish between functions and their values. The basic local thermodynamic variables are denoted by light face Greek minuscules: $\varepsilon, \psi, \eta, \vartheta, \dots$. Symbols such as $\hat{\varepsilon}, \bar{\varepsilon}, \bar{\bar{\varepsilon}} \dots$ and $\hat{\psi}, \bar{\psi}, \bar{\bar{\psi}} \dots$ represent real valued *functions* whose values are the thermodynamic variables ε and ψ .

We denote vectors and points of the three-dimensional Euclidean space \mathcal{E} by bold face Latin minuscules: $\mathbf{v}, \mathbf{x}, \mathbf{y} \dots$.

Second order tensors are denoted by light face Latin majuscules: F, U, Q, R, I . However, we reserve the symbols X and Z to represent material points of a physical body. The term tensor is used as a synonym for linear transformation. Tensors of order higher than two do not occur in this paper. For the trace of the tensor F we write $\text{tr } F$ and for the determinant of F we write $\det F$. We say that F is invertible if F has an inverse F^{-1} ; *i.e.* if $\det F \neq 0$. The transpose of F is denoted by F^T . The identity transformation is written I . For the composition, or product, of two linear transformations A and B we write simply AB .

* Hadamard stability requires (roughly) that the first variation of the integral of the elastic potential vanish, and that the second variation be non-negative, for all smooth variations in the state of strain which are compatible with a fixed boundary. This sort of stability is necessary but not sufficient for stability at fixed boundary as we define it here. In the theory of the propagation of waves in a perfectly elastic solid, Hadamard stability of a particular rest state implies the reality of all roots of the wave velocity equation for acceleration waves of arbitrary direction which might impinge on an object in that state. J. L. ERICKSEN & R. A. TOUPIN [5] have recently considered a modification of Hadamard stability in which they require that the second variation of the integral of the elastic potential be strictly positive. They use their definition of stability to prove uniqueness theorems in the theory of small deformations superimposed on large. R. HILL [15] also has recently discussed relationships between uniqueness and stability. In the third article of his "Recherches sur l'élasticité" P. DUHÉM [6] formulated several definitions of stability which are applicable to bodies with fixed and partially free surfaces; he also derived several necessary conditions on the equation of state for particular states of strain to be stable.

Let $\mathbf{h}(\mathbf{x})$ be a function for which both the range and the domain consist of either vectors or points in Euclidean space \mathcal{E} . Assume that for \mathbf{x} in some region the derivative

$$\left. \frac{d}{ds} \mathbf{h}(\mathbf{x} + s \mathbf{v}) \right|_{s=0} = \nabla \mathbf{h}(\mathbf{x}; \mathbf{v}) \quad (1)$$

exists for all \mathbf{v} and is continuous in \mathbf{x} . It is the content of a fundamental theorem of analysis that $\nabla \mathbf{h}(\mathbf{x}; \mathbf{v})$ is then a linear function of \mathbf{v} , and hence we can write

$$\nabla \mathbf{h}(\mathbf{x}; \mathbf{v}) = [\nabla \mathbf{h}(\mathbf{x})] \mathbf{v}, \quad (2)$$

where $\nabla \mathbf{h}(\mathbf{x})$ is a linear transformation (tensor), called the *gradient* of \mathbf{h} at \mathbf{x} .

Similarly, the gradient of a real valued function $\zeta(F)$ of a tensor variable F is a tensor valued function $\zeta_F(F)$ defined by the relation

$$\left. \frac{d}{ds} \zeta(F + sA) \right|_{s=0} = \text{tr} [\zeta_F(F) A], \quad (3)$$

where A is an arbitrary tensor. If Cartesian coordinates are used, and if $\|f_{ij}\|$ is the matrix of F , then the matrix of ζ_F is given by

$$\|\zeta_F(F)\| = \left\| \frac{\partial \zeta}{\partial f_{ji}} \right\|,$$

where i is the row and j the column index.

We make frequent use of the following theorem, called the *polar decomposition theorem*: Any invertible tensor F has unique decompositions

$$F = RU = VR \quad (4)$$

where R is orthogonal (i.e., $RR^T = I$) and U, V are positive definite symmetric tensors (i.e., $U = U^T, V = V^T$, and the proper numbers of U and V are all real and greater than zero). In addition, we have

$$U = R^T V R, \quad U^2 = F^T F, \quad V^2 = F F^T. \quad (5)$$

Consider a smooth (i.e., continuously differentiable) real valued function $\zeta(\mathbf{w})$ whose domain \mathcal{W} is a region in a finite dimensional vector space. The function ζ is called *strictly convex* if either of the following two equivalent conditions are satisfied:

(a) For all \mathbf{w}_1 and $\mathbf{w}_2 \neq \mathbf{w}_1$ in \mathcal{W} and all positive α, β with $\alpha + \beta = 1$, the inequality

$$\zeta(\alpha \mathbf{w}_1 + \beta \mathbf{w}_2) < \alpha \zeta(\mathbf{w}_1) + \beta \zeta(\mathbf{w}_2) \quad (6)$$

holds.

(b) For all \mathbf{w} and $\mathbf{w}^* \neq \mathbf{w}$ in \mathcal{W} the inequality

$$\zeta(\mathbf{w}^*) - \zeta(\mathbf{w}) - (\mathbf{w}^* - \mathbf{w}) \cdot \nabla \zeta(\mathbf{w}) > 0 \quad (7)$$

is satisfied.

When \mathcal{W} is a region in the space of all tensors, we use the notation of (3) and the convexity inequality (7) becomes

$$\zeta(F^*) - \zeta(F) - \text{tr} [(F^* - F) \zeta_F(F)] > 0. \quad (8)$$

For a twice continuously differentiable function $\zeta(\mathbf{w})$ to be strictly convex in \mathcal{W} , it is sufficient that the second gradient $\nabla\nabla\zeta(\mathbf{w})$ be positive definite for \mathbf{w} in \mathcal{W} . This condition is not necessary, however: if $\zeta(\mathbf{w})$ is convex, it follows only that $\nabla\nabla\zeta(\mathbf{w})$ is positive *semidefinite*.

1. Mechanical preliminaries

We give a brief summary of those concepts from the mechanics of continuous media that are relevant to the present investigation. For a detailed discussion we refer to [7] and [8].

A *body* \mathcal{B} is a smooth manifold of elements X, Z, \dots , called *material points**. A *configuration* \mathbf{f} of \mathcal{B} is a smooth one-to-one mapping of \mathcal{B} onto a region in a three-dimensional Euclidean point space \mathcal{E} . The point $\mathbf{x} = \mathbf{f}(X)$ is the *position* of the material point X in the configuration \mathbf{f} . The *mass distribution* m of \mathcal{B} is a measure defined on all Borel subsets of \mathcal{B} . For the total mass of \mathcal{B} we write $m(\mathcal{B})$. To each configuration \mathbf{f} of \mathcal{B} corresponds a mass density ρ .

Consider a neighborhood $\mathcal{N}(X)$ of a material point in a body; *i.e.*, a part of the body containing X in its interior. Let \mathbf{g} be a smooth homeomorphism of $\mathcal{N}(X)$ into the three-dimensional vector space \mathcal{V} such that X itself is mapped into the zero vector $\mathbf{0}$. The inverse mapping of \mathbf{g} is denoted by $\bar{\mathbf{g}}^{-1}$. Let \mathbf{g}_1 and \mathbf{g}_2 be two such homeomorphisms. The composition $\mathbf{g}_2 \circ \bar{\mathbf{g}}_1^{-1}$ of \mathbf{g}_2 and $\bar{\mathbf{g}}_1^{-1}$ is defined by

$$(\mathbf{g}_2 \circ \bar{\mathbf{g}}_1^{-1})(\mathbf{x}) = \mathbf{g}_2(\bar{\mathbf{g}}_1^{-1}(\mathbf{x})).$$

It is a mapping of a neighborhood of $\mathbf{0}$ onto another neighborhood of $\mathbf{0}$. We define an equivalence relation “ \sim ” among all these homeomorphisms by the condition that $\mathbf{g}_1 \sim \mathbf{g}_2$ if the gradient of the mapping $\mathbf{g}_2 \circ \bar{\mathbf{g}}_1^{-1}$ at $\mathbf{0}$ is the identity I . The resulting equivalence classes will be called the *local configurations*** M of X . If M_1 is the equivalence class of \mathbf{g}_1 and M_2 the equivalence class of \mathbf{g}_2 then the gradient at $\mathbf{0}$ of $\mathbf{g}_2 \circ \bar{\mathbf{g}}_1^{-1}$, *i.e.*

$$G = \nabla(\mathbf{g}_2 \circ \bar{\mathbf{g}}_1^{-1})(\mathbf{0}), \quad (1.1)$$

depends only on M_1 and M_2 . We write

$$G = M_2 M_1^{-1}, \quad M_2 = G M_1, \quad (1.2)$$

and call G the *deformation gradient* from M_1 to M_2 ; G is an invertible linear transformation.

It is often convenient to employ a *local reference configuration* M_r and to characterize the other local configurations

$$M = F M_r, \quad (1.3)$$

by their deformation gradients F from the local reference configuration M_r . If, in this way, two local configurations M_1 and M_2 correspond, respectively, to F_1 and F_2 then the deformation gradient G from M_1 to M_2 is given by

$$G = F_2 F_1^{-1}, \quad F_2 = G F_1. \quad (1.4)$$

* The term “particle” is often used. We prefer “material point” to avoid confusion with molecules and other physical particles.

** The term “configuration gradient” was used in [7].

The *rotation tensor* R , the *right stretch tensor** U , and the *left stretch tensor* V of a deformation gradient F are defined by the unique polar decompositions

$$F = RU = VR, \quad (1.5)$$

where R is orthogonal, while U and $V = RUR^T$ are symmetric and positive definite. We note that U and V have the same proper numbers; these proper numbers are called the *principal stretches* v_1, v_2, v_3 . A deformation gradient G is called a *pure stretch* if its rotation tensor reduces to the identity I ; *i.e.*, if G is symmetric and positive definite and hence coincides with its own right and left stretch tensors.

The mass densities at X corresponding to the local configurations M_1 and M_2 are denoted, respectively, by ρ_1 and ρ_2 . We have

$$\rho_2 = \frac{1}{|\det G|} \rho_1, \quad (1.6)$$

where G is related to M_1 and M_2 by (1.2).

2. Thermomechanic states

A global thermomechanic state, or simply a *state*, of a body \mathcal{B} is a pair $\{\mathbf{f}, \eta\}$ consisting of a configuration \mathbf{f} of \mathcal{B} and a scalar field η defined on \mathcal{B} ; η is called the *entropy distribution* of the state.

A local thermomechanic state, or simply a *local state*, of a material point X is defined as a pair (M, η) consisting of a local configuration M of X and a real number η , called the *entropy density* (per unit mass) of the local state**.

In the following we often use a local reference configuration M_* and, according to (1.3), characterize the other local configurations M by the deformation gradients F from M_* . We then use the pair (F, η) to characterize the local states.

Two local states (F, η) and (F', η') will be called *equivalent* if they differ only by a change of frame of reference. The local configuration transforms under a change of frame according to the law $F' = QF$ where Q is orthogonal. We assume that the entropy density η is *objective*; *i.e.*, it remains invariant under a change of frame. Thus, the local states (F, η) and (F', η') are equivalent if and only if

$$F' = QF, \quad \eta' = \eta \quad (2.1)$$

for some orthogonal Q .

We say that two global states $\{\mathbf{f}, \eta\}$ and $\{\mathbf{f}', \eta'\}$ are equivalent if they differ by only a change of frame. This is the case if and only if

$$\eta'(X) = \eta(X), \quad F'(X) = QF(X) \quad (2.2)$$

for all X in the body and some orthogonal tensor Q independent of X . Here, $F(X)$ and $F'(X)$ are the deformation gradients at X corresponding to \mathbf{f} and \mathbf{f}' respectively.

* The term "strain tensor" was used in [7].

** In this article, pairs in braces, $\{\}$, always refer to *global* properties; the elements of such pairs are fields over \mathcal{B} . On the other hand, pairs in brackets, $(\)$, always refer to *local* properties and have elements which are either real numbers or tensors. Note that the symbol η in $\{\mathbf{f}, \eta\}$ and (M, η) denotes different entities; in the first case η denotes a field while in the second case it denotes a number. No confusion should arise however.

