TIME-REVERSAL AND SYMMETRY IN THE THERMODYNAMICS OF MATERIALS WITH MEMORY

by

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ABSTRACT

TIME-REVERSAL AND SYMMETRY IN THE THERMODYNAMICS

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We here study, within the framework of the thermodynamics of materials with memory, the notion of invariance under timereversal. In particular, we establish conditions that are both necessary and sufficient for the infinitesmal entropy production to display such invariance.

Introduction.

In continuum thermodynamics the <u>entropy</u> production <u>rate</u> is defined through the relation¹

$$\gamma = \dot{\eta} + \operatorname{div}(\frac{q}{\theta}) - \frac{r}{\theta}$$
,

where η is the entropy, θ the temperature, q the heat flux, and r the heat supply. In view of the energy equation

$$\dot{\varepsilon} = \underbrace{S}_{\sim} \cdot \underbrace{F}_{\sim} - \operatorname{divg}_{\sim} + r,$$

where \mathcal{E} is the internal energy, $\underset{\sim}{\mathbb{S}}$ the (Piola-Kirchhoff) stress, and $\underset{\sim}{\mathbb{F}}$ the deformation gradient, we can write

$$\gamma = \dot{\eta} + \frac{1}{\theta} [\underline{s} \cdot \dot{\underline{F}} - \dot{\varepsilon}] - \frac{1}{\theta^2} \underline{q} \cdot \underline{g},$$

with

the temperature gradient.

In this paper we study materials with memory, for which ε, η, S , and \mathfrak{q} are functionals of the histories of F, θ , and \mathfrak{q} .

¹Here div is the material divergence, ∇ the material gradient.

For such materials the (total) entropy production

$$\Gamma = \int_{-\infty}^{\infty} \gamma(t) dt$$

is a functional of the underlying process

$$\mathcal{A}(t) = [F(t), \theta(t), g(t)] \quad (-\infty < t < \infty).$$

We consider processes of the form

$$(t) = [\underline{1}, \theta_{0}, \underline{0}] + \alpha [\underline{H}(t), \underline{7}(t), \underline{g}(t)] \quad (-\infty < t < \infty),$$

where the underlying site $\mathcal{A}_{0} = [1, \theta_{0}, 0]$ is natural, and show that to within an error of $o(\alpha^{2})$ as $\alpha \longrightarrow 0$ the entropy production $\Gamma[\mathcal{A}_{\alpha}]$ is approximated by α^{2} times a quantity $\Omega[\underline{H}, \mathcal{P}, \underline{g}]$, which we call the <u>infinitesmal entropy production</u> in the infinitesmal process $[\underline{H}, \mathcal{P}, \underline{g}]$.

As our main result we prove that the <u>infinitesmal</u> entropy production in each infinitesmal closed process from ω_0 is invariant under time-reversal¹ if and only if:

(a) Both the stress relaxation function² and the heat relaxation function are symmetric.

(b) The energy-strain relaxation function is equal to $-\theta$ times the stress-temperature relaxation function.

²Here the relaxation functions correspond to the derivatives of the constitutive functionals at $\mathscr{A}_{\mathcal{O}}$.

¹One should be able to determine within the framework of kinetic theory whether or not the infinitesmal entropy production is invariant; I conjecture that it is.

(c) The four remaining relaxation functions (i.e. those relating heat flux and strain, heat flux and temperature, stress and temperature gradient, energy and temperature gradient) satisfy certain symmetry conditions similar to (b).

We show that the second conclusion in (a) implies the following important result:

(d) The equilibrium conductivity tensor, $\overset{K}{\sim}_{\infty}$, is symmetric. The classical theory of heat conduction, with $\overset{K}{\sim}_{\infty}$ the underlying conductivity tensor, can be shown to be the appropriate linearized first-order approximation for <u>slow</u> processes. Thus (d) affords a rational basis for the standard assumption that the conductivity tensor in the classical theory be symmetric.¹

We also prove that (b) is equivalent to the following requirement:

(e) The entropy-strain relaxation function is equal to the negative of the stress-temperature relaxation function.

Apparently the first person to study the invariance of functionals under time-reversal was Day [1]. Working in the linearized (isothermal) theory of viscoelastic materials, Day proved that the work done in every

¹Cf. Day and Gurtin [2], who introduce a notion of thermal stability which implies the symmetry of the conductivity tensor. See also the discussion of the Onsager relations given by Truesdell [3], Lecture 7.

closed strain path starting from zero is invariant under timereversal if and only if the stress relaxation function is symmetric. Day's result motivated -- and to some extent served as a basis for -- the work presented here.

1. Preliminary definitions. Day's lemma.

Throughout this section u and w denote finite-dimensional inner product spaces. We write $\mathcal{L}(u, w)$ for the space of all linear transformations from u into w, and A[u] for the action of $A \in \mathcal{L}(u, w)$ on $u \in u$. We designate the <u>transpose</u> of $A \in \mathcal{L}(u, w)$ by A^{T} ; A^{T} is the unique transformation in $\mathcal{L}(w, u)$ with the following property:

$$\mathbf{w} \cdot \mathbf{A}[\mathbf{u}] = \mathbf{u} \cdot \mathbf{A}^{\mathrm{T}}[\mathbf{w}]$$
 for every $\mathbf{u} \in \mathbf{u}, \mathbf{w} \in \mathbf{b}$.

Here the dot on the left denotes the inner product in \mathbb{W} , the dot on the right the inner product in \mathbb{U}_{\bullet} . The inner product in $\mathfrak{L}(\mathfrak{u},\mathbb{W})$ is defined by $\underline{A} \cdot \underline{B} = \text{trace} (\underline{A} \underline{B}^{\mathrm{T}})$. Finally, we say that $\underline{A} \in \mathfrak{L}(\mathfrak{u},\mathfrak{U})$ is symmetric if $\underline{A} = \underline{A}^{\mathrm{T}}$.

