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ON THE STABILITY OF EQUILIBRIUM STATES

OF GENERAL FLUIDS

bу

Bernard D. Coleman

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Introduction

The foundations of the science of thermostatics were laid by J. Willard Gibbs[#] in his article, "A Method of Graphical Representation

#[1873, 1]; vid. The Scientific Papers, Vol. 1, pp. 33-54.

of the Thermodynamic Properties of Substances by Means of Surfaces," published in 1873. In that essay Gibbs proposed and studied a criterion for the stability of a simple fluid^{##} surrounded by a medium held at

In thermostatics, a "simple" fluid is one of uniform chemical composition, free from capillarity effects and related phenomena associated with phase boundaries. In his long memoir [1875, 1], "On the Equilibrium of Heterogeneous Systems," (here referred to as EHS) Gibbs discussed at length chemical reactions and the effects of heterogeneous composition.

fixed temperature and pressure. Assuming that the specific internal energy ϵ of a fluid in thermodynamic equilibrium is given by a function $\overline{\epsilon}$ of the specific entropy η and specific volume υ of the fluid, Gibbs gave an heuristic argument to the effect that a uniform phase with specific entropy η° and specific volume υ° is stable in an environment at temperature

 θ° and pressure p°, if for all pairs (η , υ), with either $\eta \neq \eta^{\circ}$ or $\upsilon \neq \upsilon^{\circ}$, #

$$\overline{\epsilon}(\eta,\upsilon) - \theta^{\circ}\eta + p^{\circ}\upsilon > \overline{\epsilon}(\eta^{\circ},\upsilon^{\circ}) - \theta^{\circ}\eta^{\circ} + p^{\circ}\upsilon^{\circ}.$$
(G)

[#]Vid. The Scientific Papers, Vol. 1, pp. 39-43. If (G)

holds with > replaced by \geq and reduces to an equality for some pair (η , υ) not equal to (η° , υ°), then there are two or more stable uniform phases possible at temperature θ° and pressure p° , and one is led to the theory of "coexistent phases", a subject explored at length by Gibbs, but not emphasized in the present essay. In the terminology to be developed here, (G), as written, i.e. with the sign of strict inequality for all (η , υ) \neq (η° , υ°), is equivalent to the assertion that (1) θ° and p° are chosen so that $\theta^{\circ} = \partial_{\eta} \overline{\epsilon} (\eta^{\circ}, \upsilon^{\circ})$ and $p^{\circ} = -\partial_{\upsilon} \overline{\epsilon} (\eta, \upsilon)$, and (2) ($\eta^{\circ}, \upsilon^{\circ}$) is a point of super convexity for the function $\overline{\epsilon}$.

Criteria of this type occur also in Gibbs' great memoir EHS [1875, 1] and are there related to his concept of the "stability of an isolated system".

Here, continuing and extending an investigation started with James M. Greenberg, ## I discuss the dynamical significance of Gibbs'

 $^{\#\#}$ Coleman & Greenberg [1967, 1].

criteria for stability. I seek an answer to the following question: If a uniform equilibrium state of a fluid body is stable according to the definitions of classical thermostatics, and if the body is, in some precise sense, in a "fixed environment", is it then true that every thermodynamic <u>process</u> in the body which passes near to the equilibrium state at one time must remain near to that state at all future times?

Before turning to this question, I attempt, in Chapter 1, a rigorous development of a part of classical thermostatics and show that, within the formal framework proposed by Gibbs in EHS, the inequality (G) is a sufficient condition for one type of stability and a necessary condition for another. Several of the theorems and proofs of Chapter 1 are taken, with minor modifications, from an unpublished essay which Walter Noll and I wrote together in 1958; this is the case, in particular, with Theorems 1.1 - 1.4. The other theorems of that chapter, namely 1.5 - 1.7, appear to be new in this context; they arose in an attempt to render mathematical the discussion following the expression (133) in EHS.[#]

[#]Vid. The Scientific Papers, Vol. 1, pp. 100-103.

In Chapter 2, I discuss thermodynamic processes and review the . definition of a "regular fluid".^{##} Greenberg and I introduced this class

₩vid. [1967, 1].

of fluids as a convenient, but broad generalization of the concept of a simple fluid with fading memory. The class of regular fluids includes

not only fluids with long-range memory, but also the perfect fluids and linearly viscous fluids of classical hydrodynamics. Also in Chapter 2, I try to give a precise mathematical meaning to the physical concept of a body immersed in an environment at fixed temperature and pressure; Theorem 2.1 asserts that a certain "canonical free energy" is monotone decreasing with time in every process possible in such a body.

The main results of this study are the theorems of Chapter 3. These theorems give a dynamical significance to the stability criterion (G) from thermostatics and supply an answer to the question raised above. Assuming that the equilibrium response function ϵ for a regular fluid body Z is convex for large argument, i.e. that the points in the domain \underline{D} of $\overline{\varepsilon}$ which are not points of convexity for $\overline{\varepsilon}$ are interior to a compact subset of D, I show that if (G) holds for a given pair $(\eta^{\circ}, \upsilon^{\circ})$, then the uniform equilibrium state at $(\eta^{\circ},\upsilon^{\circ})$ is dynamically stable in the following sense: If a process C of \mathcal{B} compatible with immersion of \mathcal{B} in an environment at temperature θ° and pressure p° is such that the fields over $\mathcal B$ describing the spatial distribution of internal energy, kinetic energy, specific volume, and entropy are close, in z_1 , to the corresponding uniform equilibrium fields at some time t, then in the process C these fields remain close, in \mathcal{L}_1 , to the equilibrium fields at all times after t. This is the content of Theorem 3.2. This theorem and the closely related Theorem 3.1 follow, by easy arguments, from Remark 3.3, which, in turn, rests heavily on Lemma A.2, proved in the Appendix.

The present Theorems 3.1 and 3.2 generalize and extend in two important respects the stability theorems which Greenberg and I gave in [1967, 1]. First, in the earlier work we proved stability only against the class of processes compatible with isolation of the fluid body, and that class is smaller than the class of processes compatible with immersion in an environment at fixed temperature and pressure.[#] Second, to prove

[#]This may not be obvious until the concept of "immersion" is rendered mathematical. See the discussion following Definition 2.1.

theorems about dynamical stability, Greenberg and I assumed in [1967, 1], that every uniform equilibrium state of the fluid body is thermostatically stable, i.e. that $\overline{\epsilon}$ is strictly convex throughout its domain; here I assume only that (G) holds for the given $(\eta^{\circ}, \upsilon^{\circ})$ under consideration and that $\overline{\epsilon}$ is convex for large argument. In other words, instead of assuming that every uniform equilibrium state is thermostatically stable, the present theory takes into account the physical observation that for most substances there exists in \underline{D} a precompact set \underline{S} of pairs (η, υ) for which the corresponding uniform phases are unstable or only metastable.

I urge the reader to glance now at the Appendix, for the terminology developed there is employed in Chapter $1^{\#\#}$ as well as in

 $\frac{1}{4}$ From Theorem 1.3 onward.

Chapter 3.

1. Thermostatics

The theory called the <u>thermostatics</u> of <u>simple fluids</u> rests on the assumption that, when a fluid is at equilibrium, the specific internal energy ϵ (per unit mass), the temperature θ , and the pressure p at each point X of the fluid are determined if the specific entropy η and the specific volume v are specified at X:

$$\epsilon = \overline{\epsilon}(\eta, \upsilon), \quad \theta = \overline{\theta}(\eta, \upsilon), \quad p = \overline{p}(\eta, \upsilon).$$
 (1.1)

The functions $\overline{\epsilon}$, $\overline{\theta}$, and \overline{p} , which map $(0,\infty) \times (0,\infty)$ into $(0,\infty)$, # are called the

 $#_{Physical}$ experience suggests that η and ϵ are bounded below in the sense that for each material there exist numbers b and c such that $\eta > b$ and $\epsilon > c$ always. My choice of zero for both of these bounds is arbitrary and has nothing to do with the "third law of thermodynamics"; the theorems to be proved here are independent of the choice of b and c.

equilibrium response functions for the fluid under consideration.^{##} The

The superposed bar serves to distinguish these functions from their values.

function $\overline{\epsilon}$ is assumed to be continuously differentiable, and the partial

derivatives, $\partial_{\eta} \overline{\epsilon}$ and $\partial_{\upsilon} \overline{\epsilon}$, of $\overline{\epsilon}$ determine $\overline{\theta}$ and \overline{p} through the relations

$$\overline{\theta}(\eta, \upsilon) = \partial_{\eta} \overline{\epsilon}(\eta, \upsilon), \qquad \overline{p}(\eta, \upsilon) = -\partial_{\upsilon} \overline{\epsilon}(\eta, \upsilon). \qquad (1.2)$$

It is assumed that, for each v,

$$\lim_{\eta \to \infty} \overline{\epsilon}(\eta, \upsilon) = \infty.$$
(1.3)

In thermostatics, a fluid body is a set \mathcal{B} endowed with a positive, finite, non-atomic measure \mathcal{M} , called the <u>mass measure</u> of the body. The material points X are the elements of \mathcal{B} . Attention is here confined to <u>materially</u> <u>homogeneous</u> bodies, i.e. bodies for which the response functions $\overline{\eta}$ do not vary with X. A <u>static state</u> { η, υ } of \mathcal{B} is a pair of positive \mathcal{M} -measurable functions η and υ over \mathcal{B} for which the following three integrals are finite:

$$H \stackrel{\text{def}}{=} \int_{\mathcal{B}} \eta(X) dm, \quad \forall \stackrel{\text{def}}{=} \int_{\mathcal{B}} \upsilon(X) dm, \quad \text{and} \quad E \stackrel{\text{def}}{=} \int \overline{\epsilon}(\eta(X), \upsilon(X)) dm. \quad (1.4)$$

These integrals are called the <u>total entropy</u>, the <u>total volume</u>, and the <u>total internal energy</u> of **B** for the state $\{\eta, \upsilon\}$. Two static states $\{\eta, \upsilon\}$ and $\{\eta', \upsilon'\}$ are said to be <u>equivalent</u> if there exists a measure-preserving transformation f of **B** onto **B** such that $\eta'(X) = \eta(f(X))$ and $\upsilon'(X) = \upsilon(f(X))$ for all X in **B**. [By a <u>measure-preserving transformation</u> f of **B** is meant a one-to-one mapping of **B** onto itself such that the image of each *mu*-measurable subset ϑ of **B** is *mu*-measurable and $m(f(\vartheta)) = m(\vartheta)$.] A static state of \mathcal{B} not equivalent to $\{\eta, \upsilon\}$ is said to be <u>distinct</u> from $\{\eta, \upsilon\}$.

In the present context, Gibbs' concept of <u>stable</u> <u>equilibrium</u> of <u>an</u> isolated <u>system</u>[#] may be rendered mathematical as follows.

#[1875, 1]; vid. The Scientific Papers, Vol. 1, pp. 55-353, especially pp. 56-62.

Definition 1.1. A static state $\{\eta, \upsilon\}$ of a fluid body \mathcal{B} is <u>Gibbs stable</u> <u>under isolation</u> if every static state $\{\eta', \upsilon'\}$ of \mathcal{B} which is distinct from $\{\eta, \upsilon\}$ and for which

obeys the inequality

H'
$$\stackrel{\text{def}}{=} \int_{\mathcal{B}} \eta'(X) dm < \int_{\mathcal{B}} \eta(X) dm \stackrel{\text{def}}{=} H.$$
 (1.6)

Thus a static state is said to be Gibbs stable under isolation if every distinct static state with the same total internal energy and the same total volume has a smaller total entropy. In EHS, $^{\#}$ Gibbs gave

#Vid. preceding footnote; also, [1959, 1], pp. 125, 126.

arguments to show that a necessary and sufficient condition for a state $\{\eta, \upsilon\}$ to be Gibbs stable under isolation is that it give a strict minimum to the internal energy when compared with all distinct states having the same total internal energy and volume; his arguments are rendered mathematical in the proof of the following theorem:

Theorem 1.1. A static state $\{\eta, \upsilon\}$ of a fluid body \mathcal{B} is Gibbs stable under isolation if and only if every static state of \mathcal{B} which is distinct from $\{\eta, \upsilon\}$ and obeys the equations

$$H' \stackrel{\text{def}}{=} \int_{\mathcal{B}} \eta' dm = \int_{\mathcal{B}} \eta dm \stackrel{\text{def}}{=} H,$$

$$V' \stackrel{\text{def}}{=} \int_{\mathcal{B}} \upsilon' dm = \int_{\mathcal{B}} \upsilon dm \stackrel{\text{def}}{=} V,$$

$$(1.7)$$

also obeys the inequality

$$E' \stackrel{\text{def}}{=} \int_{\mathcal{B}} \varepsilon' dm > \int_{\mathcal{B}} \varepsilon dm \stackrel{\text{def}}{=} E, \qquad (1.8)$$

where

$$\epsilon'(X) = \overline{\epsilon}(\eta'(X), \upsilon'(X))$$
 and $\epsilon(X) = \overline{\epsilon}(\eta(X), \upsilon(X)).$

Proof.[#] To show that the stated condition is necessary for Gibbs stability

[#]Cf. Coleman & Noll [1959, 1], Proof of Theorem 11, pp. 119, 120.

under isolation, let $\{\eta, \upsilon\}$ and $\{\eta', \upsilon'\}$ be two distinct states for which (1.7) holds but (1.8) fails, i.e. H' = H, V' = V, but $E' \leq E$. One can then prove that $\{\eta, \upsilon\}$ is not Gibbs stable; i.e. one can construct a state $\{\eta^*, \upsilon^*\}$, distinct from $\{\eta, \upsilon\}$, with $E^* = E$, $V^* = V$, and $H^* \geq H$. To do this, put, for each X in \mathcal{B} ,

$$v^{*}(X) = v^{*}(X)$$
 and $\epsilon^{*}(X) = \epsilon^{*}(X) + \frac{E-E^{*}}{M}$ with $M = \mathcal{M}(B) = \int d\mathcal{M}$.

