THERMODYNAMICS BASED ON A
WORK AXIOM

by

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1. Introduction.

In recent years COLEMAN [2], [3], COLEMAN and MIZEL [5], GURTIN [9] and WANG and BOWEN [14] have described rational theories of thermodynamics for materials with memory. Each of these theories adopts the Second Law, as expressed by the Clausius-Duhem inequality, as a fundamental axiom. In this paper I show that, for a broad class of materials, all the results given by these theories concerning relationships between stress, entropy and free energy can be obtained by a different approach. This approach involves taking an axiom about work as fundamental in place of the Clausius-Duhem inequality.

The materials considered here are qualitatively viscoelastic in the sense that they behave elastically in suitable fast and slow processes and also exhibit a mild kind of fading memory. We assume that a collection of histories, whose values can, for example, be thought of as strain and temperature pairs, is at our disposal and we assume that an appropriate concept of work can be introduced by way of a work functional defined for processes whose histories are in the collection. The collection of histories and the work functional are required to satisfy axioms giving precise meaning to the qualitative behaviour described above. It turns out that the generalised stress, consisting of a Piola-Kirchhoff stress and the negative of an entropy, can be constructed from the work functional and that the work done in a time interval can be represented, in the usual way, as the integral of the (generalised) stress power. In section 3 we lay down our fundamental thermodynamic axiom, which is an assertion about work.† More explicitly, let f be any history in the collection and let us consider processes F which are <u>closed connections</u> of f in the sense that the history of F up to some time s coincides with f and F assumes the value F(s) at some later time $t > s$ i.e. $F(t) = F(s)$. If the work done in the process F between the times s and t is negative we say, following BREUER and ONAT [1], that the material does useful work. Our thermodynamic axiom is the assertion that no matter which closed connection of a given history is chosen there is a finite bound on the amount of useful work which can be extracted from the history. Of course, the amount of useful work which can be extracted depends on the given history. As I have pointed out elsewhere [8], the thermodynamic axiom adopted here is implicit in, for example, Coleman's theory which is based on the Clausius-Duhem inequality.

After setting out our axioms we devote sections 4 and 5 to constructing a function which can justifiably be called a free energy function. That is to say, the existence of free energy appears as a natural outcome of the present approach. In sections 6 and 7 we discuss various ramifications of the construction and then we show, in section 8, how our concepts can be fruitfully applied to determining restrictions on the relaxation function of a linear viscoelastic material necessary for compatibility with thermodynamics. Restrictions are also found on the

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† Cf. The extensive literature relating work theorems and hyperelasticity cited by TRUESDELL and NOLL [13] .

infinitesimal relaxation function which results when the stress is approximately linear viscoelastic. In the final section we give simple examples of one dimensional viscoelastic materials compatible with thermodynamics and compute their free energy functions explicitly.

2. Preliminaries, Work, Generalised Stress.

With the aim of defining work and of formulating its properties we begin this section by introducing certain classes of functions called histories and processes.

Let H be any real finite dimensional inner product space of elements a,b,c, ... with U any non-empty connected open subset of H. Inner products in H are written as $a \cdot b$ and norms as $|a|$. Once we have chosen H and U they are to be fixed throughout our discussion. The reader should keep three examples in mind. The first, and the most important for applications to general continuum mechanics, is obtained by taking H to be the ten dimensional direct sum $\mathcal{L} \oplus$ reals, where $\mathcal{L}$ is the space of all endomorphisms on the translation space of euclidean space, and where the inner product in H is

$$(L,\sigma) \cdot (M,\tau) = \text{trace}\,(LM^T) + \sigma\tau \tag{2.1}$$

The appropriate subset is

$$U = \{(L,\sigma) \in H : \det L > 0,\ \sigma > 0\} \tag{2.2}$$

An element (F,θ) in U is interpreted as an ordered pair formed from a deformation gradient F and an absolute temperature θ. For the second example we take both H and U to be the six dimensional space of all symmetric endomorphisms on the translation space of euclidean space with inner product

$$L \cdot M = \operatorname{trace}(LM) \tag{2.3}$$

and interpret the elements of H as infinitesimal strain tensors. This example enters in applications to isothermal linear viscoelasticity. In the final section 9 one dimensional situations are treated and H and U are taken to be the real numbers, interpreted once again as strains.

Having introduced H and U let us agree to say that a function f on $(0,\infty)$ with values in U is *admissible* if f is piecewise smooth on every finite subinterval of $(0,\infty)$, and if the limits $f(0+), f(t-), f(t+)$ are in U for each $t > 0$. The constant function e^* on $(0,\infty)$ with value e in U provides a simple example of an admissible function. The concepts extension, connection and section play a crucial role in our theory. They are defined as follows. The admissible function g is an *extension* of the admissible function f if there is a number $\tau > 0$ such that $g(s+\tau) = f(s)$ for $s > 0$ and g is continuous and piecewise smooth on $(0,\tau]$. If this extension g of f is continuous at τ we say that it is a *connection* of f or, more precisely, that it *connects* f to *the value* $e = g(0+)$ in U. If in addition to being a connection of f, g has $g(0+) = f(0+)$ we say that g is a *closed connection* of f. Lastly, the admissible function g

is a section of the admissible function f if, for some $\tau > 0$, $g(s) = f(s+\tau)$ for $s > 0$.

For our purposes certain classes of admissible functions enter in a natural way. We call a class $\mathscr{P}$ of admissible functions a collection of histories and call the functions in $\mathscr{P}$ histories if $\mathscr{P}$ has the following properties:

P (i) All constant admissible functions are in $\mathscr{P}$ i.e. for each e in U the constant function e^* is in $\mathscr{P}$.

(ii) $\mathscr{P}$ is closed under extension i.e. if f is in $\mathscr{P}$ and g is an extension of f then g is in $\mathscr{P}$.

(iii) $\mathscr{P}$ is closed under section i.e. if f is in $\mathscr{P}$ and g is a section of f then g is in $\mathscr{P}$.

An example of a collection of histories is provided by the minimal collection, defined as the class of all admissible functions f with the property that f is constant on an interval (τ,∞) for some $\tau \geq 0$. Any collection of histories contains the minimal collection. From now on we assume that some fixed collection $\mathscr{P}$ of histories is available to us. It should be noted that certain linear extensions of histories are in $\mathscr{P}$: let f be any history, a any element of U and b any element of B(a), the largest open ball with centre a contained in U, and define, for some $\tau > 0$, a function g on $(0,\infty)$ by $g(s) = f(s-\tau)$ for $s > \tau$ and $g(s) = b + \frac{s}{\tau}(a-b)$ for $0 \leq s \leq \tau$. Then g is necessarily an extension of f linear on $(0,\tau)$ and, by (ii), g is in $\mathscr{P}$.

With any U-valued function F on $(-\infty,\infty)$ and any number t we can associate a function F^t defined on $(0,\infty)$ by

$$F^t(s) = F(t-s) , \quad s > 0 . \qquad (2.4)$$

If for every number t the function F^t is a history in $\mathcal{P}$ we shall say that F is a *process* and call F^t the *history of* F *up to* t. Examples of processes are provided by paths. A process F is a path if there are elements a,b in U and numbers s,t such that $u < s$ implies $F(u) = a$ and $u > t$ implies $F(u) = b$. If F is a path with $F(-\infty) = F(\infty)$ we call it a *closed path*; if it is continuous a *continuous path*.

With these preliminary definitions we can introduce work by assuming that with each process F and each open interval (s,t) on which F is smooth there is associated a number $w(F,s,t)$ called the *work done in the process* F *on the interval* (s,t). The function $w(\cdot,\cdot,\cdot)$ will sometimes be referred to as the *work functional*. The dependence of $w(F,s,t)$ on F,s and t is restricted by an axiom set out below.

The key ideas giving the work functional its structure are that, for any process F, $w(F,\cdot,\cdot)$ is additive when regarded as a set function on intervals and that, on a suitably small interval (s,t), $w(F,s,t)$ can be approximated by the work done in certain linear extensions of the history F^s. To make the latter precise let f be any history, τ any positive number, a any element of U and b any element of the open ball $B(a)$. Define a process $F(f,a,b,\tau)$ by the conditions $F^0(f,a,b,\tau) = f$, $F(f,a,b,\tau)(u) = a+\frac{u}{\tau}(b-a)$ for $0 \leq u \leq \tau$, and $F(f,a,b,\tau)(u) = b$ for $u > \tau$. Then $F(f,a,b,\tau)(0) = a$ and so $F(f,a,b,\tau)$ has a jump discontinuity at $u=0$ if $a \neq f(0+)$. Also

$F(f,a,b,\tau)(\tau) = b$. The number $w(F(f,a,b,\tau),0,\tau)$ is defined and is the work done in a process going from value a to value b at a uniform rate $(b-a)/\tau$ in the presence of the history f . As τ is made small $w(F(f,a,b,\tau),0,\tau)$ represents the work done in going from a to b at a higher and higher uniform rate. If the limit

$$\lim_{\tau \to 0+} w(F(f,a,b,\tau),0,\tau) = \Sigma(f,a,b) \tag{2.5}$$

exists we can interpret $\Sigma(f,a,b)$ as the work done in jumping instantaneously from the value a to the value b in the presence of the history f. We assume that the work done in a process on a suitably small interval can be approximated by Σ in the sense of the axiom:

W1 (i) Let f be any history in $\mathcal{P}$, and a any element of U. Then the limit in (2.5) exists and defines a function $\Sigma(f,a,\cdot)$ on $B(a)$ which is differentiable at a.

(ii) If F is any process smooth on (s,t) then the function $w(F,s,\cdot)$ can be extended to a smooth function on $[s,t]$ and can be approximated at s by Σ according to the formula

$$w(F,s,u) = \Sigma(F^s, F(s+), F(u)) + o(u-s) \quad \text{as} \quad u \to s+ .$$

Furthermore $w(F,\cdot,\cdot)$ is additive in the sense that if $s < u < v < t$ then

$$w(F,s,u) + w(F,u,v) = w(F,s,v) .$$

Part (i) of axiom WI enables us to define the *generalised stress* to be the function S on $\mathcal{P} \times U$ with values in H given by

$$S(f,a) = \text{grad}_b \Sigma(f,a,b)\Big|_{b=a} . \tag{2.6}$$

That is to say, the generalised stress enters through the smoothness assumption W1(i) on the work functional. Returning for the moment to the examples cited at the beginning of this section we note that when H is the ten dimensional space $\mathcal{L} \oplus$ reals the values of S are interpreted as ordered pairs $(P, -\eta)$ where P is a Piola-Kirchhoff stress tensor in $\mathcal{L}$ and the number η is an entropy. In the second example H is a space of symmetric endomorphisms and the values of S are interpreted as symmetric stress tensors whilst in the one dimensional case covered by the third example the values of S are real numbers.

Axiom W1 implies that the work functional can be represented in terms of the generalised stress according to the formula which is usually taken as its definition.

Proposition 1. If the process F is smooth on (s,t) with derivative $\dot{F}$ then

$$w(F,s,t) = \int_s^t S(F^u, F(u)) \cdot \dot{F}(u)\, du \,. \qquad (2.7)$$

Proof. Letting $u \to s+$ in the second equation in WI(ii) tells us that $w(F,s,s) = 0$ and so it suffices to prove that the derivative of $w(F,s,\cdot)$, which exists by hypothesis, has value $S(F^u, F(u)) \cdot F(u)$ at each u in (s,t). If F is smooth on (s,t) then it is a fortiori smooth on a subinterval (u,v) of (s,t) and so

$$w(F,u,v) = \Sigma(F^u, F(u), F(v)) + o(v-u) \,.$$

as $v \to u+$. It follows that $\Sigma(F^u, F(u), F(u)) = 0$ and consequently the definition (2.5) of the generalised stress implies

$$\Sigma(F^u, F(u), F(v)) = S(F^u, F(u)) \cdot (F(v) - F(u)) + o(|F(v) - F(u)|)$$

as $v \to u+$. Thus

$$w(F,u,v) = S(F^u,F(u))\cdot(F(v)-F(u)) + o(|F(v)-F(u)|) + o(v-u)$$

as $v \to u+$ and the result follows on observing that $w(F,s,v)-w(F,s,u) = w(F,u,v)$. Q.E.D.

It is clear that determinism has already been built into the theory via axiom W1 in the sense that the values of the work and generalised stress depend on processes through the past and not through the future. Also it is clear that the formula (2.7) can be used as the definition of *the work done in a process* F *on an interval* (s,t) *on which* F *is continuous and piece-wise smooth*. Furthermore, if F is a continuous path, its derivative $\dot{F}$ has compact support and we can define *the work done on the continuous path* F to be

$$w(F) = w(F,-\infty,\infty) .$$

We close this section by stating some smoothness assumptions on the generalised stress. Given any function Ω on $\mathcal{P} \times U$ let us define the *equilibrium response function* Ω^* *for* Ω on U by $\Omega^*(e) = \Omega(e^*,e)$ and call $\Omega(f,\cdot)$ on U the *instantaneous response function for* Ω *and the history* f. The assumptions on S are

S (i) The equilibrium response function $S^*(\cdot)$ is continuous.

(ii) For any history f in $\mathcal{P}$ the instantaneous response function $S(f,\cdot)$ is continuous.

(iii) If F is any process and t any number then

$$\lim_{u\to t\pm} S(F^u,F(u)) = S(F^t,F(t\pm))$$

3. Axioms For Work, The Thermodynamic Axiom.

We begin this section by imposing further restrictions on the work stating that our materials have a mild type of fading memory and behave elastically in certain slow and fast processes. We then give an example of a collection of histories and a work functional obeying axioms P,S,W1,W2,W3 and W4. Finally we close the section by motivating and enunciating the vital thermodynamic axiom W5 and drawing some conclusions from it.

The fading memory axiom is;

W2 (*Mild Fading Memory*). *Let* f *be any history in* $\mathcal{P}$, *let* F *be any continuous path and define a sequence of processes* F_n *by requiring that* $F_n^s = f$ *and* $F_n(t) = F(t-n)$ *for* $t \geq s$ (*see Fig.* 1). *Then*

$$w(F_n, s, \infty) \to w(F) \quad \text{as} \quad n \to \infty .$$

Axioms W3 and W4 express results of a kind which are known to hold in linear viscoelasticity (GURTIN and HERRERA [10]). W3 states that the work done in suitably retarded paths may be computed using the equilibrium response function S^* whilst W4 states that the work done in suitably accelerated processes may be computed using an instantaneous response function $S(f,\cdot)$. Before stating the axioms we make the following definitions. If F is any continuous path and s,t are any numbers such that $u < s$ implies $F(u) = F(-\infty)$ and $u > t$ implies $F(u) = F(\infty)$ then we say that a sequence of processes F_n defined by

$F_n(u) = F(-\infty)$ for $u < s$ and $F_n(u) = F(s+\frac{1}{n}(u-s))$ for $u \geq s$ is a *sequence of retardations* of F. If f is any history in $\wp$ and F,s,t are as before, we say that the sequence of processes F_n defined by requiring that $F_n^s = f$ and $F_n(u) = F(s+n(u-s))$ for $u \geq s$ (see Fig. 2) is a *sequence of accelerated processes*. The axioms are

W3 (Elastic Behaviour in Slow Processes). Let F be any continuous path and F_n the sequence of retardations of F defined above. Then

$$w(F_n) \to \int_s^t S^*(F(u))\cdot\dot{F}(u)\,du \quad \text{as} \quad n \to \infty .$$

W4 (Elastic Behaviour in Fast Processes). Let f be any history in $\wp$, F any continuous path and F_n the sequence of accelerated processes defined above. Then

$$w(F_n,s,\infty) \to \int_s^t S(f,F(u))\cdot\dot{F}(u)\,du \quad \text{as} \quad n \to \infty .$$

It is not hard to find examples of collections of histories and work functionals fulfilling all the requirements we have set down so far. For example let λ be any positive number and let $\wp$ be the class of admissible functions f with $\int_0^\infty e^{-\lambda s}|f(s)|ds < \infty$. The class $\wp$ is a collection of histories. It may be thought of as a vector space with the usual pointwise definitions of addition and scalar multiplication and then the set $\wp \times U$ can be regarded as a subset of the normed vector space $\wp \oplus H$ with norm

$$\|(f,e)\| = \int_0^\infty e^{-\lambda s}|f(s)|ds + |e| .$$

Let $S: \wp \times U \to H$ be the restriction to $\wp \times U$ of some compact function on $\wp \oplus H$ i.e. a function which is continuous and maps bounded sets into pre-compact sets. Then if we adopt the function S as the generalised stress and define work by the formula (2.7) axioms P,S,W1,W2,W3 and W4 hold. For the sake of illustrating the type of argument needed to establish that the axioms do hold we prove W4.