We use the following notation throughout this paper:

$$\begin{aligned} & \mathcal{R} &= \text{the reals,} \\ & \mathcal{R}^{+} &= \text{the strictly-positive reals,} \\ & \mathcal{V} &= \text{a finite-dimensional inner product space,} \\ & \mathcal{J} &= \mathcal{L}(\mathcal{V}, \mathcal{V}), \\ & \mathcal{J}^{+} &= \{ \underbrace{F} \in \mathcal{J} \mid \det F > 0 \}, \\ & \hat{\mathcal{J}} &= \{ \underbrace{F} \in \mathcal{J} \mid F \text{ is symmetric} \}. \end{aligned}$$

For $A \in J$ we write A u in place of A[u].

By a closed path in U starting from $u \in Ii$ we mean a smooth (continuously differentiable) function $f : ft \rightarrow -U$ such that

 $f(t) = u \quad \text{whenever} \quad t < -t \quad \text{or} \quad t > t_{0}$

for some t > 0. The time-reversal of f is the function
1 : ft->U defined by

$$\tilde{f}(t) = f(-t)$$

for every teft; clearly, ? is also a closed path in U starting from u. The history up to time t of a closed path f in U is the function f_{\cdot}^{t} : [0,00)___^U defined by

(s) = f(t-s)

for every s 2 > 0. For convenience, we write

```
P(U,u) = the set of all closed paths in U starting
from ueU,
>(U,u) = {h: [0,00) -•• U | h = f<sup>t</sup> for some f€P(U,u)
```

and some $t \in \mathbb{R}$,

.

so that H(U,u) is the set of all histories of paths in P(U,u). Given a vector ueU, we will also write u for the constant closed path in U with value u and, in addition, for the history of this path up to any time t. The precise meaning will be clear from the context.

Let U€U be fixed, and let \$: &(U,u) →-to. We say that: ~ (i) \$ is smooth in time if given any feP(U.u) the function t>-^-3>(f^t) is smooth.

(ii) Φ has a derivative SS at u if given any feP(U,o)

$$5^{*}(\underline{f}^{t}) = \lim_{\alpha \to 0} \frac{*(\underline{u} + \alpha \underline{f}^{t}) - \Phi(\underline{u})}{\alpha}$$

exists uniformly for teft, and if the function $ti \rightarrow -6\$(f)$ is continuous. Clearly, 6\\$, if it exists, is a mapping of H(U,o) into UD.

(iii) \$ has the relaxation property at u if given any feP(li,u)

$$*(u) = \lim_{t \to voo} (f^{1}).$$

The following three lemmas will be of use in the sequel. The first of these is due to Day [1]; we omit its proof, which can be found in [1]. Lemma 1 (Day). Let $A : [0, 00) \rightarrow f(U, U)$ be continuous and bounded, and, for every $f \in P(U, Q)$, let

$$3(f) = I \qquad I \qquad f(t) - A(t-s) [f(s)] ds dt.$$

Then

 $3(f) = \mathfrak{F}(\tilde{f})$

for every $f \in P(U, 0)$ if and only if A(s) jj3 symmetric for every $s \ge 0$.

Lemma 2. Let B_{\star} : [0, oo) - (E(U, U)] be continuous, and, for every $geP(U^{O})$ let

$$f^{\bar{o}}$$
 r
3(g) = -00 -00g(t)-B(t-s) [g(s)]dsdt.

<u>Then</u>

$$\mathfrak{F}(\mathfrak{g}) = \mathfrak{F}(\widetilde{\mathfrak{g}})$$
 (1)

for every geP(U,O) if and only if B(s) is symmetric for <u>every</u> $s \land 0$.

<u>Proof</u>. In view of the definition of the time-reversal $\tilde{a}^{of}v$

¹The boundedness hypothesis is necessary. Indeed, if A(s) = sW, with Wef(U,U), $W = -W^T$, then $3(f) = 3(\tilde{f}) = 0$ for every feP(U, 0).

$$\mathfrak{F}(\widetilde{\mathfrak{g}}) = \int_{\mathfrak{g}} f_{\mathfrak{g}} \mathfrak{g}(-\mathfrak{t}) - \mathfrak{B}(\mathfrak{t}-\mathfrak{s}) [\mathfrak{g}(-\mathfrak{s})] d\mathfrak{s} d\mathfrak{t},$$

and if we interchange the order of integration, we find that $-\infty$ t

$$\mathfrak{F}(\widetilde{g}) = \int_{-\infty}^{\infty} \int_{-\infty}^{t} g(t') \cdot \underline{B}(s'-t') [g(s')]dt'ds',$$
$$= \int_{-\infty}^{\infty} \int_{-\infty}^{t} g(s) - B(t-s) [g(t)]dsdt,$$
$$= \int_{-\infty}^{\infty} \int_{-\infty}^{t} 9, (t) - B(t-s)^{i}[g;(s)]dsdt.$$

Thus

$$\mathbf{\mathfrak{F}}(\mathbf{g}) - \mathbf{\mathfrak{F}}(\mathbf{\widetilde{g}}) = \int_{-00}^{\infty} \int_{-CD}^{t} g(t) - W(t-s) [g(s)] ds dt,$$
 (2)

where

$$W = B - B^T$$
.

Clearly[^] if B(s) is symmetric, then W = 0 and (1) holds.