It follows that $V^* = V' = V$ and $E^* = E' + E - E' = E$, and because $E' \leq E$, one also has $\epsilon^*(X) \geq \epsilon'(X)$. Since $\overline{\theta} = \partial_{\eta} \overline{\epsilon}$ is assumed to be always strictly positive, the function $\overline{\epsilon}(\cdot, \upsilon'(X))$ is invertible in its first variable. By (1.3),

$$\lim_{\eta\to\infty} \overline{\epsilon}(\eta, \upsilon'(X)) = \infty,$$

and therefore $\epsilon^*(X)$ is in the domain of the inverse of $\overline{\epsilon}(\cdot, v (X))$ whenever $\epsilon'(X)$ is. Hence, there exists a unique function η^* on \mathcal{B} such that

$$\epsilon^{*}(X) = \overline{\epsilon}(\eta^{*}(X), \upsilon^{\dagger}(X)) = \overline{\epsilon}(\eta^{*}(X), \upsilon^{*}(X))_{j}$$

for all X, and because $\partial_{\eta} \overline{\epsilon}$ is positive and $\epsilon^*(X) \ge \epsilon'(X)$, one has $\eta^*(X) \ge \eta'(X)$, which implies $H^* \ge H'$, where H' = H. Thus, there is produced a state $\{\eta^*, \upsilon^*\}$

with $V^* = V$, $E^* = E$, and $H^* \ge H$. Moreover, $\{\eta^*, \upsilon^*\}$ is distinct from $\{\eta, \upsilon\}$: If E' = E, then $\{\eta, \upsilon\} = \{\eta', \upsilon'\}$, and $\{\eta', \upsilon'\}$ was assumed distinct from $\{\eta, \upsilon\}$. If E' < E, then $\epsilon^*(X) > \epsilon'(X)$, which yields $\eta^*(X) > \eta'(X)$ and hence $H^* > H'$, but since H' = H, this means that η^* differs from η by more than a measure preserving transformation.

To show that the condition of the theorem is sufficient for Gibbs stability under isolation, let $\{\eta, \upsilon\}$ be a static state which is not stable. There then exists a state $\{\eta', \upsilon'\}$, distinct from $\{\eta, \upsilon\}$, which obeys (1.5) but not (1.6); i.e. E' = E, V' = V, but $H' \ge H$. One must show that $\{\eta, \upsilon\}$ does not obey the condition of the theorem; that is, one must produce a state $\{\eta^*, \upsilon^*\}$, distinct from $\{\eta, \upsilon\}$, for which $H^* = H$, $V^* = V$, but $E^* \le E$. This is easy; one need merely put, for each X in \mathcal{B} ,

 $\upsilon^*(X) = \upsilon'(X)$, and $\eta^*(X) = \lambda \eta'(X)$ with $\lambda = H/H'$. (1.9)

It follows that $V^* = V' = V$ and $H^* = \lambda H' = H$. Since $H' \ge H > 0$, one has $0 < \lambda \le 1$, and, by the positivity of $\partial_n \overline{\epsilon}$,

 $\epsilon^{*}(X) = \overline{\epsilon}(\eta^{*}(X), \upsilon^{*}(X)) = \overline{\epsilon}(\lambda \eta^{*}(X), \upsilon^{*}(X)) \leq \overline{\epsilon}(\eta^{*}(X), \upsilon^{*}(X)) = \epsilon^{*}(X).$

It follows that $E^* \leq E'$, and since $E' \approx E$, one has $E' \leq E$. Thus (1.9) defines the required state $\{\eta', \upsilon'\}$ with $H^* = H$, $\nabla^* = \nabla$, but $E^* \leq E$. Furthermore, $\{\eta^*, \upsilon^*\}$ is distinct from $\{\eta, \upsilon\}$: If H' = H, then $\lambda = 1$ and $\{\eta^*, \upsilon^*\} = \{\eta^{\prime}, \upsilon^{\prime}\}$ which is, by assumption, distinct from $\{\eta, \upsilon\}$. If H' > H, then $\eta^*(X) < \eta^{\prime}(X)$, which yields $\epsilon^*(X) < \epsilon^{\prime}(X)$ and hence $E^* < E = E^{\prime}$; i.e.

$$\int_{\mathcal{B}} \overline{\epsilon}(\eta^{*}(X), \upsilon^{*}(X)) dm < \int \overline{\epsilon}(\eta(X), \upsilon(X)) dm.$$

Clearly, this last relation contradicts the existence of a measure preserving transformation f of \mathcal{B} onto \mathcal{B} such that $\eta^*(X) = \eta(f(X))$ and $\upsilon^*(X) = \upsilon(f(X))$; q.e.d.

It is evident from Theorem 1.1 that a necessary condition for the Gibbs stability of a given static state $\{\eta, \upsilon\}$ is that the functional

$$\delta \epsilon = \int_{\mathcal{B}} \left[\partial_{\eta} \overline{\epsilon} (\eta(X), \upsilon(X)) \delta \eta(X) + \partial_{\upsilon} \overline{\epsilon} (\eta(X), \upsilon(X)) \delta \upsilon(X) \right] dm dk$$

vanish for all real-valued, *mo-measurable* functions $\delta\eta$ and $\delta\upsilon$ on \mathcal{B} obeying the conditions

$$\int_{\mathcal{B}} \delta \eta(\mathbf{X}) dm = \int_{\mathcal{B}} \delta \upsilon(\mathbf{X}) dm = 0.$$

Using the method of Lagrange multipliers, one easily deduces that $\delta \epsilon = 0$ for all such functions $\delta \eta$ and δv if and only if $\partial_{\eta} \overline{\epsilon}(\eta(X), v(X))$ and $\partial_{v} \overline{\epsilon}(\eta(X), v(X))$ are constants, independent of X. Thus, in view of (1.2), the following theorem holds.[#]

 $^{\#}$ Cf. Gibbs [1875, 1], eqs. (19) and (20).

Theorem 1.2. If a static state $\{\eta, \upsilon\}$ of \mathcal{B} is Gibbs stable under isolation, then the temperature and pressure in the state $\{\eta, \upsilon\}$ are constant over \mathcal{B} , i.e. there exist numbers θ° and p° such that

 $\overline{\theta}(\eta(X),\upsilon(X)) = \theta^{\circ}$ and $\overline{p}(\eta(X),\upsilon(X)) = p^{\circ}$, (1.10)

for almost all X in \mathcal{B} .

It is obvious that the condition (1.10), although necessary, is not sufficient for Gibbs stability.

A static state $\{\eta, \upsilon\}$ of **B** is called <u>uniform</u> if its components η and υ are constant over **B**; i.e. if there are numbers η° and υ° such that

$$\eta(\mathbf{X}) = \eta^{\circ}, \qquad \upsilon(\mathbf{X}) = \upsilon^{\circ}, \qquad (1.11)$$

for all X in \mathbb{Z} . [One can refer to the function pair $\{\eta, \upsilon\}$ obeying (1.11) as <u>the uniform static state at</u> $(\eta^{\circ}, \upsilon^{\circ})$, and denote it by $\{\eta^{\circ}, \upsilon^{\circ}\}$.] Every uniform static state obviously meets the condition (1.10); the following theorem gives a less trivial necessary condition on a uniform static state for it to be Gibbs stable. Theorem 1.3. Let $(\eta^{\circ}, \upsilon^{\circ})$ be a point in the domain of $\overline{\epsilon}$, and let n be an integer greater than 1. If the homogeneous static state at $(\eta^{\circ}, \upsilon^{\circ})$ is Gibbs stable under isolation, then for any 3n positive numbers $\alpha^{1}, \ldots, \alpha^{n}, \eta^{1}, \ldots, \eta^{n}, \upsilon^{1}, \ldots, \upsilon^{n}$ obeying

$$\sum_{i=1}^{n} \alpha^{i} = 1, \qquad \sum_{i=1}^{n} \alpha^{i} \eta^{i} = \eta^{\circ}, \qquad \sum_{i=1}^{n} \alpha^{i} \upsilon^{i} = \upsilon^{\circ}, \quad (1.12)$$

there holds the inequality

$$\overline{\epsilon}(\eta^{\circ}, \upsilon^{\circ}) < \sum_{i=1}^{n} \alpha^{i} \overline{\epsilon}(\eta^{i}, \upsilon^{i}). \qquad (1.13)$$

Proof. Choose 3n positive numbers $\alpha^1, \ldots, \alpha^n, \eta^1, \ldots, \eta^n, \upsilon^1, \ldots, \upsilon^n$ obeying (1.12). Because the mass measure *m* on **B** is positive, finite, and non-atomic, **B** has n disjoint *m*-measurable subsets, ρ^1, \ldots, ρ^n , with

$$m(\mathcal{P}^{i}) = M\alpha_{i}$$
, and hence $m\begin{pmatrix} B - \bigcup \mathcal{P}^{i} \\ i=1 \end{pmatrix} = 0,$ (1.14)

where $M = \mathcal{M}(\mathcal{B}) > 0$. Clearly, the static state $\{\eta', \upsilon'\}$ defined by

$$\eta'(X) = \eta^{i}$$
 and $\upsilon'(X) = \upsilon^{i}$ for $X \in \mathcal{P}_{i}$, (1.15)

is distinct from $\{\eta^{\circ},\upsilon^{\circ}\}$ and obeys the relations

$$\int_{\mathcal{B}} \eta' dm = M \sum_{i=1}^{n} \alpha^{i} \eta^{i} = M \eta^{\circ} = \int_{\mathcal{B}} \eta^{\circ} dm,$$
$$\int_{\mathcal{B}} \upsilon' dm = M \sum_{i=1}^{n} \alpha^{i} \eta^{i} = M \upsilon^{\circ} = \int_{\mathcal{B}} \upsilon^{\circ} dm.$$

Therefore, since $\{\eta^{\circ},\upsilon^{\circ}\}$ is stable under isolation, Theorem 1.1 yields

$$\int \overline{\epsilon} (\eta'(X), \upsilon'(X)) dm > \int \overline{\epsilon} (\eta^{\circ}, \upsilon^{\circ}) dm.$$

$$\mathcal{B}$$

The right side of this inequality is just $Me(\eta^{\circ}, \upsilon^{\circ})$; on using (1.14) and (1.15) to evaluate the left side, it is found that

$$\int_{\mathcal{B}} \overline{\epsilon}(\eta'(\mathbf{X}), \upsilon'(\mathbf{X})) dm = M \sum \overline{\epsilon}(\eta^{\mathbf{i}}, \upsilon^{\mathbf{i}}) > M \overline{\epsilon}(\eta^{\circ}, \upsilon^{\circ}),$$

which obviously implies (1.13); q.e.d.

In view of the definitions given in the Appendix [see the sentence containing (A.2) and (A.3)], the theorem just proven has the following corollary.

Corollary to Theorem 1.3. Let $(\eta^{\circ}, \upsilon^{\circ})$ be a point in the domain of $\overline{\epsilon}$. If the uniform static state at $(\eta^{\circ}, \upsilon^{\circ})$ is Gibbs stable under isolation, then $(\eta^{\circ}, \upsilon^{\circ})$ is a point of strict convexity for $\overline{\epsilon}$.

The concept of super convexity discussed in the Appendix [see (A.9)] renders elementary the formulation of a sufficient condition for Gibbs stability of a uniform state under isolation. Theorem 1.4. If $(\eta^{\circ}, \upsilon^{\circ})$ is a point of super convexity for ϵ , then the uniform static state at $(\eta^{\circ}, \upsilon^{\circ})$ is Gibbs stable under isolation.

<u>Proof</u>.[#] Let $\{\eta', \upsilon'\}$ be a static state of **B**, distinct from the uniform [#]Cf. Gibbs, The Scientific Papers, Vol. 1, pp. 100-101. The argument employed here occurs frequently in the theory of statical concepts of stability; vid., e.g., Coleman & Noll [1959, 1], p. 127.

state $\{\eta^{\circ}, \upsilon^{\circ}\}$, but with

$$\int_{\mathcal{B}} \eta'(\mathbf{X}) d\mathbf{m} = \int \eta^{\circ} d\mathbf{m}, \qquad \int_{\mathcal{B}} \upsilon'(\mathbf{X}) d\mathbf{m} = \int \upsilon^{\circ} d\mathbf{m}. \quad (1.16)$$

By (A.9), the assumption that $(\eta^{\circ}, \upsilon^{\circ})$ is a point of super convexity for $\overline{\epsilon}$ implies that, for each X in \mathcal{B}_{3}

$$\overline{\epsilon}(\eta'(X),\upsilon'(X)) \geq \overline{\epsilon}(\eta^{\circ},\upsilon^{\circ}) + (\eta'(X)-\eta^{\circ})\partial_{\eta}\overline{\epsilon}(\eta^{\circ},\upsilon^{\circ}) + (\upsilon'(X)-\upsilon^{\circ})\partial_{\upsilon}\overline{\epsilon}(\eta^{\circ},\upsilon^{\circ}). \quad (1.17)$$

Furthermore, since $\{\eta', \upsilon'\}$ is distinct from $\{\eta^{\circ}, \upsilon^{\circ}\}$, (1.17) is a strict inequality on some subset \mathcal{P} of \mathcal{B} with $\mathcal{M}(\mathcal{P}) > 0$. On integrating (1.17) over \mathcal{B} , one obtains, upon use of (1.16),

$$\int \overline{\epsilon} (\eta'(X), \upsilon'(X)) dm < \int \overline{\epsilon} (\eta^{\circ}, \upsilon^{\circ}) dm,$$

$$\mathcal{B}$$

and this inequality, in view of Theorem 1.1, shows that $\{\eta^{\circ}, \upsilon^{\circ}\}$ is Gibbs stable under isolation; q.e.d.

Definition 1.2. A uniform static state $\{\eta^{\circ}, \upsilon^{\circ}\}$ of \mathcal{B} is said to be at the frontier of stability if

- (1) $\{\eta^{\circ}, \upsilon^{\circ}\}$ is Gibbs stable under isolation, and
- (2) $(\eta^{\circ}, \upsilon^{\circ})$ is the limit of a sequence of points (η^{i}, υ^{i}) in $(0, \infty) \times (0, \infty)$ such that none of the uniform static states $\{\eta^{i}, \upsilon^{i}\}$ of \mathcal{B} is Gibbs stable under isolation.

<u>Definition</u> 1.3. A uniform static state is here said to be <u>thermostatically</u> <u>stable in the strong sense</u> if it is Gibbs stable under isolation and is not at the frontier of stability.

The following remark is an immediate consequence of the definitions just given.

Remark 1.2. The uniform static state at $(\eta^{\circ}, \upsilon^{\circ})$ is thermostatically stable in the strong sense, if and only if the domain of ϵ contains a neighborhood \underline{O} of $(\eta^{\circ}, \upsilon^{\circ})$ such that the uniform state $\{\eta, \upsilon\}$ at each point (η, υ) in \underline{O} is Gibbs stable under isolation. Theorem 1.5. If the uniform static state at $(\eta^{\circ}, \upsilon^{\circ})$ is thermostatically stable in the strong sense, then $(\eta^{\circ}, \upsilon^{\circ})$ is a point of super convexity for $\overline{\epsilon}$.