3. The caloric equation of state

A *material* is characterized by a real valued function of local states, whose values ε are called the *energy densities* (per unit mass) of the local states. We pick a fixed local reference configuration M_r and characterize the state (M, η) by the pair (F, η) where $F = M M_r^{-1}$. We write

$$\varepsilon = \hat{\varepsilon}(F, \eta). \quad (3.1)$$

It is assumed here that the function $\hat{\varepsilon}$ has continuous derivatives with respect to F and η^* .

We assume that the energy density is objective; *i.e.* invariant under a change of frame. It follows from (2.1) that the function $\hat{\varepsilon}$ must satisfy the relation

$$\hat{\varepsilon}(QF, \eta) = \hat{\varepsilon}(F, \eta) \quad (3.2)$$

for all orthogonal Q . Using the polar decomposition (1.5) and putting $Q = R^T$ in (3.2) we see that

$$\varepsilon = \hat{\varepsilon}(F, \eta) = \hat{\varepsilon}(U, \eta); \quad (3.3)$$

i.e., that the energy density is determined by the right stretch tensor U and the entropy η .

The function $\hat{\varepsilon}$ in (3.3) depends on the choice of the local reference configuration M_r . The function $\hat{\varepsilon}'$ corresponding to some other local reference configuration M'_r is related to $\hat{\varepsilon}$ by

$$\hat{\varepsilon}'(F, \eta) = \hat{\varepsilon}(FG, \eta), \quad (3.4)$$

where $G = M'_r M_r^{-1}$ is the deformation gradient from M_r to M'_r .

The equation (3.3) characterizes the thermal and mechanical properties of a material in statics. It is called the *caloric equation of state* of the material.

4. The isotropy group

It may happen that the energy function $\hat{\varepsilon}$ remains the same function if the local reference configuration M_r is changed to another local reference configuration $M'_r = HM_r$, with the same density. It follows from (3.4) that $\hat{\varepsilon}$ then satisfies the relation

$$\hat{\varepsilon}(F, \eta) = \hat{\varepsilon}(FH, \eta). \quad (4.1)$$

Since M'_r and M_r have the same density, it is clear from (1.6) that $|\det H| = 1$; *i.e.*, H is a unimodular transformation. The unimodular transformations H for which (4.1) holds form a group, called the *isotropy group* \mathcal{G} of $\hat{\varepsilon}$ or of the material defined by $\hat{\varepsilon}$. This group depends, in general, on the choice of the local reference configuration, but it can be shown that the groups corresponding to two different local configurations are always conjugate and hence isomorphic.

We say that the energy function $\hat{\varepsilon}$ defines a *simple fluid* if its isotropy group \mathcal{G} is the full unimodular group \mathcal{U} . If $\mathcal{G} = \mathcal{U}$ for one reference configuration, then $\mathcal{G} = \mathcal{U}$ for all reference configurations. A material point is called a *fluid material point* if its energy function defines a simple fluid. The caloric equation

* For the application to physical situations it is necessary to limit the domain of $\hat{\varepsilon}$ to a region in the space of local configurations and an interval on the η -axis. We do not supply the mathematical details which may arise in the consideration of limitations of this kind.

of state (3.3) then reduces to the form

$$\hat{\varepsilon} = \hat{\varepsilon}(F, \eta) = \bar{\varepsilon}(v, \eta), \quad (4.2)$$

where

$$v = \frac{1}{\varrho} = \left| \det F \right| \frac{1}{\varrho_r} \quad (4.3)$$

is the *specific volume* of the local configuration $M = FM_r$; ϱ and ϱ_r are the mass densities corresponding to M and M_r . The function $\bar{\varepsilon}$ in (4.2) does not depend on the choice of the reference configuration.

We say that a material point is an *isotropic material point* if the isotropy group of its energy function $\hat{\varepsilon}$, relative to some local reference configuration, contains the orthogonal group \mathcal{O} . Those local reference configurations of the material point for which \mathcal{G} contains \mathcal{O} are said to be *undistorted*. A simple fluid is isotropic, and all of its local configurations are undistorted. For any isotropic material, it follows from (3.2) and (4.1) that $\hat{\varepsilon}$ satisfies the relation

$$\hat{\varepsilon}(QUQ^T, \eta) = \hat{\varepsilon}(U, \eta) \quad (4.4)$$

for all symmetric and positive definite U and all orthogonal Q , provided the local reference configuration for $\hat{\varepsilon}$ is undistorted. Taking $Q = R$, so that $V = RUR^T$ is the left stretch tensor, we see that for isotropic material points the caloric equation of state (3.3) may be written in the form

$$\varepsilon = \hat{\varepsilon}(F, \eta) = \hat{\varepsilon}(V, \eta). \quad (4.5)$$

It is a further consequence of (4.4) that for each fixed value of η , ε may be expressed as a symmetric function of the three principal stretches v_1, v_2, v_3 :

$$\varepsilon = \hat{\varepsilon}(F, \eta) = \hat{\varepsilon}(V, \eta) = \bar{\varepsilon}(v_1, v_2, v_3; \eta) = \bar{\varepsilon}(v_j, \eta). \quad (4.6)$$

It may also be expressed as a function of the three principal invariants I_V, II_V, III_V of V and U :

$$\varepsilon = \hat{\varepsilon}(V, \eta) = \bar{\varepsilon}(I_V, II_V, III_V; \eta). \quad (4.7)$$

We say that the energy function $\hat{\varepsilon}$ defines a *simple solid* if its isotropy group \mathcal{G} is contained as a subgroup in the orthogonal group \mathcal{O} . A material point is called a *solid material point* if its energy function $\hat{\varepsilon}$, relative to some local configuration as a reference, defines a simple solid. The local reference configurations with this property are again called the *undistorted* states of the solid material point. For an *isotropic simple solid*, the isotropy group \mathcal{G} is identical to the orthogonal group \mathcal{O} .

Throughout the rest of this paper, whenever we discuss isotropic materials it is to be understood that the local reference configuration for the energy density function is undistorted, unless the reference configuration is explicitly specified.

5. Forces, stresses, and work

A *system of forces* is a system of vector valued measures, one for each part of the body \mathcal{B} under consideration*. One must distinguish between contact and body forces. The contact force acting across an oriented surface element in \mathcal{B} will be denoted by $d\mathbf{c}$.

* For a detailed axiomatic treatment cf. [8].

Definition of mechanical equilibrium. *In order that a body \mathcal{B} be in mechanical equilibrium under a given system of forces, two conditions must be fulfilled for each part \mathcal{P} of \mathcal{B} : (a) the sum of the forces acting on \mathcal{P} must vanish, and (b) the sum of the moments, about any point, of the forces acting on \mathcal{P} must vanish.*

The condition (a), called the *force condition*, depends only on the body and the force system, not on the configuration of the body. The condition (b), called the *moment condition*, does depend on the configuration of the body; *i.e.*, for a given force system, the moment condition may be satisfied for one configuration but not for another.

The force condition alone implies that, for each configuration, the contact forces $d\mathbf{c}$ arise from a stress-tensor S , so that

$$d\mathbf{c} = S\mathbf{n}dA, \quad (5.1)$$

where \mathbf{n} is the unit normal vector of the oriented surface element and dA its area in the configuration under consideration. For fixed contact forces $d\mathbf{c}$, the stress tensor S will be different for different configurations.

We consider now a neighborhood $\mathcal{N}(X)$ of a material point X and assume that a system of contact forces $d\mathbf{c}$ is given for $\mathcal{N}(X)$. Let \mathbf{f}_r be a fixed reference configuration and \mathbf{f} some other configuration of $\mathcal{N}(X)$. If $d\mathbf{c}$ is such that the force condition is satisfied, then (5.1) is valid for all configurations; we can write for the reference configuration \mathbf{f}_r , in particular,

$$d\mathbf{c} = S_r\mathbf{n}_r dA_r, \quad (5.2)$$

where \mathbf{n}_r is the unit normal of the oriented surface element in the reference configuration \mathbf{f}_r , and dA_r is the area of the surface element in \mathbf{f}_r . We denote the position vector, in the configuration \mathbf{f} , of a typical material point Z in $\mathcal{N}(X)$, relative to the position of X as origin, by \mathbf{p} , and we consider the tensor K defined by

$$K = \frac{1}{v(\mathcal{N}(X))} \int_{\overline{\mathcal{N}(X)}} \mathbf{p} \otimes d\mathbf{c}, \quad (5.3)$$

where $\overline{\mathcal{N}(X)}$ denotes the boundary surface of $\mathcal{N}(X)$ and $v(\mathcal{N}(X))$ the volume of $\mathcal{N}(X)$ in the configuration \mathbf{f} , and where \otimes denotes a tensor product. If the force condition is satisfied, the relation (5.1) is valid, and we have

$$K^T = \frac{1}{v(\mathcal{N}(X))} \int_{\overline{\mathcal{N}(X)}} S\mathbf{n} \otimes \mathbf{p} dA.$$

In the limit as $\mathcal{N}(X)$ shrinks to X , we obtain, after using Green's theorem,

$$S^T = \lim_{\mathcal{N}(X) \rightarrow X} K. \quad (5.4)$$

The same argument, with the configuration \mathbf{f} replaced by the reference configuration \mathbf{f}_r , gives

$$S_r^T = \lim_{\mathcal{N}(X) \rightarrow X} \frac{1}{v_r(\mathcal{N}(X))} \int_{\overline{\mathcal{N}(X)}} \mathbf{p}_r \otimes d\mathbf{c}, \quad (5.5)$$

where $v_r(\mathcal{N}(X))$ is the volume of $\mathcal{N}(X)$ in the reference configuration and \mathbf{p}_r the position vector, in the reference configuration, of a typical material point Z

in $\mathcal{N}(X)$, relative to the position of X as origin. The position vector \mathbf{p} of Z in the configuration \mathbf{f} is related to \mathbf{p}_r by the relation

$$\mathbf{p} = F \mathbf{p}_r + o(|\mathbf{p}_r|) \quad (5.6)$$

where F is the gradient at X of the deformation from \mathbf{f}_r to \mathbf{f} and where

$$\lim_{d \rightarrow 0} \frac{o(d)}{d} = 0.$$

Substitution of (5.6) into (5.3) and use of (5.4) and (5.5) yields

$$S = \frac{\rho}{\rho_r} F S_r, \quad (5.7)$$

where ρ and ρ_r are, respectively, the mass densities at X in the configurations \mathbf{f} and \mathbf{f}_r .

The skew part of K , defined by (5.3), is the moment about X , per unit volume, of the contact forces $d\mathbf{c}$ acting on $\mathcal{N}(X)$ in the configuration \mathbf{f} . If the moment condition is satisfied for the configuration \mathbf{f} , then the total moment (*i.e.* the moment of the contact forces *and* the body forces) about X in \mathbf{f} must vanish. Since the moment per unit volume about X of the body forces on $\mathcal{N}(X)$ goes to zero as $\mathcal{N}(X)$ shrinks to X , it follows from (5.4) that S must be symmetric if the moment condition is satisfied in \mathbf{f} .

We say that a material point X is in *local mechanical equilibrium*, when the body is in a given configuration and under a given force system, if the stress tensor S exists at X and is symmetric.

The local behavior at X of a system of contact forces is completely determined by the tensor S_r defined by (5.2). It is called the *Kirchhoff tensor** of the system. For a given force system, the Kirchhoff tensor depends only on the choice of the reference configuration and remains the same if the actual configuration is changed. From (5.7) we see that the existence of the Kirchhoff tensor S_r and the symmetry of $F S_r$ are necessary and sufficient conditions for local mechanical equilibrium at a material point in the local configuration determined by F .

In order that a body \mathcal{B} in a configuration \mathbf{f} be in mechanical equilibrium, it is not sufficient that all its material points be in local mechanical equilibrium; *i.e.*, that the stress tensor exist and be symmetric at each material point. Global mechanical equilibrium will prevail only if, in addition, Cauchy's law

$$\operatorname{div} S + \rho \mathbf{b} = \mathbf{0} \quad (5.8)$$

is satisfied. In this equation, S , ρ , and the density \mathbf{b} of the body forces are to be regarded as fields with domain $\mathbf{f}(\mathcal{B})$.