If f,F,s,t,F_n are all as in the statement of W4 then

$$w(F_n,s,\infty) = \int_s^\infty S(F_n^{\,u},F_n(u))\cdot\dot{F}_n(u)\,du .$$

On making the change of variable $v = s + n(u-s)$ it follows that

$$w(F_n,s,\infty) = \int_s^t S(F_n^{\,s+\frac{1}{n}(v-s)},F(v))\cdot\dot{F}(v)\,dv .$$

Let us show next that for each v in (s,t)

$$S(F_n^{\,s+\frac{1}{n}(v-s)},F(v)) \to S(f,F(v)) , \quad \text{as} \quad n \to \infty ,$$

by showing that, as $n \to \infty$,

$$\|(F_n^{\,s+\frac{1}{n}(v-s)},F(v)) - (f,F(v))\| = \int_0^\infty e^{-\lambda\sigma}|F_n^{\,s+\frac{1}{n}(v-s)}(\sigma) - f(\sigma)|\,d\sigma \to 0 \tag{3.1}$$

and appealing to the continuity of S. We have

$$\int_0^\infty e^{-\lambda\sigma}|F_n^{s+\frac{1}{n}(v-s)}(\sigma) - f(\sigma)|d\sigma = \int_0^\infty e^{-\lambda\sigma}|F_n(s+\tfrac{1}{n}(v-s)-\sigma) - f(\sigma)|d\sigma$$

$$= \int_0^{\frac{1}{n}(v-s)} e^{-\lambda\sigma}|F(v-n\sigma) - f(\sigma)|d\sigma$$

$$+ \int_{\frac{1}{n}(v-s)}^\infty e^{-\lambda\sigma}|f(\sigma-\tfrac{1}{n}(v-s)) - f(\sigma)|d\sigma$$

$$\leq \max_u |F(u)| \int_0^{\frac{1}{n}(v-s)} e^{-\lambda\sigma}d\sigma + \int_0^{\frac{1}{n}(v-s)} e^{-\lambda\sigma}|f(\sigma)|d\sigma$$

$$+ e^{-\frac{\lambda}{n}(v-s)} \int_0^\infty e^{-\lambda\sigma}|f(\sigma+\tfrac{1}{n}(v-s) - f(\sigma)|d\sigma$$

$$\to 0 \text{ as } n\to\infty \text{ for each } v \text{ in } (s,t) ,$$

which proves (3.1). Furthermore, we have the estimate

$$\|(F_n^{s+\frac{1}{n}(v-s)}, F(v))\| = |F(v)| + \int_0^\infty e^{-\lambda\sigma}|F_n^{s+\frac{1}{n}(v-s)}(\sigma)|d\sigma$$

$$= |F(v)| + \int_0^{\frac{1}{n}(v-s)} e^{-\lambda\sigma}|F(v-n\sigma)|d\sigma$$

$$+ \int_{\frac{1}{n}(v-s)}^\infty e^{-\lambda\sigma}|f(\sigma-\tfrac{1}{n}(v-s))|d\sigma$$

$$\leq \max_u |F(u)| \left[1 + \int_0^{\frac{1}{n}(v-s)} e^{-\lambda\sigma}d\sigma\right]$$

$$+ e^{-\frac{\lambda}{n}(v-s)} \int_0^\infty e^{-\lambda\sigma}|f(\sigma)|d\sigma$$

$$\leq (1+\tfrac{1}{\lambda})\max_u |F(u)| + \int_0^\infty e^{-\lambda\sigma}|f(\sigma)|d\sigma ,$$

holding for all v in (s,t) and all $n = 1,2,3 \ldots$ and so, by the compactness of S, the set

$$\left\{|S(F_n^{s+\frac{1}{n}(s-v)}, F(v))| \;:\; v \text{ in } (s,t),\; n = 1,2,3 \ldots\right\}$$

is bounded. Accordingly, the sequence of functions

$v \to S(F_n^{s+\frac{1}{n}(v-s)}, F(v))$ converges pointwise to the function $v \to S(f,F(v))$ on (s,t) and is uniformly bounded. The dominated convergence theorem now implies that W4 holds.

The motivation for the final axiom, which is our only axiom of a thermodynamical character, arises from considerations of the following sort. Suppose that f in $\mathcal{P}$ is any history. Let us examine processes F with the property that $F^s = f$ for some s and that F^t is a closed connection of f for some $t > s$ and let us compute the work $w(F,s,t)$ for each process of this type. For example we might define F by requiring that $F^s = f$ and $F(u) = f(0+)$ on (s,t) and in this case $w(F,s,t) = 0$ no matter what f is. If it happens that $w(F,s,t) < 0$ we say, following BREUER and ONAT [1], that *the material does useful work of amount* $-w(F,s,t)$. The following question then arises. Given the history f and given any number $N < 0$, no matter how large $|N|$ is, can we find a process F of the above type such that $w(F,s,t) < N$ i.e. such that the useful work is as large as we please? It does not seem reasonable to expect that this is possible and the last axiom is just the assertion that it is indeed impossible. More precisely, if we define **the minimal work in closed connections of the history** f to be the number

$$\mathfrak{m}(f) = \inf\{w(F,s,t) \; : \; F^s = f,\ F^t \text{ is a closed connection of } f\} \tag{3.2}$$

our assumption is

W5 (*Thermodynamic Axiom*). *For each history* f *in* $\mathcal{P}$, $\mathfrak{m}(f) > -\infty$.

A simple case in which W5 holds occurs when the generalised stress is **hyperelastic** by which we mean that there is some smooth real-valued potential K on U with gradient grad $K(e) = S(f,e)$ for every history f and every e in U. In this case the minimal work $\mathfrak{m}(f) = 0$ for every history f. An example of a collection of histories and a work functional obeying axioms P,S,W1,W2,W3,W4,W5 is discussed in the final section 9. We close this section by proving a number of miscellaneous results following rapidly from W5.

Theorem 1.

(1) For each history f in $\mathcal{P}$, $\mathfrak{m}(f) \leq 0$.

(2) For each e in U, $\mathfrak{m}(e^*) = 0$.

(3) If F,G are continuous paths with $F(-\infty) = G(\infty)$ and $F(\infty) = G(-\infty)$ then $w(F) + w(G) \geq 0$.

(4) If F is any continuous closed path then $w(F) \geq 0$.

Proof. (1) The process F defined by $F^0 = f$ and $F(u) = f(0+)$ for $u \geq 0$ has the property that F^t is a closed connection of f for any $t > 0$ and $w(F,s,t) = 0$, which proves (1).

(2),(3),(4). Suppose that F,G are continuous paths with $F(-\infty) = G(\infty) = a$, say, and $F(\infty) = G(-\infty) = b$, say. Choose a number s such that $t > s$ implies $F(t) = F(\infty)$ and define a sequence of paths F_n by requiring that $F_n^s = F^s$ and $F_n(t) = G(t-n)$ for $t \geq s$. For every large integer n, F_n is a continuous closed path with $F_n(-\infty) = F_n(\infty) = a$ (see Fig. 3) and consequently given any large n there is a number $t > s$, which depends on n, such that F_n^t is a closed connection of the constant history a^*. Thus

$$w(F_n) \geq \mathfrak{m}(a^*) .$$

But

$$w(F_n) = w(F_n,-\infty,s) + w(F_n,s,\infty) = w(F) + w(F_n,s,\infty)$$

and, by axiom W2,

$$w(F_n,s,\infty) \to w(G) \quad \text{as } n \to \infty .$$

Thus

$$w(F) + w(G) \geq \mathfrak{m}(a^*) . \tag{3.3}$$

In the special case $G = F$ and $F(-\infty) = F(\infty) = a$ we deduce that

$$2w(F) \geq \mathfrak{m}(a^*) .$$

Taking the least upper bound over all continuous closed paths F of this type gives

$$2\mathfrak{m}(a^*) \geq \mathfrak{m}(a^*) ,$$

which, by axiom W5, implies

$$\mathfrak{m}(a^*) \geq 0 .$$

Combining this inequality with (1) gives (2) and then (3) follows from (2) and (3.3). Finally (4) is a special case of (3) with $G = F$. Q.E.D.

The result (4) of Theorem 1 was established by COLEMAN [2] . In section 7 it will be extended to a result about paths which are not necessarily continuous.

4. Potentials For The Equilibrium And Instantaneous Response.

Throughout this section and the next we suppose that some collection of histories $\mathcal{P}$ and some work functional w are available to us. We speak always of the same $\mathcal{P}$ and the same w so that the adjective unique is to be taken as meaning 'uniquely determined by the choice of $\mathcal{P}$ and w.' Our primary object is to construct a free energy function for w. The construction is carried out in the next section and depends on knowing two functions $\pi(\cdot)$ and $\Phi(f,\cdot)$, the first being a potential for the equilibrium response function $S^*(\cdot)$ and the second a potential for the instantaneous response function $S(f,\cdot)$ corresponding to a history f. This section is devoted to the preliminary matter of showing that these potentials exist.

The first Lemma suffices to establish the existence of a potential in certain circumstances.

Lemma 1. *Suppose that* $T : U \to H$ *is a continuous function and that there is an element* e *in* U *with the property that the set of numbers*

$$\left\{ \int T(F(u))\cdot\dot{F}(u)\,du \; : \; F \text{ is a continuous path with } F(-\infty)=F(\infty)=e \right\} \tag{4.1}$$

is bounded below. Then there is a smooth real-valued function Γ *on* U *with* $\operatorname{grad}\Gamma = T$.

Proof. Since U is connected it suffices to show that if F is any continuous path with $F(-\infty) = F(\infty) = e$ then

$$\int T(F(u))\cdot\dot{F}(u)\,du = 0 \; .$$

If m is the greatest lower bound of the set (4.1) then

$$\int T(F(u)\cdot\dot{F}(u)du \geq m$$

for any path F of the required kind. Choosing s and t so that $u < s$ implies $F(u) = e$ and $u > t$ implies $F(u) = e$ and writing $F'(u) = F(t-u)$, $-\infty < u < \infty$, produces another path F' of this type. For this path

$$m \leq \int T(F'(u))\cdot\dot{F}'(u)du \quad = \quad -\int T(F(u))\cdot\dot{F}(u)du$$

and so

$$0 \leq \left|\int T(F(u))\cdot\dot{F}(u)du\right| \leq -m \ .$$

Also if F_n is a path which has value e everywhere except on $n(=1,2,3, \ldots\ldots)$ intervals of length $t-s$, on each of which it coincides with a translate of the restriction of F to (s,t), then F_n is of the required kind and

$$0 \leq n\left|\int T(F(u))\cdot\dot{F}(u)du\right| \quad = \quad \left|\int T(F_n(u))\cdot\dot{F}_n(u)du\right| \leq -m \ ,$$

which implies the result. Q.E.D.

It is convenient to parallel definition (3.2) and define *the minimal work in connections of the history* f *to* e in U to be

$$\mathfrak{m}(f,e) = \inf\{w(F,s,t) \ : \ F^s = f, \ F^t \text{ connects } f \text{ to } e\}. \tag{4.2}$$

Of course, $\mathfrak{m}(f) = \mathfrak{m}(f,f(0+))$. We are now in a position to prove that the equilibrium response function S^* is derivable from a potential π .

Lemma 2. *There is a smooth real-valued function* π *on* U, *unique up to an additive constant, such that, for any history* f *and any* a,b *in* U,

(1) $S^* = \text{grad}\ \pi$

(2) $\mathfrak{m}(a^*,b) = \pi(b) - \pi(a)$

(3) $\mathfrak{m}(f,a) = \pi(a) - \pi(f(0+)) + \mathfrak{m}(f)$

Proof. (1),(2). Let a,b be any elements of U and let F be any continuous path with $F(-\infty) = a$, $F(\infty) = b$. Construct from F a sequence of retardations F_n as in the statement of axiom W3. Each F_n is a continuous path with $F_n(-\infty) = a$ and $F_n(\infty) = b$ and so

$$w(F_n) \geq \mathfrak{m}(a^*,b) .$$

On letting $n \to \infty$ and using axiom W3 we deduce that

$$\int S^*(F(t)) \cdot \dot{F}(t)\,dt \geq \mathfrak{m}(a^*,b) . \qquad (4.3)$$

In particular, if $\tilde{F}$ is any closed continuous path with $\tilde{F}(-\infty) = \tilde{F}(\infty) = a$ we must have

$$\int S^*(\tilde{F}(t)) \cdot \dot{\tilde{F}}(t)\,dt \geq \mathfrak{m}(a^*,a) = \mathfrak{m}(a^*) = 0 .$$

and a direct application of Lemma 1 and the continuity of S^* shows that there is a smooth real-valued potential π on U with grad $\pi = S^*$. Furthermore, the connectedness of U implies that S^* determines π to within an arbitrary constant.

Since the potential π exists we can perform the integration in (4.3) explicitly and find the inequality

$$\pi(b) - \pi(a) \geq \mathfrak{m}(a^*,b) , \qquad (4.4)$$

holding for all elements a,b in U. Interchanging a and b gives

$$\pi(a) - \pi(b) \geq \mathfrak{m}(b^*,a) . \qquad (4.5)$$

However, according to (3) of Theorem 1, if F is any continuous path with $F(-\infty) = a$, $F(\infty) = b$ and G is any continuous path with $G(-\infty) = b$, $G(\infty) = a$ then

$$w(F)+w(G) \geq 0 \ .$$

Taking greatest lower bounds over all F,G of this type gives

$$\mathfrak{m}(a^*,b)+\mathfrak{m}(b^*,a) \geq 0 \tag{4.6}$$

and combining (4.4),(4.5) and (4.6) shows that

$$\pi(b)-\pi(a) \geq \mathfrak{m}(a^*,b) \geq -\mathfrak{m}(b^*,a) \geq \pi(b)-\pi(a) \ ,$$

which proves (2).