Proof. By the present hypothesis and Remark 1.2, in the domain of $\overline{\epsilon}$ there is a neighborhood $\underline{0}$ of $(\eta^{\circ}, \upsilon^{\circ})$ such that the uniform static state at each point in $\underline{0}$ is Gibbs stable under isolation. It follows from the Corollary to Theorem 1.3 that each point in $\underline{0}$ is a point of strict convexity for $\overline{\epsilon}$. Thus, $(\eta^{\circ}, \upsilon^{\circ})$ is interior to the set of strict convexity for $\overline{\epsilon}$, and, by Remark A.3, $(\eta^{\circ}, \upsilon^{\circ})$ is a point of super convexity for $\overline{\epsilon}$; q.e.d.

Since the gradient of $\overline{\sqrt{\epsilon}}$ is the ordered pair $(\partial_{\eta}\overline{\epsilon}, \partial_{\overline{\sqrt{\epsilon}}})$, it follows from (1.2) that

$$\nabla \overline{\epsilon} = (\overline{\theta}, -\overline{p}), \qquad (1.18)$$

and, by (A.9), the theorem just proven has the following corollary.

Corollary to Theorem 1.5. If the uniform static state at $(\eta^{\circ}, \upsilon^{\circ})$ is thermostatically stable in the strong sense, then for each pair (υ, η) in the domain of $\overline{\epsilon}$ with either $\eta \neq \eta^{\circ}$ or $\upsilon \neq \upsilon^{\circ}$

$$\varepsilon(\eta, \upsilon) > \overline{\varepsilon}(\eta^{\circ}, \upsilon^{\circ}) + (\eta - \eta^{\circ})\theta^{\circ} - (\upsilon - \upsilon^{\circ})p^{\circ}, \qquad (1.19)$$

where

$$\theta^{\circ} = \overline{\theta}(\eta^{\circ}, \upsilon^{\circ}), \qquad p^{\circ} = \overline{p}(\eta^{\circ}, \upsilon^{\circ}). \qquad (1.20)$$

It is evident that this corollary can be reformulated as follows.

Remark 1.3. Let $\theta^{\circ} > 0$ and $p^{\circ} > 0$ be given, and let $\overline{\phi}$ be the function on $(0,\infty) \times (0,\infty)$ defined by

$$\overline{\phi}(\eta, \upsilon) \stackrel{\text{def}}{=} \overline{\epsilon}(\eta, \upsilon) - \theta^{\circ}\eta + p^{\circ}\upsilon. \qquad (1.21)$$

If there is a point $(\eta^{\circ}, \upsilon^{\circ})$ in the domain of $\overline{\epsilon}$ such that the uniform static state at $(\eta^{\circ}, \upsilon^{\circ})$ has temperature θ° and pressure p° and is thermostatically stable in the strong sense, then $\overline{\phi}$ attains a strict, global minimum at $(\eta^{\circ}, \upsilon^{\circ})$, i.e. for all $\eta > 0$ and $\upsilon > 0$,

$$(\eta, \upsilon) \neq (\eta^{\circ}, \upsilon^{\circ}) \implies \overline{\phi}(\eta, \upsilon) > \overline{\phi}(\eta^{\circ}, \upsilon^{\circ}). \qquad (1.22)$$

It is evident that if, for a given $\theta^{\circ} > 0$ and $p^{\circ} > 0$, there exists a point $(\eta^{\circ}, \upsilon^{\circ})$ obeying (1.22) then it is <u>unique</u>. Thus we have

Remark 1.4. At a given temperature and pressure, there can be at most one uniform static state of \mathcal{B} that is thermostatically stable in the strong sense.

This last result is refined considerably in Theorem 1.7 below. The proof of that theorem employs a condition which, in addition to (1.10), must be fulfilled by every static state that is Gibbs stable under isolation, whether uniform or not. This new necessary condition for stability is given in Theorem 1.6. Since the proof of Theorem 1.6 would be long if set down in full detail, and since Theorem 1.6 is employed only in the demonstration of Theorem 1.7, a theorem which is not applied in subsequent chapters, I give here only a brief outline of the proof of Theorem 1.6.

Theorem 1.6. Let $\{\eta, \upsilon\}$ be a static state of **B**. If $\{\eta, \upsilon\}$ is Gibbs stable under isolation, then for almost all X in **B**, $(\eta(X), \upsilon(X))$ is a point of convexity for $\overline{\epsilon}$.

Sketch of the Proof.[#] Let \mathscr{S} be the set of points X in \mathscr{B} for which $(\eta(X), \upsilon(X))$ is not a point of convexity for $\overline{\epsilon}$. The theorem is proved by showing that if $\mathfrak{m}(\mathscr{S}) > 0$, then $\{\eta, \upsilon\}$ is not Gibbs stable under isolation. Now, when $\mathfrak{m}(\mathscr{S}) > 0$, there exists a pair (η^1, υ^1) which is the image $(\eta(Y), \upsilon(Y))$ of a point Y in \mathscr{S} and is such that, for each $\delta > 0$,

 $m(\mathcal{Q}_{\delta}) > 0$, where $\mathcal{Q}_{\delta} = \left\{ X \mid X \in \mathcal{S}, |\eta(X) - \eta^{1}| < \delta, \text{ and } |\upsilon(X) - \upsilon^{1}| < \delta \right\}.$

[#]One can show that if a static state of a simple fluid is Gibbs stable under isolation, then the state is a combination of, at most, three uniform phases; i.e. if $\{\eta, \upsilon\}$ is Gibbs stable under isolation, then, for some $n \leq 3$, \mathcal{B} has n subsets \mathcal{P}_i , with $\mathcal{M}(\mathcal{B} - \bigcup_{i=1}^n \mathcal{P}_i) = 0$, such that the restriction of $\{\eta, \upsilon\}$ to each \mathcal{P}_i is a constant function. The attentive reader will notice that if I had proved this familiar consequence of the "phase rule" before taking up Theorem 1.6, then the proof I outline for Theorem 1.6 could be simplified drastically. In fact, Theorem 1.6 can be strengthened to read as follows: If $\{\eta, \upsilon\}$ is a static state of \mathcal{B} that is Gibbs stable under isolation, then for almost all X in \mathcal{B} , $(\eta(X), \upsilon(X))$ is a point of strict convexity for $\overline{\epsilon}$.

Since (η^1, υ^1) is not a point of convexity for $\overline{\epsilon}$, there exist a number α , with $0 < \alpha < 1$, and points (η^2, υ^2) , (η^3, υ^3) in the domain of $\overline{\epsilon}$, such that

$$\eta^1 = \alpha \eta^2 + \beta \eta^3$$
, $\upsilon^1 = \alpha \upsilon^2 + \beta \upsilon^3$, $\beta = 1 - \alpha$,

and

$$\overline{\epsilon}(\eta^1, \upsilon^1) > \alpha \overline{\epsilon}(\eta^2, \upsilon^2) + \beta \overline{\epsilon}(\eta^3, \upsilon^3).$$

Furthermore, by the continuity of $\overline{\epsilon}$, there exist a number $\delta > 0$ and points (η^4, υ^4) , (η^5, υ^5) in the domain of $\overline{\epsilon}$, such that

$$\frac{1}{m(\mathcal{A}_{\delta})}\int_{\mathcal{S}_{\delta}}\eta(\mathbf{X})dm = \alpha\eta^{4} + \beta\eta^{5}, \qquad \frac{1}{m(\mathcal{A}_{\delta})}\int_{\mathcal{S}_{\delta}}\upsilon(\mathbf{X})dm = \alpha\upsilon^{5} + \beta\upsilon^{5},$$

and

$$\overline{\epsilon}(\eta(\mathbf{X}),\upsilon(\mathbf{X})) > \alpha \overline{\epsilon}(\eta^4,\upsilon^4) + \beta \overline{\epsilon}(\eta^5,\upsilon^5)$$

for all X in $\mathcal{Q}_{\delta}^{}.$ Let \mathbf{P}^{1} and \mathbf{P}^{2} be two subsets of $\mathcal{Q}_{\delta}^{}$ with

$$\begin{aligned} &\mathcal{Q}_{\delta} = \mathcal{P}^{1} \cup \mathcal{P}_{j}^{2} \\ &\mathcal{m}(\mathcal{P}^{1}) = \alpha \mathcal{m}(\mathcal{Q}_{\delta}), \qquad \mathcal{m}(\mathcal{P}^{2}) = \beta \mathcal{m}(\mathcal{Q}_{\delta}), \end{aligned}$$

and let the static state $\{\eta^{\,\prime}\,,\upsilon^{\,\prime}\,\}$ be defined as follows:

$$\eta'(\mathbf{X}) = \begin{cases} \eta(\mathbf{X}) \text{ for } \mathbf{X} \in \mathbf{\mathcal{B}} - \mathbf{\mathcal{A}}_{\delta}, \\ \eta^{4} \text{ for } \mathbf{X} \in \mathbf{\mathcal{P}}^{1}, \\ \eta^{5} \text{ for } \mathbf{X} \in \mathbf{\mathcal{P}}^{2}, \end{cases} \quad \upsilon'(\mathbf{X}) = \begin{cases} \upsilon(\mathbf{X}) \text{ for } \mathbf{X} \in \mathbf{\mathcal{B}} - \mathbf{\mathcal{A}}_{\delta}, \\ \upsilon^{4} \text{ for } \mathbf{X} \in \mathbf{\mathcal{P}}^{1}, \\ \upsilon^{5} \text{ for } \mathbf{X} \in \mathbf{\mathcal{P}}^{2}. \end{cases}$$

It is easily verified that

$$\int_{\mathcal{B}} \eta' dm = \int_{\mathcal{B}} \eta dm , \qquad \int_{\mathcal{B}} \upsilon' dm = \int_{\mathcal{B}} \upsilon dm ,$$

while

$$\int \overline{\epsilon} (\eta'(X), \upsilon'(X)) dm < \int \overline{\epsilon} (\eta(X), \upsilon(X)) dm.$$

Hence, in view of Theorem 1.1, the state $\{\eta,\upsilon\}$ is not Gibbs stable under isolation; q.e.d.

Theorem 1.7. If $\{\eta^{\circ}, \upsilon^{\circ}\}$ is a uniform static state of \mathcal{B} that is thermostatically stable in the strong sense, then there is no static state of \mathcal{B} that (1) is Gibbs stable under isolation, (2) has the same temperature and pressure as $\{\eta^{\circ}, \upsilon^{\circ}\}$, and (3) is distinct from $\{\eta^{\circ}, \upsilon^{\circ}\}$.

In other words, if $\{\eta^{\circ}, \upsilon^{\circ}\}$ is a uniform static state that is thermostatically stable in the strong sense, and if $\{\eta, \upsilon\}$ is a static state of \mathcal{B} distinct from $\{\eta^{\circ}, \upsilon^{\circ}\}$ with

$$\overline{\theta}(\eta(X),\upsilon(X)) = \overline{\theta}(\eta^{\circ},\upsilon^{\circ}), \qquad \overline{p}(\eta(X),\upsilon(X)) = \overline{p}(\eta^{\circ},\upsilon^{\circ}). \quad (1.23)$$

for almost all X in \mathcal{B} , then $\{\eta, \upsilon\}$ cannot be Gibbs stable under isolation.

Proof. Since $\{\eta^{\circ}, \upsilon^{\circ}\}$ is thermostatically stable in the strong sense, it follows from Theorem 1.5 that $(\eta^{\circ}, \upsilon^{\circ})$ is a point of super convexity for $\overline{\epsilon}$. In view of (1.18), the equations (1.23) can be written

$$\nabla \overline{\epsilon} (\eta(X), \upsilon(X)) = \nabla \overline{\epsilon} (\eta^{\circ}, \upsilon^{\circ}),$$

and hence Remark A.5 here asserts that if X is such that (1.23) holds and

$$(\eta(X), \upsilon(X)) \neq (\eta^{\circ}, \upsilon^{\circ}),$$
 (1.24)

then $(\eta(X), \upsilon(X))$ is not a point of convexity for $\overline{\epsilon}$. If $\{\eta, \upsilon\}$ is distinct from $\{\eta^{\circ}, \upsilon^{\circ}\}$, then (1.24) holds for each X in some set $\mathscr{S} \subset \mathscr{B}$ with $\mathfrak{m}(\mathscr{S}) > 0$, and if, further, (1.23) holds for almost all X in \mathscr{B} , then there is a subset \mathscr{S}' of \mathscr{S} with $\mathfrak{m}(\mathscr{S}') = \mathfrak{m}(\mathscr{S}) > 0$, such that, for each X in \mathscr{J}' , $(\eta(X), \upsilon(X))$ is not a point of convexity for $\overline{\epsilon}$. But, Theorem 1.6 states that if it is not true that $(\eta(X), \upsilon(X))$ is a point of convexity for $\overline{\epsilon}$ at almost every X in \mathscr{B} , then $\{\eta, \upsilon\}$ cannot be stable under isolation; q.e.d.

In view of Theorem 1.2, the theorem just proven has the following

Corollary. If the uniform static state of \mathcal{B} at $(\eta^{\circ}, \upsilon^{\circ})$ is thermostatically stable in the strong sense, then no static state $\{\eta, \upsilon\}$ of \mathcal{B} , which is distinct from $\{\eta^{\circ}, \upsilon^{\circ}\}$ but has $(\eta(X), \upsilon(X)) = (\eta^{\circ}, \upsilon^{\circ})$ for all X in some set $\mathcal{T} \subset \mathcal{B}$ with $m(\mathcal{T}) > 0$, can be Gibbs stable under isolation. Or, in words closer to those used by Gibbs: If the uniform state of \mathbb{Z} at $(\eta^{\circ}, \upsilon^{\circ})$ is stable under isolation and is not at the frontier of stability, then there is no non-uniform state of \mathbb{Z} that is stable under isolation and has a uniform phase at $(\eta^{\circ}, \upsilon^{\circ})$.

Proof. If $\{\eta, \upsilon\}$ is as described, it is distinct from the uniform state $\{\eta^{\circ}, \upsilon^{\circ}\}$, but obeys (1.23) for all X in a set \mathscr{T} with $\mathscr{m}(\mathscr{T}) > 0$. Hence, by Theorem 1.2, if $\{\eta, \upsilon\}$ is Gibbs stable under isolation, $\{\eta^{\circ}, \upsilon^{\circ}\}$ obeys (1.23) for almost all X in \mathscr{B} . But since $\{\eta^{\circ}, \upsilon^{\circ}\}$ is thermostatically stable in the strong sense, Theorem 1.7 asserts that if $\{\eta, \upsilon\}$ is distinct from $\{\eta^{\circ}, \upsilon^{\circ}\}$ and obeys (1.23), then $\{\eta, \upsilon\}$ cannot be Gibbs stable under isolation; q.e.d.