Conversely, suppose that (1) holds. Since $\underset{\sim}{B}$ is continuous, and since each of the (smooth) functions $\underset{\sim}{gGP(U, 0)}$ has compact support, (1) must hold for every piecewise continuous function $g : \& -^U$ with compact support. Let $f,? \in ft^+$ with f < A,

let $\underline{a}, \underline{b} \in u$, and let $\underline{g} : \mathbb{R} \longrightarrow u$ be defined as follows: $\underline{g}(t) = 0$ for t < 0, $\underline{g}(t) = \underline{a}$ for $0 \le t \le \varepsilon$, $\underline{g}(t) = \underline{0}$ for $\varepsilon < t < \lambda$, $\underline{g}(t) = \underline{b}$ for $\lambda \le t \le \lambda + \varepsilon$, $\underline{g}(t) = 0$ for $t > \lambda + \varepsilon$. For this choice of \underline{g} , (1) and (2) imply that

$$0 = \int_{0}^{\varepsilon} \int_{0}^{t} \underbrace{\mathbf{a}}_{\varepsilon} \underbrace{\mathbf{W}}_{\varepsilon}(t-s) \begin{bmatrix} \mathbf{a} \end{bmatrix} ds dt + \int_{\lambda}^{\lambda+\varepsilon} \int_{\lambda}^{t} \underbrace{\mathbf{b}}_{\varepsilon} \underbrace{\mathbf{W}}_{\varepsilon}(t-s) \begin{bmatrix} \mathbf{b} \end{bmatrix} ds dt + \int_{\lambda}^{\lambda+\varepsilon} \int_{0}^{\varepsilon} \underbrace{\mathbf{b}}_{\varepsilon} \underbrace{\mathbf{W}}_{\varepsilon}(t-s) \begin{bmatrix} \mathbf{a} \end{bmatrix} ds dt.$$

Since $\underline{W} = -\underline{W}^{\mathrm{T}}$, the first two terms on the right vanish. Thus if we divide through by ε^2 and let $\varepsilon \rightarrow 0$, we deduce that $\underline{b} \cdot \underline{W}(\lambda) \underline{a} = 0$, and, since $\underline{a}, \underline{b}$, and λ were chosen arbitrarily, $\underline{W} = 0$. This yields the desired result: $\underline{B}(s) = \underline{B}(s)^{\mathrm{T}}$ for all $s \geq 0$. \Box

Lemma 3. Let $C : [0,\infty) \longrightarrow \mathcal{L}(\mathfrak{u},\mathfrak{w})$ and $D : [0,\infty) \longrightarrow \mathcal{L}(\mathfrak{w},\mathfrak{u})$ be continuous, and, for every $f \in \mathcal{P}(\mathfrak{u}, \mathcal{O})$, $g \in \mathcal{P}(\mathfrak{w}, \mathcal{O})$, let

$$\mathfrak{F}(\mathfrak{f},\mathfrak{g}) = \int_{-\infty}^{\infty} \int_{-\infty}^{t} {\{\mathfrak{f}(t) \cdot \mathfrak{D}(t-s) [\mathfrak{g}(s)] + \mathfrak{g}(t) \cdot \mathfrak{C}(t-s) [\mathfrak{f}(s)]\}} ds dt.$$

Then

$$\mathfrak{F}(\mathfrak{f},\mathfrak{g}) = \mathfrak{F}(\widetilde{\mathfrak{f}},\widetilde{\mathfrak{g}}) \tag{3}$$

for every
$$f \in P(u, 0)$$
, $g \in P(w, 0)$ if and only if

$$C(s) = -D(s)^{T} + constant$$
(4)

<u>for every</u> $s \ge 0$.

<u>Proof</u>. We proceed as in the proof of Lemma 1:

$$\mathfrak{F}(\widetilde{\mathfrak{f}},\widetilde{\mathfrak{g}}) = -\int_{-\infty}^{\infty} \int_{-\infty}^{t} \{ \frac{\mathfrak{f}}{\mathfrak{f}}(-\mathfrak{t}) \cdot \underbrace{\mathbb{D}}(\mathfrak{t}-\mathfrak{s}) [\mathfrak{g}(-\mathfrak{s})] + \mathfrak{g}(-\mathfrak{t}) \cdot \underbrace{\mathbb{C}}(\mathfrak{t}-\mathfrak{s}) [\frac{\mathfrak{f}}{\mathfrak{c}}(-\mathfrak{s})] \} d\mathfrak{s} d\mathfrak{t},$$
$$= -\int_{-\infty}^{\infty} \int_{-\infty}^{t} \{ \frac{\mathfrak{f}}{\mathfrak{c}}(\mathfrak{t}) \cdot \underbrace{\mathbb{C}}(\mathfrak{t}-\mathfrak{s})^{\mathrm{T}} [\mathfrak{g}(\mathfrak{s})] + \mathfrak{g}(\mathfrak{t}) \cdot \underbrace{\mathbb{D}}(\mathfrak{t}-\mathfrak{s})^{\mathrm{T}} [\frac{\mathfrak{f}}{\mathfrak{c}}(\mathfrak{s})] \} d\mathfrak{s} d\mathfrak{t}.$$

Thus

$$\mathfrak{F}(\underline{f},\underline{g}) - \mathfrak{F}(\underline{\tilde{f}},\underline{\tilde{g}}) = \int_{-\infty}^{\infty} \int_{-\infty}^{t} {\{\underline{t}(t) \cdot \underline{M}(t-s) [\underline{g}(s)] + \underline{g}(t) \cdot \underline{M}(t-s)^{T} [\underline{t}(s)]\}} ds dt,$$
(5)

where

$$\underline{M} = \underline{D} + \underline{C}^{\mathrm{T}}.$$

Assume first that (4.1) holds, or equivalently that $M_{\sim} = \text{constant}$. Choose $f \in \mathcal{P}(u, 0)$, $g \in \mathcal{P}(w, 0)$. Then, since f has compact support,

$$\int_{-\infty}^{\infty} \int_{-\infty}^{t} \underline{g}(t) \cdot \underline{M}^{\mathrm{T}}[\dot{\underline{f}}(s)] \mathrm{d}s \mathrm{d}t = \int_{-\infty}^{\infty} \underline{g}(t) \cdot \underline{M}^{\mathrm{T}}[\underline{f}(t)] \mathrm{d}t.$$