We consider now a smooth one-parameter family of configurations $\mathbf{f}(s)$ with deformation gradients $F(s)$ at X . The *work per unit mass* done on $\mathcal{N}(X)$ by the contact forces $d\mathbf{c}$ along the path of configurations $\mathbf{f}(s)$ from $s = s_1$ to $s = s_2$ is defined by

$$w = \frac{1}{m(\mathcal{N}(X))} \int_{s_1}^{s_2} \left[\int_{\mathcal{N}(X)} \frac{d\mathbf{p}}{ds} \cdot d\mathbf{c} \right] ds, \quad (5.9)$$

* Cf. TRUESDELL [9], (26.5).

where $m(\mathcal{N}(X))$ is the mass of $\mathcal{N}(X)$ and $\mathbf{p}(s)$ denotes the position vector, in the configuration $\mathbf{f}(s)$, of a typical material point in $\mathcal{N}(X)$. Assuming that the contact forces $d\mathbf{c}$ are independent of s , we obtain

$$w = \frac{1}{m(\mathcal{N}(X))} \left[\int_{\mathcal{N}(X)} \mathbf{p}(s_2) \cdot d\mathbf{c} - \int_{\mathcal{N}(X)} \mathbf{p}(s_1) \cdot d\mathbf{c} \right]. \quad (5.10)$$

Observing (5.3), (5.4) and (5.7), and taking the limit $\mathcal{N}(X) \rightarrow X$, we get

$$\rho_r w = \text{tr} [F(s_2) S_r] - \text{tr} [F(s_1) S_r]. \quad (5.11)$$

This relation shows that $-\frac{1}{\rho_r} \text{tr}(F S_r)$ has the physical meaning of the potential energy, per unit mass, of the local contact forces.

6. Definition of thermal equilibrium

A *force temperature pair* for a material point X is a pair (S_r, ϑ) consisting of a tensor S_r , to be interpreted as the Kirchhoff tensor of a system of contact forces at X , and a real number ϑ , to be interpreted as the temperature at X .

Let a force temperature pair (S_r, ϑ) be given and consider the function

$$\hat{\lambda}(F, \eta) = \hat{\varepsilon}(F, \eta) - \frac{1}{\rho_r} \text{tr}(F S_r) - \eta \vartheta. \quad (6.1)$$

To help motivate the definition of thermal equilibrium given below, we make the following remarks. According to (5.11) the term $-\frac{1}{\rho_r} \text{tr}(F S_r)$ is the potential energy, per unit mass, of the local contact forces. The term $-\eta \vartheta$ may be interpreted as a thermal potential energy. Thus, the value $\lambda = \hat{\lambda}(F, \eta)$ gives a kind of free energy per unit mass of the local state (F, η) when under the action of the force temperature pair (S_r, ϑ) .

Definition of thermal equilibrium. *The local state (F, η) is called a **state of thermal equilibrium under a given force temperature pair** (S_r, ϑ) if*

- (a) *the stress tensor $S = (\rho/\rho_r) F S_r$ is symmetric,*
- (b) *the inequality*

$$\hat{\lambda}(F^*, \eta^*) > \hat{\lambda}(F, \eta) \quad (6.2)$$

holds for all states $(F^, \eta^*) \neq (F, \eta)$ such that*

$$F^* = G F, \quad (6.3)$$

where G is symmetric and positive definite.

The condition (a) means that F corresponds to a local configuration in local mechanical equilibrium (cf. § 5). The condition (b) means that a change of state increases the free energy λ provided that the configuration of the changed state is related to the original configuration by a pure stretch G (cf. § 1).

7. Conditions for thermal equilibrium

In this section we show that, for a local state (F, η) to be a state of thermal equilibrium under the force temperature pair (S_r, ϑ) , the following three conditions

are necessary and sufficient:

(α) The stress tensor $S = \frac{\rho}{\rho_r} F S_r$ is given by the *stress relation* *

$$S = \rho F \hat{e}_F(F, \eta). \tag{7.1}$$

(β) The temperature ϑ is given by the *temperature relation*

$$\vartheta = \hat{e}_\eta(F, \eta). \tag{7.2}$$

(γ) The inequality

$$\hat{e}(F^*, \eta^*) - \hat{e}(F, \eta) - \text{tr}[(F^* - F) \hat{e}_F(F, \eta)] - (\eta^* - \eta) \hat{e}_\eta(F, \eta) > 0 \tag{7.3}$$

holds if $(F^*, \eta^*) \neq (F, \eta)$ and F^* is related to F by $F^* = GF$, where G is positive definite and symmetric.

We assume first that (F, η) is a state of thermal equilibrium and prove the validity of (α), (β), and (γ). By (6.2) and (6.3), the function $\hat{\lambda}(GF, \eta^*)$ of the symmetric tensor variable G and the scalar variable η^* has a minimum for $G = I$ and $\eta^* = \eta$. By a theorem of calculus, it follows that the derivatives of $\hat{\lambda}(GF, \eta^*)$ with respect to G and η^* must vanish for $G = I$ and $\eta^* = \eta$. If we set the derivative of $\hat{\lambda}(GF, \eta^*)$ with respect to η^* equal to zero at $\eta^* = \eta$, we obtain the temperature relation (7.2). The gradient of $\hat{\lambda}(GF, \eta^*)$ with respect to G may be computed using the formula (3) of the mathematical preliminaries and (6.4); we obtain the equation

$$\text{tr} \left\{ \left[F \hat{e}_F(F, \eta) - \frac{1}{\rho_r} F S_r \right] A \right\} = 0, \tag{7.4}$$

which is valid for arbitrary symmetric tensors A . Using (5.7) the equation (7.4) may be rewritten in the form

$$\text{tr} \{ [\rho F \hat{e}_F(F, \eta) - S] A \} = 0. \tag{7.5}$$

By the condition (a) of the definition of thermal equilibrium, S is symmetric. It follows from (3.2) and Theorem I of reference [10], p. 42, that $\rho F \hat{e}_F(F, \eta)$ is also symmetric. Thus, the tensor $\rho F \hat{e}_F(F, \eta) - S$ is symmetric. On the other hand, (7.5) can be valid for arbitrary symmetric A only if $\rho F \hat{e}_F(F, \eta) - S$ is skew; whence it follows that $\rho F \hat{e}_F(F, \eta) - S$ must vanish, which proves (7.1). The inequality (7.3) is obtained simply by substitution of (7.1) and (7.2) into the inequality (6.2), after $\hat{\lambda}$ is replaced by its definition (6.1).

We assume now that the conditions (α), (β), and (γ) are satisfied. It then follows from (7.1), (3.2) and the theorem of reference [10] mentioned above that the stress tensor S must be symmetric, so that condition (a) of the definition of thermal equilibrium is satisfied. Furthermore, the Kirchhoff tensor is given by

$$S_r = \rho_r \hat{e}_F(F, \eta). \tag{7.6}$$

Substitution of (7.6) and (7.2) into the inequality (7.3) gives the inequality (6.2); hence condition (b) of the definition of equilibrium is also satisfied.

* This is the familiar stress-strain relation of finite elasticity theory (cf. [10], (16.4)).

8. The fundamental postulates

We are now able to lay down our two fundamental postulates:

Postulate I. For every local state (F, η) for which $\hat{\varepsilon}(F, \eta)$ is defined there exists a force temperature pair (S_r, ϑ) such that (F, η) is a state of thermal equilibrium under (S_r, ϑ) .

Postulate II. The energy function $\hat{\varepsilon}(F, \eta)$ is strictly increasing in η for each fixed F .

Postulate I and the results of the previous section yield the following theorems:

Theorem 1. The force temperature pair (S_r, ϑ) which makes the local state (F, η) a state of thermal equilibrium is given by

$$S_r = \rho_r \hat{\varepsilon}_F(F, \eta), \quad (8.1)$$

$$\vartheta = \hat{\varepsilon}_\eta(F, \eta). \quad (8.2)$$

Theorem 2. The energy function $\hat{\varepsilon}$ obeys the inequality

$$\hat{\varepsilon}(F^*, \eta^*) - \hat{\varepsilon}(F, \eta) - \text{tr}[(F^* - F) \hat{\varepsilon}_F(F, \eta)] - (\eta^* - \eta) \hat{\varepsilon}_\eta(F, \eta) > 0 \quad (8.3)$$

for any two local states (F, η) and (F^*, η^*) , in the domain of definition of $\hat{\varepsilon}$, which are related by

$$F^* = GF, \quad (8.4)$$

where G is symmetric and positive definite.

The discussion of the previous section shows that Theorem 2 is equivalent to Postulate I. In fact, if we are given a state (F, η) , we can define a force temperature pair (S_r, ϑ) according to (8.1) and (8.2) and then use the inequality (8.3) to prove that (F, η) is in equilibrium under (S_r, ϑ) .

The inequality (8.3) of Theorem 2 is a restricted convexity condition on the function $\hat{\varepsilon}$. If we take, in particular, $F^* = F$, then (8.3) reduces to

$$\hat{\varepsilon}(F, \eta^*) - \hat{\varepsilon}(F, \eta) - (\eta^* - \eta) \hat{\varepsilon}_\eta(F, \eta) > 0 \quad (8.5)$$

for $\eta^* \neq \eta$. This inequality is the content of the following corollary to Theorem 2:

Theorem 3. For each fixed local configuration, the energy density is given by a strictly convex function of the entropy density.

This theorem is equivalent to the statement that $\hat{\varepsilon}_\eta(F, \eta)$ must be a strictly increasing function of η for each fixed F . It follows that the equation (8.2) can be solved for η in a unique manner:

$$\eta = \tilde{\eta}(F, \vartheta). \quad (8.6)$$

Here, $\tilde{\eta}$ is a strictly increasing function* of ϑ for each F . The fact that (8.6) is obtained by solving (8.2) for η is expressed by the identity

$$\hat{\varepsilon}_\eta[F, \tilde{\eta}(F, \vartheta)] = \vartheta. \quad (8.7)$$

* The specific heat c at fixed strain is given by $c = \vartheta \tilde{\eta}_\vartheta(F, \vartheta)$. Hence, it is a consequence of Theorem 3 that c/ϑ is never negative and, for each F , is strictly positive except possibly for a nowhere dense set of values of ϑ .

If we take $\eta^* = \eta$ in (8.3), we obtain

$$\hat{\varepsilon}(F^*, \eta) - \hat{\varepsilon}(F, \eta) - \text{tr}[(F^* - F) \hat{\varepsilon}_F(F, \eta)] > 0; \quad (8.8)$$

this inequality holds whenever $F^* = GF$, where $G \neq I$ is symmetric and positive definite.

A local state (F, η) is called a *natural state* if the corresponding stress (8.1) vanishes. Keeping the entropy fixed, we may use the local configuration of the natural state as the reference configuration, so that $F = I$ and $\hat{\varepsilon}_F(I, \eta) = \frac{1}{\rho} S = 0$. In this case, the inequality (8.8), by (8.4), reduces to

$$\hat{\varepsilon}(G, \eta) > \hat{\varepsilon}(I, \eta), \quad (8.9)$$

which is valid for arbitrary symmetric and positive definite $G \neq I$. Replacing G by the right stretch tensor U of an arbitrary deformation gradient F and using (3.3), we see that

$$\hat{\varepsilon}(F, \eta) \geq \hat{\varepsilon}(I, \eta); \quad (8.10)$$

this expression becomes an equality only when F is orthogonal; *i.e.*, when (F, η) is equivalent to (I, η) . Hence, the *energy density is smallest in a natural state*. It should be pointed out that this observation, though important for the theory of simple solids, is vacuous for fluids. For, we shall prove in § 11 that the stress on a fluid material point in thermal equilibrium is always a strictly positive pressure; thus, for a fluid there is no natural state.