Another, and more obvious, corollary to Theorem 1.7, is Remark 1.4.

2. Thermodynamic Processes and Regular Fluids

Let us now turn from the theory of static states to the general theory of processes, i.e. from thermo<u>statics</u> to thermo<u>dynamics</u>. In a dynamical theory, a body \mathcal{B} has more structure than in the statical theory of Chapter 1: \mathcal{B} is now not only endowed with a mass-measure, but is also a smooth manifold. Smooth injective mappings of \mathcal{B} into a three-dimensional Euclidean space are called <u>configurations</u> of \mathcal{B} , and each <u>motion</u> χ of \mathcal{B} is a one-parameter family of configurations; the parameter, is of course, the <u>time</u>, and is denoted by t. Furthermore, in thermodynamics, pairs of fields of given type, such as two specific entropy fields η and η' , cannot always be considered equivalent if they differ by only a mass preserving transformation of \mathcal{B} .

A <u>thermodynamic process</u> C of a body **B** is a collection of functions of X and t compatible with the laws of balance of momentum and energy. At the level of generality sought here, each thermodynamic process consists of six functions: (1) the motion χ , with $\chi = \chi(X,t)$ called the <u>position</u> at time t of the material point X; (2) the <u>specific internal</u> <u>energy</u> ϵ ; (3) the <u>specific entropy</u> η ; (4) the <u>temperature</u> θ , which is assumed to be positive; (5) the <u>heat flux vector</u> q; and (6) the symmetric

<u>Cauchy stress tensor</u> \underline{T} .[#] When these six fields suffice to describe a

[#]In this essay attention is confined to situations in which all acting mechanical forces are contact forces, and all heat flow into a region is by direct flux through the region's bounding surface. In particular, it is assumed that gravitational body forces are absent and that there is no heat transfer by radiation.

thermodynamic process, the laws of <u>balance</u> <u>of momentum</u> and <u>balance</u> <u>of</u> <u>energy</u> take the forms

$$\frac{\mathrm{d}}{\mathrm{dt}} \int_{\mathcal{P}} \dot{\mathbf{x}} \, \mathrm{d} \, \boldsymbol{m} = \int_{\partial \mathcal{P}} \operatorname{Tn} \, \mathrm{da}, \qquad (2.1)$$

$$\frac{\mathrm{d}}{\mathrm{dt}} \int_{\mathcal{P}} \left(\varepsilon + \frac{1}{2} \dot{\mathbf{x}}^2 \right) \mathrm{d}\boldsymbol{m} = \int_{\partial \mathcal{P}} \left(\dot{\mathbf{x}} \cdot \underline{\mathrm{Tn}} - \underline{q} \cdot \underline{\mathbf{n}} \right) \mathrm{d}\boldsymbol{a}.$$
(2.2)

These integral relations are assumed to hold at all times t, $-\infty < t < \infty$, and in all parts^{##} ρ of \mathcal{B} ; here n is the exterior unit normal vector

##A part P of B is a subset of the closure of B with certain properties of regularity which I need not list here; cf. Noll [1958, 2]. Of course, B itself belongs to the set of parts of B.

to the surface $\partial \boldsymbol{\rho}$ of $\boldsymbol{\rho}$ in the configuration at time t, da is the element of surface area in this configuration, $\dot{\mathbf{x}} = (\dot{\mathbf{x}} \cdot \dot{\mathbf{x}})^{1/2}$ is the magnitude of $\dot{\mathbf{x}}$, and the superposed dot denotes the material time derivative. Many types of processes are imaginable. The theorems to be proved in Chapter 3 concern processes possible in fluid bodies which from some time, say t = 0, onward are either isolated or immersed in an environment held at a fixed temperature and pressure.

Definition 2.1. Let $\theta^{\circ} > 0$ and $p^{\circ} > 0$ be assigned. If a process C of a body \mathcal{B} is such that, at each time $t \ge 0$,

$$(\theta - \theta^{\circ})\mathbf{q} \cdot \mathbf{n} \geq 0 \quad \text{for all} \quad \mathbf{X} \in \partial \mathcal{B}$$
 (2.3)

and

$$\int_{\mathcal{B}} \dot{\mathbf{x}} \cdot \underline{\mathbf{T}} \mathbf{n} \, d\mathbf{a} = -\dot{\mathbf{V}} \mathbf{p}^{\circ} \quad \text{with} \quad \mathbf{V} = \int_{\mathcal{B}} \upsilon \, d\mathbf{m} \, \mathcal{J}, \qquad (2.4)$$

then C is said to be <u>compatible</u> with <u>immersion</u> of \mathcal{B} in an <u>environment</u> at <u>temperature</u> θ° and <u>pressure</u> p° , from time zero onward.

The condition (2.3) asserts that if the material point X on the surface of \mathcal{B} has a temperature $\begin{cases} \text{greater} \\ \text{less} \end{cases}$ than θ° , then heat does not flow $\begin{cases} \text{into} \\ \text{out of} \end{cases}$ \mathcal{B} at X. This condition is met, trivially, in the extreme cases in which (1) \mathcal{B} is thermally isolated, $(\underline{q} \cdot \underline{n} \equiv 0)$, and (2) the surface of \mathcal{B} is held at the constant temperature θ° .[#] If \mathcal{B}

[#]Cf. Koiter [1967, 4].

pt
is in an environment which is held at the constant and uniform temperature θ° , then (2.3) is expected to be a consequence of the second law of thermodynamics, under reasonable constitutive assumptions for the transfer of heat across the surface of \mathcal{B} . For example, if one assumes that for each point on the surface of \mathcal{B} ,[#]

 $q \cdot n = k(\theta - \theta^{\circ}),$

[#]Employing thermal boundary conditions of this type, Serrin [1959, 2] has proved uniqueness theorems for the flow of classical viscous fluids with heat conduction.

then the second law requires that k be not negative, and (2.3) is obeyed.

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The condition (2.4) asserts that Vp° is a potential for the total work done by the contact forces acting on \mathcal{B} . This condition is met, for example, when \mathcal{B} is mechanically isolated, i.e. when $\dot{V} = 0$ and $\dot{x} \cdot Tn = 0$ on the surface of \mathcal{B} ; a special case of a process compatible with mechanical isolation is one in which \mathcal{B} fills a rigid container to which it adheres, so that the velocity \dot{x} is zero at the bounding surface of \mathcal{B} . Processes which are not compatible with isolation, but yet obey (2.4), occur in a body confined in a piston chamber, provided that the force F exerted by the piston on \mathcal{B} is positive and constant in time; then $p^{\circ} = F/A$, with A the cross-sectional area of the piston [see Fig. 1.1].

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area A = V/l. Here
$$\int \dot{\mathbf{x}} \cdot \mathbf{Tn} \, d\mathbf{a} = -F\dot{l} = -p^{\circ}\dot{\mathbf{V}}$$
.

The <u>Clausius-Duhem</u> inequality asserts that, at each instant of time and for each part P of \mathcal{B} ,

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{P} \eta \,\mathrm{d}m\nu \geq -\int_{O} \frac{q}{\theta} \,\underline{n} \,\mathrm{d}a. \qquad (2.5)$$

Given two positive numbers θ° , p° , and a process C of \mathcal{B} , one can define, at each time t, a number $\Phi(t)$ by

$$\Phi(t) = \int_{\mathcal{B}} \left(\epsilon(X,t) - \theta^{\circ} \eta(X,t) + p^{\circ} \upsilon(X,t) + \frac{1}{2} \dot{x}^{2}(X,t) \right) dm . \quad (2.6)$$

I call $\Phi(t)$ the <u>canonical free-energy of</u> \mathcal{B} , <u>at time</u> t, <u>under an</u> <u>environment at temperature</u> θ° and pressure p° .

Theorem 2.1.[#] It is a direct consequence of the balance law (2.2) and [#]Theorems related to 2.1 are given by Ericksen [1966, 2], Koiter [1967, 4], and Coleman & Dill [1968, 2].

the Clausius-Duhem inequality (2.5), that if C is a process of \mathcal{B} compatible with immersion of \mathcal{B} in an environment at temperature θ° and pressure p° (from time zero onward), and if Φ is the canonical free-energy of \mathcal{B} under such an environment, then in the process C

$$\frac{\mathrm{d}}{\mathrm{d}t} \Phi(t) \leq 0$$

for each $t \geq 0$.

Proof. When (2.4) holds, (2.2) yields

$$\frac{\mathrm{d}}{\mathrm{dt}} \int_{\mathcal{B}} \left(\varepsilon + \frac{1}{2} \dot{x}^2 + p^\circ \upsilon \right) \mathrm{d}m\upsilon = -\int_{\partial \mathcal{B}} q \cdot \underline{n} \mathrm{d}a. \qquad (2.7)$$

Since θ and θ° are positive, (2.3) implies

$$\frac{1}{\theta^{\circ}}\int_{\partial \mathcal{B}} \mathbf{q} \cdot \mathbf{n} \, \mathrm{da} \geq \int_{\partial \mathcal{B}} \frac{1}{\theta} \mathbf{q} \cdot \mathbf{n} \, \mathrm{da},$$

and hence, by (2.5),

$$\theta^{\circ} \frac{d}{dt} \int_{\mathcal{B}} \eta dm \geq -\int_{\mathcal{B}} q \cdot \underline{n} da.$$
 (2.8)

Substitution of (2.7) into (2.8) yields

$$\frac{\mathrm{d}}{\mathrm{dt}}\int_{\mathcal{B}} \left(\varepsilon + \frac{1}{2}\dot{\mathbf{x}}^2 + \mathbf{p}^{\circ}\upsilon - \theta^{\circ}\eta\right) \mathrm{d}m\upsilon \leq 0;$$

q.e.d.

Let a motion of \mathcal{B} be given, and let \underline{x} be the position in space of the material point X at time t, which may be interpreted as the present time. Suppose that at time $\tau \leq t$ the same material point X occupied the position $\underline{\xi}$. For the dependence of $\underline{\xi}$ on \underline{x} , t, and τ , one can write

$$\xi = \chi_t(x,\tau).$$

The function $\mathbf{C}_{\mathbf{p}}^{\mathsf{t}}$ defined by

$$C_{\mathcal{A}}^{t}(s) = F(s)^{T}F(s), \quad \text{with} \quad F(s) = \nabla \chi_{X \sim t}(x, t-s), \quad 0 < s < \infty, \quad (2.9)$$

may be called the past history[#] (up to time t) of the relative strain at

[#]Cf. Coleman [1964, 2], §9, p. 251.

X; this function maps $(0,\infty)$ into the set of symmetric positive definite tensors. The value $C_{\rho}^{t}(s)$ of C_{ρ}^{t} is the right Cauchy-Green tensor at X at time t-s, computed using the configuration at time t as reference.^{##}

##Cf. Noll [1958, 2].

The <u>past history</u> (up to t) of <u>the specific entropy</u> at X is the positive function η_{p}^{t} on $(0,\infty)$ given by

$$\eta_{\mu}^{t}(s) = \eta(X, t-s), \qquad 0 < s < \infty.$$
 (2.10)

A <u>material</u> is characterized by constitutive assumptions which restrict the class of the processes that can occur in a body comprised of the material. For example, a <u>simple fluid</u> is defined by four functions e, t, \mathfrak{T} , and \mathfrak{q} , called <u>constitutive functionals</u>; a thermodynamic process is said to be <u>admissible</u> in such a fluid if, at each point X and each time t, the values of ϵ , θ , \mathfrak{T} , and \mathfrak{q} at X,t are given by the equations

$$\epsilon = e(\eta, \upsilon; \eta^{t}_{\rho}, \mathcal{C}^{t}_{\rho}),$$

$$\theta = t(\eta, \upsilon; \eta^{t}_{\rho}, \mathcal{C}^{t}_{\rho}),$$

$$T = \mathfrak{X}(\eta, \upsilon; \eta^{t}_{\rho}, \mathcal{C}^{t}_{\rho}),$$

$$q = q(\eta, \upsilon, \nabla_{\mathfrak{X}} \theta; \eta^{t}_{\rho}, \mathcal{C}^{t}_{\rho}),$$
(2.11)

where the numbers η , υ , and the vector $\nabla_{\underline{x}} \theta$ are present values, i.e., values at X,t, while the functions $C_{\underline{x}}^{t}$ and $\eta_{\underline{p}}^{t}$ are the past histories defined in (2.9) and (2.10).[#]

[#]The concept of a simple fluid was introduced by Noll [1958, 2] in a context in which thermodynamic variables do not occur. The full set of equations (2.11) was presented and studied in my essay [1964, 1] (vid., particularly, pp. 31 & 43).

In our paper of 1963, Walter Noll and I developed a procedure for finding the limitations which the second law of thermodynamics places on constitutive assumptions. The theory proposed there renders mathematical the often vaguely stated <u>second law</u> by interpreting it to be the assertion that, for every admissible process in a body comprised of a given material, the <u>Clausius-Duhem inequality must hold at all times and in all parts of</u> <u>the body</u>.^{##} Clearly, under such an interpretation, the second law must

In that paper [1963, 1] account was taken of long-range influences, such as body forces and heat supply by radiation, which are here assumed absent.

imply restrictions on constitutive functionals, such as e, t, \mathfrak{X} , and \mathfrak{q} in (2.11). In my essay of 1964, I found these restrictions for e, t, \mathfrak{X} ,

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and q, under the hypothesis that these functionals obey the principle of \sim fading memory[#]. There is no need to list here all the results obtained

[#]This is a postulate of smoothness introduced in [1960, 1] and [1961, 1], and developed from a set of elementary axioms in [1966, 1]. Generalizations of the theory of fading memory, with applications to thermodynamics, are explored in [1967, 3], [1968, 3-5], and [1970, 1].

in that study, but I should like to state those which contribute to an understanding of the generality of the concept of a "regular fluid", to be defined later in this chapter.

Let 1^{\dagger} and 1^{\dagger} be the constant functions on $(0,\infty)$ equal, respectively, to the number 1 and the unit tensor 1:

$$1^{\dagger}(s) \equiv 1, \qquad 1^{\dagger}(s) = 1, \qquad 0 < s < \infty.$$

If a region containing the point X has remained in its present configuration at all times $\tau \leq t$, or has been subjected to only rigid motion, then $C_{,\rho}^{t} = 1^{\dagger}$ at X; if the specific entropy at X has remained constant at its present value η for all $\tau \leq t$, then $\eta_{,\rho}^{t} = \eta 1^{\dagger}$ at X; therefore, I call the function $\overline{\epsilon}$, defined by

$$\overline{\epsilon}(\eta,\upsilon) \stackrel{\text{def}}{=} e(\eta,\upsilon; \eta 1^{\dagger}, \underline{1}^{\dagger}), \qquad (2.12)$$

the equilibrium response function for the internal energy (or, to be

briefer, the <u>equilibrium energy function</u>) for the simple fluid under consideration. Among the consequences of the second law is the following inequality, which the functional e obeys throughout its domain:[#]

$$e(\eta, v; \eta^{t}_{\rho, \rho}, \mathcal{C}^{t}_{\rho}) \leq \overline{\epsilon}(\eta, v).$$
 (2.13)

In words: For a simple fluid with fading memory, of all past histories, that corresponding to perpetual rest at the present configuration and entropy gives the smallest value to the internal energy.