Further, an integration by parts confirms that

$$\int_{-\infty}^{\infty} \int_{-\infty}^{t} \dot{f}(t) \cdot M[\underline{g}(s)] ds dt = \int_{-\infty}^{\infty} \dot{f}(t) \cdot \int_{-\infty}^{t} M[\underline{g}(s)] ds dt$$
$$= -\int_{-\infty}^{\infty} f(t) \cdot M[\underline{g}(t)] dt,$$

and we conclude from (5) and the last two equations that (3) holds.

conversely, suppose that (3) holds for every $fe^{\rho}(u, o)$, $ge^{\rho}(u, o)$. Then, since $fe^{\rho}(u, o)$ and $ge^{\rho}(u, o)$ has each of the (smooth) functions $fe^{\rho}(u, o)$ and $ge^{\rho}(u, o)$ has compact support, (3) must hold for every piecewise continuous function $g: \mathfrak{R} \longrightarrow \mathfrak{W}$ with compact support, and each continuous and piecewise smooth function $f: \mathfrak{R} \longrightarrow \mathfrak{U}$ with compact support. Such a pair of functions is defined as follows: let $\varepsilon, \lambda \in \mathfrak{R}^+$ with $\varepsilon < \lambda$, let ge^{μ} , g(t) = 0 for t < 0, $g(t) = \mathfrak{a}$ for $0 \le t \le \varepsilon$, g(t) = 0 for $t > \varepsilon$, and let $f(t) = \int_{0}^{t} h(s) ds$ for all te^{μ} , where h(t) = 0 for t < 0, $h(t) = \mathfrak{b}$ for $0 \le t \le \varepsilon$, h(t) = 0 for $t > \lambda + \varepsilon$. For this choice of g and f, (3) and (5) yield

$$0 = \int_{0}^{\varepsilon} \int_{0}^{t} \underbrace{\mathbf{b}}_{0} \cdot \underbrace{\mathbf{M}}_{0} (t-s) \begin{bmatrix} \mathbf{a} \end{bmatrix} ds dt - \int_{\lambda}^{\lambda+\varepsilon} \int_{0}^{\varepsilon} \underbrace{\mathbf{b}}_{0} \cdot \underbrace{\mathbf{M}}_{0} (t-s) \begin{bmatrix} \mathbf{a} \end{bmatrix} ds dt + \int_{0}^{\varepsilon} \int_{0}^{t} \underbrace{\mathbf{a}}_{0} \cdot \underbrace{\mathbf{M}}_{0} (t-s)^{T} \begin{bmatrix} \mathbf{b} \end{bmatrix}.$$

If we divide this relation by ε^2 and let $\varepsilon \rightarrow 0$, we arrive at

$$b \cdot M(0) [a] = b \cdot M(\lambda) [a],$$

which implies (4), since $a \in w$, $b \in u$, and $\lambda \in \mathbb{R}^+$ were chosen arbitrarily.

2. States. Closed processes.

By a site we mean a triplet of the form

 $\mathcal{A} = [F, \theta, g],$

where $\mathbf{F} \in \mathbf{J}^+$ is the <u>deformation gradient</u>, $\theta \in \mathbb{R}^+$ <u>the temperature</u>, and $\mathbf{g} \in \mathbf{V}$ the <u>temperature gradient</u>; if $\mathbf{g} = \mathbf{0}$, then \checkmark is called an <u>equilibrium site</u>. Throughout this paper θ_0 <u>is a fixed</u> <u>temperature</u>, and \sim_0 <u>is the equilibrium site</u>

$$\boldsymbol{A}_{\boldsymbol{O}} = [\underline{1}, \theta_{\boldsymbol{O}}, \underline{0}],$$

so that $\cancel{}_{0}$ corresponds to holding the body in the reference configuration at the temperature θ_{0} . By an infinitesmal site we mean a triplet of the form

$$\mathcal{L} = [\mathrm{H}, \mathcal{L}, \mathrm{g}],$$

where $\underset{\sim}{\text{He}}$ is the <u>displacement gradient</u>, $\mathscr{P} \in \mathbb{R}$ the <u>temperature</u> <u>change</u>, and $g \in V$ the <u>temperature</u> gradient; we call

$$E_{\sim} = \frac{1}{2} (H_{\sim} + H_{\sim}^{T})$$
 (6)

the infinitesmal strain. For convenience, we write

\$ = the set of all sites, \$ = the set of all infinitesmal sites. A one-parameter family $\mathscr{A}(t) = [F(t), \theta(t), g(t)]$ (- $\infty < t < \infty$) of sites is called a <u>closed process</u> if $\mathscr{A}(\cdot)$ is a closed path in g starting from \mathscr{A}_{0} ; i.e., if $\mathscr{A}(\cdot) \in \mathbb{P}(g, \mathscr{A}_{0})$. On the other hand, a one-parameter family $\mathscr{A}(t) = [H(t), \mathscr{P}(t), g(t)]$ (- $\infty < t < \infty$) of infinitesmal sites is an <u>infinitesmal closed process</u> if $\mathscr{A}(\cdot)$ is a closed path in \mathscr{I} starting from zero; i.e., if $\mathscr{A}(\cdot) \in \mathbb{P}(\mathfrak{I}, 0)$.