We note that the restriction (8.4) on the inequality (8.3) of Theorem 2 is essential for application of the present theory to physical situations. This restriction means that the local configurations corresponding to F^* and F must be related by a pure stretch. If, for example, these local configurations were related by a rotation so that $F^* = QF$, with Q an orthogonal transformation, then the left side of (8.8) would reduce to $\text{tr}[(Q - I)F \hat{\varepsilon}_F(F, \eta)]$, since $\hat{\varepsilon}(F^*)$ would equal $\hat{\varepsilon}(F)$ by (3.2). The stress relation (7.1) shows that the left side of (8.8) would then become $\frac{1}{\rho} \text{tr}[(Q - I)S]$. One can show that this expression can be made negative by an appropriate choice of Q if S has at least one negative proper number. Thus, the inequality (8.8), were it to hold for arbitrary pairs F, F^* , would exclude the possibility of thermal equilibrium under compression stresses, which is certainly not in accord with experience*.

9. An alternative axiomatization

In this section we hope to make clear our reasons for assuming Postulate II and to motivate further our definition of equilibrium.

It follows from Postulate II that, for each fixed F , the caloric equation of state has a unique solution for η :

$$\eta = \hat{\eta}(F, \varepsilon), \quad (9.1)$$

and that the function $\hat{\eta}$ is strictly increasing in ε for each F . This one-to-one correspondence between ε and η at each F makes it possible to give an alternative

* It has also been pointed out by HILL [15] that an assumption of unrestricted convexity of $\hat{\varepsilon}$ in the deformation gradient would lead to unacceptable physical behavior.

axiomatization of our present theory of thermostatics by taking ε and F as independent variables and defining thermal equilibrium in terms of the function $\hat{\eta}$. In such a formulation a local thermomechanic state is characterized by a pair (F, ε) , and thermal equilibrium is defined as follows:

Alternative definition of thermal equilibrium. *The local state (F, ε) is called a state of thermal equilibrium under the force temperature pair (S_r, ϑ) , with $\vartheta \neq 0$, if*

- (a) *the stress tensor $S = (\rho/\rho_r) F S_r$ is symmetric,*
- (b) *the inequality*

$$\hat{\eta}(F, \varepsilon) > \hat{\eta}(F^*, \varepsilon^*) + \frac{1}{\vartheta \rho_r} \text{tr} [(F^* - F) S_r] - \frac{\varepsilon^* - \varepsilon}{\vartheta} \tag{9.2}$$

holds for all states $(F^, \varepsilon^*) \neq (F, \varepsilon)$ such that $F^* = GF$, where G is symmetric and positive definite.*

Theorem 4. *The definition of thermal equilibrium given in § 6 and the alternative definition of thermal equilibrium are equivalent (for $\vartheta \neq 0$) if Postulate II is assumed.*

Proof. In § 7 we showed that, under the original definition of § 6, in order for a state (F, η) to be a state of thermal equilibrium for the force temperature pair (S_r, ϑ) it is necessary that

$$\vartheta = \hat{\varepsilon}_\eta(F, \eta). \tag{9.3}$$

By a very similar argument it can be shown, using the alternative definition of thermal equilibrium, that in order for the state (F, ε) to be a state of thermal equilibrium it is necessary that

$$\frac{1}{\vartheta} = \hat{\eta}_\varepsilon(F, \varepsilon). \tag{9.4}$$

Now, by Postulate II, the functions $\hat{\varepsilon}$ and $\hat{\eta}$ are strictly increasing in η and ε , respectively, for fixed F . Hence, ϑ cannot be negative if (S_r, ϑ) is to be a force temperature pair for some state of thermal equilibrium, regardless of which of the two definitions is used. Since we here assume $\vartheta \neq 0$, we have $\vartheta > 0$, and (9.2) can be multiplied by ϑ and then rearranged to give

$$-\vartheta \hat{\eta}(F^*, \varepsilon^*) - \frac{1}{\rho_r} \text{tr}(F^* S_r) + \varepsilon^* > -\vartheta \hat{\eta}(F, \varepsilon) - \frac{1}{\rho_r} \text{tr}(F S_r) + \varepsilon. \tag{9.5}$$

Noting the relations

$$\begin{aligned} \eta^* &= \hat{\eta}(F^*, \varepsilon^*), & \eta &= \hat{\eta}(F, \varepsilon), \\ \varepsilon^* &= \hat{\varepsilon}(F^*, \eta^*), & \varepsilon &= \hat{\varepsilon}(F, \eta), \end{aligned} \tag{9.6}$$

and (6.1), we see that (9.5) is equivalent to (6.2). The requirement that $(F, \eta) \neq (F^*, \eta^*)$ and the requirements on $G = F^* F^{-1}$ are the same for (6.2) and (9.5). The condition (a) is obviously the same in both definitions; hence the definitions are equivalent, q. e. d.

From a certain point of view the alternative definition of thermal equilibrium given in this section is more fundamental than the original definition of § 6. The alternative definition is more closely related to the physical notion that, since entropy tends to increase, equilibrium states should be, in some sense, states of maximum entropy. The definition of § 6 is closely related to the idea, which is often used in mechanics, that equilibrium states should be, in some

sense, states of minimum potential. It should be emphasized that the two definitions are equivalent only if Postulate II is assumed; *i.e.*, only if states of negative temperature are excluded. Of course, negative temperatures never occur in continuum mechanics, but there are subjects in which they do occur (*cf.* [11], [12]). Statistical mechanical considerations suggest that for systems capable of negative temperatures a practical definition of thermal equilibrium should be based on the idea of maximum entropy.

10. Infinitesimal deformations from an arbitrary state

Here we consider the classical theory of *infinitesimal deformations* from an arbitrary initial configuration. We make no attempt to justify the use of the theory of infinitesimal deformations as an approximation to the theory of finite deformations.

In the theory of infinitesimal deformations one considers cases in which $F^* = GF$ is obtained from F by superimposing an infinitesimal deformation. The *infinitesimal strain tensor* E is defined as the *symmetric part* of $G - I$.

In the special case in which G is positive definite and symmetric (*i.e.*, when F^* is related to F by a pure stretch) we have

$$E = G - I, \quad (10.1)$$

and the excess energy $\hat{\varepsilon}(GF, \eta) - \hat{\varepsilon}(F, \eta)$ is a function of E alone:

$$\sigma(E) = \hat{\varepsilon}(GF, \eta) - \hat{\varepsilon}(F, \eta). \quad (10.2)$$

Equation (10.2) is valid approximately even when G is not symmetric.

In the infinitesimal theory it is assumed (i) that (10.2) is valid exactly for all G and (ii) that the excess energy is exactly given by the sum,

$$\sigma(E) = \sigma_1(E) + \sigma_2(E), \quad (10.3)$$

of a term $\sigma_1(E)$ linear in E and a term $\sigma_2(E)$ quadratic in E .

By taking the gradient of (10.2) with respect to E and then putting $E = 0$, it is easily shown that the linear term $\sigma_1(E)$ must be given by

$$\sigma_1(E) = \text{tr}[EF \hat{\varepsilon}_F(F, \eta)]. \quad (10.4)$$

Hence, using the stress relation (7.4), we have

$$\sigma_1(E) = \frac{1}{\rho} \text{tr}(ES), \quad (10.5)$$

where S is the stress of the original state (F, η) .

Now, the fundamental inequality (8.8) may be written

$$\hat{\varepsilon}(GF, \eta) - \hat{\varepsilon}(F, \eta) - \text{tr}[(G - I)F \hat{\varepsilon}_F(F, \eta)] > 0. \quad (10.6)$$

From (10.1), (10.2) we get

$$\sigma(E) - \text{tr}[EF \hat{\varepsilon}_F(F, \eta)] > 0, \quad (10.7)$$

and it follows from (10.3), (10.4) and (10.5) that

$$\sigma_2(E) = \sigma(E) - \frac{1}{\rho} \text{tr}(ES) > 0. \quad (10.8)$$

This inequality is the content of the following theorem:

Theorem 5. *For an infinitesimal deformation superimposed, at fixed entropy, on an arbitrary state, the excess energy is the sum of a positive definite quadratic form in the infinitesimal strain tensor E of the superimposed strain and a linear term $\frac{1}{\rho} \text{tr}(ES)$, where ρ is the density and S the stress corresponding to the original state.*

If the original state is a natural state in which the stress vanishes, the above theorem reduces to the familiar statement that the strain energy is a positive definite quadratic form in the infinitesimal strain tensor. For isotropic materials, this statement is equivalent to following well known inequalities for the Lamé constants:

$$\mu > 0, \quad 3\lambda + 2\mu > 0, \tag{10.9}$$

which state that the shear modulus and the compression modulus must be positive.

11. Simple fluids

For simple fluids we have, by (4.2) and (4.3),

$$\hat{\varepsilon}(F, \eta) = \bar{\varepsilon}(|\det F| v_r, \eta), \tag{11.1}$$

where $v_r = 1/\rho_r$ is the specific volume in the reference configuration. Taking the gradient of (11.1) with respect to F , we obtain

$$\hat{\varepsilon}_F(F, \eta) = \bar{\varepsilon}_v(v, \eta) v F^{-1}, \tag{11.2}$$

where $v = |\det F| v_r$. On substituting (11.2) into the fundamental inequality (8.3) and using (8.4), we obtain

$$\bar{\varepsilon}(v^*, \eta^*) - \bar{\varepsilon}(v, \eta) - v \bar{\varepsilon}_v(v, \eta) \text{tr}(G - I) - (\eta^* - \eta) \bar{\varepsilon}_\eta(v, \eta) > 0, \tag{11.3}$$

which must hold for all positive definite symmetric $G = FF^{*-1}$ whenever either $G \neq I$ or $\eta \neq \eta^*$.

We assume now that $v^* = v$; i.e., that $|\det F^*| = |\det F|$, which means that G is unimodular. We also choose $\eta^* = \eta$. Then (11.3) reduces to

$$-v \bar{\varepsilon}_v(v, \eta) \text{tr}(G - I) > 0, \tag{11.4}$$

which must be valid for all symmetric positive definite unimodular tensors $G \neq I$. Let g_1, g_2, g_3 be the proper numbers of G . We then have

$$g_i > 0, \quad g_1 g_2 g_3 = 1 \tag{11.5}$$

and

$$\text{tr}(G - I) = g_1 + g_2 + g_3 - 3. \tag{11.6}$$

Using the fact that the arithmetic mean is greater than the geometric mean,

$$\frac{g_1 + g_2 + g_3}{3} > \sqrt[3]{g_1 g_2 g_3}, \tag{11.7}$$

we see that (11.5) and (11.6) imply

$$\text{tr}(G - I) > 0. \tag{11.8}$$

Hence, it follows from (11.4) that

$$\bar{\varepsilon}_v(v, \eta) < 0 \quad (11.9)$$

for all v and η for which $\bar{\varepsilon}$ is defined. Thus, $\bar{\varepsilon}(v, \eta)$ must be a strictly decreasing function of v for each fixed η .

Substitution of (11.2) into (7.1) shows that the stress relation reduces to

$$S = -\bar{p}(v, \eta) I, \quad (11.10)$$

where

$$\bar{p}(v, \eta) = -\bar{\varepsilon}_v(v, \eta) \quad (11.11)$$

is the hydrostatic pressure. By (11.9) it is positive.

For further exploitation of (11.3) we choose $G = \alpha I$, $\alpha > 0$. Since

$$\alpha^3 = |\det G| = \left| \frac{\det F^*}{\det F} \right| = \frac{v^*}{v},$$

we have

$$G = \left(\sqrt[3]{\frac{v^*}{v}} \right) I. \quad (11.12)$$

Substitution of (11.12) into (11.3) yields the inequality

$$\bar{\varepsilon}(v^*, \eta^*) - \bar{\varepsilon}(v, \eta) - 3v\bar{\varepsilon}_v(v, \eta) \left(\sqrt[3]{\frac{v^*}{v}} - 1 \right) - (\eta^* - \eta)\bar{\varepsilon}_\eta(v, \eta) > 0, \quad (11.13)$$

which must be valid for all v, v^*, η, η^* except, of course, when both $v = v^*$ and $\eta = \eta^*$. In order to understand the significance of this inequality we introduce the new variable

$$v = \sqrt[3]{v} \quad (11.14)$$

and define the function $\bar{\bar{\varepsilon}}$ by

$$\bar{\varepsilon}(v, \eta) = \bar{\bar{\varepsilon}}(\sqrt[3]{v}, \eta). \quad (11.15)$$

A straightforward calculation shows that (11.13) is equivalent to the inequality

$$\bar{\bar{\varepsilon}}(v^*, \eta^*) - \bar{\bar{\varepsilon}}(v, \eta) - (v^* - v)\bar{\bar{\varepsilon}}_v(v, \eta) - (\eta^* - \eta)\bar{\bar{\varepsilon}}_\eta(v, \eta) > 0, \quad (11.16)$$

which states that $\bar{\bar{\varepsilon}}(v, \eta)$ is strictly convex in v and η jointly. If $\bar{\bar{\varepsilon}}(v, \eta)$ happens to possess continuous second derivatives, it follows that the matrix

$$\begin{vmatrix} \bar{\bar{\varepsilon}}_{vv} & \bar{\bar{\varepsilon}}_{v\eta} \\ \bar{\bar{\varepsilon}}_{\eta v} & \bar{\bar{\varepsilon}}_{\eta\eta} \end{vmatrix} \quad (11.17)$$

must be positive semi-definite.