The equilibrium response functions for the temperature, stress, and heat flux are defined by equations analogous to (2.12):

$$\overline{\theta}(\eta, \upsilon) \stackrel{\text{def}}{=} t(\eta, \upsilon; \eta 1^{\dagger}, \underline{1}^{\dagger}),$$

$$\overline{\underline{I}}(\eta, \upsilon) \stackrel{\text{def}}{=} \underline{\mathfrak{X}}(\eta, \upsilon; \eta 1^{\dagger}, \underline{1}^{\dagger}), \qquad (2.14)$$

$$\overline{\underline{q}}(\eta, \upsilon, \nabla_{\underline{x}} \theta) \stackrel{\text{def}}{=} \underline{q}(\eta, \upsilon, \nabla_{\underline{x}} \theta; \eta 1^{\dagger}, \underline{1}^{\dagger}).$$

It is easily shown that the principle of material frame-indifference $^{\#\#}$

Moll [1958, 2]; he there used the term "objectivity" instead of "frame-indifference". implies that the functions $\overline{\underline{T}}$ and $\overline{\underline{q}}$ have the forms[#]

$$\overline{\underline{T}}(\eta, \upsilon) = -p\underline{1}, \qquad p = \overline{p}(\eta, \upsilon),$$

$$\overline{\underline{q}}(\eta, \upsilon, \nabla_{\underline{x}} \theta) = -\kappa \nabla_{\underline{x}} \theta, \qquad \kappa = \overline{\kappa}(\upsilon, \varepsilon, \nabla_{\underline{x}} \theta).$$
(2.15)

#Vid., e.g., [1964, 4], Proposition 7, pp. 96, 97, and [1963, 1], p. 177.

It is a consequence of the second law that the functional e must determine the functionals \mathfrak{T} and t through a formula called the <u>generalized stress</u> <u>relation</u>.^{##} I need not review here the several definitions required to

##[1964, 1], Theorem 6, p. 33.

formulate this relation for arbitrary past histories $C_{\rho\nu}^{t}$ and $\eta_{\rho\nu}^{t}$, but I should like to remind the reader that, for a simple fluid with fading memory, it is a consequence of (2.13) and the generalized stress relation that the equilibrium response functions $\overline{\epsilon}$, $\overline{\theta}$, and \overline{p} must obey (1.2).

###[1964, 1], Remark 23, p. 35.

The concept of a "uniform static state", which plays a central role in classical thermostatics, can be given a meaning in thermodynamics through the following definition. Definition 2.2. A uniform static state of a body \mathcal{B} is an admissible process of \mathcal{B} in which

 $\eta(X,t) = \text{const.}, v(X,t) = \text{const.}, \text{ and } \dot{x}(X,t) = 0,$

for all X in \mathcal{B} and all t in $(-\infty,\infty)$.

The apparatus required to specify the class of materials called "regular fluids"[#] has now been assembled.

#Cf. Coleman & Greenberg [1967, 1].

Definition 2.3. A body \mathcal{B} is comprised of a <u>regular</u> fluid if there exists a differentiable function $\overline{\epsilon}$ mapping $(0,\infty) \times (0,\infty)$ into $(0,\infty)$ such that

(i) for each pair $(\eta^{\circ}, \upsilon^{\circ})$ of positive numbers, there is a unique uniform static state of \mathcal{B} with $\eta = \eta^{\circ}$ and $\upsilon = \upsilon^{\circ};^{\#}$

[#]<u>Unique</u> here means the following: If χ , ϵ , η , θ , q, and \underline{T} are the six functions of X and t describing an admissible process of \mathcal{B} with $\eta(X,t) \equiv \eta^{\circ}, \ \upsilon(X,t) \equiv \upsilon^{\circ}, \ \text{and} \ \partial_{t}\chi(X,t) = \underline{0}, \ \text{then } \epsilon, \ \eta, \ \theta, \ q, \ \text{and } \underline{T} \ \text{are}$ completely determined once η° and υ° are given, and χ is determined to within a constant unimodular transformation, i.e. to within a transformation of the form $\chi(X,t) \to U\chi(X,t) + c$, with c a vector and \underline{V} a tensor obeying $|\det \underline{V}| = 1$. in this state (regarded as a process), for all X and t,

$$\epsilon(\mathbf{X}, \mathbf{t}) = \epsilon^{\circ} \stackrel{\text{def}}{=} \overline{\epsilon}(\eta^{\circ}, \upsilon^{\circ}),$$

$$\theta(\mathbf{X}, \mathbf{t}) = \theta^{\circ} \stackrel{\text{def}}{=} \overline{\theta}(\eta^{\circ}, \upsilon^{\circ}), \text{ with } \overline{\theta} = \partial_{\eta}\overline{\epsilon},$$

$$\underline{T}(\mathbf{X}, \mathbf{t}) = -\mathbf{p}^{\circ}\underline{1}, \text{ with } \mathbf{p}^{\circ} \stackrel{\text{def}}{=} \overline{p}(\eta^{\circ}, \upsilon^{\circ}), \overline{\mathbf{p}} = -\partial_{\upsilon}\overline{\epsilon},$$

$$\underline{q}(\mathbf{X}, \mathbf{t}) = \underline{0};$$

$$(2.16)$$

(ii) in every admissible thermodynamic process of ${\mathcal B}$

$$\epsilon(X,t) \geq \epsilon(\eta(X,t),\upsilon(X,t)),$$
 (2.17)

for all X and t.

The function $\overline{\epsilon}$ in (2.16) and (2.17) is called the <u>equilibrium</u> <u>energy</u> <u>function</u> for the regular fluid.

Remark 2.1. Every simple fluid with fading memory is a regular fluid.

Proof. Let a simple fluid with fading memory be given, let \mathscr{B} be a body comprised of this fluid, and define $\overline{\epsilon}$, $\overline{\theta}$, $\overline{\underline{T}}$, and $\overline{\underline{q}}$ by (2.12) and (2.14). Then, (2.15) holds, and, according to the italicized observation made above about the generalized stress relation, $\overline{\theta} = \partial_n \overline{\epsilon}$ and $\overline{p} = -\partial_v \overline{\epsilon}$. Let $\eta^{\circ} > 0$ and $\upsilon^{\circ} > 0$ be given, let $\chi(X,t)$ be such that both $\dot{\chi}(X,t) \equiv 0$ and $\upsilon(X,t) \equiv \upsilon^{\circ}$, and put $\epsilon(X,t) \equiv \overline{\epsilon}(\eta^{\circ},\upsilon^{\circ}), \ \eta(X,t) \equiv \eta^{\circ}, \ \theta(X,t) \equiv \overline{\theta}(\eta^{\circ},\upsilon^{\circ}),$ $q \equiv 0$, and $\underline{T}(X,t) \equiv -\overline{p}(\eta^{\circ}, \upsilon^{\circ})\underline{1}$. The six (constant) functions χ , ϵ , η , heta, q, and T so constructed obviously obey the balance laws (2.1) and (2.2) and hence form a <u>thermodynamic process</u> of \mathcal{B} ; furthermore, by (2.12), (2.14), and (2.15), this process obeys (2.11) and hence is admissible. Moreover, the present construction completely determines ϵ , η , heta, q, and \mathtt{T} as functions of X and t, and determines ${\underline{\chi}}$ to within a constant unimodular transformation; i.e. the admissible thermodynamic process ($\chi \in \eta, \theta, q, T$) constructed here is the only one with $\eta \equiv \eta^{\circ}$, $v \equiv v^{\circ}$, and $\dot{x} \equiv 0$. Therefore, there exists a unique uniform static state of \mathcal{B} with $\eta = \eta^{\circ}$ and $\upsilon = \upsilon^{\circ}$, and this state obeys (2.16). In view of (2.13), it is obvious that (2.17) holds for every admissible thermodynamic process of \mathcal{B} . Thus, for an arbitrarily given simple fluid with fading memory, the function $\overline{\epsilon}$ of (2.12) obeys items (i) and (ii) of the Definition 2.3; q.e.d.

Since each perfect (i.e. "elastic") fluid is a special case of a simple fluid with fading memory, every perfect fluid is a regular fluid. It is not difficult to show that the class of regular fluids also includes all linearly viscous fluids (with or without heat conduction).[#] For these

[#]The consequences of the second law for the constitutive equations of these and related materials are discussed in [1963, 1] and [1964, 3].

classical materials, (2.17) reduces to an equation. The theory of materials with internal state variables $^{\#\#}$ yields additional examples of

regular fluids. Thus, the theory of regular fluids may be considered a broad generalization of the theory of simple fluids with fading memory.

Since, by assumption, for a regular fluid the uniform static state mentioned in item (i) of Definition 2.3 exists for each pair $(\eta^{\circ}, \upsilon^{\circ})$ in $(0, \infty) \times (0, \infty)$ and is uniquely determined by $(\eta^{\circ}, \upsilon^{\circ})$, one may refer to this state as <u>the uniform static state at</u> $(\eta^{\circ}, \upsilon^{\circ})$ and denote it by $\{\eta^{\circ}, \upsilon^{\circ}\}$, just as is done in thermostatics. One may, furthermore, here continue to refer to every pair $\{\eta, \upsilon\}$ of positive *mu*-measurable functions over \mathcal{B} which renders finite the three integrals in (1.4) as a <u>static</u> <u>state</u> of \mathcal{B} , albeit it is not true that every static state so obtained occurs in a thermodynamic process in which the functions χ , η , ϵ , θ , q, and <u>T</u> are constant in time.[#] Of course, "Gibbs stability under isolation"

#For this reason, some physicists prefer to refer to certain static states as "virtual states".

and "thermostatic stability in the strong sense" become then formal concepts whose dynamical significance must be demonstrated. Such demonstrations are given in the following chapter, where it is shown that if \mathcal{B} is a regular fluid body with $\overline{\epsilon}$ convex for large argument, then each uniform static state $\{\eta^{\circ}, \upsilon^{\circ}\}$ of \mathcal{B} that is thermostatically stable in the strong sense, according to Definition 1.3, is, when interpreted as a process, also dynamically stable against a class of admissible processes compatible with immersion of \mathcal{B} in an environment at the temperature $\theta^{\circ} = \overline{\theta}(\eta^{\circ}, \upsilon^{\circ})$ and the pressure $p^{\circ} = \overline{p}(\eta^{\circ}, \upsilon^{\circ})$.

3. Dynamical Stability

Employing the important inequality (2.17) and Theorem 1.5 in the form of Remark 1.3, one can derive a lower bound for the canonical free energy Φ of a regular fluid body \mathcal{B} under an environment at temperature θ° and pressure p° , provided there is a uniform static state $\{\eta^{\circ}, \upsilon^{\circ}\}$ of \mathcal{B} that (1) is thermostatically stable in the strong sense, according to Definition 1.3, and (2) gives to \mathcal{B} the temperature θ° and the pressure p° . Indeed, the lower bound for Φ is just Φ° , the canonical free energy of the fluid in the state $\{\eta^{\circ}, \upsilon^{\circ}\}$, regarded as a process. This is the main content of Remark 3.2 below, which is an immediate consequence of the following observation.

Remark 3.1. Let η° , υ° , ε° , θ° , and p° be the values of η , υ , ε , θ , and p in a uniform static state $\{\eta^{\circ}, \upsilon^{\circ}\}$ of a regular fluid body \mathcal{B} , and let $\eta(X,t)$, $\upsilon(X,t)$, and $\varepsilon(X,t)$ be the values assumed by η , υ , and ε at some given time t and material point X in an arbitrary admissible thermodynamic process C of \mathcal{B} . Put

$$\phi^{\circ} \stackrel{\text{def}}{=} \epsilon^{\circ} - \theta^{\circ} \eta^{\circ} + p^{\circ} \upsilon^{\circ}$$
(3.1)

and

$$\zeta(X,t) \stackrel{\text{def}}{=} \epsilon(X,t) - \theta^{\circ}\eta(X,t) + p^{\circ}\upsilon(X,t). \qquad (3.2)$$

If the state $\{\eta^{\circ}, \upsilon^{\circ}\}$ is thermostatically stable in the strong sense, then

and the sign of inequality holds here whenever $\eta(X,t) \neq \eta^{\circ}$, $\upsilon(X,t) \neq \upsilon^{\circ}$, or $\epsilon(X,t) \neq \epsilon^{\circ}$.

42.

Proof. Let $\overline{\phi}$ be the function defined in equation (1.21) of Remark 1.3, i.e.

$$\overline{\phi}(\eta,\upsilon) = \overline{\epsilon}(\eta,\upsilon) - \theta^{\circ}\eta + p^{\circ}\upsilon, \qquad (3.3)$$

with $\overline{\epsilon}$ the equilibrium energy function for \mathcal{B} . Then

$$\phi^{\circ} = \overline{\phi}(\eta^{\circ}, \upsilon^{\circ}),$$

and since, by (2.17),

$$\overline{\epsilon}(\eta(X,t),\upsilon(X,t)) \leq \epsilon(X,t),$$

it follows that

$$\overline{\phi}(\eta(\mathbf{X},t),\upsilon(\mathbf{X},t)) \leq \zeta(\mathbf{X},t), \qquad (3.4)$$

with equality holding only when $\epsilon(X,t) = \overline{\epsilon}(\eta(X,t),\upsilon(X,t))$. Hence the conclusion (1.22) of Remark 1.3 here implies

$$\overline{\phi}(\eta^{\circ}, \upsilon^{\circ}) \leq \overline{\phi}(\eta(X, t), \upsilon(X, t)) \leq \zeta(X, t),$$

and $\overline{\phi}(\eta^{\circ}, \upsilon^{\circ}) = \overline{\phi}(\eta(X, t), \upsilon(X, t))$ only when $\eta(X, t) = \eta^{\circ}$ and $\upsilon(X, t) = \upsilon^{\circ}$; q.e.d.