Proposition 1. If $\mathscr{A}(\cdot)$ is a closed process, and if $\mathscr{A}(\cdot)$ is an infinitesmal closed process, then $\mathscr{A}(\cdot) + \alpha \mathscr{A}(\cdot)$ is a closed process for all sufficiently small α .

<u>Proof</u>. Let $\mathcal{A}(\cdot) = [\underline{F}(\cdot), \theta(\cdot), \underline{g}(\cdot)], \quad \dot{\mathcal{A}}(\cdot) = [\underline{H}(\cdot), \mathcal{V}(\cdot), \underline{g}'(\cdot)].$ Clearly, $\mathcal{A}(\cdot) + \alpha \, \dot{\mathcal{A}}'(\cdot)$ is a closed path starting from \mathcal{A}_{O} with the requisite degree of smoothness. We have only to show that $\mathcal{A}(\cdot) + \alpha \, \dot{\mathcal{A}}'(\cdot)$ has values in § for all sufficiently small α , or equivalently that

det [F(t) +
$$\alpha$$
H(t)] > 0, θ (t) + $\alpha \vartheta$ (t) > 0 (7)

for all $t \in \mathbb{R}$ and all sufficiently small α . Since $F(t) \in \mathfrak{T}^+$, $\theta(t) \in \mathbb{R}^+$, the result (7) follows from the continuity of the functions $F(\cdot)$, $\theta(\cdot)$, $H(\cdot)$, and $\mathcal{P}(\cdot)$, and the fact that these functions are constant outside a compact time interval.

3. <u>Constitutive relations</u>. <u>Time-reversal symmetry</u>.

In this paper we study materials defined by constitutive relations giving the <u>stress</u> S(t), the <u>internal energy</u> $\mathcal{E}(t)$, the <u>entropy</u> $\eta(t)$, and the <u>heat flux</u> g(t) at time t when the site-history \mathcal{A}^{t} is known:

$$\begin{split} & \underbrace{s}(t) = \widehat{s}(a^{t}), \qquad \varepsilon(t) = \widehat{\varepsilon}(a^{t}), \\ & \eta(t) = \widehat{\eta}(a^{t}), \qquad q(t) = \widehat{q}(a^{t}). \end{split}$$
(8)

Here the <u>response functionals</u> \hat{s} , $\hat{\epsilon}$, $\hat{\eta}$, and \hat{g} have $\#(\mathbf{s}, \boldsymbol{\omega}_{o})$ as their common domain and \Im , \Re , \Re , and ψ as their respective co-domains. We assume that:

(A) all four response functionals are smooth in time;

(B) \hat{s} , $\hat{\varepsilon}$, and \hat{g} have derivatives $\delta \hat{s}$, $\delta \hat{\varepsilon}$, and $\delta \hat{g}$ at ω_{0} , and $\delta \hat{s}$ has symmetric values;¹

- (C) $\hat{\varepsilon}$ and $\hat{\eta}$ have the relaxation property at \mathscr{A}_{0} ;
- (D) Δ_0 is a natural site in the sense that

 $\hat{s}(\omega_{0}) = 0, \quad \hat{g}(\omega_{0}) = 0.$

Let $\mathcal{A}(\cdot) = [\underline{F}(\cdot), \theta(\cdot), \underline{g}(\cdot)]$ be a closed process. We define the entropy production $\Gamma[\mathcal{A}(\cdot)]$ on $\mathcal{A}(\cdot)$ by

$$\Gamma\{\mathscr{A}(\cdot)\} = \int_{-\infty}^{\infty} \left[\dot{\eta} + \frac{1}{\theta}(\underline{s}\cdot\dot{\underline{F}} - \dot{\epsilon}) - \frac{1}{\theta^{2}}\underline{g}\cdot\underline{g}\right]dt, \qquad (9)$$

¹Since S is the Piola-Kirchhoff stress, its response functional must satisfy the relation

$$\hat{\underline{s}}(\boldsymbol{\rho}^{t})\underline{F}(t)^{T} = \underline{F}(t)\hat{\underline{s}}(\boldsymbol{\rho}^{t})^{T} \qquad (*)$$

in every closed process (see, e.g., Truesdell and Noll [4], Eq. (43A.8)); this, in turn, leads to our assumption that $\delta \hat{S}$ have symmetric values. Here we do not find it necessary to make the stronger assumption (*).

where S, £, 77, and q are defined on ft by (8).

Proposition 2. Let $>0/(#) = [F(, \cdot), 9(\cdot), g(\cdot)]$ be a closed process. Then

$$rr^{(.)} = \prod_{r=0}^{r^{00}} T(S-F - \frac{e}{r} - \frac{S^{*}}{r})dt.$$
 (10)

<u>Proof</u>. Since $>v(\cdot)$ is a closed process, we conclude from (C) that



Similarly,

$$^{0} - I < t >^{dt} = J T^{dt} " I - H^{dt}$$

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and these relations, with (9), imply (10). CZ3 Let $X^{(\#)} = [H(\ll) j^{(')})^{(\#)}$ be an infinitesmal closed

process, and let

$$\underline{s}_{x}(t) = \hat{s}_{s} \hat{s} f^{*}$$
, $e_{1}(t) = \hat{5}_{t}(xv^{t})$, $_{31}(t) = \hat{s}_{g} t^{*}$.
(ID

We define the infinitesmal entropy production flf (/(•) } on ~(•) by

$$\Omega\{\mathcal{A}(\cdot)\} = \int_{0}^{\infty} \int_{-\infty}^{\infty} g_{1} \cdot g_{2} dt, \quad (12)$$

where E is the infinitesmal strain (6). The next theorem motivates this definition.