We summarize in the following theorem:

Theorem 6. *For a simple fluid in thermal equilibrium, the stress S reduces to a hydrostatic pressure $S = -\bar{p}(v, \eta)I$. The pressure $\bar{p}(v, \eta) = -\bar{\varepsilon}_v(v, \eta)$ is always positive. The energy density $\bar{\varepsilon}(v, \eta)$ is a strictly convex function of the cube root v of the specific volume and the entropy η jointly.*

It is not hard to show that, for simple fluids, the positivity of $\bar{p}(v, \eta)$ and the convexity of $\bar{\varepsilon}(v, \eta)$ are not only necessary but also sufficient conditions for the validity of the fundamental inequality (11.3). Hence, these conditions are also sufficient conditions for the validity of Postulate I for simple fluids.

12. Isotropic materials

For isotropic materials in general, if we pick an undistorted state as reference, we have, by (4.5),

$$\hat{\varepsilon}(F, \eta) = \hat{\varepsilon}(VR, \eta) = \hat{\varepsilon}(V, \eta), \tag{12.1}$$

where V is the left stretch tensor, defined by the polar decomposition $F = VR$. On computing the gradient of (12.1) with respect to V , we find

$$\hat{\varepsilon}_F(F, \eta) = R^T \hat{\varepsilon}_V(V, \eta). \tag{12.2}$$

If we substitute (12.2) into (7.1) and again use $F = VR$, we see that the stress relation may be written in the form

$$S = \rho V \hat{\varepsilon}_V(V, \eta) = \rho \hat{\varepsilon}_V(V, \eta) V. \tag{12.3}$$

On substituting (8.4), (12.1) and (12.2) into the fundamental inequality (8.3) and observing that

$$\hat{\varepsilon}(F^*) = \hat{\varepsilon}(GF) = \hat{\varepsilon}(GVR) = \hat{\varepsilon}(GV),$$

we obtain

$$\hat{\varepsilon}(GV, \eta^*) - \hat{\varepsilon}(V, \eta) - \text{tr}[(G - I) V \hat{\varepsilon}_V(V, \eta)] - (\eta^* - \eta) \hat{\varepsilon}_\eta(V, \eta) > 0. \tag{12.4}$$

This inequality must be valid for all η, η^* and all symmetric and positive definite G and V , except, of course, when both $\eta = \eta^*$ and $G = I$.

We consider now the special case when G and V commute; *i.e.*, when

$$V^* = GV \tag{12.5}$$

is symmetric. In this case the tensors V and V^* have an orthonormal basis of proper vectors in common. The matrices of V and V^* , relative to this basis, are

$$\|V\| = \begin{vmatrix} v_1 & 0 & 0 \\ 0 & v_2 & 0 \\ 0 & 0 & v_3 \end{vmatrix}, \quad \|V^*\| = \begin{vmatrix} v_1^* & 0 & 0 \\ 0 & v_2^* & 0 \\ 0 & 0 & v_3^* \end{vmatrix}, \tag{12.6}$$

where the v_i and the v_i^* are the proper numbers of V and V^* , respectively. The matrix of $\hat{\varepsilon}_V(V, \eta)$ is

$$\|\hat{\varepsilon}_V(V, \eta)\| = \begin{vmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_2 & 0 \\ 0 & 0 & \varepsilon_3 \end{vmatrix}, \tag{12.7}$$

where

$$\varepsilon_i = \bar{\varepsilon}_i(v_j, \eta) = \frac{\partial}{\partial v_i} \bar{\varepsilon}(v_j, \eta) \tag{12.8}$$

are the partial derivatives of the function (4.6). Substitution of (12.5), (4.6), (12.6), and (12.7) into (12.4) gives the inequality

$$\bar{\varepsilon}(v_j^*, \eta^*) - \bar{\varepsilon}(v_j, \eta) - \sum_{i=1}^3 (v_i^* - v_i) \bar{\varepsilon}_i(v_j, \eta) - (\eta^* - \eta) \bar{\varepsilon}_\eta(v_j, \eta) > 0, \tag{12.9}$$

which is valid except when $\eta^* = \eta$ and $v_i = v_i^*$ for all i . We have thus proved*

* We have shown that for isotropic materials the inequality (12.9) is a *necessary* condition for validity of the fundamental inequality (8.3). At the present time, it is an open matter as to whether (12.9) is *sufficient* for the validity of (8.3) in the isotropic case, or whether further inequalities which are independent of (12.9) can be deduced from Postulate I for isotropic materials.

Theorem 7. For an isotropic material, the energy density $\bar{\epsilon}(v_j, \eta)$ is a strictly convex function of the principal stretches v_j and the entropy density η jointly.

If $\bar{\epsilon}$ happens to be twice continuously differentiable, it follows that the matrix

$$\begin{vmatrix} \bar{\epsilon}_{11} & \bar{\epsilon}_{12} & \bar{\epsilon}_{13} & \bar{\epsilon}_{1\eta} \\ \bar{\epsilon}_{21} & \bar{\epsilon}_{22} & \bar{\epsilon}_{23} & \bar{\epsilon}_{2\eta} \\ \bar{\epsilon}_{31} & \bar{\epsilon}_{32} & \bar{\epsilon}_{33} & \bar{\epsilon}_{3\eta} \\ \bar{\epsilon}_{\eta 1} & \bar{\epsilon}_{\eta 2} & \bar{\epsilon}_{\eta 3} & \bar{\epsilon}_{\eta\eta} \end{vmatrix} \quad (12.10)$$

is positive semidefinite. Here the indices 1, 2, 3, and η denote the derivatives of $\bar{\epsilon}$ with respect to v_1, v_2, v_3 , and η , respectively.

A corollary of the convexity inequality (12.9) is

Theorem 8. For an isotropic material, the functions $\bar{\epsilon}_i(v_j, \eta)$, defined by (12.8), have the property that $v_i > v_k$ implies $\bar{\epsilon}_i(v_j, \eta) > \bar{\epsilon}_k(v_j, \eta)$.

Proof. Without loss of generality, we take $i=1$ and $k=2$. We then choose $v_1^* = v_2$, $v_2^* = v_1$, $v_3^* = v_3$, and $\eta^* = \eta$. Since $\bar{\epsilon}(v_j, \eta)$ is a symmetric function of the principal stretches v_j (cf. § 4), and since the v_j^* differ from the v_j only by their order, we have

$$\bar{\epsilon}(v_j^*, \eta) = \bar{\epsilon}(v_j, \eta).$$

Hence (12.9) reduces to

$$-(v_2 - v_1)\bar{\epsilon}_1(v_j, \eta) - (v_1 - v_2)\bar{\epsilon}_2(v_j, \eta) > 0;$$

i.e.,

$$(v_1 - v_2) [\bar{\epsilon}_1(v_j, \eta) - \bar{\epsilon}_2(v_j, \eta)] > 0.$$

Thus, if $v_1 > v_2$, then $\bar{\epsilon}_1(v_j, \eta) > \bar{\epsilon}_2(v_j, \eta)$, q.e.d.

In an isotropic material, the left stretch tensor V and the stress tensor S have an orthonormal basis e_i of proper vectors in common. The e_i determine the principal axes of stress. It follows from (12.3), (12.6), and (12.7) that the principal stresses are given by

$$s_i = \rho v_i \bar{\epsilon}_i(v_j, \eta). \quad (12.11)$$

When measured per unit area in the undistorted reference state, these principal stresses must be replaced by

$$s'_i = \rho_r \bar{\epsilon}_i(v_j, \eta). \quad (12.12)$$

Hence Theorem 8 has the following simple physical interpretation:

Theorem 8a. If, at a given value η , the principal stretch v_i is greater than the principal stretch v_k , then the principal stress, measured per unit area in the undistorted reference state, in the direction of v_i is greater than that in the direction of v_k .

It should be noted that the statement of this theorem does not necessarily remain valid if the principal stresses are measured per unit area of the deformed state*, except when these stresses are all positive; *i.e.*, except in a state of pure tension.

* Such a statement was proposed as a postulate by M. BAKER & J. L. ERICKSEN [13]. In our theory, only the modification given by Theorem 8a is valid. Related inequalities have been studied by J. BARTA [14].

13. The free energy

It is often useful to employ the deformation gradient F and the temperature ϑ , rather than F and the entropy η , as the independent variables. This is possible because, by (8.2) and (8.6), there is a one-to-one correspondence between η and ϑ for each fixed F .

The *free energy function* $\tilde{\psi}$ is defined by

$$\tilde{\psi}(F, \vartheta) = \hat{\varepsilon}[F, \tilde{\eta}(F, \vartheta)] - \vartheta \tilde{\eta}(F, \vartheta), \quad (13.1)$$

where the entropy function $\tilde{\eta}$ is defined in (8.6) as the unique solution of the equation (8.2). The values ψ of the free energy function $\tilde{\psi}$ are called *free energy densities**.

Differentiation of (13.1) with respect to F , using the chain rule, gives

$$\tilde{\psi}_F(F, \vartheta) = \hat{\varepsilon}_F[F, \tilde{\eta}(F, \vartheta)] + \hat{\varepsilon}_\eta[F, \tilde{\eta}(F, \vartheta)] \tilde{\eta}_F(F, \vartheta) - \vartheta \tilde{\eta}_F(F, \vartheta).$$

It follows from (8.7) that the last two terms cancel, so that

$$\tilde{\psi}_F(F, \vartheta) = \hat{\varepsilon}_F[F, \tilde{\eta}(F, \vartheta)]. \quad (13.2)$$

Differentiation of (13.1) with respect to ϑ gives

$$\tilde{\psi}_\vartheta(F, \vartheta) = -\tilde{\eta}(F, \vartheta). \quad (13.3)$$

From Theorems 1 and 2, (13.2), and (13.3) we get

Theorem 9. *For the force temperature pair (S_r, ϑ) to make the local state (F, η) a state of thermal equilibrium, it is necessary and sufficient that S_r and η be given by*

$$S_r = \rho_r \tilde{\psi}_F(F, \vartheta), \quad (13.4)$$

$$\eta = -\tilde{\psi}_\vartheta(F, \vartheta). \quad (13.5)$$

On multiplying (13.4) on the left by $(\rho/\rho_r)F$ and noting that $S = (\rho/\rho_r)FS_r$, we get the following form for the stress relation:

$$S = \rho F \tilde{\psi}_F(F, \vartheta). \quad (13.6)$$

Assuming that two temperatures ϑ, ϑ^* and two deformation gradients F, F^* are given, we now put

$$\begin{aligned} \eta &= \tilde{\eta}(F, \vartheta) = -\tilde{\psi}_\vartheta(F, \vartheta) \\ \eta^* &= \tilde{\eta}(F^*, \vartheta^*) = -\tilde{\psi}_\vartheta(F^*, \vartheta^*). \end{aligned} \quad (13.7)$$

By substituting (13.1)–(13.7) into the fundamental inequality (8.3) of Theorem 2, we obtain

Theorem 10. *The free energy function $\tilde{\psi}$ obeys the inequality*

$$\tilde{\psi}(F^*, \vartheta^*) - \tilde{\psi}(F, \vartheta) - \text{tr}[(F^* - F)\tilde{\psi}_F(F, \vartheta)] - (\vartheta^* - \vartheta)\tilde{\psi}_\vartheta(F^*, \vartheta^*) > 0 \quad (13.8)$$

for any two pairs (F, ϑ) and $(F^*, \vartheta^*) \neq (F, \vartheta)$ in the domain of definition of $\tilde{\psi}$ which are related by

$$F^* = GF, \quad (13.9)$$

where G is symmetric and positive definite.