A direct corollary of this remark is

Remark 3.2. Let \mathcal{B} be a regular fluid body, let $\{\eta^{\circ}, \upsilon^{\circ}\}$ be a uniform static state of \mathcal{B} that is thermostatically stable in the strong sense, and let ε° , θ° , and p° be the specific internal energy, the temperature, and the pressure of \mathcal{B} in the state $\{\eta^{\circ}, \upsilon^{\circ}\}$, i.e.

$$\epsilon^{\circ} = \overline{\epsilon}(\eta^{\circ}, \upsilon^{\circ}), \qquad \theta^{\circ} = \overline{\theta}(\eta^{\circ}, \upsilon^{\circ}), \qquad p^{\circ} = \overline{p}(\eta^{\circ}, \upsilon^{\circ}). \qquad (3.5)$$

Put

$$\Phi^{\circ} \stackrel{\text{def}}{=} \int \phi^{\circ} dm = M \phi^{\circ}$$
(3.6)

where

$$\phi^{\circ} \stackrel{\text{def}}{=} \epsilon^{\circ} - \theta^{\circ} \eta^{\circ} + p^{\circ} \upsilon^{\circ}.$$

If $\epsilon(X,t)$, $\eta(X,t)$, $\upsilon(X,t)$, and $\dot{\chi}(X,t)$ are values assumed by ϵ , η , υ , and $\dot{\chi}$ in an arbitrary admissible process C of \mathcal{B} , and \underline{if}

$$\phi(\mathbf{X},t) \stackrel{\text{def}}{=} \epsilon(\mathbf{X},t) - \theta^{\circ}\eta(\mathbf{X},t) + p^{\circ}\upsilon(\mathbf{X},t) + \frac{1}{2}\dot{\mathbf{x}}^{2}(\mathbf{X},t), \quad (3.7)$$

then

$$\phi(\mathbf{X},\mathbf{t}) \geq \phi^{\circ} \tag{3.8}$$

for <u>all X in \mathcal{B} and <u>all</u> t, and consequently, at each time t, for the process C,</u>

$$\Phi(t) \geq \Phi^{\circ}, \qquad (3.9)$$

where

$$\Phi(t) \stackrel{\text{def}}{=} \int \phi(X,t) dm u. \qquad (3.10)$$

Moreover, equality holds in (3.9) only if

$$\epsilon(X,t) = \epsilon^{\circ}, \eta(X,t) = \eta^{\circ}, \text{ and } \upsilon(X,t) = \upsilon^{\circ}, \text{ a.e. in } \mathcal{B}.$$

Of course, $\Phi(t)$ is the <u>canonical free-energy</u> of \mathcal{B} at time t under an environment at temperature θ° and pressure p° ; [see (2.6)]. The number Φ° is the canonical free energy of \mathcal{B} , under the same environment, in the uniform static state $\{\eta^{\circ}, \upsilon^{\circ}\}$, regarded as a process of \mathcal{B} .[#]

[#]Since (3.5) holds here, it would be in accord with common usage to call Φ° "the Gibbs free energy of **B** in the static state { $\eta^{\circ}, \upsilon^{\circ}$ }", or "the equilibrium Gibbs free energy of **B** at $\theta^{\circ}, p^{\circ}$ ".

If there are four numbers a, b, c, and d, obeying $0 < a \le b < \infty$, $0 < c \le d < \infty$, such that every point in $(0,\infty) \times (0,\infty) - (a,b) \times (c,d)$ is a point of convexity for $\overline{\epsilon}$, then $\overline{\epsilon}$ is said to be <u>convex for large argument</u>.[#]

[#]It is easily verified that for a function with domain $(0,\infty) \times (0,\infty)$ this definition agrees with the Definition A.1.

When $\overline{\epsilon}$ is convex for large argument, Remark 3.2 can be strengthened as follows.

Remark 3.3. For each regular fluid body \mathcal{B} whose equilibrium energy function $\overline{\epsilon}$ is convex for large argument, there exists a function $\delta(\omega, \eta^{\circ}, \upsilon^{\circ})$ such that:

(i)
$$\delta(\omega,\eta^{\circ},\upsilon^{\circ}) > 0$$
 for $\omega > 0$, $\eta^{\circ} > 0$, and $\upsilon^{\circ} > 0$;

(ii) <u>if</u> the uniform static state of \mathcal{B} at $(\eta^{\circ}, \upsilon^{\circ})$ is thermostatically stable in the strong sense, <u>if</u> ϵ° , θ° , and p° are given by (3.5), and <u>if</u> C is an admissible process of \mathcal{B} with

$$\Phi(t) - \Phi^{\circ} < \delta(\omega, \eta^{\circ}, \upsilon^{\circ}),$$

where $\Phi(t)$ and Φ° are defined as in Remark 3.2, <u>then</u> in the process *C*, at time t,

$$\theta^{\circ} \int_{\mathcal{B}} |\eta(X,t) - \eta^{\circ}| dm < \omega, \qquad p^{\circ} \int_{\mathcal{B}} |\upsilon(X,t) - \upsilon^{\circ}| dm < \omega,$$

$$\frac{1}{2} \int_{\mathcal{B}} \dot{x}^{2}(X,t) dm < \omega, \quad \text{and} \quad \int_{\mathcal{B}} |\varepsilon(X,t) - \varepsilon^{\circ}| dm < \omega.$$

$$(3.11)$$

Proof. Suppose that the uniform static state at $(\eta^{\circ}, \upsilon^{\circ})$ is thermostatically stable in the strong sense, let $\omega > 0$ be assigned, let ϵ° , θ° , and p° be given by (3.5), and let $\Phi(t)$ and Φ° be as in Remark 3.2. Then

$$\Phi(t) - \Phi^{\circ} = \int_{\mathcal{B}} [\phi(X,t) - \phi^{\circ}] dm = \int_{\mathcal{B}} [\zeta(X,t) - \phi^{\circ}] dm + \frac{1}{2} \int_{\mathcal{B}} \dot{x}^{2}(X,t) dm, \quad (3.12)$$

with $\phi(X,t)$ defined in (3.7), ϕ° in (3.1), and $\zeta(X,t)$ in (3.2). By Remark 3.1,

$$\zeta(X,t) - \phi^{\circ} \geq 0,$$

and therefore (3.12) yields

$$\Phi(t) - \Phi^{\circ} \geq \frac{1}{2} \int_{\mathcal{B}} \dot{x}^{2}(X, t) d\mathcal{M}. \qquad (3.13)$$

Furthermore, since \dot{x}^2 is never negative, (3.12) yields also

$$\Phi(t) - \Phi^{\circ} \geq \int_{\mathcal{B}} [\zeta(X, t) - \phi^{\circ}] dm',$$

and, by (3.4), this implies

$$\Phi(t) - \Phi^{\circ} \geq \int_{\mathcal{B}} [\bar{\phi}(\eta, \upsilon) - \phi^{\circ}] dm, \qquad (3.14)$$

where I have written η for $\eta(X,t)$ and υ for $\upsilon(X,t)$, and $\overline{\phi}$ is as in (3.3). Let

$$y_1 = (\eta - \eta^\circ)\theta^\circ, \qquad y_2 = (\upsilon - \upsilon^\circ)p^\circ, \qquad y_2 = (y_1, y_2), \qquad (3.15)$$

$$f(\mathbf{y}) \stackrel{\text{def}}{\sim} \overline{\phi}\left(\frac{\mathbf{y}_1}{\theta^\circ} + \eta^\circ, \frac{\mathbf{y}_2}{p^\circ} + \upsilon^\circ\right) - \phi^\circ = \overline{\phi}(\eta, \upsilon) - \phi^\circ. \quad (3.16)$$

In terms of the function f, (3.14) becomes

$$\Phi(t) - \Phi^{\circ} \geq \int_{\mathcal{B}} f(y) dm . \qquad (3.17)$$

By (3.1) and (3.3),

$$f(y) = \overline{\epsilon} \left(\frac{y_1}{\theta^{\circ}} + \eta^{\circ}, \frac{y_2}{p^{\circ}} + \upsilon^{\circ} \right) - \epsilon^{\circ} + y_1 + y_2, \qquad (3.18)$$

and because $\overline{\epsilon}$ is defined and differentiable on $(0,\infty) \times (0,\infty)$, f is defined and differentiable for all y in the set

$$\underline{\mathbf{D}} = (-\eta^{\circ}\theta^{\circ}, \infty) \times (-\upsilon^{\circ}\mathbf{p}^{\circ}, \infty).$$

Of course, since $\overline{\phi}(\eta^{\circ}, \upsilon^{\circ}) = \phi^{\circ}$, (3.16) yields

f(0) = 0,

and it follows from Remark 1.3 that f is positive definite on \underline{D} in the sense of the Definition A.2. As it is here assumed that $\overline{\epsilon}$ is convex for large argument, it is clear from (3.18) that f is too; [see the Definition A.1]. Thus, f meets the hypothesis of Lemma A.2, and there exists an $\iota > 0$ such that

$$\int_{\mathcal{B}} f(\underline{y}) dm < \iota \implies \int_{\mathcal{B}} ||\underline{y}|| dm < \frac{\omega}{2},$$

or, by (3.17), (3.15), and (A.12),

$$\Phi(t) - \Phi^{\circ} < \iota \implies \theta^{\circ} \int_{\mathcal{B}} |\eta - \eta^{\circ}| \, dm + p^{\circ} \int_{\mathcal{B}} |\upsilon - \upsilon^{\circ}| \, dm < \frac{\omega}{2} \, . \quad (3.19)$$

It follows from the conclusion (3.8) of Remark 3.2 that $(3.12)_1$ can be written

$$\Phi(t) - \Phi^{\circ} = \int_{\mathcal{B}} |\phi - \phi^{\circ}| dm, \qquad (3.20)$$

where ϕ stands for $\phi(X,t)$. In view of (3.1) and (3.7),

$$\epsilon - \epsilon^{\circ} = \phi - \phi^{\circ} + (\eta - \eta^{\circ})\theta^{\circ} - (\upsilon - \upsilon^{\circ})p^{\circ} - \frac{1}{2}\dot{x}^{2},$$

and therefore, by the triangle inequality, (3.20), and (3.13),

$$\int_{\mathcal{B}} |\epsilon - \epsilon^{\circ}| dm \leq \int_{\mathcal{B}} |\phi - \phi^{\circ}| dm + \theta^{\circ} \int_{\mathcal{B}} |\eta - \eta^{\circ}| dm + p^{\circ} \int_{\mathcal{B}} |\upsilon - \upsilon^{\circ}| dm + \frac{1}{2} \int_{\mathcal{B}} \dot{x}^{2} dm$$

$$\leq 2[\Phi(t) - \Phi^{\circ}] + \theta^{\circ} \int_{\mathcal{B}} |\eta - \eta^{\circ}| dm + p^{\circ} \int_{\mathcal{B}} |\upsilon - \upsilon^{\circ}| dm . \quad (3.21)$$

It is a direct consequence of (3.13), (3.19), and (3.21) that if one puts

 $\delta = \min(\iota, \omega/4),$

then δ is positive, and all four of the inequalities in (3.11) hold whenever $\Phi(t) - \Phi^{\circ}$ is less than δ . Of course the δ so obtained depends on not only ω but also η° and υ° , i.e. $\delta = \delta(\omega, \eta^{\circ}, \upsilon^{\circ})$. The argument just given rests on the assumption that $\{\eta^{\circ}, \upsilon^{\circ}\}$, the uniform static state at $(\eta^{\circ}, \upsilon^{\circ})$, is thermostatically stable in the strong sense; if $\{\eta^{\circ}, \upsilon^{\circ}\}$ is not stable in this manner, then let $\delta(\omega, \eta^{\circ}, \upsilon^{\circ})$ have any convenient positive value, such as 1 or ω . Thus one obtains a function $\delta(\omega, \eta^{\circ}, \upsilon^{\circ})$ with the properties (i) and (ii); q.e.d. The main results of this study, Theorems 3.1 and 3.2 below, are easy consequences of the remark just proven and Theorem 2.1.

In both Theorem 3.1 and Theorem 3.2, a regular fluid body is supposed assigned in advance, and, for each pair $(\theta^{\circ}, p^{\circ})$ of positive numbers, $\mathfrak{S}(\theta^{\circ}, p^{\circ})$ denotes the class of admissible thermodynamic processes of \mathcal{B} that are compatible with immersion of \mathcal{B} in an environment at temperature θ° and pressure p° from time t = 0 onward.[#]

#Vid. Definition 2.1.

Theorem 3.1. Let θ° , p° , and ϵ° be the values of the temperature, the pressure, and the specific internal energy in a uniform static state $\{\eta^{\circ}, \upsilon^{\circ}\}$ of a regular fluid body \mathcal{B} for which the equilibrium energy function is convex for large argument. If $\{\eta^{\circ}, \upsilon^{\circ}\}$ is thermostatically stable in the strong sense, then given any $\omega > 0$, there exists a $\delta = \delta(\omega, \eta^{\circ}, \upsilon^{\circ}) > 0$ such that each process in $\mathfrak{C}(\theta^{\circ}, p^{\circ})$ which, at any one time $t \geq 0$, satisfies

$$\Phi(t) - \Phi^{\circ} < \delta, \qquad (3.22)$$

with $\Phi(t)$ and Φ° defined as in Remark 3.2, must also satisfy

$$\frac{1}{2} \int_{\mathcal{B}} \dot{\mathbf{x}}^{2} (\mathbf{X}, \tau) d\boldsymbol{m} < \omega, \qquad \int_{\mathcal{B}} |\epsilon (\mathbf{X}, \tau) - \epsilon^{\circ}| d\boldsymbol{m} < \omega, \\ \theta^{\circ} \int_{\mathcal{B}} |\eta (\mathbf{X}, \tau) - \eta^{\circ}| d\boldsymbol{m} < \omega, \quad \text{and} \quad p^{\circ} \int_{\mathcal{B}} |\upsilon (\mathbf{X}, \tau) - \upsilon^{\circ}| d\boldsymbol{m} < \omega, \end{cases}$$
(3.23)

for <u>all</u> $\tau \ge t$.

Proof. Let $\delta = \delta(\omega, \eta^{\circ}, \upsilon^{\circ})$ be as in Remark 3.3. Of course, by item (i) of that remark, δ is then always positive. Now, according to Theorem 2.1, for $\tau \ge 0$, $\Phi(\tau)$ does not increase with τ in any process *C* belonging to $\mathfrak{C}(\theta^{\circ}, p^{\circ})$. Hence if *C* in $\mathfrak{C}(\theta^{\circ}, p^{\circ})$ obeys (3.22) at some time $t \ge 0$, then for the process *C*,

$$\Phi(\tau) - \Phi^{\circ} < \delta, \qquad (3.24)$$

at each time $\tau \ge t$. But, by item (ii) of Remark 3.3, if (3.24) holds at time τ , then (3.23) also holds at time τ ; q.e.d.