Theorem 1. Let v(') be. an infinitesmal closed process; and let $\Delta_{\alpha}(\cdot) = \Delta_{0} + \alpha \Delta(\cdot)$.

Then 1

$$\Gamma\{\boldsymbol{\mathcal{A}}_{\alpha}(\boldsymbol{\cdot})\} = a^{2} \mathrm{fi}\{\boldsymbol{\hat{-}}(\boldsymbol{-})\} + o(a^{2}) \quad \mathrm{as} \quad \alpha \rightarrow 0.$$

Proof, Let

$$\omega(\cdot) = [\underline{H}(\cdot), \mathscr{V}(\cdot), \underline{g}(\cdot)],$$

$$\boldsymbol{\omega}_{\alpha}(\cdot) = [F_{\alpha}(\cdot), \theta_{\alpha}(\cdot), g_{\alpha}(\cdot)] = [\frac{1}{2} + \alpha H(\cdot), \theta_{\alpha} + \alpha A(\cdot) + \alpha A(\cdot)].$$
(13)

By (6), $(11)_v$ and (B),

If we let

$$S_{\alpha}(t) = \hat{S}(\omega_{\alpha}^{t}), \quad \varepsilon_{\alpha}(t) = \hat{\varepsilon}(\omega_{\alpha}^{t}), \quad \varepsilon_{0} = \hat{\varepsilon}(\omega_{0}), \quad g_{\alpha}(t) = \hat{g}(\omega_{\alpha}^{t})$$
(14)

and choose $t_{o} > 0$ such that $x^{(0)} = 0$ outside $[-t_{o}, t_{o}]$, then we conclude from (10), (12), and the above relations that

¹By Proposition 1 J/J (•) lies in the domain of T for all a sufficiently small a.

$$\Omega\{\boldsymbol{\omega}(\cdot)\} - \frac{1}{\alpha^{2}} \Gamma\{\boldsymbol{\omega}_{\alpha}(\cdot)\} = \int_{-t_{0}}^{t_{0}} \left[\left(\frac{s_{1}}{\theta_{0}} - \frac{s_{\alpha}}{\alpha\theta_{\alpha}}\right) \cdot \dot{H} - \left(\frac{\varepsilon_{1}}{\theta_{0}^{2}} - \frac{[\varepsilon_{\alpha} - \varepsilon_{0}]}{\alpha\theta_{\alpha}^{2}}\right) \dot{\boldsymbol{\psi}} + \left(\frac{g_{1}}{\theta_{0}^{2}} - \frac{g_{\alpha}}{\alpha\theta_{\alpha}^{2}}\right) \cdot g\right] dt + \frac{\varepsilon_{0}}{\alpha^{2}} \int_{-t_{0}}^{t_{0}} \frac{\dot{\theta}_{\alpha}}{\theta_{\alpha}^{2}} dt. \quad (15)$$

Since $\theta_{\alpha}(t) = \theta_{0}$ outside $[-t_{0}, t_{0}]$,

$$\int_{-t_0}^{t_0} \frac{\frac{\partial}{\partial t}}{\frac{\partial}{\partial t}} dt = -\int_{-t_0}^{t_0} \frac{d}{dt} (\frac{1}{\theta}) dt = 0.$$

Next, the properties of the infinitesmal closed path $\mathcal{A}(\cdot)$, (B), (D), (13), and (14) imply that as $\alpha \longrightarrow 0$

$$\begin{split} \theta_{\alpha}(t) &\longrightarrow \theta_{0} > 0, \qquad \frac{1}{\alpha} \underset{\sim}{\mathrm{s}}_{\alpha}(t) \longrightarrow \underset{1}{\mathrm{s}}_{1}(t), \\ \frac{1}{\alpha} [\varepsilon_{\alpha}(t) - \varepsilon_{0}] &\longrightarrow \varepsilon_{1}(t), \qquad \frac{1}{\alpha} \underset{\alpha}{\mathrm{g}}_{\alpha}(t) \longrightarrow \underset{1}{\mathrm{g}}_{1}(t), \end{split}$$

uniformly for teR. Thus, since \dot{H} , $\dot{\mathcal{V}}$, and g are bounded on $(-t_0, t_0)$, if we take the limit as $\alpha \rightarrow 0$ in (15), we are led to the desired result.

Theorem 2. Assume that the entropy production Γ is invariant under time-reversal; i.e.,

 $\Gamma\{\mathscr{A}(\cdot)\} = \Gamma\{\widetilde{\mathscr{A}}(\cdot)\} \text{ for every closed process } \mathscr{A}(\cdot).$

Then the infinitesmal entropy production Ω is invariant under time-reversal; i.e.,

 $\Omega\{\mathscr{A}(\cdot)\} = \Omega\{\widetilde{\mathscr{A}}(\cdot)\} \text{ for every infinitesmal closed process} \qquad \mathscr{A}(\cdot).$ (16)

<u>Proof</u>. Let $\mathcal{A}(\cdot)$ be an infinitesmal closed process, and let

$$\mathscr{A}_{\alpha}(\cdot) = \mathscr{A}_{\alpha} + \alpha \mathscr{A}(\cdot).$$

Then

$$\widetilde{\mathcal{A}}_{\alpha}(\cdot) = \mathcal{A}_{0} + \alpha \widetilde{\mathcal{A}}(\cdot),$$

and therefore, by hypothesis and Theorem 1,

$$\Omega\{ \boldsymbol{\omega}(\boldsymbol{\cdot}) \} = \lim_{\alpha \to 0} \frac{1}{\alpha^2} \Gamma\{ \boldsymbol{\omega}_{\alpha}(\boldsymbol{\cdot}) \} = \lim_{\alpha \to 0} \frac{1}{\alpha^2} \Gamma\{ \boldsymbol{\widetilde{\omega}}_{\alpha}(\boldsymbol{\cdot}) \} = \Omega\{ \boldsymbol{\widetilde{\omega}}(\boldsymbol{\cdot}) \}.$$

4. <u>Consequences of invariance under time-reversal</u>.