* The term "Helmholtz free energy per unit mass" would also be in accord with common usage.

As Theorem 2, so also Theorem 10 is equivalent to Postulate I.

If in (13.8) we take the special case $F^* = F$ and interchange ϑ and ϑ^* , we obtain

$$\tilde{\psi}(F, \vartheta^*) - \tilde{\psi}(F, \vartheta) - (\vartheta^* - \vartheta) \tilde{\psi}_\vartheta(F, \vartheta) < 0. \quad (13.10)$$

This inequality, which is valid for all F and all $\vartheta^* \neq \vartheta$, states that the free energy function $\tilde{\psi}(F, \vartheta)$ is *strictly concave* in ϑ for each F .

Putting $\vartheta^* = \vartheta$ in (13.8) gives the following restricted convexity of $\tilde{\psi}$ in F :

$$\tilde{\psi}(F^*, \vartheta) - \tilde{\psi}(F, \vartheta) - \text{tr}[(F^* - F) \tilde{\psi}_F(F, \vartheta)] > 0, \quad (13.11)$$

the restriction being the condition (13.9).

The considerations and results of § 11 and § 12 on simple fluids and isotropic materials remain valid if the energy function $\hat{\epsilon}$ is replaced by the free energy function $\tilde{\psi}$, except that the convexity of $\hat{\epsilon}(F, \eta)$ in η corresponds to the concavity of $\tilde{\psi}(F, \vartheta)$ in ϑ . We summarize the relevant results.

For a simple fluid, the free energy density reduces to a function of the specific volume v and the temperature ϑ only:

$$\psi = \tilde{\psi}(F, \vartheta) = \bar{\psi}(v, \vartheta). \quad (13.12)$$

The stress reduces to a hydrostatic pressure given by

$$S = -\bar{p}(v, \vartheta) I, \quad \bar{p}(v, \vartheta) = -\bar{\psi}_v(v, \vartheta). \quad (13.13)$$

The pressure is always positive. The function $\bar{\psi}$, giving the free energy as a function of the cube root ν of the specific volume and the temperature,

$$\bar{\bar{\psi}}(\nu, \vartheta) = \bar{\psi}(\nu^3, \vartheta), \quad (13.14)$$

satisfies the inequality

$$\bar{\bar{\psi}}(\nu^*, \vartheta^*) - \bar{\bar{\psi}}(\nu, \vartheta) - (\nu^* - \nu) \bar{\bar{\psi}}_\nu(\nu, \vartheta) - (\vartheta^* - \vartheta) \bar{\bar{\psi}}_\vartheta(\nu^*, \vartheta^*) > 0. \quad (13.15)$$

This inequality implies that $\bar{\bar{\psi}}(\nu, \vartheta)$ is strictly convex in ν for each ϑ and strictly concave in ϑ for each ν .

For isotropic materials in general, the free energy reduces to a function of the temperature ϑ and the three principal stretches v_1, v_2, v_3 , computed relative to an undistorted state:

$$\tilde{\psi}(F, \vartheta) = \bar{\psi}(v_1, v_2, v_3; \vartheta). \quad (13.16)$$

The function $\bar{\psi}$ is symmetric and strictly convex in the variables v_1, v_2, v_3 ; $\bar{\psi}$ is strictly concave in ϑ . Theorems 8 and 8a remain valid if $\bar{\epsilon}$ is replaced by $\bar{\psi}$; *i.e.*, if the temperature, rather than the entropy is fixed at a given value. The stress relation may be written in the form

$$S = \rho V \tilde{\psi}_V(V, \vartheta), \quad (13.17)$$

where V is the left stretch tensor.

The forms, (13.6), (13.13), and (13.17), of the stress relation are useful in discussing experiments involving equilibrium states for which the temperature is controlled, while the forms, (7.1), (11.10), and (12.3), are appropriate for discussing experiments involving equilibrium states for which the entropy is controlled.

14. Thermal stability

Consider a body \mathcal{B} and a global thermomechanic state $\{\mathbf{f}, \eta\}$ of \mathcal{B} , defined by a configuration \mathbf{f} of \mathcal{B} and an entropy distribution η of \mathcal{B} ; (cf. § 2). Let the caloric equation of state of the material point X of \mathcal{B} be given by

$$\varepsilon(X) = \hat{\varepsilon}[F(X), \eta(X); X]. \quad (14.1)$$

Here $F(X)$ is the deformation gradient at X of the configuration \mathbf{f} relative to some reference configuration \mathbf{f}_r . We do not assume that the body is homogeneous, and hence the function $\hat{\varepsilon}$ may depend explicitly on X as indicated in (14.1). The *total entropy* of \mathcal{B} in the given state is defined by

$$H = \int_{\mathcal{B}} \eta(X) dm \quad (14.2)$$

and the *total internal energy* of \mathcal{B} by

$$E = \int_{\mathcal{B}} \hat{\varepsilon}[F(X), \eta(X); X] dm. \quad (14.3)$$

In this section we shall deal with situations in which the deformation gradient $F(X)$ is kept fixed at each X while the entropy field $\eta = \eta(X)$ is varied. It will not be necessary to make the dependence of ε on F explicit, and the following abbreviated notation will be convenient:

$$\hat{\varepsilon}[F(X), \eta(X); X] = \varepsilon(X, \eta(X)). \quad (14.4)$$

Definition of thermal stability. Let $\{\mathbf{f}, \eta\}$ be a state of \mathcal{B} and let E and H be, respectively, the total internal energy and total entropy corresponding to the state $\{\mathbf{f}, \eta\}$. We say that $\{\mathbf{f}, \eta\}$ is a **thermally stable** state of \mathcal{B} if every other state $\{\mathbf{f}, \eta^*\}$, with the same configuration as $\{\mathbf{f}, \eta\}$ and the same total entropy as $\{\mathbf{f}, \eta\}$,

$$H^* = \int_{\mathcal{B}} \eta^*(X) dm = H = \int_{\mathcal{B}} \eta(X) dm, \quad (14.5)$$

has a greater total internal energy than the state $\{\mathbf{f}, \eta\}$; i.e.,

$$E^* = \int_{\mathcal{B}} \varepsilon(X, \eta^*(X)) dm > E = \int_{\mathcal{B}} \varepsilon(X, \eta(X)) dm. \quad (14.6)$$

We give another condition, equivalent to the one given above, which could also be used to define thermal stability.

Theorem 11. A state $\{\mathbf{f}, \eta\}$ of \mathcal{B} is thermally stable if and only if every other state $\{\mathbf{f}, \eta^*\}$ with the same configuration as $\{\mathbf{f}, \eta\}$ and the same total energy as $\{\mathbf{f}, \eta\}$,

$$E^* = \int_{\mathcal{B}} \varepsilon(X, \eta^*(X)) dm = E = \int_{\mathcal{B}} \varepsilon(X, \eta(X)) dm, \quad (14.7)$$

has a lower total entropy than the state $\{\mathbf{f}, \eta\}$; i.e.,

$$H = \int_{\mathcal{B}} \eta(X) dm > H^* = \int_{\mathcal{B}} \eta^*(X) dm. \quad (14.8)$$

Proof. We show that the hypothesis of Theorem 11 is necessary for thermal stability by showing that if there exists a state $\{\mathbf{f}, \eta_1\}$ (with η_1 not identical to η) which obeys the equation (14.7) of Theorem 11 but violates (14.8), then there must exist a state $\{\mathbf{f}, \eta_2\}$ (with η_2 not identical to η) which obeys the equation

(14.5) of the definition of thermal stability but which does not obey (14.6). Let η_1 be the entropy density distribution which obeys (14.7) but not (14.8); we construct η_2 as follows:

$$\eta_2(X) = \eta_1(X) + \frac{H - H_1}{m(\mathcal{B})}, \quad (14.9)$$

where H_1 is the total entropy corresponding to η_1 . The total entropy corresponding to η_2 is

$$H_2 = \int_{\mathcal{B}} \eta_2(X) dm = H. \quad (14.10)$$

Hence, the state $\{f, \eta_2\}$ obeys the equation (14.5) of the definition. We have assumed that η_2 is not identical to η and that $H_1 \geq H$. If $H_1 = H$, then η_2 is the same as η_1 and hence different from η . In this trivial case of $\eta_2 = \eta_1$, it follows from the fact that η_1 obeys (14.7) that

$$\int_{\mathcal{B}} \varepsilon(X, \eta_2(X)) dm = \int_{\mathcal{B}} \varepsilon(X, \eta_1(X)) dm = \int_{\mathcal{B}} \varepsilon(X, \eta(X)) dm. \quad (14.11)$$

If $H_1 > H$, then $\eta_2(X) < \eta_1(X)$ for all X in \mathcal{B} . It then follows from Postulate II of § 8 and the assumption that η_1 obeys (14.7) that

$$\int_{\mathcal{B}} \varepsilon(X, \eta_2(X)) dm < \int_{\mathcal{B}} \varepsilon(X, \eta_1(X)) dm = \int_{\mathcal{B}} \varepsilon(X, \eta(X)) dm. \quad (14.12)$$

It is clear from (14.12) that η_2 is not identical to η . Hence, whenever $H_1 \geq H$, we have, by the construction (14.9), a state $\{f, \eta_2\}$ with η_2 different from η but with $H_2 = H$ and

$$E_2 = \int_{\mathcal{B}} \varepsilon(X, \eta_2(X)) dm \leq \int_{\mathcal{B}} \varepsilon(X, \eta(X)) dm = E. \quad (14.13)$$

Thus, a violation of the hypothesis of Theorem 11 implies the existence of a state different from $\{f, \eta\}$ which obeys (14.5) yet violates (14.6).

The sufficiency of the hypothesis of Theorem 11 is proved analogously by starting with a state which obeys (14.5) of the definition, but not (14.6), and then using Postulate II to construct a state which obeys (14.7) of the theorem, but which violates (14.8).

The main result of the present section is the following theorem:

Theorem 12. *A state $\{f, \eta\}$ of a body is thermally stable if and only if it is of uniform temperature; i.e., if and only if*

$$\vartheta = \varepsilon_{\eta}(X, \eta(X)) \quad (14.14)$$

is a constant, independent of the material point X .

Proof. To show the necessity of $\vartheta = \text{constant}$, we observe that, by (14.6), the function $\eta(X)$ is the solution of the variational problem

$$\int_{\mathcal{B}} \varepsilon(X, \eta^*(X)) dm = \text{Minimum} \quad (14.15)$$

subject to the constraint (14.5). It follows that the first variation of

$$\int_{\mathcal{B}} [\varepsilon(X, \eta^*(X)) - \alpha \eta^*(X)] dm \quad (14.16)$$

must vanish for $\eta^* = \eta$. Here α is a constant Lagrange parameter. We obtain

$$\alpha = \varepsilon_{\eta}(X, \eta(X)) = \vartheta = \text{constant}. \quad (14.17)$$

To prove the sufficiency of $\vartheta = \text{constant}$, we substitute the function values $F(X)$, $\eta(X)$ and $\eta^*(X)$ for F , η and η^* in the convexity inequality (8.5). Using the abbreviation (14.4) and the equation (14.14), we get

$$\varepsilon(X, \eta^*(X)) - \varepsilon(X, \eta(X)) - [\eta^*(X) - \eta(X)] \vartheta \geq 0. \quad (14.18)$$

This inequality must be strict for some X if η^* and η are different continuous functions. If ϑ is a constant and if (14.5) holds, then integration of (14.18) over the body \mathcal{B} gives the inequality (14.6), which proves that $\{\mathbf{f}, \eta\}$ is thermally stable, *q. e. d.*

15. Mechanical stability

Consider a state $\{\mathbf{f}, \eta\}$ of a body \mathcal{B} . According to Postulate I of § 8 it is possible to find a temperature field ϑ and a stress field S such that every material point of \mathcal{B} is in *thermal equilibrium* for the force temperature field defined by S and ϑ . In fact, S and ϑ are given by the stress relation (7.1) and the temperature relation (7.2), respectively. If a field of body forces \mathbf{b} is given, then the state $\{\mathbf{f}, \eta\}$ will be a state of *mechanical equilibrium* if Cauchy's condition

$$\text{Div } S + \rho \mathbf{b} = 0 \quad (15.1)$$

holds. If $\{\mathbf{f}, \eta\}$ is such that every material point is in thermal equilibrium, it is always possible to choose \mathbf{b} such that the state $\{\mathbf{f}, \eta\}$ is a state of mechanical equilibrium. We need only to define \mathbf{b} by (15.1). We say that the fields S , ϑ , and \mathbf{b} , given by (7.1), (7.2) and (15.1)*, make $\{\mathbf{f}, \eta\}$ a state of equilibrium. We call S , ϑ and \mathbf{b} , respectively, the stress, temperature, and body force fields of $\{\mathbf{f}, \eta\}$.