Theorem 3.2. Let \mathcal{B} be a regular fluid body with an equilibrium energy function $\overline{\epsilon}$ that is convex for large argument. If \mathcal{B} has, at a given temperature θ° and a given pressure p° , a uniform static state $\{\eta^{\circ}, \upsilon^{\circ}\}$ that is thermostatically stable in the strong sense, then this uniform static state is unique and is dynamically stable in the following sense. Given any $\omega > 0$, there exists $\lambda = \lambda(\omega, \theta^{\circ}, p^{\circ}) > 0$ such that if a process C in $\mathfrak{C}(\theta^{\circ}, p^{\circ})$ has

$$\frac{1}{2} \int_{\mathcal{B}} \dot{x}^{2}(X,t) dm < \lambda, \qquad \int_{\mathcal{B}} |\epsilon(X,t)-\epsilon^{\circ}| dm < \lambda \qquad (\epsilon^{\circ} = \overline{\epsilon}(\eta^{\circ}, \upsilon^{\circ})), \\ \theta^{\circ} \int_{\mathcal{B}} |\eta(X,t)-\eta^{\circ}| dm < \lambda, \quad \text{and} \quad p^{\circ} \int_{\mathcal{B}} |\upsilon(X,t)-\upsilon^{\circ}| dm < \lambda, \end{cases}$$

$$(3.25)$$

at any one time t ≥ 0 , then C must obey (3.23) for <u>all</u> $\tau \geq t$.

Proof. Let $\{\eta^{\circ}, \upsilon^{\circ}\}$ be a uniform static state of \mathcal{B} , with the given temperature θ° and pressure p° , that is thermostatically stable in the strong sense, and let C be in $\mathfrak{S}(\theta^{\circ}, p^{\circ})$. It follows immediately from Remark 1.4 that $\{\eta^{\circ}, \upsilon^{\circ}\}$ is unique. Furthermore, it is clear from Remark 3.2 [see also (3.20)] that at each time t, in the process C,

$$\Phi(t) - \Phi^{\circ} = \iint_{\mathcal{B}} |\phi(X,t) - \phi^{\circ}| d_{\mathcal{M}},$$

where, by (3.1) and (3.7),

$$\phi(\mathbf{X},\mathbf{t}) - \phi^{\circ} = \frac{1}{2} \dot{\mathbf{x}}^{2}(\mathbf{X},\mathbf{t}) + \epsilon(\mathbf{X},\mathbf{t}) - \epsilon^{\circ} - [\eta(\mathbf{X},\mathbf{t}) - \eta^{\circ}]\theta^{\circ} + [\upsilon(\mathbf{X},\mathbf{t}) - \upsilon^{\circ}]p^{\circ}.$$

Hence the triangle inequality yields

$$\Phi(t) - \Phi^{\circ} \leq \int_{\mathcal{B}} \frac{1}{2} \dot{x}^{2}(X, t) dm + \int_{\mathcal{B}} |\epsilon(X, t) - \epsilon^{\circ}| dm + \theta^{\circ} \int |\eta(X, t) - \eta^{\circ}| dm + p^{\circ} \int |\upsilon(X, t) - \upsilon^{\circ}| dm,$$

and, if one puts

$$\lambda = \lambda(\omega, \theta^{\circ}, p^{\circ}) = \frac{1}{4} \delta(\omega, \eta^{\circ}, v^{\circ})$$

with $\delta(\omega, \eta, \upsilon^{\circ})$ as in Theorem 3.1, then λ is not only positive but is also such that (3.25) implies (3.22). But, Theorem 3.1 asserts that if C satisfies (3.22) with $t \ge 0$, then C must obey (3.23) for all $\tau \ge t$; q.e.d.

Appendix: On the theory of functions with points of convexity

I here attempt to lay out in a systematic manner some results from analysis that play a vital role in thermostatics and thermodynamics. Few of the arguments employed here are new; nearly all of them occur in the theory of convex functions, although, in a certain sense, the present subject can be regarded as a generalization of that classical theory. The emphasis is laid on relations which, if they were to hold globally, would characterize a convex or strictly convex function, but which occur here only as properties of a function and single point in its domain.

Let <u>R</u> be the set of real numbers, let <u>R</u>ⁿ, with $n \ge 1$, be the space of n-tuples of elements of <u>R</u>, and let <u>D</u> be a convex[#] open subset

 $\frac{\#}{A}$ subset \underline{S} of a vector space is called <u>convex</u> if whenever \underline{x} and \underline{y} are in \underline{S} and α obeys $0 < \alpha < 1$, the vector $\alpha \underline{x} + (1-\alpha) \underline{y}$ is in \underline{S} .

of \underline{R}^n . Although the present discussion employs only the assumption that the given set \underline{D} is convex and open in \underline{R}^n ,^{##} in applications to thermodynamics

##From Remark A.6 onward, I further assume that the vector 0 = (0, ..., 0)is in <u>D</u>; this, however, is done only to permit use of the convenient normalization f(0) = 0, for real-valued functions on <u>D</u>.

53.

 $\underline{\underline{D}}$ is usually a set of type

$$\underline{\mathbf{D}} = \left\{ \underbrace{\mathbf{x}}_{i} = (\mathbf{x}_{1}, \dots, \underbrace{\mathbf{x}}_{n}) \mid \mathbf{x}_{i} > -\mathbf{b}_{i} \right\} = (-\mathbf{b}_{1}, \infty) \times \cdots \times (-\mathbf{b}_{n}, \infty) \quad (A.1)$$

where the b_i are given non-negative numbers. Let f be a differentiable function mapping \underline{D} into \underline{R} . A point \underline{z} in \underline{D} is called a <u>point of convexity</u> for f if

$$f(z) \leq \alpha f(x) + \beta f(y),$$
 (A.2)

whenever $\underset{\sim}{x}$ and $\underset{\sim}{y}$ in $\underset{\simeq}{\underline{D}}$ are such that

$$z = \alpha x + \beta y, \qquad \alpha + \beta = 1, \qquad \alpha > 0, \qquad \beta > 0.$$
 (A.3)

If

$$f(z) < \alpha f(x) + \beta f(y),$$
 (A.4)

whenever (A.3) holds, then \underline{z} is called a <u>point of strict convexity</u> for f.

Remark A.1. A point z in \underline{D} is a point of convexity for f if and only if, for each x in \underline{D}_{2}

$$f(\underline{x}) \geq f(\underline{z}) + (\underline{x} - \underline{z}) \cdot \nabla f(\underline{z}), \qquad (A.5)$$

with $\nabla f(z)$ the gradient of f at z.

Proof. Suppose first that (A.5) holds, and let $x \in \alpha$ and $y \in \alpha$ obey (A.3). For $\alpha > 0$ and $\beta > 0$, (A.5) yields,

$$\begin{array}{l} \alpha f(\underline{x}) \geq \alpha f(\underline{z}) + \alpha(\underline{x} - \underline{z}) \cdot \nabla f(\underline{z}), \\ \beta f(\underline{y}) \geq \beta f(\underline{z}) + \beta(\underline{y} - \underline{z}) \cdot \nabla f(\underline{z}). \end{array} \right\}$$
(A.6)

Adding these relations one obtains

$$\alpha f(\underline{x}) + \beta f(\underline{y}) \geq (\alpha + \beta) f(\underline{z}) + (\alpha \underline{x} + \beta \underline{y} - (\alpha + \beta) \underline{z}) \cdot \nabla f(\underline{z}). \quad (A.7)$$

It follows from (A.3) that (A.7) reduces to (A.2), and hence z is a point of convexity for f.

Starting now with the assumption that \underline{z} is a point of convexity, let <u>h</u> be an arbitrary vector with $\underline{z} + \underline{h}$ in <u>D</u>, and for each β in (0,1), put

$$x = z - \beta h$$
, $y = z + \alpha h$, $\alpha = 1 - \beta$.

Clearly, $\underset{\sim}{x}$ and $\underset{\sim}{y}$ so defined obey (A.3) and hence (A.2), which may be written

$$f(\underline{x}) - f(\underline{z}) \geq f(\underline{x}) - [\alpha f(\underline{x}) + \beta f(\underline{y})] = [f(\underline{x}) - f(\underline{y})]\beta.$$

Thus,

$$\frac{f(z-\beta\underline{h}) - f(z)}{\beta} \geq f(z-\beta\underline{h}) - f(z+(1-\beta)\underline{h}).$$
(A.8)

By the definition of $\nabla f(z)$,

$$\lim_{\beta \to 0} \frac{f(\underline{z} - \beta \underline{h}) - f(\underline{z})}{\beta} = -\nabla f(\underline{z}) \cdot \underline{h},$$

and since (A.8) holds for all β in (0,1),

$$-\nabla f(z) \cdot h \geq f(z) - f(z+h).$$

By the arbitrariness in the choice of h, this last relation is the same as (A.5); q.e.d.

I say that a point \underline{z} in \underline{D} is a point <u>of super convexity</u> for f if, for each \underline{x} in \underline{D} ,

$$x \neq z \implies f(x) > f(z) + (x-z) \cdot \nabla f(z).$$
(A.9)

Remark A.2. Each point of super convexity for f is also a point of strict convexity for f.

<u>Proof.</u> Let \underline{z} be a point of super convexity for f. If \underline{x} and \underline{y} obey (A.3), then $\underline{x} \neq \underline{z}$ and $\underline{y} \neq \underline{z}$, and, by (A.9), the relations (A.6) hold with the sign of inequality. Hence the sign of inequality holds also in (A.7), which then reduces to (A.4); q.e.d. The accompanying figure shows part of the graph of a smooth function f mapping $(-b,\infty)$ into $\underset{=}{R}$, with z = 0 a point of strict convexity. For this function

$$f(a) = f(0) + (a-0)\nabla f(0),$$

ø

i.e. z = 0 is <u>not</u> a point of super convexity for f. Thus it is not in general true that a given point of strict convexity is a point of super convexity. It is, however, well known that if <u>every</u> point in the domain \underline{D} of f is a point of strict convexity, i.e. if f is a strictly convex function, then every point in \underline{D} is a point of super convexity. A slightly more general result of this type is given in Remark A.3.

Let \underline{Z} be the set of all points in \underline{D} which are points of strict convexity for f. A point \underline{z} is said to be <u>interior</u> to the set of strict <u>convexity</u> for f, if \underline{z} is in the interior of \underline{Z} , i.e. if there is a neighborhood \underline{O} of \underline{z} in \underline{D} such that each \underline{x} in \underline{O} (including \underline{z}) is in \underline{Z} .

Remark A.3. If z is interior to the set of strict convexity for f, then z is a point of super convexity for f.



Fig. 2

<u>Proof</u>. Since \underline{z} is interior to the set of strict convexity for f, for some neighborhood \underline{O} of \underline{z} , each \underline{x} in \underline{O} is a point of strict convexity for f. Now, suppose \underline{z} is not a point of super convexity for f. Then, \underline{D} contains a point y, other than \underline{z} , for which

$$f(y) \leq f(z) + (y-z) \cdot \nabla f(z).$$

But, since \underline{z} is a point of convexity, Remark A.1 yields

$$f(y) \geq f(z) + (y-z) \cdot \nabla f(z),$$

and therefore

$$f(\underline{y}) = f(\underline{z}) + (\underline{y} - \underline{z}) \cdot \nabla f(\underline{z}).$$
(A.10)

Let α , with $0 < \alpha < 1$, be such that the point

$$\underset{\sim}{\mathbf{x}} = \alpha \underset{\sim}{\mathbf{y}} + \beta \underset{\sim}{\mathbf{z}}, \qquad \beta = 1 - \alpha$$

is in \underline{O} , and hence is a point of strict convexity. Of course, since \underline{z} is a point of convexity,

$$f(\underline{x}) \geq f(\underline{z}) + (\underline{x}-\underline{z}) \cdot \nabla f(\underline{z}).$$

On multiplying (A.10) by α and subtracting the result from this last relation, one obtains

$$\begin{split} f(\underline{x}) &- \alpha f(\underline{y}) \geq (1 - \alpha) f(\underline{z}) + [\underline{x} - (\alpha y + (1 - \alpha) \underline{z})] \cdot \nabla f(\underline{z}) &= \beta f(\underline{z}) + \underline{0} \cdot \nabla f(\underline{z}); \\ \\ \text{i.e.} & f(\underline{x}) \geq \alpha f(\underline{y}) + \beta f(\underline{z}), \end{split}$$

which contradicts the fact that \underline{x} is a point of strict convexity. Hence, the supposition that \underline{z} is not a point of super convexity leads to a contradiction; q.e.d.

The following remark gives another condition on a point of convexity sufficient to assure that it be a point of super convexity. This condition, although it is not directly employed in the present essay, is worth mentioning because it has a familiar geometrical interpretation.

<u>Remark</u> A.4. Let \underline{z} in \underline{D} be a point of convexity for f. If \underline{D} contains no point \underline{y} of convexity for f such that $\nabla f(\underline{y}) = \nabla f(\underline{z})$ and $\underline{y} \neq \underline{z}$, then \underline{z} is a point of super convexity for f.

In other words, if a point \underline{z} of convexity for f is not a point of super convexity, then there must exist another point of convexity at which f has the same gradient as at \underline{z} . Actually, the argument given below proves the following slightly stronger proposition: If \underline{z} is a point of convexity for f, then the hyperplane ℓ tangent to f at \underline{z} never crosses f; if it touches f at another point \underline{y} , then ℓ is tangent to f at \underline{y} , and \underline{y} is a point of convexity; of course, if ℓ does not touch f at any point other than \underline{z} , then \underline{z} is a point of super convexity. Proof. Since \underline{z} is a point of convexity, (A.5) holds for all \underline{x} in \underline{D} . Thus, the present remark will be proved if it is shown that each point \underline{y} in \underline{D} for which (A.10) holds is such that $\nabla f(\underline{y}) = \nabla f(\underline{z})$ and is also a point of convexity for f. Let \underline{y} be a point in \underline{D} obeying (A.10), and let \underline{h} be an arbitrary vector in \underline{R}^n . Because \underline{D} is an open set, there is a $\delta > 0$ such that, for each ω in (0, δ), the vector $\underline{y} + \omega \underline{h}$ is in \underline{D} , and (A.5) yields

$$f(\underline{y}+\omega\underline{h}) \geq f(\underline{z}) + (\underline{y}+\omega\underline{h}-\underline{z})\cdot\nabla f(\underline{z}),$$

which, by (A.10), can be written

$$\frac{f(\underline{y}+\omega\underline{h}) - f(\underline{y})}{\omega} - \underline{h} \cdot \nabla f(\underline{z}) \geq 0.$$

Since this last relation holds for all ω in (0, δ), it implies

$$[\nabla f(y) - \nabla f(z)] \cdot h \geq 0,$$

and, since <u>h</u> was chosen arbitrarily, one can conclude that $\nabla f(\underline{y}) = \nabla f(\underline{z})$. Because (A.5) holds for all <u>x</u> in <u>D</u>, it now follows from (A.10) that

$$f(\underline{x}) \geq f(\underline{z}) + (\underline{x}-\underline{z}) \cdot \nabla f(\underline{z}) = f(\underline{y}) + (\underline{x}-\underline{y}) \cdot \nabla f(\underline{z}) = f(\underline{y}) + (\underline{x}-\underline{y}) \cdot \nabla f(\underline{y}),$$

for all \underline{x} in \underline{D} , and thus, in view of Remark A.1, \underline{y} is a point of convexity for f; q.e.d.