In this section we establish conditions that are both necessary and sufficient for the <u>infinitesmal</u> entropy production to be invariant under time-reversal.

We call

$$\Lambda = (E, \mathcal{V}) \tag{17}$$

the generalized (infinitesmal) strain,

 $\sum_{n \geq 1} = (\theta_{0} S_{1}, - \varepsilon_{1})$

the <u>generalized</u> (infinitesmal) <u>stress</u>. In terms of these quantities the first two relations in (11) take the form

$$\sum_{n=1}^{\infty} (t) = \delta \hat{\Sigma} (\mathbf{A}^{t}), \qquad (18)$$

where

$$\delta \hat{\Sigma} = (\theta_{\delta} \delta \hat{S}, -\delta \hat{\epsilon}).$$
 (19)

The quantities \bigwedge_{\sim} and $\sum_{\sim 1}^{\Sigma}$ are both elements of

 $w = \hat{\mathfrak{I}}_{\times}\mathfrak{R};$

if we take the natural inner product in this space, we can rewrite (12) in the form

$$\prod_{g_{0}} \left\{ \begin{array}{c} \mathbf{A} \left\{ \mathbf{f} \right\} \right\} = \int_{g_{0}}^{h} \mathbf{f} \left\{ \mathbf{f} \right\} = \int_{g_{0}^{h} \mathbf{f} \left\{ \mathbf{f} \right\} =$$

We now assume that:

(E) there exist continuous functions

with G bounded, such that given any infinitesmal closed process $\omega(\cdot) = [H(\cdot), \mathcal{O}(\cdot), g(\cdot)],$

$$\delta \hat{\Sigma}(\Delta?) = J \overset{t}{G(t-s)} [\dot{A}(s)]ds + j \overset{t}{L(t-s)} [g(s)]ds,$$

-00" -00~ (21)

$$\delta \hat{g}(\mathcal{A}^{t}) = \int_{-00}^{t^{\star}} J(t-s) \left[A(s) \right] ds + \int_{-00}^{t^{fc}} K(t-s)g(s) ds$$

with A given by (16) and E by (6).¹ We call G the <u>generalized</u> <u>stress relaxation function</u>, K the <u>heat relaxation function</u>. Our

¹By (17) a dependence on A leads to a dependence on H only through \sim **> t ^ its symmetric part, E. That, e.g., E (t) = $5f(x^{\wedge})$ should be independent of the skew part of H is a consequence of (D) and the principle of material frame-xndifference (see, e.g., Truesdell and Noll [4], Eq. (41.23)). It is important to note that in our theory $S_1(t)$ and C_1 (t) are independent of the present values A(t) and g(t) of the generalized strain-rate and the temperature gradient (see (11), (17), and:(21)). Thus our theory does not include, as <u>special cases</u>, (con¹ t on next page) main result is

Theorem 3. A necessary and sufficient condition that the infinitesmal entropy production be invariant under time-reversal is that the following three statements be true for every $s \ge 0$:

(i) The generalized stress relaxation function G(s) is symmetric.

(ii) <u>The heat relaxation function</u> K(s) is symmetric. (iii) $L(s) = J(s)^{T} + constant$.

<u>Proof.</u> By (19)-(21),

$$\theta_{0}^{2} \Omega\{ \mathcal{A}(\cdot) \} = \int_{-\infty}^{\infty} \int_{-\infty}^{t} \{ \dot{\Lambda}(t) \cdot \underline{G}(t-s) [\dot{\Lambda}(s)] + \dot{\Lambda}(t) \cdot \underline{L}(t-s) [\underline{g}(s)]$$

$$(22)$$

$$- q(t) \cdot J(t-s) [\dot{\Lambda}(s)] - q(t) \cdot K(t-s)q(s) \} dsdt,$$

and we conclude from Lemmas 1-3 that (i)-(iii) imply (16).

Conversely, assume that (16) holds. We consider first only infinitesmal closed processes with g = 0. For such processes (22)

(con't)

Fourier heat conductors or Navier-Stokes fluids. Under reasonable assumptions, however, we recover both of these theories as <u>limiting</u> <u>cases</u> for slow processes (see, e.g., Coleman and Noll [5]). We do not allow for a specific dependence on $\dot{\Lambda}(t)$ or g(t), since such a dependence leads to infinite speeds of propagation for disturbances (see, e.g. the discussions given by Gurtin and Pipkin [6] and Truesdell [3], Lecture 4).

and Lemma 1 imply that (i) must hold. Similarly, processes with $\bigwedge_{\sim} = \bigcirc_{\sim}$ in conjunction with Lemma 2 lead to (ii). By (i), (ii), Lemma 1, Lemma 2, and (22), (16) implies that

 $\Phi\{ \mathcal{A}(\cdot) \} = \Phi\{ \widetilde{\mathcal{A}}(\cdot) \}$ for every infinitesmal process $\mathcal{A}(\cdot)$,

where

$$\Phi\{ \mathscr{A}(\cdot) \} = \int_{-\infty}^{\infty} \int_{-\infty}^{t} \{ \dot{\Lambda}(t) \cdot \underline{L}(t-s) [\underline{g}(s)] - \underline{g}(t) \cdot \underline{J}(t-s) [\dot{\Lambda}(s)] \} ds dt,$$

The result (iii) now follows from this fact and Lemma 3.