(3). To prove (3) we prove both

$$\mathfrak{m}(f,a) \geq \pi(a)-\pi(f(0+))+\mathfrak{m}(f) \tag{4.7}$$

and

$$\mathfrak{m}(f,a) \leq \pi(a)-\pi(f(0+))+\mathfrak{m}(f) \ . \tag{4.8}$$

Let F be any process with $F^s = f$, with F^t connecting f to a and let G be any continuous path with $G(-\infty) = a$ and $G(\infty) = f(0+)$. Define a sequence of processes F_n by requiring that $F_n{}^t = F^t$ and that $F_n(u) = G(u-n)$ for $u \geq t$ (see Fig.4(a)). Then for any large integer n there is a number $t'(n)$ with $F_n{}^{t'}$ a closed connection of f. Thus

$$\mathfrak{m}(f) \leq w(F_n,s,\infty) \ = \ w(F,s,t)+w(F_n,t,\infty) \ .$$

On letting $n \to \infty$ and using axiom W2 we deduce that

$$\mathfrak{m}(f) \leq w(F,s,t)+w(G) \ .$$

Taking the greatest lower bound over all such G and using (2) of this Lemma gives

$$\mathfrak{m}(f) \leq w(F,s,t)+\pi(f(0+))-\pi(a)$$

and now taking the greatest lower bound over all such processes F yields the inequality (4.7) .

To prove the converse inequality (4.8) let F be any process with $F^s = f$ and F^t a closed connection of f. If G is any continuous path with $G(-\infty) = f(0+)$ and $G(\infty) = a$ we can define a sequence of processes F_n by the conditions $F_n^t = F^t$ and $F_n(u) = G(u-n)$ for $u \geq t$ (see Fig. 4(b)). This time it follows that

$$\mathfrak{m}(f,a) \leq w(F_n,s,\infty) = w(F,s,t)+w(F_n,t,\infty) .$$

Letting $n \to \infty$, using axiom W2 and taking the greatest lower bound over all such paths G gives, in precisely the same way as above, the inequality

$$\mathfrak{m}(f,a) \leq w(F,s,t)+\pi(a)-\pi(f(0+)) ,$$

from which (4.8) may be deduced. Q.E.D.

Incidentally we have shown more than is claimed in the statement of Lemma 2. If F is any continuous path with $F(-\infty) = a$ and $F(\infty) = b$ and if the sequence of retardations F_n is defined as in the statement of axiom W3 then

$$w(F_n) \to \int S^*(F(t))\cdot\dot{F}(t)dt = \pi(b)-\pi(a) = \mathfrak{m}(a^*,b) .$$

That is to say we have proved

Corollary 1. Given any elements a,b in U and any $\epsilon > 0$ we can construct a continuous path G with $G(-\infty) = a$ and $G(\infty) = b$ such that

$$w(G) < \mathfrak{m}(a^*,b) + \epsilon$$

by taking G to be a suitable retardation of any continuous path F with $F(-\infty) = a$ and $F(\infty) = b$.

The results (3) of Lemma 2 and (1) of Theorem 1 show that

$$\mathfrak{m}(f,e) = \pi(e) - \pi(f(0+)) + \mathfrak{m}(f) \leq \pi(e) - \pi(f(0+)) ,$$

and so $\mathfrak{m}(f,e) < 0$ if $\pi(e) < \pi(f(0+))$. Accordingly we have

Corollary 2. If f is any history and if e in U satisfies $\pi(e) < \pi(f(0+))$ then there is a process F such that $F^s = f$, F^t connects f to e and $w(F,s,t) < 0$ i.e. we can extract useful work from a history f by choosing a suitable process connecting f to any e with $\pi(e) < \pi(f(0+))$.

The final Lemma of this section shows that if f is any history in $\mathcal{P}$ the corresponding instantaneous response function $S(f,\cdot)$ is derivable from a potential. We choose to impose a normalising condition which ensures that the potential is unique and we discuss its physical significance after proving the Lemma.

Lemma 3. There is a unique real valued function Φ on $\mathcal{P} \times U$ having both of the following properties:

(1) for each f in $\mathcal{P}$, the function $\Phi(f,\cdot)$ on U is smooth with gradient

$$\text{grad } \Phi(f,\cdot) = S(f,\cdot) ,$$

(2) for each f in $\mathcal{P}$, $\Phi(f,f(0+)) = 0$.

<u>Proof</u>. Let f be any history and F any closed continuous path with $F(-\infty) = F(\infty) = f(0+)$. If the sequence of accelerated processes F_n is the sequence considered in the statement of axiom W4 then F_n^t is a closed connection of f and so, by the definition of $\mathfrak{m}(f)$,

$$w(F_n, s, \infty) \geq \mathfrak{m}(f) .$$

Letting $n \to \infty$ and using W4 implies that

$$\int S(f, F(u)) \cdot \dot{F}(u)\, du \geq \mathfrak{m}(f)$$

for any continuous path F meeting the condition $F(-\infty) = F(\infty) = f(0+)$. The assumed continuity of $S(f,\cdot)$ and Lemma 1 now implies that there is a function ϕ on $\mathcal{P} \times U$ with the property (1). If we define

$$\Phi(f,a) = \phi(f,a) - \phi(f, f(0+))$$

then Φ satisfies both (1) and (2). This Φ must be unique for if $\bar{\Phi}$ also satisfies (1) and (2), then by (1), $\Phi(f,a) - \bar{\Phi}(f,a)$ is independent of a and, by (2), has value 0. The result follows. Q.E.D.

In order to appreciate the physical significance of the potential Φ let us suppose that a history f and an element e in U are given. Let us choose any continuous path F with $F(-\infty) = f(0+)$ and $F(\infty) = e$ and construct a sequence of accelerated processes F_n from f and F as in the statement of W4. The sequence F_n converges pointwise to a process $\tilde{F}$ with $\tilde{F}^s = f$, $\tilde{F}(s) = f(0+)$ and $\tilde{F}(u) = e$ for $u > s$ so that $\tilde{F}$ has a jump discontinuity of amount $e - f(0+)$ at s. On using W4 and Lemma 3 we deduce that as $n \to \infty$

$$w(F_n, s, \infty) \to \int S(f, F(u)) \cdot \dot{F}(u)\, du = \Phi(f,e) - \Phi(f, f(0+)) = \Phi(f,e) .$$

In other words: <u>the number</u> $\Phi(f,e)$ <u>can be interpreted as the work done in traversing the jump discontinuity of amount</u> $e - f(0+)$ <u>in the process</u> $\tilde{F}$.

5. The Free Energy.

This section contains our most important results. We shall show that for any choice of a collection of histories and a work functional satisfying axioms S,W1,W2,W3,W4,W5 one can define a function with properties which justify calling it free energy. Our definition is: the real-valued function Ψ defined on $\mathcal{P} \times U$ by the relation

$$\Psi(f,e) = \pi(f(0+)) - \mathfrak{m}(f) + \Phi(f,e) \tag{5.1}$$

is called the *free energy*. The definition can be written out in words as

{the free energy corresponding to the history f and present value e}

= {the equilibrium potential corresponding to the value f(0+)}

- {the minimal work in closed connections of f}

+ {the work done in traversing a jump discontinuity of amount e-f(0+) in the presence of the history f}

Of course, if $e = f(0+)$ there is no discontinuity and the third term in the definition disappears. Each of the functions $\pi(\cdot)$, $\Phi(\cdot,\cdot)$, $\mathfrak{m}(\cdot)$ and $\mathfrak{m}(\cdot,\cdot)$ can be expressed in terms of the free energy Ψ and the equilibrium free energy Ψ^* according to the formulae set down in

<u>Proposition</u> 2. <u>For any history</u> f <u>and any</u> e <u>in</u> U <u>the following results hold</u>:

(1) $\pi(e) = \Psi^*(e)$

(2) $\Phi(f,e) = \Psi(f,e) - \Psi(f,f(0+))$

(3) $\mathfrak{m}(f) = \Psi^*(f(0+)) - \Psi(f,f(0+))$

(4) $\mathfrak{m}(f,e) = \Psi^*(e) - \Psi(f,f(0+))$

The proofs of these results are simple applications of (2) of Theorem 1, (3) of Lemma 2 and (2) of Lemma 3.

The justification for the name free energy is the wealth of properties displayed in Theorem 2.

Theorem 2. *For the free energy* Ψ *the following statements hold*:

(1) *for each history* f *the instantaneous response function* $\Psi(f,\cdot)$ *is smooth with gradient*

$$\operatorname{grad} \Psi(f,\cdot) = S(f,\cdot) ,$$

(2) *the equilibrium response function* Ψ^* *is smooth with gradient*

$$\operatorname{grad} \Psi^* = S^* ,$$

(3) *for each history* f ,

$$\Psi(f,f(0+)) \geq \Psi^*(f(0+)) ,$$

(4) *if the process* F *is continuous and piecewise smooth on the open interval* (s,t) *and continuous at* s *and* t *then*

$$w(F,s,t) \geq \Psi(F^t,F(t)) - \Psi(F^s,F(s)) ,$$

(5) *if the process* F *is continuous and piecewise smooth on* (s,t) *and continuous at* s *and* t *then the function* $u \to \psi(u) = \Psi(F^u,F(u))$ *is differentiable almost everywhere on* (s,t) *and at each* u *in* (s,t) *at which* $\dot{\psi}(u)$ *exists*

$$S(F^u,F(u)) \cdot \dot{F}(u) \geq \dot{\psi}(u) .$$

Proof. (1) This property follows from the definition of Ψ and the construction of $\Phi(f,\cdot)$ as a potential for $S(f,\cdot)$.
(2) Property (2) is implied by (1) of Proposition 2 and the construction of $\pi(\cdot)$ as a potential for $S^*(\cdot)$.
(3) The result (3) of Proposition 2 can be written

$$\Psi(f,f(0+)) - \Psi(f(0+)) = -\mathfrak{m}(f) ,$$

from which (3) follows since (1) of Theorem 1 tells us that $\mathfrak{m}(f) \leq 0$.
(4) Let F,s,t be as in the statement of (4) and let G be any process for which $G^t = F^t$, G is continuous and piecewise smooth on $[s,\infty)$ and for which there is some $u > t$ such that $u' > u$ implies $G(u') = F(s)$ (see Fig. 5) . The history G^u is a closed connection of F^s and consequently

$$\mathfrak{m}(F^s) \leq w(G,s,\infty) = w(F,s,t) + w(G,t,\infty) .$$

On noting that G^u also connects F^t to $F(s)$ and taking the greatest lower bound over all such G we deduce the inequality

$$\mathfrak{m}(F^s) \leq w(F,s,t)+\mathfrak{m}(F^t,F(s)) ,$$

which, by (3) of Lemma 2, implies

$$w(F,s,t) \geq (\pi(F(t))-\mathfrak{m}(F^t))-(\pi(F(s))-\mathfrak{m}(F^s)) .$$

Since F is continuous at s and t, $\Phi(F^s,F(s)) = \Phi(F^t,F(t)) = 0$ and the result follows on using the definition of Ψ .
(5) If F is continuous and piecewise smooth on (s,t) and continuous at s and t and $s \leq u < u' \leq t$ then F is continuous and piecewise smooth on (u,u') and continuous at u,u' so that (4) holds and we can write

$$\int_u^{u'} S(F^v,F(v))\cdot\dot{F}(v)\,dv \geq \psi(u')-\psi(u) .$$

which implies

$$\psi(u') - \int_s^{u'} S(F^v, F(v)) \cdot \dot{F}(v)\,dv \leq \psi(u) - \int_s^u S(F^v, F(v)) \cdot \dot{F}(v)\,dv \ .$$

In other words the function

$$u \to \psi(u) \ - \int_s^u S(F^v, F(v)) \cdot \dot{F}(v)\,dv$$

is monotone decreasing on $[s,t]$. By Lebesgue's theorem it has a non-positive derivative almost everywhere and this proves (5) . Q.E.D.

The properties (1),(2),(3),(4) and (5) of the free energy are, of course, familiar results in theories of thermodynamics† which introduce free energy as a primitive concept and adopt the Clausius-Duhem inequality as a starting point. In fact the relation (1) is what COLEMAN [2] calls the generalised stress relation and (2) is its counterpart in equilibrium. Property (3) is the assertion that among all histories f ending with a given value $e = f(0+)$ the constant history e^* gives the least free energy, which is the form of the result given by COLEMAN. Property (4) is the integrated dissipation inequality and the local inequality (5) is the form assumed by the Clausius-Duhem inequality in homothermal processes.

It now appears that there are certain notable features of the present theory of thermodynamics which deserve to be emphasised. For the sake of concreteness let us think of the first example introduced in Section 2 with H a certain ten dimensional

†See, for example, COLEMAN [2], COLEMAN and MIZEL [5], GURTIN [9] and WANG and BOWEN [14] .

space and where the pairs (F,θ) in U consist of a deformation gradient F and an absolute temperature θ. Our procedure takes work as primitive and then stress and entropy are defined in terms of the work functional. Furthermore on the basis of the thermodynamical axiom W5 we construct a free energy function related to the stress and entropy by familiar rules. It should be noted too that we do not need balance laws for linear momentum, moment of momentum and energy - they are quite irrelevant to our purpose.

We conclude this section by proving two more theorems. The first characterises hyperelastic materials within the class of materials considered here. We know already that if the generalised stress is hyperelastic, if f is any history and if F is a process with $F^s = f$ and F^t a closed connection of f then $w(F,s,t) \geq 0$; in fact equality holds here. The converse statement is also true and is given in

Theorem 3. Suppose that for every history f and every process F, with $F^s = f$ and F^t a closed connection of f, the work $w(F,s,t) \geq 0$. Then the generalised stress is hyperelastic.

Proof. The hypotheses imply that the minimal work $\mathfrak{m}(f) = 0$ for any history f and, consequently, if the process F is continuous at u, $\Psi(F^u,F(u)) = \Psi^*(F(u))$. It suffices to show that, for any history f and any e in U, $S(f,e) = S^*(e)$ for then, by Theorem 2, $S(f,e) = \text{grad}\, \Psi^*(e)$, which proves the result. Given any a in $B(e)$, the largest open ball with centre e contained in U, define a process F by requiring that $F^O = f$, $F(u) = e+ua$ for $0 \leq u \leq 1$ and $F(u) = e+a$ for $u > 1$. For s,t in $0 < s < t < 1$ (4) of Theorem 2 implies

$$\int_s^t S(F^u, F(u)) \cdot a \, du \geq \Psi(F^t, F(t)) - \Psi(F^s, F(s))$$

$$= \Psi^*(e+ta) - \Psi^*(e+sa) \quad .$$

Dividing throughout by $(t-s)$ and letting $t \to s+$ gives

$$S(F^s, F(s)) \cdot a \geq S^*(e+sa) \cdot a$$

and now letting $s \to 0+$ and using the smoothness assumptions S on the generalised stress gives

$$(S(f,e) - S^*(e)) \cdot a \geq 0$$

for every a in $B(e)$ and this implies the result. Q.E.D.

Finally we prove a theorem relating the present theory to the work of various authors who have studied the restrictions which are imposed on constitutive relations by assumptions about work. The assumption that non-negative work must be performed to perturb a 'system' from an equilibrium state was used by KÖNIG and MEIXNER [11] in their study of one dimensional constitutive relations and they called constitutive relations with this property dissipative. More recently, GURTIN and HERRERA [10] and SHU and ONAT [12] have investigated conditions on the relaxation function of a linear viscoelastic material necessary for it to be dissipative. Let us agree to say that an element e in U is *locally stable* if e lies in a *stability* neighbourhood N in U with $\Psi^*(e) \leq \Psi^*(a)$ for every a in N and turn to proving

Theorem 4.