Remark A.4 has the following converse.

Remark A.5. If z is a point of convexity for f, if y is a point of super convexity for f, and if $\nabla f(y) = \nabla f(z)$, then y = z.

Proof. Suppose $y \neq z$. Since z is a point of convexity, Remark A.1 yields

$$f(y) \geq f(z) + (y-z) \cdot \nabla f(z),$$

and since y is a point of super convexity,

$$f(z) > f(y) + (z-y) \cdot \nabla f(y).$$

Addition of these relations yields

$$0 > (\underline{y}-\underline{z}) \cdot [\nabla f(\underline{z}) - \nabla f(\underline{y})],$$

which is impossible, because $\nabla f(z) - \nabla f(y) = 0$. Hence y = z; q.e.d.

Henceforth, let us assume that the point $\underline{0} = (0, \dots, 0)$ is in \underline{D} . When \underline{D} has the form (A.1), this assumption will be met if $b_i > 0$ for $i = 1, \dots, n$. For Remarks A.6 and A.7, and Lemmata A.1 and A.2 below, it is not necessary to assume that f is differentiable on \underline{D} . <u>Remark</u> A.6. Suppose $f(\underline{0}) = 0$, and let \underline{z} in $\underline{\mathbb{R}}^n$ be given. If for some $\mu > 0$ the vector $\mu \underline{z}$ is a point of convexity for f, then for each $\nu \ge \mu$ with $\nu \underline{z}$ in \underline{D} ,

$$\frac{f(\nu_z)}{\nu} \geq \frac{f(\mu_z)}{\mu} . \qquad (A.11)$$

Proof.[#] If $\nu = \mu$, (A.11) is trivially true; hence one can assume $\nu > \mu$. #The argument used here is well known; cf. Eggleston [1958, 1], p. 47.

Since μz is a point of convexity for f,

$$f(\mu z) \leq \alpha f(x) + (1-\alpha)f(y),$$

whenever $\underset{\sim}{x}$ and $\underset{\sim}{y}$ are in $\underline{\underline{D}},$ and

$$\mu z = \alpha x + (1-\alpha)y, \qquad 0 < \alpha < 1.$$

Hence, if

$$\alpha = \mu/\nu, \qquad x = \nu z, \qquad y = 0,$$

then

$$f(\mu z) \leq \frac{\mu}{\nu} f(\nu z) + (1 - \frac{\mu}{\nu}) f(0),$$

which, because f(0) = 0, reduces to (A.11); q.e.d.
The proof just given obviously can be tightened to yield

Remark A.7. Suppose $f(\underline{0}) = 0$. If $\mu \underline{x}$, with $\mu > 0$, $\underline{x} \neq \underline{0}$, is a point of strict convexity for f, then, for each $\nu > \mu$ with $\nu \underline{x}$ in <u>D</u>,

$$\frac{f(\nu x)}{\nu} > \frac{f(\mu x)}{\mu}$$

<u>Definition</u> A.1. A function f mapping <u>D</u> into <u>R</u> is <u>convex</u> for <u>large</u> <u>argument</u> if there exists an open set <u>S</u> in $\underline{\mathbb{R}}^n$, with closure <u>S</u>, such that

- (1) $\underline{\underline{S}}$ is a compact subset of $\underline{\underline{D}}$,
- (2) every point in $\underline{D} \underline{S}$ is a point of convexity for f.

Definition A.2. If f(x) > 0, for all x in D with $x \neq 0$, then f is said to be <u>positive</u> <u>definite</u> on D.

In the statements of Lemmata A.1 and A.2 below, a norm $\|\cdot\|$ on \mathbb{R}^n is employed. Although the choice of norm is immaterial to the proofs given, it is worth mentioning that in applications $\|\cdot\|$ is the function defined by

$$\|\mathbf{y}\| = |\mathbf{y}_1| + |\mathbf{y}_2| + \dots + |\mathbf{y}_n|,$$
 (A.12)

where, of course, $y = (y_1, \dots, y_n)$ and $|y_i|$ is the absolute value of y_i .

Lemma A.1. Let f be a continuous function mapping \underline{D} into \underline{R} with $f(\underline{0}) = 0$. If f is convex for large argument and positive definite on \underline{D} , then for each d > 0 there exists an A = A(d) > 0 such that

$$\inf_{\underline{\mathbf{T}}_{\underline{\mathbf{d}}}} \frac{f(\underline{\mathbf{x}})}{\|\underline{\mathbf{x}}\|} \ge \mathbf{A}$$
(A.13)

where

$$\underline{\underline{T}}_{d} = \{ \underline{x} \mid \underline{x} \in \underline{\underline{D}} \text{ and } \| \underline{x} \| \ge d \}.$$
 (A.14)

<u>Proof.</u> By assumption, \underline{D} is an open subset of $\underline{\mathbb{R}}^n$, and $\underline{0}$ is in \underline{D} . Let \underline{S} be the precompact open set in the Definition A.1. Clearly, there exists an open set \underline{M} such that $\underline{0}$ is in \underline{M} , \underline{S} is a subset of \underline{M} , and the closure \underline{M} of \underline{M} is a compact subset of \underline{D} . Let d > 0 be given. Since $\underline{0}$ is not in \underline{T}_d , and f is positive definite, we have

$$\frac{f(\mathbf{x})}{\|\mathbf{x}\|} > 0, \qquad (A.15)$$

for each \underline{x} in $\underline{\underline{T}}_d,$ and since $\underline{\underline{T}}_d\cap \underline{\underline{M}}$ is compact, if we put

$$B(d) = \begin{cases} 1 \text{ when } \underline{\underline{T}}_{d} \cap \underline{\underline{M}} = \phi, \\ \vdots & f \\ \underline{\underline{T}}_{d} \cap \underline{\underline{M}} & \underline{\underline{f}(\underline{x})} \\ \underline{\underline{T}}_{d} \cap \underline{\underline{M}} & \|\underline{x}\| \end{cases} \text{ when } \underline{\underline{T}}_{d} \cap \underline{\underline{M}} \neq \phi, \end{cases}$$

then

$$B(d) > 0.$$
 (A.16)

Of course, $\underline{\underline{D}} = \underline{\underline{M}} \cup (\underline{\underline{D}} - \underline{\underline{M}})$, and therefore $\underline{\underline{T}}_d$ is contained in $(\underline{\underline{T}}_d \cap \underline{\underline{M}}) \cup (\underline{\underline{D}} - \underline{\underline{M}})$, which implies that

$$\inf_{\underline{\mathbf{I}}_{d}} \frac{\mathbf{f}(\underline{\mathbf{x}})}{\|\underline{\mathbf{x}}\|} \geq \min \left\{ \begin{array}{l} \mathbf{B}(\mathbf{d}), & \inf_{\mathbf{f}} \frac{\mathbf{f}(\underline{\mathbf{z}})}{\|\underline{\mathbf{z}}\|} \\ & \underline{\mathbf{D}} - \underline{\mathbf{M}} \\ \end{array} \right\}. \tag{A.17}$$

To estimate the second term in parenthesis above, let \underline{F} be the frontier of \underline{M} , i.e. $\underline{F} = \underline{M} - \underline{M}$. Since $\underline{0}$ is not in \underline{F} , (A.15) holds for each \underline{x} in \underline{F} , and since \underline{F} is compact, if one puts

$$\gamma = \inf_{\underline{F}} \frac{f(\underline{x})}{\|\underline{x}\|}, \qquad (A.18)$$

one has

$$\gamma > 0. \tag{A.19}$$

Furthermore, because \underline{F} is a subset of \underline{D} which does not intersect \underline{S} , each point in \underline{F} is a point of convexity for f. Now, suppose \underline{z} is in $\underline{D} - \underline{M}$. Then $\underline{z} \neq \underline{0}$, and, for some μ in (0,1), the vector $\mu \underline{z}$ is in \underline{F} , and by (A.18),

$$\frac{f(\mu z)}{\|\mu z\|} \geq \gamma. \tag{A.20}$$

Since μz is a point of convexity for f, Remark A.6 yields

$$\frac{f(z)}{1} \geq \frac{f(\mu z)}{\mu} ,$$

i.e.

$$\frac{\mathbf{f}(\underline{z})}{\|\underline{z}\|} \geq \frac{\mathbf{f}(\underline{\mu}\underline{z})}{\|\underline{\mu}\|_{\underline{z}}\|} = \frac{\mathbf{f}(\underline{\mu}\underline{z})}{\|\underline{\mu}\underline{z}\|},$$

and, by (A.20),

$$\frac{f(z)}{\|z\|} \geq \gamma.$$

Thus

$$\inf_{\underline{D}} \frac{f(\underline{z})}{\|\underline{z}\|} \geq \gamma.$$
(A.21)

It follows from (A.16), (A.19), (A.21), and (A.17) that A(d), defined by

A
$$\underline{\det}$$
 min{B(d), γ },

is positive and obeys (A.13); q.e.d.

Lemma A.1 is employed to prove

Lemma A.2. Let \mathscr{B} be a set endowed with a finite, positive measure \mathcal{MV} , and let f be a continuous function mapping \underline{D} into \underline{R} with $f(\underline{0}) = 0$. If f is convex for large argument and positive definite on \underline{D} , then for each $\epsilon > 0$ there exists a $\delta > 0$ such that every \mathcal{MV} -measurable function g mapping \mathscr{B} into \underline{D} with[#]

$$\int_{\mathcal{B}} \mathbf{f} \circ \mathbf{g} \, \mathrm{d} \mathbf{m} < \delta, \qquad (A.22)$$

 $\frac{\#}{f \circ g}$ denotes the function mapping \mathcal{B} into $\underline{\mathbb{R}}$ defined by $f \circ \underline{g}(X) = f(\underline{g}(X))$.

obeys

$$\int_{\mathcal{B}} \|g\| d_{\mathcal{M}} < \epsilon.$$
 (A.23)

Proof.[#] Let $\epsilon > 0$ be given, and then put, for each *mu*-measurable function [#]The proof given here employs an argument used by Coleman and Greenberg in a less general context: vid. [1967, 1], Proof of Remark 4.2.

g taking \mathcal{B} into \underline{D} ,

$$\mathcal{S} = \left\{ X \mid X \in \mathcal{B} \text{ and } \|_{\mathfrak{S}}(X) \| < \frac{\epsilon}{2M} \right\},$$
$$\widetilde{\mathcal{S}} = \mathcal{B} - \mathcal{S} = \left\{ X \mid X \in \mathcal{B} \text{ and } \|_{\mathfrak{S}}(X) \| \ge \frac{\epsilon}{2M} \right\},$$

with M = m(B). Clearly,

$$\int_{\mathcal{B}} \|g\| \, dm = \mathcal{L}_1 + \mathcal{L}_2, \qquad (A.24)$$

where

$$\boldsymbol{\ell}_1 = \int_{\boldsymbol{\beta}} \|\boldsymbol{g}\| \, \mathrm{d}\boldsymbol{m} \,, \qquad \boldsymbol{\ell}_2 = \int_{\boldsymbol{\beta}} \|\boldsymbol{g}\| \, \mathrm{d}\boldsymbol{m} \,,$$

and, by the definition of β ,

$$\boldsymbol{\ell}_1 \leq \frac{\epsilon}{2} . \tag{A.25}$$

Now, since fog does not vanish anywhere on $\widetilde{\mathscr{S}}$, one can write

$$\mathcal{L}_{2} = \int_{\widetilde{g}} \frac{\|\mathbf{g}\|}{\mathbf{f} \circ \mathbf{g}} \mathbf{f} \circ \mathbf{g} \, \mathrm{d} \mathbf{m} \, .$$

By Lemma A.1 and the assumptions made here about f,

$$\sup_{\widetilde{\underline{S}}} \frac{\|\underline{g}\|}{f \circ g} \stackrel{\underline{def}}{=} \sup_{X \in \widetilde{\underline{S}}} \frac{\|\underline{g}(X)\|}{f(\underline{g}(X))} = \frac{1}{A(\frac{\epsilon}{2M})},$$

where

$$A\left(\frac{\epsilon}{2M}\right) > 0.$$
 (A.26)

Hence

$$\mathcal{L}_{2} \geq \frac{1}{A\left(\frac{\epsilon}{2M}\right)} \int_{\mathcal{B}} f \circ g dm,$$

and, in view of (A.24) and (A.25),

$$\int_{\mathcal{B}} \|\underline{g}\| \, d\boldsymbol{m} \leq \frac{\underline{\epsilon}}{2} + \frac{1}{A\left(\frac{\underline{\epsilon}}{2M}\right)} \int_{\mathcal{B}} \underline{f} \circ \underline{g} \, d\boldsymbol{m} \, .$$

It is evident from (A.26) and this last relation that if one puts

$$\delta \quad \stackrel{\underline{\mathsf{def}}}{=} \quad \frac{\epsilon}{2} \operatorname{A} \left(\frac{\epsilon}{2\mathrm{M}} \right) ,$$

then δ is positive when ε is, and (A.23) holds when (A.22) holds; q.e.d.

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Double underlining, as in \underline{D} , \underline{S} , \underline{F} , \underline{M} , \underline{Z} , \underline{O} , \underline{T}_d , etc., indicates that the symbol is to be set in sans serif type, using the Latin alphabet.

Single underlining denotes, as usual, italic type.

Wavy underlining, as in χ , χ , χ , χ , χ , T, etc., indicates that the symbol is to be set in boldface type.

Superposed bars, as in $\overline{\epsilon}$, $\overline{\theta}$, \overline{p} , $\overline{\underline{S}}$, $\overline{\underline{M}}$, $\overline{\underline{T}}$, $\overline{\underline{q}}$, $\overline{\kappa}$, etc., are to be printed as shown.