We investigate the possible meaning that can be given to the statement that an equilibrium state $\{\mathbf{f}, \eta\}$ is *stable*. First, we require that it be *thermally stable* which, according to Theorem 12, means that the temperature ϑ must be uniform. In addition, we require that some condition of *mechanical stability* be satisfied. One must distinguish between various types of *isothermal mechanical stability* and *adiabatic mechanical stability*.

In the case of isothermal mechanical stability, one compares the given equilibrium state $\{\mathbf{f}, \eta\}$ with a class of states $\{\mathbf{f}^*, \eta^*\}$ corresponding to the same uniform temperature $\vartheta = \hat{\vartheta}(F, \eta)$ as the given state. Each of these states is characterized by its configuration \mathbf{f}^* alone, because the corresponding entropy distribution is then determined by

$$\eta = \hat{\eta}(F^*, \vartheta). \quad (15.2)$$

External forces or boundary conditions must be prescribed for each of the comparison configurations \mathbf{f}^* . The configuration \mathbf{f} is called *stable* if the increase in the total free energy would always be greater than the work done on the body by the external forces if the configuration were to be deformed into any of the comparison configurations \mathbf{f}^* . We give more precise definitions in two special cases.

Definition of isothermal stability at fixed boundary (IFB stability). *An equilibrium state $\{\mathbf{f}, \eta\}$ is called IFB stable if $\{\mathbf{f}, \eta\}$ has a uniform temperature ϑ*

and if for every state $\{\mathbf{f}^*, \eta\}$ which satisfies the following conditions:

- (a) \mathbf{f}^* lies in a prescribed neighborhood* of \mathbf{f} ,
- (b) $\mathbf{f}^*(X) = \mathbf{f}(X)$, when X belongs to $\bar{\mathcal{B}}$,
- (c) the temperature corresponding to $\{\mathbf{f}^*, \eta\}$ is equal to ϑ for all X in \mathcal{B} ,

the following inequality holds:

$$\int_{\mathcal{B}} \{\psi(F^*) - \psi(F) - \mathbf{b} \cdot (\mathbf{f}^* - \mathbf{f})\} dm \geq 0. \quad (15.4)$$

Here $\bar{\mathcal{B}}$ is the boundary of \mathcal{B} , and $\psi(F)$ is an abbreviation for

$$\psi(F) = \tilde{\psi}(F(X), \vartheta; \dot{X}); \quad (15.5)$$

$F^*(X)$ and $F(X)$ are the deformation gradients at X for the configurations \mathbf{f}^* and \mathbf{f} , respectively, both computed relative to the same fixed reference configuration. As in § 14, we do not assume that the body is homogeneous, and hence the function $\tilde{\psi}$ may depend explicitly on X .

We say that $\{\mathbf{f}, \eta\}$ is *strictly IFB stable* if the inequality (15.4) is strict whenever $\{\mathbf{f}^*, \eta^*\}$ obeys (a), (b) and (c) and is such that $\mathbf{f}^* \neq \mathbf{f}$.

Note that the surface tractions do no work if the boundary is fixed and that $-\int_{\mathcal{B}} \mathbf{f}^* \cdot \mathbf{b} dm$ is a potential of the work done by the body forces if these are held at their values $\mathbf{b}(X)$ in the equilibrium state $\{\mathbf{f}, \eta\}$.

The type of stability considered is affected by the prescription of the neighborhood in the requirement (a) of the definition of IFB stability. A global state may be stable with respect to some (small) neighborhood without being stable with respect to other (larger) neighborhoods.

Definition of isothermal stability at fixed surface tractions (IFT stability). An equilibrium state $\{\mathbf{f}, \eta\}$ is called **IFT stable** if $\{\mathbf{f}, \eta\}$ has a uniform temperature ϑ and if for every state $\{\mathbf{f}^*, \eta\}$ which satisfies the following conditions:

- (a) \mathbf{f}^* lies in a prescribed neighborhood of \mathbf{f} ,
- (b) the temperature corresponding to $\{\mathbf{f}^*, \eta\}$ is equal to ϑ for all X in \mathcal{B} ,

the following inequality holds:

$$\Gamma = \int_{\mathcal{B}} \{\psi(F^*) - \psi(F) - \mathbf{b} \cdot (\mathbf{f}^* - \mathbf{f})\} dm - \int_{\bar{\mathcal{B}}} (\mathbf{f}^* - \mathbf{f}) \cdot \mathbf{S} \mathbf{n} dA \geq 0. \quad (15.6)$$

Here $\bar{\mathcal{B}}$ is the boundary surface of the region occupied by \mathcal{B} in the configuration \mathbf{f} ; dA is the element of that surface; and \mathbf{n} is the exterior unit normal.

Note that $-\int_{\bar{\mathcal{B}}} \mathbf{f}^* \cdot \mathbf{S} \mathbf{n} dA$ is a potential of the work done by the surface tractions if they are held at their values in the equilibrium state $\{\mathbf{f}, \eta\}$.

An IFT stable state is always also IFB stable. This follows from the fact that the surface integral in (15.6) gives no contribution if the boundary condition (15.3) holds, so that the inequalities (15.4) and (15.6) become the same in this case.

* A neighborhood of \mathbf{f} of a configuration is defined by the metric

$$\delta(\mathbf{f}, \mathbf{f}^*) = \sup_{X \in \mathcal{B}} \{|\mathbf{f}^*(X) - \mathbf{f}(X)| + |F^{*-1}(X)F(X) - I|\}$$

over the space of all configurations.

If the inequality (15.6) holds for all states which obey items (a) and (b) of the definition of IFT stability and is, furthermore, a strict inequality for all such states for which $F^*(X) \neq F(X)$ for at least one material point X , then we say that $\{f, \eta\}$ is *strictly IFT stable against deformations and rotations*. For in that case (15.6) can reduce to an equality only if f^* is related to f by a simple rigid translation.

To investigate adiabatic mechanical stability, one compares the given equilibrium state $\{f, \eta\}$ with a class of states which correspond to the same total entropy as $\{f, \eta\}$. We again consider two special cases.

Definition of adiabatic stability at fixed boundary (AFB stability). An equilibrium state $\{f, \eta\}$ is called **AFB stable** if $\{f, \eta\}$ is thermally stable and if for every state $\{f^*, \eta^*\}$ which satisfies the following conditions:

- (a) f^* lies in a prescribed neighborhood of f ,
- (b) $f^*(X) = f(X)$, when X belongs to $\bar{\mathcal{B}}$,
- (c) $\int_{\mathcal{A}} \eta^*(X) dm = \int_{\mathcal{A}} \eta(X) dm$,

the following inequality holds:

$$\int_{\mathcal{A}} \{\hat{\varepsilon}[F^*(X), \eta^*(X); X] - \hat{\varepsilon}[F(X), \eta(X); X] - \mathbf{b} \cdot (f^* - f)\} dm \geq 0. \quad (15.7)$$

If the inequality in (15.7) is strict for all $\{f^*, \eta^*\}$ satisfying (a), (b) and (c) and for which $f^* \neq f$, then we say that $\{f, \eta\}$ is *strictly AFB stable*.

Theorem 13. A thermally stable equilibrium state $\{f, \eta\}$ is AFB stable if and only if for every state $\{f^*, \eta^*\}$ which satisfies the following conditions:

- (a) f^* lies in a prescribed neighborhood of f ,
- (b) $f^*(X) = f(X)$ when X belongs to $\bar{\mathcal{B}}$,
- (c) $\int_{\mathcal{A}} \{\hat{\varepsilon}(F^*(X), \eta^*(X); X) - \mathbf{b} \cdot f^*\} dm = \int_{\mathcal{A}} \{\hat{\varepsilon}(F(X), \eta(X); X) - \mathbf{b} \cdot f\} dm$, (15.8)

the following inequality holds:

$$\int_{\mathcal{A}} \eta^*(X) dm \leq \int_{\mathcal{A}} \eta(X) dm. \quad (15.9)$$

Furthermore, $\{f, \eta\}$ is strictly AFB stable if and only if (15.9) is a strict inequality for every state $\{f^*, \eta^*\} \neq \{f, \eta\}$ obeying (a), (b) and (c).

We omit the proof of Theorem 13 because it is analogous to that of Theorem 11. Of course, the validity of Theorem 13 requires the assumption of Postulate II.

Definition of adiabatic stability at fixed surface tractions (AFT stability). An equilibrium state $\{f, \eta\}$ is called **AFT stable** if it is thermally stable and if for every state $\{f^*, \eta^*\}$ which satisfies the following conditions:

- (a) f^* is in a prescribed neighborhood of f ,
- (b) $\int_{\mathcal{A}} \eta^*(X) dm = \int_{\mathcal{A}} \eta(X) dm$,

the following inequality holds:

$$\int_{\mathcal{A}} \{\hat{\varepsilon}[F^*(X), \eta^*(X); X] - \hat{\varepsilon}[F(X), \eta(X); X] - \mathbf{b} \cdot (f^* - f)\} dm - \int_{\bar{\mathcal{A}}} (f^* - f) \cdot \mathbf{S} n dA \geq 0. \quad (15.10)$$

It will be noticed that a state which is AFT stable is always AFB stable.

If the inequality (15.10) holds for all states which obey (a) and (b) and is a strict inequality for all such states for which $F^*(X) \neq F(X)$ for at least one X , then we say that $\{\mathbf{f}, \eta\}$ is *strictly AFT stable against deformations and rotations*.

It is clear that, in analogy to Theorem 13, an alternative, but equivalent, definition of AFT stability can be formulated in which a stable state is defined to be one of maximum entropy among all those states for which (15.10) reduces to an equality.

The definitions of IFB, IFT, AFB and AFT stability given above are applicable only to those physical situations in which the body force field $\mathbf{b} = \mathbf{b}(X)$ is independent of the comparison configuration \mathbf{f}^* . If one is interested in studying cases in which the body force on X depends on X and is also a functional of \mathbf{f}^* , one can modify the definitions of stability by connecting the comparison state \mathbf{f}^* to \mathbf{f} by means of a continuous one-parameter family \mathbf{f}_s , $0 \leq s \leq 1$, $\mathbf{f}_0 = \mathbf{f}$, $\mathbf{f}_1 = \mathbf{f}^*$ and replacing the term

$$-\int_{\mathcal{B}} \mathbf{b} \cdot (\mathbf{f}^* - \mathbf{f}) \, dm$$

in (15.4), (15.6), (15.7), (15.8) and (15.10) by

$$-\int_{\mathcal{B}} \int_0^1 \mathbf{b}(X, \mathbf{f}_s) \cdot \frac{\partial \mathbf{f}_s(X)}{\partial s} \, ds \, dm.$$

If the body force on each material point is derivable from a single-valued potential, then the integral exhibited above is independent of the parametrization, and is simply the difference in the potentials at \mathbf{f} and \mathbf{f}^* .

In the definitions of IFT and AFT stability, we assumed that not only the body forces but also the contact forces at the surface do not depend on the comparison configuration. One can also study, in a way analogous to that outlined above for the body forces, those cases in which the surface tractions depend on the comparison configuration.