(1) *If F is any continuous path then*

$$w(F) \geq \Psi^*(F(\infty)) - \Psi^*(F(-\infty)) \ .$$

(2) *Let e in U be locally stable and let F be a continuous process with* $F^o = e^*$. *Then there is a number* $\epsilon > 0$ *such that t in* $(0,\epsilon)$ *implies*

$$w(F,o,t) \geq 0 \ .$$

Proof. (1) If F is a continuous path then, for all large numbers t, F^t connects the constant history $F(-\infty)^*$ to $F(\infty)$ and so

$$w(F) \geq \mathfrak{m}(F(-\infty)^*, F(\infty)) \ .$$

The result follows on using (2) of Lemma 2.

(2) Let N be a stability neighbourhood for e. The continuity of F enables us to choose $\epsilon > 0$ so that t in $(0,\epsilon)$ implies that F(t) is in N. An application of (1) now shows that

$$w(F,o,t) \geq \Psi^*(F(t)) - \Psi^*(e) \geq 0 \ . \qquad \text{Q.E.D.}$$

6. Optimal Processes.

For each history f and each e in U the numbers $\mathfrak{m}(f)$ and $\mathfrak{m}(f,e)$ are defined as the greatest lower bounds of certain sets in (3.2) and (4.2). It may happen that there is a process F which attains the greatest lower bound in the sense that there are numbers s,t with $s < t$, $F^s = f$, F^t connecting f to e and

$$w(F,s,t) = \mathfrak{m}(f,e) \; .$$

We shall call any process with these properties an *optimal process for* f *and* e. An optimal process extracts all the useful work possible from the history f in processes connecting it to e. Whether optimal processes exist or not would seem to be a question decided by the detailed structure of the collection of histories $\mathcal{P}$, the work functional w and the pair f and e and we shall not enter into this question here. Our purpose is to prove a theorem describing certain features of optimal processes, assuming that they exist. Of course, optimal processes do exist in certain cases. For example, if the generalised stress is hyper-elastic any process connecting f to e is optimal. Also, for any work functional we know that if f is the constant history e^* the constant process with value e is optimal because $\mathfrak{m}(e^*) = 0$. Even if no optimal process for f and e exists the definition (4.2) of the minimal work $\mathfrak{m}(f,e)$ does guarantee that for any $\epsilon > 0$ there is a process F_ϵ with

$$\mathfrak{m}(f,e) \leq w(F_\epsilon,s,t) < \mathfrak{m}(f,e)+\epsilon \; ,$$

and it would be of great interest if alternative characterisations of F_ϵ could be found. The Corollary 1 to Lemma 2 provides such a characterisation in the simple case where f is a constant history.

We turn to proving Theorem 5 which gives necessary and sufficient conditions for a process to be optimal.

Theorem 5. Let f be any history, e any element of U and f a process with $F^s = f$ and with F^t connecting f to e. Then F is optimal for f and e i.e. $w(F,s,t) = \mathfrak{m}(f,e)$ if and only if each of the following conditions holds:

(1) at t the free energy and generalised stress assume their equilibrium values i.e.

$$\Psi(F^t,F(t)) = \Psi^*(e) \quad \text{and} \quad S(F^t,F(t)) = S^*(e) \ ,$$

(2) on the interval (s,t) the internal dissipation vanishes i.e. for each u in (s,t)

$$S(F^u,F(u))\cdot\dot{F}(u) = \dot{\psi}(u) \ ,$$

where $\psi(u) = \Psi(F^u,F(u))$.

Proof. Firstly we show that conditions (1) and (2) are necessary for F to be optimal.

(1) If we choose any process G with $G^{t'}$ a closed connection of F^t for some $t' > t$ then $G^{t'}$ also connects f to e and consequently

$$w(G,s,t') \geq \mathfrak{m}(f,e) \ .$$

But, if F is optimal,

$$w(G,s,t') = w(F,s,t)+w(G,t,t') = \mathfrak{m}(f,e)+w(G,t,t')$$

and we deduce that $w(G,t,t') \geq 0$ for any such G, which implies

$$\mathfrak{m}(F^t) = 0 \ . \tag{6.1}$$

Using (6.1), the definition (5.1) of the free energy and noting that $F^t(0+) = F(t-) = e$ gives the first result in (1), namely

$$\Psi(F^t, F(t)) = \Psi^*(e) \tag{6.2}$$

one consequence of (6.1) and (6.2) is that for any element b in U

$$\mathfrak{m}(F^t, b) = \Psi^*(b) - \Psi^*(F^t(0+)) + \mathfrak{m}(F^t) = \Psi^*(b) - \Psi^*(e) \ .$$

Now choose any a in the open ball $B(e)$ and define a process $\tilde{G}$ by requiring that $\tilde{G}^t = F^t$, $\tilde{G}(u) = e+(u-t)a$ for $t \leq u \leq t+1$ and $\tilde{G}(u) = e+a$ for $u > t+1$. Then for any u in $(t,t+1)$ we have, by (4) of Theorem 2,

$$\int_t^u S(\tilde{G}^v, \tilde{G}(v)) \cdot a \, dv = w(\tilde{G},t,u) \geq \mathfrak{m}(\tilde{G}^t, \tilde{G}(u)) = \Psi^*(e+(u-t)a) - \Psi^*(e) \ .$$

Dividing throughout by $(u-t)$ and letting $u \to t+$ gives

$$S^*(e) \cdot a \leq S(\tilde{G}^t, \tilde{G}(t)) \cdot a = S(F^t, F(t)) \cdot a$$

and this inequality can hold for all a in $B(e)$ only if the second result of (1) holds.

(2) By hypothesis, $w(F,s,t) = \mathfrak{m}(f,e)$ and, by (3) of Lemma 2,

$$\mathfrak{m}(f,e) = \Psi^*(e) - \Psi^*(f(0+)) + \mathfrak{m}(f) \ .$$

However, we have already proved that $\psi(t) = \Psi^*(e)$ and it follows from the definition of free energy that $\psi(s) = \Psi^*(f(0+)) - \mathfrak{m}(f)$. Consequently

$$w(F,s,t) = \psi(t) - \psi(s) \ . \tag{6.3}$$

If we now choose any numbers u, u' in $s < u < u' < t$ then the integrated dissipation inequality (4) of Theorem 2 applied to each of the intervals $(s,u),(u,u'),(u',t)$ states that

$$w(F,s,u) \geq \psi(u)-\psi(s); \; w(F,u,u') \geq \psi(u')-\psi(u); \; w(F,u',t) \geq \psi(t)-\psi(u')$$

and these inequalities are compatible with equation (6.3) only if equality holds in each of them. In particular

$$\int_u^{u'} S(F^v,F(v))\cdot\dot{F}(v)\,dv = \psi(u')-\psi(u)$$

and so ψ is differentiable on (s,t) and the result (2) holds.

To prove the sufficiency of conditions (1) and (2) we observe that integration of the equation in (2) produces equation (6.3) Condition (1) tells us that $\psi(t) = \Psi^*(e)$ and also, by the definition of free energy, $\psi(s) = \Psi^*(f(0+))-\mathfrak{m}(f)$. Thus

$$w(F,s,t) = \Psi^*(e)-\Psi^*(f(0+))+\mathfrak{m}(f) = \mathfrak{m}(f,e)$$

and F is optimal for f and e. Q.E.D.

7. Extending The Definition of Work.

Let us agree to say that a process F has a *small discontinuity* at t if F(t+) is in the open ball B(F(t-)). If F does have a small discontinuity at t then the line segment joining F(t-) and F(t+) lies entirely in U. Of course if U = H every discontinuity of a process is small. Thus far we have defined the work w(F,s,t) for a process F and an open interval (s,t) on which F is continuous and piecewise smooth. In this section we show that provided we make a further smoothness assumption on the work the structure of our theory suggests a natural definition of work for a process and a finite open interval on which the process is piecewise smooth and has small discontinuities. In short, we can handle processes with a finite number of small discontinuities provided that for the purposes of computing work these processes can be approximated by processes which are linear near the discontinuities. It turns out that the results (3) and (4) of Theorem 2 and the result (1) of Theorem 4 can be extended to discontinuous processes. The extended form of (1) of Theorem 4 is used in Section 8 to obtain restrictions on the relaxation function of a linear viscoelastic material necessary for compatibility with thermodynamics.

The extra assumption we need concerns a process with a single small discontinuity and may be motivated in the following way. Let F be a process which is smooth on the intervals (s,u) and (u,t) and has a small discontinuity at u. For each integer $n > 1/(t-u)$ define a process F_n (see Fig. 6) by requiring that F_n coincide with F on $(-\infty,u)$ and $(u+\frac{1}{n},\infty)$ and that on $[u,u+\frac{1}{n}]$

$$F_n(v) = F(u-)+n(v-u)F(u+\tfrac{1}{n})-F(u-)) \ .$$

Then F_n is continuous and piecewise smooth on (s,t) and linear on $[u,u+\frac{1}{n}]$ and

$$\begin{aligned} w(F_n,s,t) &= w(F_n,s,u)+w(F_n,u,u+\tfrac{1}{n})+w(F_n,u+\tfrac{1}{n},t) \\ &= w(F,s,u) + \int_u^{u+\frac{1}{n}} S(F_n{}^v,F_n(v))\cdot\dot{F}_n(v)\,dv + w(F_n,u+\tfrac{1}{n},t) \\ &= w(F,s,u) \\ &\quad + \int_0^1 S(F_n^{u+\frac{1}{n}\lambda},F(u-)+\lambda(F(u+\tfrac{1}{n})-F(u-)))\cdot(F(u+\tfrac{1}{n})-F(u-))\,d\lambda \\ &\quad + w(F_n,u+\tfrac{1}{n},t) \end{aligned} \tag{7.1}$$

It is reasonable to expect, with mild assumptions on the generalised stress S, that on letting $n \to \infty$ in the equation (7.1) we obtain

$$\lim_{n\to\infty} w(F_n,s,t) = w(F,s,u) + \int_0^1 S(F^u,F(u-)+\lambda(F(u+)-F(u-))\cdot(F(u+)-F(u-))\,d\lambda + w(F,u,t) \ . \tag{7.2}$$

By the definition of the potential Φ the right hand side of (7.2) can be rewritten as

$$w(F,s,u) + \Phi(F^u,F(u+)) + w(F,u,t) \ .$$

The limit $\lim_{n\to\infty} w(F_n,s,t)$ certainly exists and has the value (7.2) in the example cited in section 3 where the collection of histories $\mathcal{P}$ is a certain normed vector space of admissible functions and the generalised stress S is a compact H-valued function on $\mathcal{P} \times U$. We proceed by assuming the result explicitly:

W6. _Let_ F _be a process which is smooth on_ (s,u) _and_ (u,t) _and has a small discontinuity at_ u. _If_ F_n _is the sequence of processes defined above then_

$$\lim_{n\to\infty} w(F_n,s,t) = w(F,s,u)+\Phi(F^u,F(u+))+w(F,u,t) \ . \tag{7.3}$$

With this axiom we can extend the definition of work. Suppose that the process F is piecewise smooth on the interval (s,t) with small discontinuities at $u_1,---,u_k$ in (s,t) and is continuous at every other point of (s,t). For notational convenience write $s = u_o$ and $t = u_{k+1}$. Corresponding to each choice of a k-tuple $(n_1,---,n_k)$ of large integers define the k processes

$$F_{n_1\cdots\cdots n_k}, F_{n_2\cdots n_k}, \ \cdots\cdots, \ F_{n_{k-1}n_k}, F_{n_k}$$

according to the following prescription: Define $F_{n_1\cdots\cdots n_k}$ to be that process which is continuous and piecewise smooth on (u_o,u_{k+1}) which coincides with F on the open intervals $(-\infty,u_1)$, $(u_i+\frac{1}{n_i},u_{i+1})$, $1 \le i \le k-1$, $(u_k+\frac{1}{n_k},\infty)$ and is linear on the closed intervals $[u_i,u_i+\frac{1}{n_i}]$, $1 \le i \le k$. Define the $(k-1)$ remaining processes inductively by demanding that $F_{n_m\cdots n_k}$ coincide with F on $(-\infty,u_m)$ and with $F_{n_{m-1}\cdots n_k}$ on $[u_m,\infty)$ for $2 \le m \le k$ (see Fig. 7). Then repeated application of axiom W6 shows that, for $1 \le m \le k$,

$$\lim_{n_m\to\infty} w(F_{n_m\cdots n_k},u_{m-1},u_{k+1}) = w(F,u_{m-1},u_m)+\Phi(F^{u_m},F(u_m+)) + w(F_{n_{m+1}\cdots n_k},u_m,u_{k+1}) \ .$$

Adding these k equations together tells us that the multiple limit

$$\lim_{n_k\to\infty} \cdots \lim_{n_1\to\infty} w(F_{n_1\cdots n_k}, u_o, u_{k+1}) \tag{7.4}$$

exists and has value

$$\sum_{i=o}^{k} w(F,u_i,u_{i+1}) + \sum_{i=1}^{k} \Phi(F^{u_i}, F(u_i+)) \ . \tag{7.5}$$

In the case $k = 1$ the expression (7.5) reduces to the right side of (7.3) and furthermore $F_{n_1\cdots n_k} \to F$ pointwise everywhere, with the possible exception of the points of discontinuity $u_1,\ldots,u_k$, as $n_1,\ldots,n_k \to \infty$. Accordingly we take the expression (7.5) as the definition of $w(F,s,t)$, *the work done in the process* F *on* (s,t). If F is any path we shall write, as before, $w(F) = w(F,s,t)$ where s is negative and large and t is positive and large. The utility of the definition is illustrated by

Theorem 6.

(1) *If* f *is any history in* $\wp$ *and* e *is any element of* $B(f(0+))$ *then*

$$\Psi(f,e) \geq \Psi^*(e) \ .$$

(2) *Let* F *be any process continuous at* s *and* t, *piecewise smooth on* (s,t) *and with all its discontinuities in* (s,t) *small. Then*

$$w(F,s,t) \geq \Psi(F^t,F(t)) - \Psi(F^s,F(s)) \ .$$

(3) *If* F *is any path whose discontinuities are small then*

$$w(F) \geq \Psi^*(F(\infty)) - \Psi^*(F(-\infty)) \ .$$

Proof. (1) Let f_e in $\mathcal{P}$ be the extension of f defined by $f_e(u) = e$, for $0 \leq u \leq 1$, and $f_e(u) = f(u-1)$ for $u > 1$ and let F be any process connecting f_e to $f(0+)$, with $F^s = f_e$ and $F(t) = f(0+)$ (see Fig. 8). If $e \neq f(0+)$, $F(u)$ has a discontinuity at $u = s-1$. Let F_n be the sequence of processes approximating F constructed in extending the definition of work. Then each history $F_n{}^t$ is a closed connection of f with $F_n{}^{s-1} = f$ and so

$$w(F_n, s-1, t) \geq \mathfrak{m}(f) .$$

On letting $n \to \infty$ we deduce, since F is constant on $(s-1, s)$, that

$$\Phi(f,e) + w(F,s,t) \geq \mathfrak{m}(f) .$$

Now $F^s = f_e$ and F^t connects f_e to $f(0+)$ and so on taking the greatest lower bound over all such processes F we deduce, on using (3) of Lemma 2, that

$$\Phi(f,e) + \pi(f(0+)) - \pi(e) + \mathfrak{m}(f_e) \geq \mathfrak{m}(f) .$$

But $\mathfrak{m}(f_e) \leq 0$ and so

$$\pi(f(0+)) - \mathfrak{m}(f) + \Phi(f,e) \geq \pi(e) ,$$

which implies the required result.

(2) Choose any process G coinciding with F on $(-\infty, t)$ and with G^u a closed connection of F^t for some $u > t$. Construct an approximating multiple sequence $G_{n_1 \cdots n_k}$ for G on (s,u)

in the manner described in extending the definition of work. Then each $G^u_{n_1 \cdots n_k}$ connects F^s to $F(t)$ and so

$$w(G^u_{n_1 \cdots n_k}, s, u) \geq \mathfrak{m}(F^s, F(t)) \ .$$

On taking the multiple limit $\lim_{n_k \to \infty} \ldots \lim_{n_1 \to \infty}$ it follows that

$$\mathfrak{m}(F^s, F(t)) \leq w(G,s,u) \quad = \quad w(F,s,t) + w(G,t,u) \ .$$

Taking the greatest lower bound over all such processes G yields

$$\mathfrak{m}(F^s, F(t)) \leq w(F,s,t) + \mathfrak{m}(F^t)$$

and the result follows on using the continuity of F at s and t and the definition of the free energy.

(3) Let F be any path whose discontinuities are small and construct the multiple sequence $F_{n_1 \cdots n_k}$ as in extending the definition of work. Each $F_{n_1 \cdots n_k}$ is a continuous path with $F_{n_1 \cdots n_k}(-\infty) = F(-\infty)$ and $F_{n_1 \cdots n_k}(\infty) = F(\infty)$ and so, by (1) of Theorem 4,

$$w(F_{n_1 \cdots n_k} \geq \Psi^*(F(\infty)) - \Psi^*(F(-\infty)) \ .$$

Since $w(F) = \lim_{n_k \to \infty} \ldots \lim_{n_1 \to \infty} w(F_{n_1 \cdots n_k})$ the result follows. Q.E.D.

The result (1) of Theorem 6 extends (3) of Theorem 2 and the result (2) is an extension of the integrated dissipation inequality (4) of Theorem 2. When written out in full it reads

$$\int_s^t S(F^u,F(u))\cdot\dot{F}(u)\,du + \sum_{u\in(s,t)}\Phi\,(F^u,F(u+)) \geq \Psi(F^t,F(t)) - \Psi(F^s,F(s))\ .$$

The result (3) of this Theorem extends (1) of Theorem 4. We close the section by proving a Corollary which is used in the next section.

Corollary.

(1) If F is any closed path whose discontinuities are small then $w(F) \geq 0$.

(2) If F is any piecewise constant closed path whose discontinuities are small then

$$\sum_{-\infty<t<\infty} \Phi(F^t,F(t+)) \geq 0\ . \qquad (7.6)$$

Proof. (1) is a special case of (3) of the theorem, whilst (2) is a direct consequence of (1) and the definition of $w(F)$. Q.E.D.

8. Restrictions On Linear Viscoelasticity.

Throughout this section we will assume $U = H$ so that every discontinuity of a process is small. The theory of linear viscoelasticity corresponds to taking U and H to be the six dimensional space of symmetric endomorphisms of a three dimensional inner product space.

For the purpose of obtaining restrictions on the relaxation function of a linear viscoelastic material it suffices to work with the minimal collection of histories $\mathcal{P}$, defined previously as the class of admissible functions f on $(0,\infty)$ with f constant on some subinterval (t,∞). We choose to think of $\mathcal{P}$ as a vector space with the usual pointwise definitions of addition and scalar multiplication. By a *relaxation function* we mean any smooth function $\mathfrak{J}$ on $[0,\infty)$ whose values are endomorphisms of H and $\int_0^\infty |\dot{\mathfrak{J}}(s)|ds < \infty$. For any relaxation function $\mathfrak{J}(\infty) = \lim_{s\to\infty} \mathfrak{J}(s)$ necessarily exists.

Any relaxation function $\mathfrak{J}$ induces a linear function S on the direct sum $\mathcal{P} \oplus H$ with values in H defined by the constitutive relation for a linear viscoelastic material, namely

$$S(f,e) = \mathfrak{J}(0)e + \int_0^\infty \dot{\mathfrak{J}}(s)f(s)ds \, . \qquad (8.1)$$

It can be verified that if we adopt S as the stress and define work by formula (2.7) then axioms S,W1,W2,W3,W4 and W6 hold. If it happens too that the thermodynamic axiom W5 holds we say that $\mathfrak{J}$ is *compatible with thermodynamics*. Examples of one dimensional relaxation functions compatible with thermodynamics are discussed in the final section 9. The results of sections 4 and 7 provide certain interesting conditions necessary for compatibility with thermodynamics. They are given in

<u>Theorem</u> 7. <u>If the relaxation function</u> $\mathfrak{J}$ <u>is compatible with thermodynamics then</u>

(1) $\mathfrak{J}(0)$ <u>and</u> $\mathfrak{J}(\infty)$ <u>are symmetric</u>

(2) $\mathfrak{J}(0)-\mathfrak{J}(\infty) \geq \pm (\mathfrak{J}(s)-\mathfrak{J}(\infty))^{\dagger}$ <u>for</u> $0 \leq s \leq \infty$.

(3) $\dot{\mathfrak{J}}(0) \leq 0$.

<u>Proof</u>. (1) The definition (8.1) shows that, for any e in H,

$$S(0^*,e) = \mathfrak{J}(0)e \ , \ S^*(e) = \mathfrak{J}(\infty)e \ .$$

By hypothesis, the results of Lemmas 2 and 3 apply and the symmetry of $\mathfrak{J}(0)$ and $\mathfrak{J}(\infty)$ is immediate.

(2) To prove (2) we use the Corollary to Theorem 6. The potential $\Phi(f,\cdot)$ for the instantaneous response $S(f,\cdot)$ is given by the formula

$$\Phi(f,e) = \frac{1}{2}(\mathfrak{J}(0)e\cdot e-\mathfrak{J}(0)f(0+)\cdot f(0+))+(e-f(0+))\cdot\int_0^{\infty}\dot{\mathfrak{J}}(s)f(s)ds \ . \tag{8.2}$$

For any integer $N > 1$, any $N+1$ numbers $t_o < t_1 < \ldots < t_N$ and any N elements $e_1,\ldots,e_N$ of H we can construct a piece-wise constant closed path F with $F(s) = 0$ for $s \leq t_o$ and $s > t_N$ and $F(s) = e_k$ for $t_{k-1} < s \leq t_k$, $1 \leq k \leq N$. Direct computation shows that for this F the inequality (7.6) becomes

$$\sum_{k=1}^{N} (\mathfrak{J}(0)-\mathfrak{J}(t_k-t_{k-1}))e_k\cdot e_k$$
$$+\sum_{k=2}^{N}\sum_{m=1}^{k-1} (\mathfrak{J}(t_k-t_m)-\mathfrak{J}(t_k-t_{m-1})-\mathfrak{J}(t_{k-1}-t_m)+\mathfrak{J}(t_{k-1}-t_{m-1}))e_m\cdot e_k$$
$$\geq 0 \tag{8.3}$$

---

†We use the notation $L \gtrless M$ to mean that $L-M$ is positive / negative semi-definite.

In the inequality (8.3) set $N = 2$, $t_2 - t_o = s$ and $e_1 = e_2 = e$. This produces the inequality

$$(\mathfrak{J}(0) - \mathfrak{J}(s))e \cdot e \geq 0 ,$$

holding for all e in H, and proves that $\mathfrak{J}(0) \geq \mathfrak{J}(s)$ or, as we prefer to write it,

$$\mathfrak{J}(0) - \mathfrak{J}(\infty) \geq + (\mathfrak{J}(s) - \mathfrak{J}(\infty)) \tag{8.4}$$

for all s in $0 \leq s \leq \infty$. To prove

$$\mathfrak{J}(0) - \mathfrak{J}(\infty) \geq - (\mathfrak{J}(s) - \mathfrak{J}(\infty)) \tag{8.5}$$

we take the following special choices of N, the t_k and the e_k:

(i) $N = 2N' + 1 \geq 3$ is odd,

(ii) for given $s,t > 0$ define $t_o < t_1 < \ldots < t_{2N'+1}$ by requiring that $t_k = t_o + \frac{1}{2}k(s+t)$ if k is even and that $t_k = t_o + \frac{1}{2}(k-1)(s+t) + t$ if k is odd,

(iii) for given e in H define $e_k = 0$ if k is even and $e_k = (-1)^{(k-1)/2} e$ if k is odd.

If we now employ the symbol Σ' to denote that the indicated summation is over odd integers only the inequality (8.3) becomes

$$\sum_{k=1}^{2N'+1}{}' (\mathfrak{J}(0) - \mathfrak{J}(t)) e_k \cdot e_k$$
$$- \sum_{k=3}^{2N'+1}{}' \sum_{m<k}{}' (\mathfrak{J}(\tfrac{1}{2}(k-m)(s+t)+t) - 2\mathfrak{J}(\tfrac{1}{2}(k-m)(s+t))$$
$$+ \mathfrak{J}(\tfrac{1}{2}(k-m)(s+t)-t) e_m \cdot e_k \geq 0 .$$

On letting $t \to \infty$, using (iii) and dividing throughout by N' the latter inequality becomes

$$(\mathfrak{J}(s) - \frac{2N'+1}{N'}\mathfrak{J}(\infty) + \frac{N'+1}{N'}\mathfrak{J}(0))e\cdot e \geq 0 \ ,$$

holding for all integers $N' > 1$ and all e in H. On letting $N' \to \infty$ we deduce (8.5) and so (2) is proved.

(3) This result is an immediate consequence of (2) and the assumed differentiability of $\mathfrak{J}$. Q.E.D.

Aside from an arbitrary additive constant, the equilibrium free energy for the linear viscoelastic material defined by (8.1) must have the form

$$\Psi^*(e) = \tfrac{1}{2}\mathfrak{J}(\infty)e\cdot e \quad .$$

If we assume that 0 in H is locally stable, in the sense of section 5, then $\mathfrak{J}(\infty)$ is positive semi-definite and it follows from (2) of Theorem 7 that $\mathfrak{J}(0)$ is positive semi-definite. The positive semi-definiteness of $\mathfrak{J}(0)$ and the negative semi-definiteness of $\dot{\mathfrak{J}}(0)$ are significant results for the theory of plane acceleration waves in linear viscoelastic materials since they guarantee that these waves are damped in time.† Results similar in nature to those in Theorem 7 have been given by GURTIN and HERRERA [10] on the assumption that the work done, starting from equilibrium, is always non-negative i.e. that the material is dissipative. They establish the symmetry and positive semi-definiteness of $\mathfrak{J}(0)$†† and $\mathfrak{J}(\infty)$ and obtain, in place of (2) of Theorem 7,

$$\mathfrak{J}(0) \geq \pm\, \mathfrak{J}(s) \quad .$$

†Cf. COLEMAN and GURTIN [4].

††The symmetry of $\mathfrak{J}(0)$ was also established by SHU and ONAT [12] using the same assumption about work as GURTIN and HERRERA [10].

It should be noted that (2) of Theorem 7 implies the latter inequalities whenever $\mathfrak{J}(\infty)$ is positive semi-definite.

Finally we consider cases in which the stress S has a more general form than (8.1) but nevertheless can be approximated by a linear viscoelastic law in certain circumstances. It turns out that the restrictions given in Theorem 7 must also apply to the resulting infinitesimal relaxation function if S itself is to be compatible with thermodynamics. As before we take $U = H$ and work with the minimal collection of histories throughout.

We assume then that we have a work functional for the minimal collection of histories satisfying axioms S,W1,W2,W3,W4,W5 and W6, that the stress S is defined by (2.6) and the free energy by (5.1). Let e_o be some element of H. We add one assumption:

(A)[†] <u>For histories close to</u> e_o^* <u>and present values close to</u> e_o, S <u>can be approximated in the form</u>

$$S(f,e) = S^*(e_o) + S_{\mathfrak{J}}(f,e) + T(f,e)$$

<u>where</u>

$$S_{\mathfrak{J}}(f,e) = \mathfrak{J}(0)(e-e_o) + \int_0^\infty \dot{\mathfrak{J}}(s)(f(s)-e_o)\,ds ,$$

<u>for some relaxation function</u> $\mathfrak{J}$, <u>and where</u>

$$T(f,e) = o(\sup_s |f(s)-e_o| + |e-e_o|)$$

<u>as</u> $$\sup_s |f(s)-e_o| + |e-e_o| \to 0$$

[†]Vid. COLEMAN and NOLL [6],[7] and COLEMAN [3] for a discussion of the circumstances in which an approximation of this type is valid.

It is easy to see that if $\mathfrak{J}$ in (A) exists then it is unique; we call $\mathfrak{J}$ the infinitesimal relaxation function at e_o. We can now state and prove Theorem 8.

Theorem 8. If (A) holds then the infinitesimal relaxation function satisfies the conditions (1), (2) and (3) of Theorem 7.

Proof. (1) If the gradient of the instantaneous free energy $\Psi(e_o^*,\cdot)$ is denoted by grad $\Psi(e_o^*,\cdot)$, in the usual way, then, by (1) of Theorem 2 and assumption (A),

$$\begin{aligned}\text{grad } \Psi(e_o^*,e) &= S(e_o^*,e)\\ &= S^*(e_o)+\mathfrak{J}(0)(e-e_o)+T(e_o^*,e)\\ &= S^*(e_o)+\mathfrak{J}(0)(e-e_o)+o(|e-e_o|)\end{aligned}$$

for all e in some neighbourhood of e_o. It follows that $\Psi(e_o^*,\cdot)$ is twice differentiable at e_o with second gradient $\mathfrak{J}(0)$, which must be symmetric. In a similar way,

$$\text{grad } \Psi^*(e) = S^*(e) = S^*(e_o)+\mathfrak{J}(\infty)(e-e_o)+o(|e-e_o|)$$

in some neighbourhood of e_o so that $\Psi^*(\cdot)$ is twice differentiable at e_o with symmetric second gradient $\mathfrak{J}(\infty)$.

(2), (3). Firstly we show that if F is any continuous closed path with $F(-\infty) = F(\infty) = e_o$ then

$$\int S_{\mathfrak{J}}(F^u,F(u))\cdot\dot{F}(u)\,du \geq 0 \ . \qquad (8.6)$$

To prove this, define, for each $\lambda > 0$, the continuous path F_λ by

$$F_\lambda(u) = e_o+\lambda(F(u)-e_o) \ .$$

Then, by assumption (A), we have that

$$S(F^u_\lambda, F_\lambda(u)) = S^*(e_o) + \lambda\, S_{\mathfrak{J}}(F^u, F(u)) + T(F^u_\lambda, F_\lambda(u))$$

and so

$$\begin{aligned} w(F_\lambda) &= \int S(F^u_\lambda, F_\lambda(u)) \cdot \dot{F}_\lambda(u)\,du \\ &= \lambda \int S^*(e_o) \cdot \dot{F}(u)\,du + \lambda^2 \int S_{\mathfrak{J}}(F^u, F(u)) \cdot \dot{F}(u)\,du \\ &\qquad + \lambda \int T(F^u_\lambda, F_\lambda(u)) \cdot \dot{F}(u)\,du \,. \end{aligned}$$

But

$$\int S^*(e_o) \cdot \dot{F}(u)\,du = 0$$

and, since F is bounded, $T(F^u_\lambda, F_\lambda(u)) = o(\lambda)$ as $\lambda \to 0$ and so

$$w(F_\lambda) = \lambda^2 \int S_{\mathfrak{J}}(F^u, F(u)) \cdot \dot{F}(u)\,du + o(\lambda^2) \,.$$

By our assumptions on S, (4) of Theorem 1 applies and we have

$$w(F_\lambda) \geq 0 \,.$$

It follows that

$$\int S_{\mathfrak{J}}(F^u, F(u)) \cdot \dot{F}(u)\,du + o(1) \geq 0 \qquad \text{as } \lambda \to 0 \,,$$

which implies the required result (8.6).