Theorem 14. *A state which has isothermal stability of a certain type also has adiabatic stability of the corresponding type.*

Proof. Consider a state $\{\mathbf{f}, \eta\}$ which has a uniform temperature ϑ and which has isothermal stability of a particular type. Let \mathbf{f}^* be a configuration which satisfies the boundary conditions, if any, for the appropriate comparison configurations. Define the entropy field η_1 by

$$\eta_1(X) = \tilde{\eta}(F^*(X), \vartheta), \quad (15.11)$$

where F^* is the deformation gradient field corresponding to the configuration \mathbf{f}^* . By (13.1) we have

$$\tilde{\psi}(F^*, \vartheta) - \tilde{\psi}(F, \vartheta) = \hat{\varepsilon}(F^*, \eta_1) - \hat{\varepsilon}(F, \eta) - (\eta_1 - \eta) \vartheta. \quad (15.12)$$

Here F corresponds to \mathbf{f} . Let η^* be any entropy distribution satisfying the condition

$$\int_{\mathcal{B}} \eta^*(X) \, dm = \int_{\mathcal{B}} \eta(X) \, dm, \quad (15.13)$$

which is required for comparison states in adiabatic stability. Define the field β by

$$\beta = \hat{\varepsilon}(F^*, \eta^*) - \hat{\varepsilon}(F^*, \eta_1) - (\eta^* - \eta_1) \vartheta. \quad (15.14)$$

From (8.5) we get $\beta(X) \geq 0$
 for all X . From (15.12) we have

$$\tilde{\psi}(F^*, \vartheta) - \tilde{\psi}(F, \vartheta) = \hat{\varepsilon}(F^*, \eta^*) - \hat{\varepsilon}(F, \eta) - \beta - (\eta^* - \eta) \vartheta. \quad (15.15)$$

We integrate (15.15) over \mathcal{B} . According to (15.13) we get no contribution from the term $-(\eta^* - \eta) \vartheta$; hence, since β is non-negative,

$$\int_{\mathcal{B}} [\tilde{\psi}(F^*, \vartheta) - \tilde{\psi}(F, \vartheta)] dm \leq \int_{\mathcal{B}} [\hat{\varepsilon}(F^*, \eta^*) - \hat{\varepsilon}(F, \eta)] dm. \quad (15.16)$$

Since the work W done by the external forces in going from f to f^* is the same in adiabatic and isothermal stability, it follows from (15.16) that if

$$\int_{\mathcal{B}} [\tilde{\psi}(F^*, \vartheta) - \tilde{\psi}(F, \vartheta)] dm - W \quad (15.17)$$

is non-negative, then

$$\int_{\mathcal{B}} [\hat{\varepsilon}(F^*, \eta^*) - \hat{\varepsilon}(F, \eta)] dm - W \quad (15.18)$$

is non-negative (and strictly positive when (15.17) is strictly positive). Hence, the isothermal stability of $\{f, \eta\}$ implies the corresponding adiabatic stability for $\{f, \eta\}$, *q. e. d.*

Although in writing our proof of Theorem 14 we have used a notation which implies that \mathcal{B} is homogeneous, it is clear that the same argument is valid when \mathcal{B} is not homogeneous.

It appears to us that the converse of Theorem 14 need not be true, *i. e.*, an equilibrium state may have adiabatic stability without being isothermally stable.

16. Gibbs' thermostatistics of fluids

We now consider a type of stability which was proposed by GIBBS* for fluids free from body forces. GIBBS states** that he had in mind a physical situation in which the fluid is "enclosed in a rigid envelop which is non-conducting to heat and impermeable to all the components of the fluid". A body which may be regarded as being in such an envelop is usually called an "isolated system".

Definition of G stability*.** *An equilibrium state $\{f, \eta\}$ of a fluid body \mathcal{B} is called G stable if the following condition is satisfied. Let $\{f^*, \eta^*\}$ be any other state with the same total volume and the same total entropy as $\{f, \eta\}$,*

$$\int_{\mathcal{B}} v^* dm = \int_{\mathcal{B}} v dm, \quad \int_{\mathcal{B}} \eta^* dm = \int_{\mathcal{B}} \eta dm, \quad (16.1)$$

* See the section of [I] which is entitled "Internal stability of homogeneous fluids as indicated by the fundamental equations", (b), pp. 100–115, particularly the subsection entitled "Stability with respect to continuous changes of phase" (b), pp. 105–111.

** [I] (b), p. 100.

*** In this definition we again restrict ourselves to those physical situations in which fluctuations in chemical composition are suppressed. We have in mind situations in which chemical reactions are prohibited and in which the fluid is either homogeneous or does not allow diffusion. For fluids the homogeneous case is the one of practical importance. Situations in which flow is permitted but diffusion is prohibited are rare.

then $\{f, \eta\}$ has a lower total internal energy than $\{f^*, \eta^*\}$,

$$\int_{\mathcal{B}} \bar{\varepsilon}[v^*(X), \eta^*(X); X] dm > \int_{\mathcal{B}} \bar{\varepsilon}[v(X), \eta(X); X] dm, \quad (16.2)$$

unless $v^*(X) = v(X)$ and $\eta^*(X) = \eta(X)$ for all X in \mathcal{B} .

In (16.1) v and v^* denote the specific volume fields for \mathcal{B} corresponding to the configurations f and f^* .

In the following alternative definition f and ε are taken as the independent variables, and the permitted comparison states are such that the total internal energy and total volume of the body are conserved during the variations. This alternative formulation may suggest to the reader why G stability is regarded as being appropriate for discussing the physics of *isolated systems* composed of fluids:

Alternative definition of G stability. *An equilibrium state $\{f, \varepsilon\}$ of a fluid body \mathcal{B} is called G stable if any other state $\{f^*, \varepsilon^*\}$ with the same total volume and the same total internal energy as $\{f, \varepsilon\}$,*

$$\int_{\mathcal{B}} v^* dm = \int_{\mathcal{B}} v dm, \quad \int_{\mathcal{B}} \varepsilon^* dm = \int_{\mathcal{B}} \varepsilon dm, \quad (16.3)$$

has a higher total entropy,

$$\int_{\mathcal{B}} \hat{\eta}[v^*(X), \varepsilon^*(X); X] dm < \int_{\mathcal{B}} \hat{\eta}[v(X), \varepsilon(X); X] dm, \quad (16.4)$$

unless $v^*(X) = v(X)$ and $\varepsilon^*(X) = \varepsilon(X)$ for all X in \mathcal{B} .

The function $\hat{\eta}$ in (16.4) is obtained by solving $\varepsilon = \bar{\varepsilon}(v, \eta; X)$ for η , which is possible in a unique way because $\bar{\varepsilon}$ is strictly increasing in η .

The proof of the equivalence of the two definitions of G stability is analogous to the one given for Theorem 11 of § 14 in the case of thermal stability; one must again use Postulate II of § 8.

The main result of this section is

Theorem 15. *An equilibrium state $\{f, \eta\}$ of a fluid body is G stable if and only if its temperature and pressure are uniform.*

Proof. To prove that the condition is necessary we observe that the functions v, η are solutions of the variational problem

$$\int_{\mathcal{B}} \bar{\varepsilon}(v^*, \eta^*; X) dm = \text{Minimum} \quad (16.5)$$

subject to the constraints (16.1). Therefore, the first variation of

$$\int_{\mathcal{B}} [\bar{\varepsilon}(v^*, \eta^*; X) - \lambda \eta^* - \mu v^*] dm$$

must vanish for $v^* = v$ and $\eta^* = \eta$. Here λ and μ are constant Lagrange parameters. It follows that

$$\bar{\varepsilon}_{\eta}(v, \eta; X) = \lambda = \text{constant}, \quad \bar{\varepsilon}_v(v, \eta; X) = \mu = \text{constant}. \quad (16.6)$$

Hence, by (8.2) and (11.11), both the temperature, $\vartheta = \bar{\varepsilon}_{\eta}(v, \eta; X)$, and the pressure, $p = -\bar{\varepsilon}_v(v, \eta; X)$ are uniform over \mathcal{B} .

To prove the sufficiency of the condition of the theorem, we assume that ϑ and p are uniform and that (16.1) holds. From the convexity inequality (11.16),

the inequality (11.9), and the fact that $v = v^3$, $v > 0$, is a convex function of v , one can easily infer that $\bar{\varepsilon}(v, \eta)$ must be convex in v and η . Hence, the inequality

$$\bar{\varepsilon}(v^*, \eta^*; X) - \bar{\varepsilon}(v^*, \eta; X) - (v^* - v) \bar{\varepsilon}_v(v, \eta; X) - (\eta^* - \eta) \bar{\varepsilon}_\eta(v, \eta; X) \geq 0 \quad (16.7)$$

is valid at all material points X in \mathcal{B} ; (16.7) cannot reduce to an equality for all X unless $v(X) = v^*(X)$ and $\eta(X) = \eta^*(X)$ for all X . Since $p = -\varepsilon_v(v, \eta)$ and $\vartheta = \bar{\varepsilon}_\eta(v, \eta)$ are independent of X , integration of (16.7) over \mathcal{B} gives

$$\int_{\mathcal{B}} \{ \bar{\varepsilon}(v^*, \eta^*; X) - \bar{\varepsilon}(v, \eta; X) \} dm + p \int_{\mathcal{B}} (v^* - v) dm - \vartheta \int_{\mathcal{B}} (\eta^* - \eta) dm > 0.$$

The condition (16.1) states that the last two terms vanish and hence that (16.2) holds, q. e. d.

In his discussion of the stability of homogeneous fluids, GIBBS used a definition of stability which is identical to what we have called G stability, except that he did not demand, as we do, that $\{f, \eta\}$ be an equilibrium state*. GIBBS was able to prove that uniform values of $\bar{\varepsilon}_\eta(v, \eta)$ and $\bar{\varepsilon}_v(v, \eta)$ are necessary for his stability and, furthermore, that the inequality (16.7) is also necessary. He also realized that the constancy of $\bar{\varepsilon}_\eta$ and $\bar{\varepsilon}_v$ over \mathcal{B} and the validity of (16.7) are sufficient for his stability. If he had gone a step further and postulated that for homogeneous fluids stable states exist for every value of v and η for which $\bar{\varepsilon}$ is defined, he would have obtained (16.7) as a property of the function $\bar{\varepsilon}$. Such a procedure, however, cannot yield the statements, made in Theorem 6, that $-\bar{\varepsilon}_v$ is positive and that $\bar{\varepsilon}$ is jointly and strictly convex in v and η .

We conclude with

Theorem 16. *An equilibrium state $\{f, \eta\}$ of a fluid body \mathcal{B} is G stable if and only if both of the following conditions hold:*

- (a) *The temperature corresponding to $\{f, \eta\}$ is uniform.*
- (b) *Any other state $\{f^*, \eta^*\}$ with the same total volume,*

$$\int_{\mathcal{B}} v^* dm = \int_{\mathcal{B}} v dm, \quad (16.8)$$

and the same uniform temperature ϑ has a higher total free energy,

$$\int_{\mathcal{B}} \bar{\psi}(v^*, \vartheta; X) dm > \int_{\mathcal{B}} \bar{\psi}(v, \vartheta; X) dm, \quad (16.9)$$

unless $v^(X) = v(X)$ for all X in \mathcal{B} .*

Proof. The proof that the conditions (a) and (b) are sufficient for the G stability of $\{f, \eta\}$ is completely analogous to the proof of Theorem 14 of § 15.

The necessity of the condition (a) for the G stability of $\{f, \eta\}$ follows from Theorem 15. To prove that (b) is necessary we assume that $\{f, \eta\}$ is stable. We consider another state $\{f^*, \eta^*\}$ which obeys (16.8) and which has the uniform temperature ϑ . Since $v = v^3$ is a convex function of v for $v > 0$, and $\bar{\psi}_v(v, \vartheta) < 0$, the inequality (13.15) implies that

$$\bar{\psi}(v^*, \vartheta; X) - \bar{\psi}(v, \vartheta; X) - (v^* - v) \bar{\psi}_v(v, \vartheta; X) \geq 0; \quad (16.10)$$

* GIBBS does not use either our Postulate I or our definition of (local) thermal equilibrium.

(16.10) cannot reduce to equality for all X unless $v(X) = v^*(X)$ for all X . Now, since we are assuming that $\{f, \eta\}$ is stable, it follows from Theorem 15 and (13.13) that $\bar{\psi}_v(v, \vartheta; X)$ is independent of X . Thus, by (16.8), if we compute the mass integral of (16.10) over \mathcal{B} , the last term on the left makes no contribution, and we get (16.9). Hence, when $\{f, \eta\}$ is G stable, the condition (b) is valid, q.e.d.

This theorem shows that for G stability of fluids adiabatic and isothermal stability are equivalent.

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