Next we observe that, since $\mathfrak{J}(0)$ is symmetric, the function Φ defined on $\mathcal{P} \times H$ by

$$\begin{aligned} \Phi(f,e) &= \tfrac{1}{2}\mathfrak{J}(0)(e-e_o)\cdot(e-e_o) - \tfrac{1}{2}\mathfrak{J}(0)(f(0+)-e_o)\cdot(f(0+)-e_o) \\ &\qquad + (e-f(0+)) \cdot \int_0^\infty \dot{\mathfrak{J}}(s)(f(s)-e_o)\,ds \end{aligned}$$

is a potential for $S_{\mathfrak{J}}$, in the sense that grad $\Phi(f,\cdot) = S(f,\cdot)$ and $\Phi(f,f(0+)) = 0$. It is now not difficult to show, on the basis of (8.6), that if F is any piecewise constant closed path with $F(-\infty) = F(\infty) = e_o$ then the inequality (7.6) holds. (The proof of (7.6) depends on approximating F by continuous closed paths which are linear near the discontinuities of F). From the inequality (7.6) we now deduce that the infinitesimal relaxation function satisfies the inequality (8.3) and the proof of properties (2) and (3) proceeds precisely as in Theorem 7. Q.E.D.

The restrictions placed on infinitesimal relaxation functions by thermodynamics have been considered previously by COLEMAN [3] who showed that $\mathfrak{J}(0)-\mathfrak{J}(\infty)$ is symmetric and positive semi-definite. If we impose the additional assumption that e_o is locally stable then, since, as we have seen, the second gradient of Ψ^* at e_o is $\mathfrak{J}(\infty)$ it follows that $\mathfrak{J}(\infty)$ is positive semi-definite and hence, by Theorem 8, that $\mathfrak{J}(0)$ is positive semi-definite and

$$\mathfrak{J}(0) \geq \pm \mathfrak{J}(s) \quad \text{for} \quad s \geq 0 .$$

In other words, we recover results obtained by GURTIN and HERRERA [10] for the purely linear viscoelastic case if we make the assumption that e_o is locally stable.

9. One Dimensional Linear Viscoelasticity.

In this section we discuss one dimensional linear viscoelasticity, which corresponds to taking both U and H to be the real numbers, and confine our attention to relaxation functions of the form

$$\mathfrak{J}(t) = \sum_{k=0}^{N} \gamma_k e^{-\lambda_k t} \qquad (9.1)$$

where the λ's are ordered so that $0 < \lambda_0 < \ldots < \lambda_N$ and $\gamma_0, \ldots, \gamma_N > 0$. We take the vector space of all admissible real-valued functions f on $(0,\infty)$ with

$$\int_0^\infty e^{-\lambda_0 s} |f(s)| ds < \infty$$

to be the collection of histories $\mathcal{P}$ and endow the direct sum $\mathcal{P} \oplus$ reals with the norm

$$\|(f,e)\| = |e| + \int_0^\infty e^{-\lambda_0 s} |f(s)| ds .$$

The stress is taken to be the linear form S defined on $\mathcal{P} \oplus$ reals by

$$S(f,e) = \mathfrak{J}(0)e + \int_0^\infty \dot{\mathfrak{J}}(s) f(s) ds . \qquad (9.2)$$

In fact S is a continuous form and, in particular, is a compact map. It follows, as we have seen previously, that if we define work by the formula (2.7) the axioms P,S,W1,W2,W3,W4 hold. Our object is to establish that the thermodynamic axiom W5 also holds and, moreover, to produce explicit expressions for the free energy.

Relaxation functions of type (9.1) have been considered previously by BREUER and ONAT [1] in their work on maximum recoverable work in linear viscoelasticity. They obtained an integral equation of Wiener-Hopf type as a necessary condition on a process giving the maximum work recoverable from a given history and showed how, for relaxation functions of type (9.1), one can obtain a formal solution of the equation. Their solution is formal in the sense that the derivative of the process maximizing the recoverable work has a Dirac δ-function singularity and so corresponds to no actual connection in our sense.

Before entering into the details of proving compatibility with thermodynamics and evaluating the free energy let us outline the approach to the problem presented here. Let f be any history in $\mathcal{P}$ and e any number and let $\mathcal{C}(f,e)$ be the class of processes with $F^0 = f$ and with the property that for some $\tau > 0$, F^τ connects f to e and $t \geq \tau$ implies $F(t) = F(\tau) = e$. Then, by definition, the minimal work

$$\mathfrak{m}(f,e) \quad = \quad \inf\{w(F,0,\infty): \quad F \text{ in } \mathcal{C}(f,e)\}$$

and

$$\mathfrak{m}(f) = \mathfrak{m}(f,f(0+)) \quad .$$

Firstly we establish $\mathfrak{m}(f) > -\infty$, that is to say W5 holds, and in the course of proving that result we obtain a particular lower bound, $\ell(f)$ say, for the set

$$\{w(F,0,\infty): \quad F \text{ in } \mathcal{C}(f,f(0+))\}$$

and we wish to show that this lower bound is actually the greatest lower bound $\mathfrak{m}(f)$. To do this we notice that for the particular relaxation function $\mathfrak{J}$ of (9.1) $\mathfrak{J}(\infty) = 0$ and so we can take the equilibrium potential π of Lemma 2 to be identically zero. The result (3) of Lemma 2 then tells us that

$$\mathfrak{m}(f,e) = \mathfrak{m}(f) ,$$

for every number e. As the next step we choose a convenient number e_o and construct a sequence of processes F_n in $\mathcal{C}(f,e_o)$ for which $w(F_n,0,\infty) \to \ell(f)$. It must follow that $\ell(f) = \mathfrak{m}(f)$ and in this way we get an explicit formula for $\mathfrak{m}(f)$ from which one can easily write down the free energy by using the definition (5.1). We turn to the details.

If the process F is in some class $\mathcal{C}(f,e)$ the stress at $t \geq 0$ is

$$\begin{aligned} S(F^t,F(t)) &= \mathfrak{I}(0)F(t) + \int_0^\infty \dot{\mathfrak{I}}(s)F^t(s)\,ds \\ &= \alpha_f(t) + \int_0^t \mathfrak{I}(t-s)\dot{F}(s)\,ds , \end{aligned} \tag{9.3}$$

where $\alpha_f(\cdot)$ is defined on $[0,\infty)$ by

$$\alpha_f(t) = \mathfrak{I}(t)f(0+) + \int_0^\infty \mathring{\mathfrak{I}}(t+s)f(s)\,ds$$

and is determined by f and $\mathfrak{I}$. In this case

$$\alpha_f(t) = \sum_{k=0}^{N} \gamma_k \left\{ f(0+) - \lambda_k \int_0^\infty e^{-\lambda_k s} f(s)\,ds \right\} e^{-\lambda_k t} , \tag{9.4}$$

It follows from (9.3) that

$$w(F,0,\infty) = \int_0^\infty \alpha_f(t)\dot{F}(t)\,dt + \frac{1}{2}\int_0^\infty \int_0^\infty \mathfrak{I}(|t-s|)\dot{F}(s)\dot{F}(t)\,ds\,dt \tag{9.5}$$

In order to proceed further we need the following Lemma which is due to BREUER and ONAT [1] .

<u>Lemma</u> 4. <u>There are numbers</u> $\beta_o, \beta_1, \ldots, \beta_N, \mu_1, \ldots, \mu_N$, <u>depending on</u> f <u>and</u> $\mathfrak{J}$, <u>with</u> $0 < \mu_1 < \ldots < \mu_N$ <u>such that the integral equation</u>

$$\int_o^\infty \mathfrak{J}(|t-s|)\beta_f(s)\,ds + \beta_o\, \mathfrak{J}(t) = \alpha_f(t) \quad , \quad t \geq 0 \tag{9.6}$$

<u>is solved by the function</u>

$$\beta_f(s) = \sum_{k=1}^{N} \beta_k e^{-\mu_k s} \quad . \tag{9.7}$$

To prove this result BREUER and ONAT choose $\mu_1, \ldots, \mu_N$ as the N positive distinct roots of the equation

$$Q(\mu) \equiv \sum_{k=0}^{N} \frac{\gamma_k \lambda_k}{\lambda_k^2 - \mu^2} = 0 \tag{9.8}$$

and $\beta_o, \ldots, \beta_N$ to satisfy the linear equations

$$\beta_o - \sum_{k=1}^{N} \frac{\beta_k}{\lambda_i - \mu_k} = \gamma_i \left\{ f(0+) - \lambda_i \int_o^\infty e^{-\lambda_i s} f(s)\,ds \right\} \quad , \quad i = 0, 1, \ldots, N \ , \tag{9.9}$$

and it is a simple matter to verify that with these choices the integral equation is satisfied.

Now let F be any process in some class $C(f,e)$. Noting the following facts (i) $\dot{F}$ has compact support on $[0,\infty)$, (ii) $\int_o^\infty |\beta_f(s)|ds < \infty$, (iii) $0 \leq \mathfrak{J}(|t-s|) \leq \mathfrak{J}(0)$, (iv) $\mathfrak{J}$ is of positive type, we have that for any positive integer n

$$0 \leq \frac{1}{2}\int_0^\infty \int_0^\infty \mathfrak{J}(|t-s|)\,(\dot{F}(s)+2\beta_o(\tfrac{n}{\pi})^{\frac{1}{2}} e^{-ns^2}+\beta_f(s))$$

$$\times(\dot{F}(t)+2\beta_o(\tfrac{n}{\pi})^{\frac{1}{2}} e^{-nt^2}+\beta_f(t))\,dsdt$$

$$= \frac{1}{2}\int_0^\infty \int_0^\infty \mathfrak{J}(|t-s|)\ \dot{F}(s)\dot{F}(t)\,dsdt$$

$$+ \int_0^\infty \left[\int_0^\infty \mathfrak{J}(|t-s|)\,2\beta_o(\tfrac{n}{\pi})^{\frac{1}{2}} e^{-ns^2} ds-\beta_o\mathfrak{J}(t)+\alpha_f(t)\right]\dot{F}(t)\,dt$$

$$+\frac{1}{2}\int_0^\infty \left[\int_0^\infty \mathfrak{J}(|t-s|)\,2\beta_o(\tfrac{n}{\pi})^{\frac{1}{2}} e^{-ns^2} ds-\beta_o\mathfrak{J}(t)+\alpha_f(t)\right]$$

$$\times\left[2\beta_o(\tfrac{n}{\pi})^{\frac{1}{2}} e^{-nt^2}+\beta_f(t)\right]\,dt$$

$$= w(F,0,\infty) + \int_0^\infty \left[\int_0^\infty \{\mathfrak{J}(|t-s|)-\mathfrak{J}(t)\}\,2\beta_o(\tfrac{n}{\pi})^{\frac{1}{2}} e^{-ns^2} ds\right]\dot{F}(t)\,dt$$

$$+\frac{1}{2}\int_0^\infty \left[\int_0^\infty \{\mathfrak{J}(|t-s|)-\mathfrak{J}(t)\}\,2\beta_o(\tfrac{n}{\pi})^{\frac{1}{2}} e^{-ns^2} ds+\alpha_f(t)\right]$$

$$\times\left[2\beta_o(\tfrac{n}{\pi})^{\frac{1}{2}} e^{-nt^2}+\beta_f(t)\right]\,dt$$

$$= w(F,0,\infty) + \frac{1}{2}\beta_o\alpha_f(0) + \frac{1}{2}\int_0^\infty \alpha_f(t)\,\beta_f(t)\,dt$$

$$+\frac{1}{2}\int_0^\infty \{\alpha_f(t)-\alpha_f(0)\}\,2\beta_o(\tfrac{n}{\pi})^{\frac{1}{2}} e^{-nt^2} dt$$

$$+\int_0^\infty \left[\int_0^\infty \{\mathfrak{J}(|t-s|)-\mathfrak{J}(t)\}\,2\beta_o(\tfrac{n}{\pi})^{\frac{1}{2}} e^{-ns^2} ds\right]\dot{F}(t)\,dt$$

$$+\frac{1}{2}\int_0^\infty \left[\int_0^\infty \{\mathfrak{J}(|t-s|)-\mathfrak{J}(t)\}\,2\beta_o(\tfrac{n}{\pi})^{\frac{1}{2}} e^{-ns^2} ds\right]\left[2\beta_o(\tfrac{n}{\pi})^{\frac{1}{2}} e^{-nt^2}+\beta_f(t)\right] dt\ . \tag{9.10}$$

The mean value theorem applied to any smooth function $\xi(\cdot)$ with bounded derivative $\dot{\xi}(\cdot)$ tells us that

$$|2\int_0^\infty \{\xi(t-s)-\xi(t)\}(\tfrac{n}{\pi})^{\frac{1}{2}} e^{-ns^2} ds|$$

$$\leq \max_u |\dot{\xi}(u)| \int_0^\infty 2(\tfrac{n}{\pi})^{\frac{1}{2}} e^{-ns^2} s ds = \max_u |\dot{\xi}(u)| (\pi n)^{-\frac{1}{2}},$$

and employing this inequality in (9.10) enables us to deduce the following estimate: <u>there is a positive number</u> $A(f,\mathfrak{J})$ <u>such that if</u> F <u>is any process in some class</u> $\mathcal{C}(f,e)$ <u>and</u> n <u>is any positive integer then</u>

$$0 \leq \frac{1}{2}\int_0^\infty \int_0^\infty \mathfrak{J}(|t-s|)(\dot{F}(s)+2\beta_0(\tfrac{n}{\pi})^{\frac{1}{2}} e^{-ns^2} + \beta_f(s))$$

$$\times (\dot{F}(t)+2\beta_0(\tfrac{n}{\pi})^{\frac{1}{2}} e^{-nt^2} + \beta_f(t)) ds dt$$

$$= w(F,0,\infty) + \tfrac{1}{2}\beta_0\alpha_f(0) + \frac{1}{2}\int_0^\infty \alpha_f(t)\beta_f(t)dt + \Omega(F,f,\mathfrak{J},n) \qquad (9.11)$$

<u>where</u>

$$|\Omega(F,f,\mathfrak{J},n)| \leq A(f,\mathfrak{J})\left[1+\int_0^\infty |\dot{F}(t)|dt\right] \frac{1}{n^{\frac{1}{2}}}. \qquad (9.12)$$

One consequence of this estimate, which follows on letting $n \to \infty$, is that for each F in $\mathcal{C}(f,f(0+))$

$$w(F,0,\infty) \geq -\tfrac{1}{2}\beta_0\alpha_f(0) + \frac{1}{2}\int_0^\infty \alpha_f(t)\beta_f(t)dt > -\infty,$$

i.e. the thermodynamic axiom W5 holds and the minimal work in closed connections of f satisfies

$$\mathfrak{m}(f) \geq -\tfrac{1}{2}\beta_0\alpha_f(0) - \frac{1}{2}\int_0^\infty \alpha_f(t)\beta_f(t)dt. \qquad (9.13)$$

In fact we can show that equality holds in (9.12). As remarked above, if suffices to exhibit a sequence of processes F_n in $\mathcal{C}(f,e_o)$, for some e_o, with

$$w(F_n,0,\infty) \to -\tfrac{1}{2}\beta_o\alpha_f(0) - \tfrac{1}{2}\int_o^\infty \alpha_f(t)\beta_f(t)\,dt\ , \quad \text{as} \quad n\to\infty\ .$$

We choose e_o to be the number

$$e_o = f(0+) - \beta_o - \int_o^\infty \beta_f(u)\,du$$

and define the sequence of processes F_n in $\mathcal{C}(f,e_o)$ by

$$F_n(s) = \begin{cases} f(0+) - \dfrac{2\beta_o}{\pi^{1/2}}\displaystyle\int_o^{n^{1/2}s} e^{-u^2}du - \int_o^s \beta(u)\,du\ , & 0 \le s \le n\ , \\ F_n(n) + \dfrac{(s-n)}{n}(e_o - F_n(n))\ , & n < s \le 2n\ , \\ e_o\ , & s > 2n\ . \end{cases}$$

It is clear from the definitions of e_o and F_n that $F_n(n) \to e_o$ as $n\to\infty$, and it is straightforward to verify that

$$0 \le \frac{1}{2}\int_o^\infty\int_o^\infty \mathfrak{J}(|t-s|)\,(\dot{F}_n(s) + 2\beta_o(\tfrac{n}{\pi})^{1/2} e^{-ns^2} + \beta_f(s))$$

$$\times\ (\dot{F}_n(t) + 2\beta_o(\tfrac{n}{\pi})^{1/2} e^{-nt^2} + \beta_f(t))\,ds\,dt$$

$$= \frac{1}{2}\int_n^\infty\int_n^\infty \mathfrak{J}(|t-s|)\,(\dot{F}_n(s) + 2\beta_o(\tfrac{n}{\pi})^{1/2} e^{-ns^2} + \beta_f(s))$$

$$\times\ (\dot{F}_n(t) + 2\beta_o(\tfrac{n}{\pi})^{1/2} e^{-nt^2} + \beta_f(t))\,ds\,dt$$

$$\le \frac{1}{2}\mathfrak{J}(0)\left[|e_o - F_n(n)| + \frac{2\beta_o}{\pi^{1/2}}\int_{n^{3/2}}^\infty e^{-u^2}du + \int_n^\infty |\beta_f(u)|\,du\right]^2$$

$$= o(1) \quad \text{as} \quad n\to\infty\ .$$

Thus equation (9.11) tells us that

$$w(F_n,0,\infty)+\frac{1}{2}\beta_o\alpha_f(0)+\frac{1}{2}\int_o^\infty \alpha_f(t)\beta_f(t)\,dt+\Omega(F_n,f,\mathfrak{J},n) = o(1), \text{ as } n\to\infty . \tag{9.14}$$

But

$$\int_o^\infty |\dot{F}_n(t)|dt = \int_o^{2n} |\dot{F}_n(t)|dt$$

$$\leq \int_o^n \{2\beta_o(\tfrac{n}{\pi})^{\frac{1}{2}} e^{-nt^2} + |\beta_f(t)|\}dt + \int_n^{2n} \frac{1}{n}|e_o-F_n(n)|dt$$

$$\leq \beta_o + \int_o^\infty |\beta_f(t)|dt + |e_o-F_n(n)| = O(1), \text{ as } n\to\infty,$$

and so the estimate (9.12) tells us that

$$\Omega(F_n,f,\mathfrak{J},n) = o(1) , \quad \text{as} \quad n\to\infty \tag{9.15}$$

On combining (9.15) and (9.14) we deduce that, as $n\to\infty$,

$$w(F_n,0,\infty) \to -\frac{1}{2}\beta_o\alpha_f(0) -\frac{1}{2}\int_o^\infty \alpha_f(t)\beta_f(t)\,dt ,$$

which proves that equality holds in (9.13) and completes the proof.

The results of this section are summarised in Theorem 9.

Theorem 9. *If* $0 < \lambda_o < \ldots < \lambda_N$ *and* $\gamma_o, \ldots, \gamma_N > 0$, *the one dimensional relaxation function* $\mathfrak{J}(t) = \sum_{k=0}^{N} \gamma_k e^{-\lambda_k t}$ *is compatible with thermodynamics. Given any history* f *with* $\int_o^\infty e^{-\lambda_o s}|f(s)|ds < \infty$ *and any number* e *define* $\alpha_f(\cdot)$ *by equation* (9.4) *and* $\beta_f(\cdot)$ *by equations* (9.7), (9.8), *and* (9.9).

Then the free energy is

$$\Psi(f,e) = \frac{1}{2}\beta_o \alpha_f(0) + \frac{1}{2}\int_0^\infty \alpha_f(t)\beta_f(t)\,dt$$

$$+ \frac{1}{2}\mathfrak{I}(0)(e^2 - f(0+)^2) + (e - f(0+))\int_0^\infty \dot{\mathfrak{I}}(s)f(s)\,ds \; .$$

The sequence of processes F_n which ultimately extracts the maximum recoverable work from the history f has the point-wise limit $F(s) = \lim_{n\to\infty} F_n(s)$ with $F^0 = f$, $F(0) = f(0+)$ and $F(s) = f(0+) - \beta_o - \int_0^s \beta_f(u)\,du$ for $s > 0$. That is to say, F jumps instantaneously from the value $f(0+)$ to the value $f(0+) - \beta_o$ at 0 and thereafter decays exponentially to the value $F(\infty) = f(0+) - \beta_o - \int_0^\infty \beta_f(u)\,du = e_o$. This behaviour agrees with that found by BREUER and ONAT [1].

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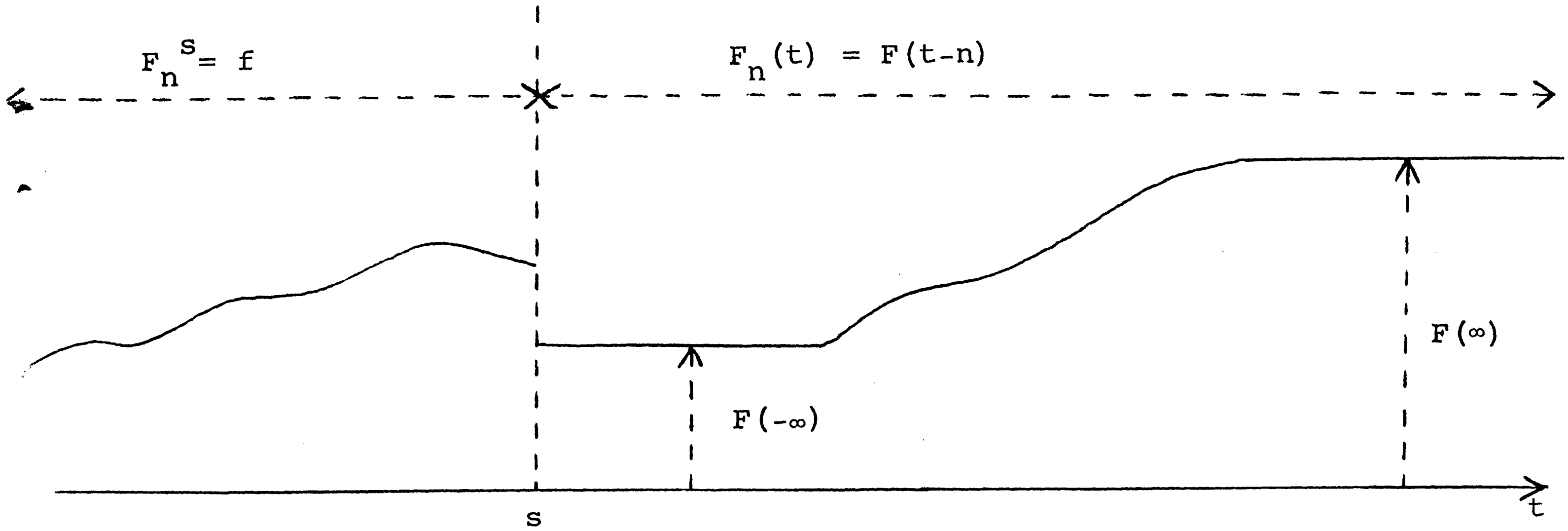
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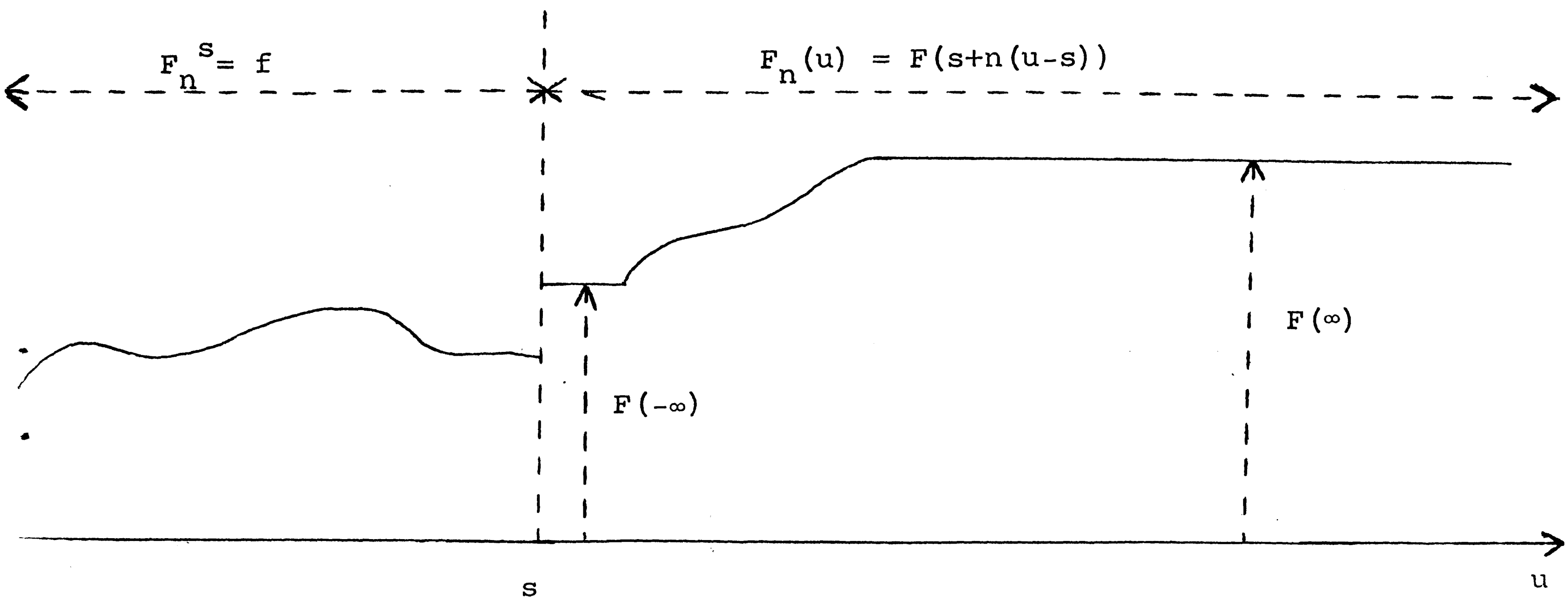
$F_n(t) = F(t-n)$
$F(\infty)$
$F(-\infty)$
s
t

Fig. 1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$F(-\infty)$
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Fig. 2

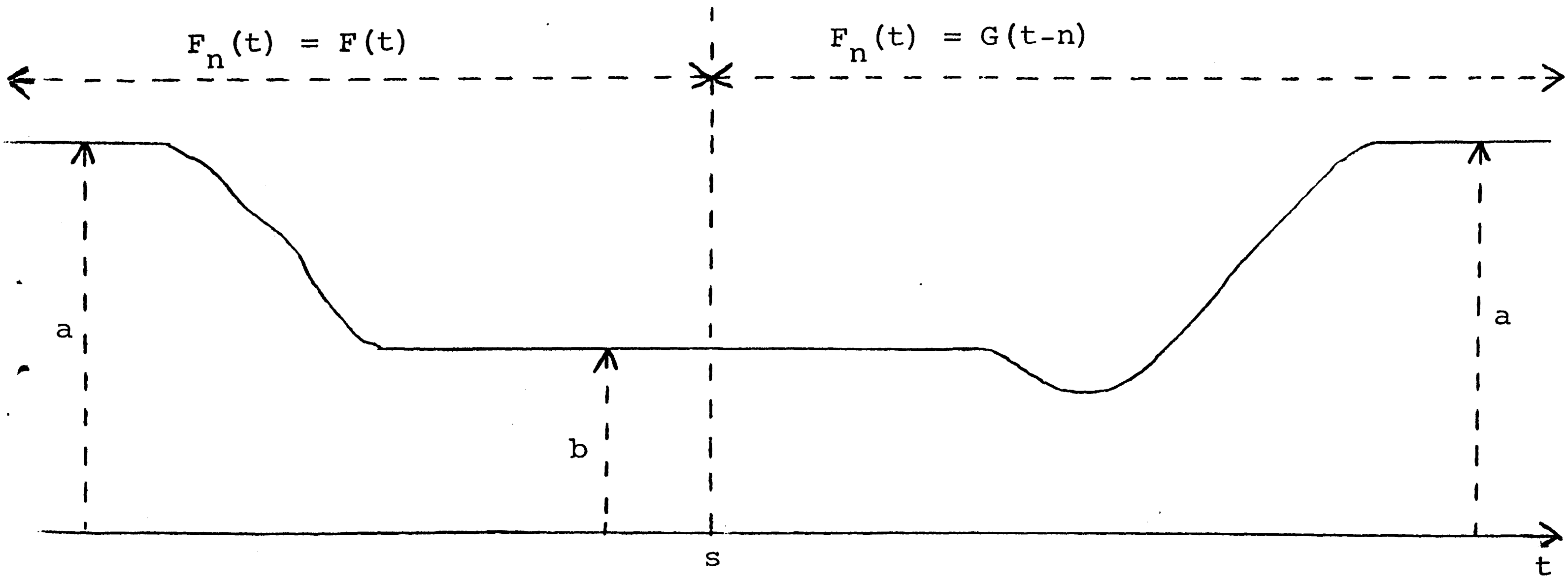


Fig. 3

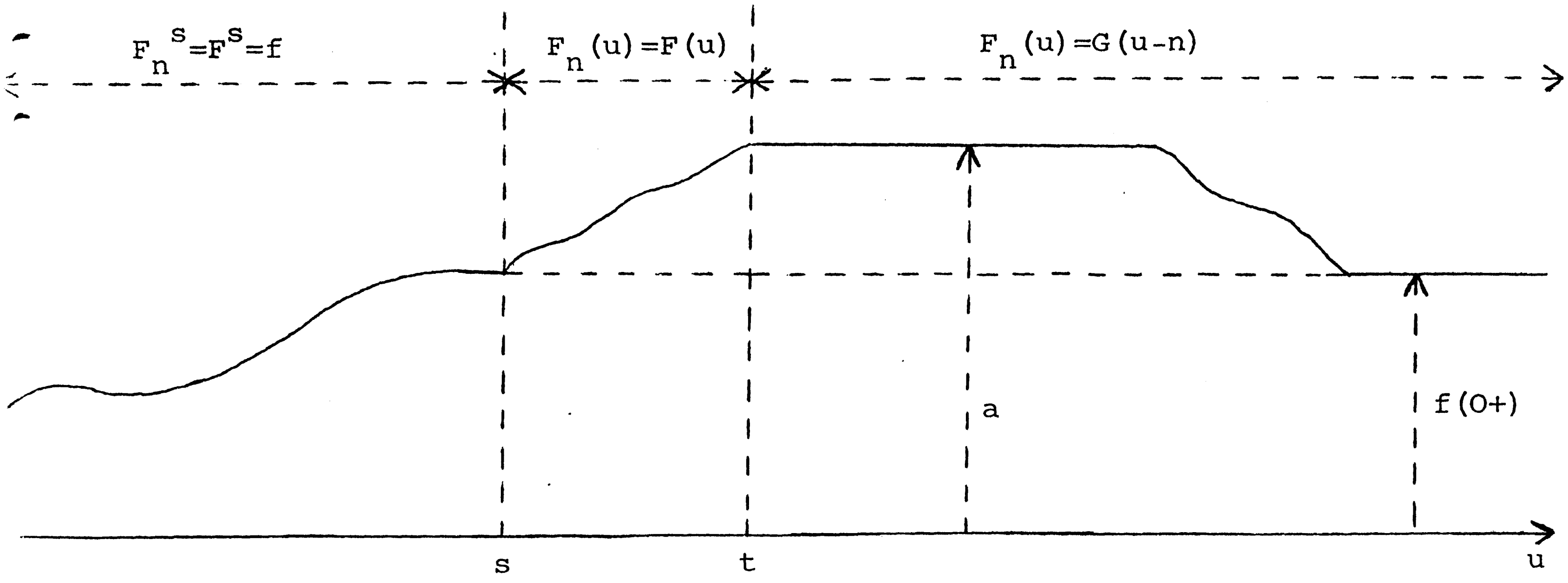


Fig. 4(a)

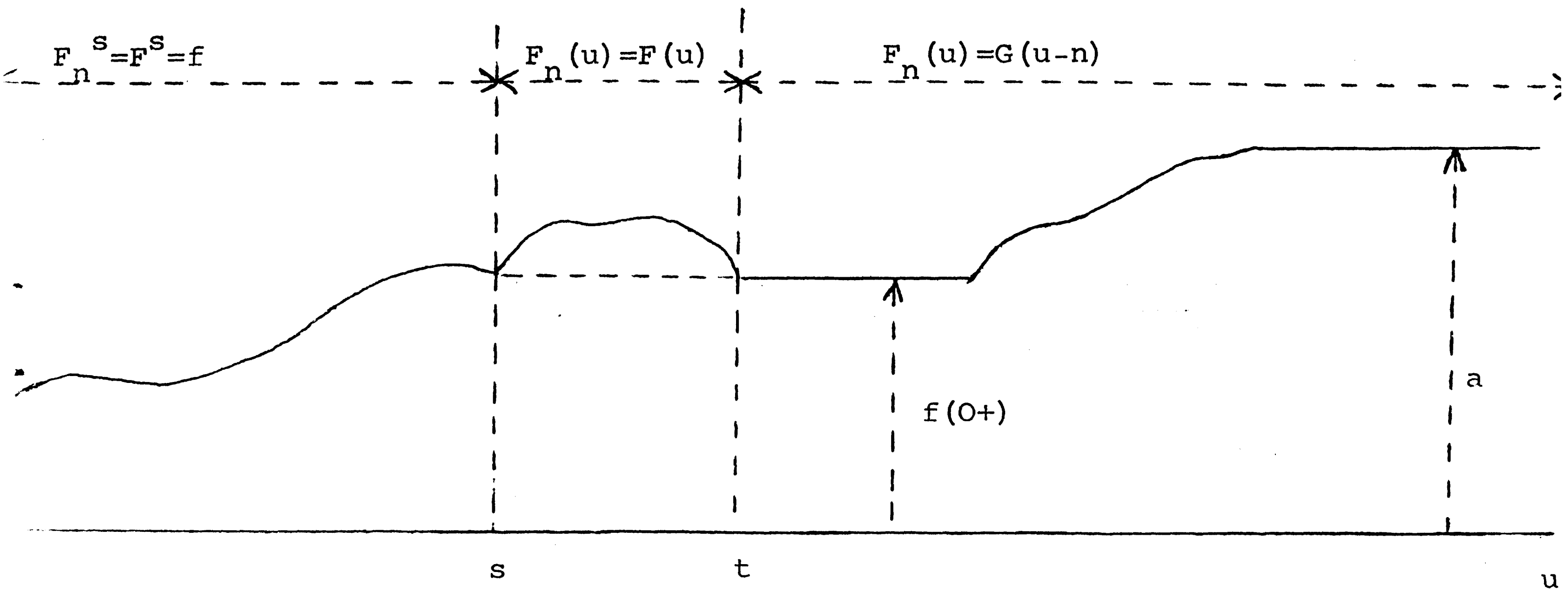


Fig. 4(b)

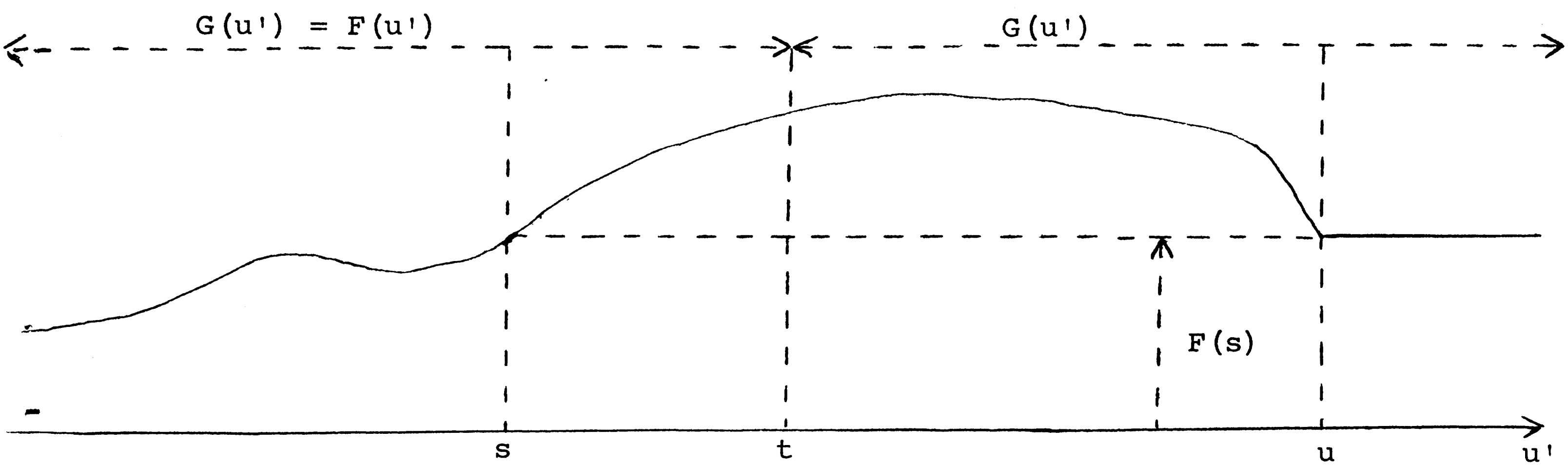
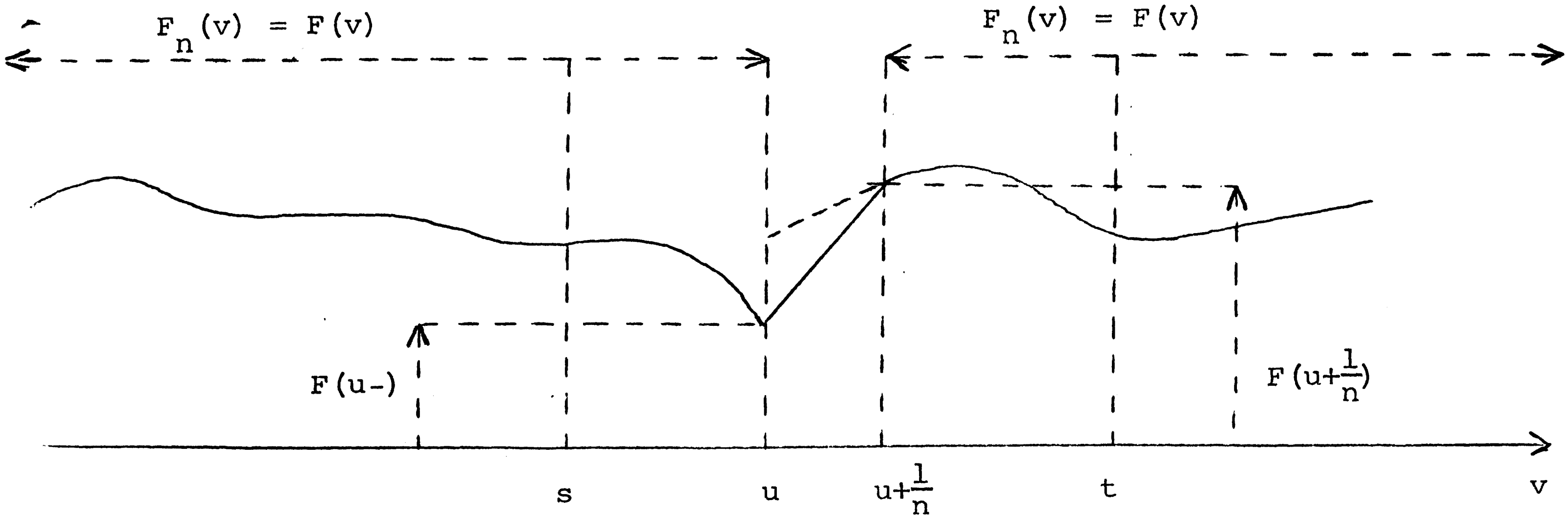


Fig. 5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$F_n(v) = F(v)$
$F(u-)$
$F(u+\frac{1}{n})$
s
u
$u+\frac{1}{n}$
t
v

Fig. 6

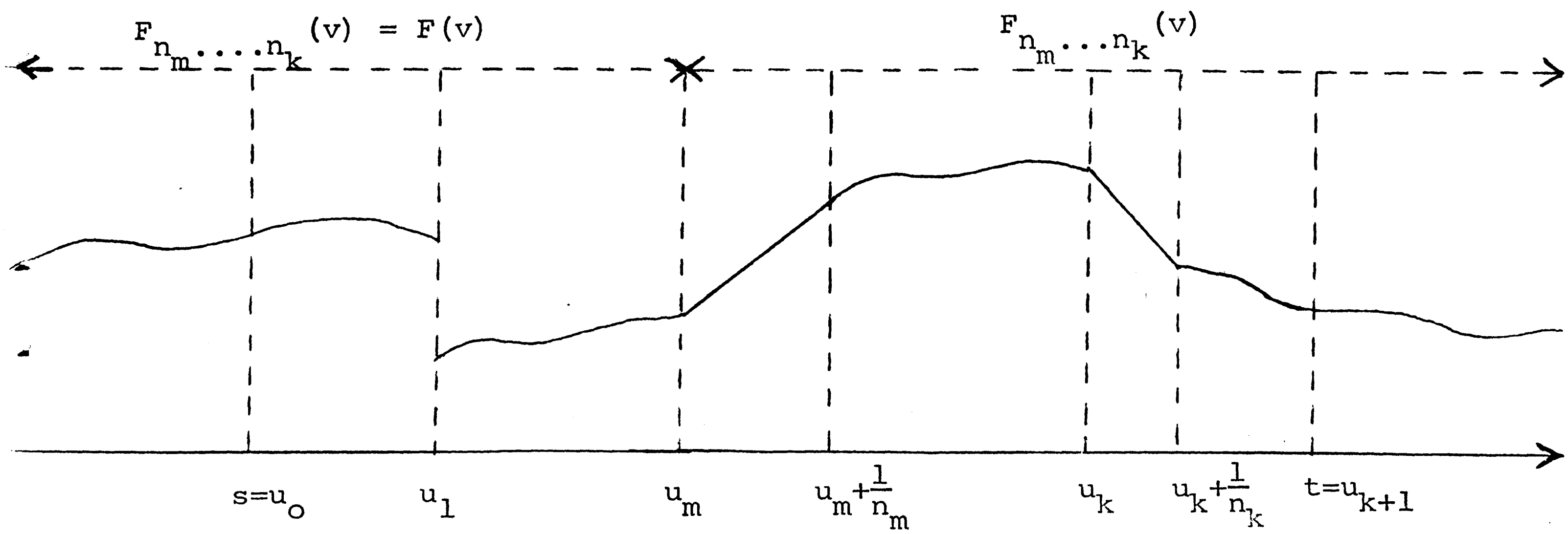
$F_{n_m \ldots n_k}(v) = F(v)$
$F_{n_m \ldots n_k}(v)$
$s=u_o$
u_1
u_m
$u_m+\frac{1}{n_m}$
u_k
$u_k+\frac{1}{n_k}$
$t=u_{k+1}$

Fig. 7

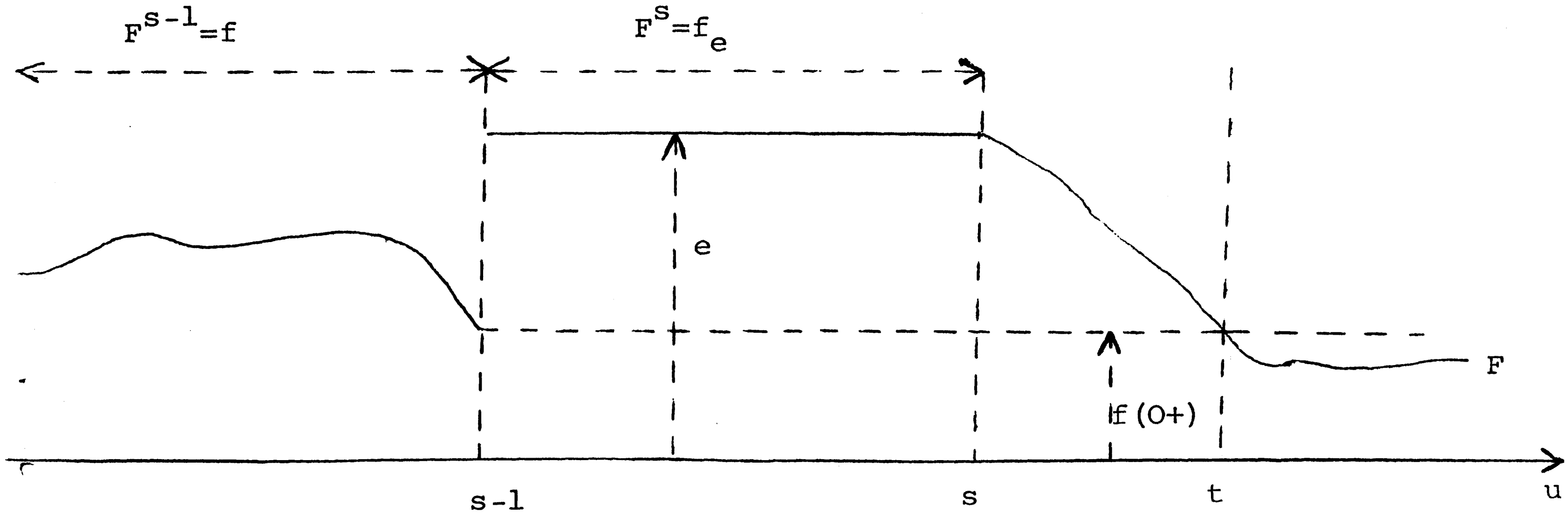

Fig. 8