We assume for the remainder of the paper that the infinitesmal entropy production is invariant under time-reversal, ¹ so that (i)-(iii) of Theorem 3 hold.

We call

$$K_{-\infty} = \int_{0}^{\infty} K(s) ds,$$

provided it exists, the <u>equilibrium conductivity tensor</u>. Formally, $g_1 = K g$ is the infinitesmal heat flux arising from a temperature gradient that had always been constant. A direct consequence of (ii) of Theorem 3 is the following important result:

Corollary 1. The equilibrium conductivity tensor, K_{∞} , if it exists, is symmetric.

¹In view of Theorem 2, this will be true whenever Γ is invariant under time-reversal.

The equations (21) can also be written in the somewhat less abbreviated form:

$$\delta g(\uparrow) = \mathbf{\dot{f}} \quad G^{\uparrow}t-s) \quad [\mathbf{\dot{E}}(s)]ds + \mathbf{\dot{f}} \quad G_{\uparrow}(t-s)^{\uparrow}(s)ds + \mathbf{J} \quad L^{\uparrow}_{-co} t-s) \quad [_{s}(s)]ds,$$

$$\delta \mathbf{\hat{e}}(\checkmark t) = \int_{-\infty}^{t} G_{3}(t-s) \cdot \mathbf{\dot{E}}(s)ds + \int_{-\infty}^{t} G_{4}(t-s) \cdot \mathbf{\dot{\sigma}}(s)ds + \mathbf{J} \quad \bigwedge_{-\infty}^{A} 2(t-s) \cdot \mathbf{g}(s)ds,$$

$$\delta \mathbf{\dot{g}}(\checkmark f) = \mathbf{J} \quad \mathbf{J}_{\mathbf{x}}(t-s) \quad [\mathbf{\dot{E}}(s)]ds + \mathbf{J} \quad \mathbf{J} \quad \mathbf{\dot{\sigma}}_{-\infty} \quad \mathbf{\dot{\sigma}}(s)ds + \mathbf{J} \quad \mathbf{\dot{\sigma}}_{-\infty} \quad \mathbf{\dot{\sigma}}(s)ds + \mathbf{J} \quad \mathbf{\dot{\sigma}}_{-\infty} \quad \mathbf{\dot{\sigma}}(s)ds + \mathbf{J} \quad \mathbf{\dot{\sigma}}_{-\infty} \quad \mathbf{\dot{\sigma}}(s)ds,$$

$$\delta \mathbf{\dot{g}}(\checkmark f) = \mathbf{J} \quad \mathbf{J}_{\mathbf{x}}(t-s) \quad [\mathbf{\dot{E}}(s)]ds + \mathbf{J} \quad \mathbf{J} \quad \mathbf{\dot{\sigma}}_{-\infty} \quad \mathbf{\dot{\sigma}}(s)ds + \mathbf{J} \quad \mathbf{\dot{\sigma}}_{-\infty} \quad \mathbf{\dot{\sigma}}(s)ds + \mathbf{J} \quad \mathbf{\dot{\sigma}}_{-\infty} \quad \mathbf{\dot{\sigma}}(s)ds + \mathbf{J} \quad \mathbf{\dot{\sigma}}_{-\infty} \quad \mathbf{\dot{\sigma}}(s)ds,$$

$$(23)$$
Here, for each $s \uparrow 0$, G . $(s) ef(\mathbf{\dot{s}}, \mathbf{\ddot{s}})$; $G_{\circ}(s) \uparrow G_{\circ}(s) \in \mathbf{\dot{c}}$; L , $(s) \mathbf{c} \mathbf{\dot{s}}(\mathbf{\dot{v}}, \mathbf{\dot{s}})$;
 $G.(s) eR; \quad \uparrow_{0}(s), \mathbf{j}_{-}(s) eV; \quad \mathbf{j}_{-}(s) ef(\mathbf{f}, U); \quad K(s)_{e} JT. \quad In view of (17),$
the relaxation functions in (21) and (23) are related as follows

(using an obvious notation):

$$\mathfrak{g} \longleftrightarrow \begin{bmatrix} \mathfrak{g}_{\circ} \mathfrak{g}_{1} & \mathfrak{g}_{\circ} \mathfrak{g}_{2} \\ -\mathfrak{g}_{\circ} \mathfrak{g}_{1} & -\mathfrak{g}_{4} \end{bmatrix} , \quad \mathfrak{g}_{\circ} \longleftrightarrow \begin{bmatrix} \mathfrak{g}_{\circ} \mathfrak{L}_{1} \\ -\mathfrak{L}_{2} \end{bmatrix} * \mathtt{i} * \star \star \mathtt{m}^{[\texttt{fii} 2]'}$$

thus we have

Corollary 2. For every s > 0:

- (i) G-(s) j∕§.<u>symmetric</u>,
- (ii) $e_0 f_2(s) = -G_3(s)$, (iii) $9_0 L_1(s) = J_1(s)^T + constant$, (iv) $\xi_2(s) = -j_2(s) + constant$.

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Condition (i) asserts that <u>the stress relaxation function is</u> <u>symmetric</u>; (ii) is the interesting requirement that <u>the energy-strain</u> relaxation function be equal to -6 <u>times the stress-temperature</u> <u>q</u> <u>relaxation function</u>.

Let us assume, for the time being, that $L_{\infty}(\infty)$, $I_{2}(\infty)$, $J_{1}(GO)$, and $J_{2}(\infty)$ exist. Then the response of the material to the equilibrium history $g(s) \equiv \text{constant}$ will exist only if $L_{1}(\infty) = 0$ and $\hat{J}_{2}(\infty) = 0$. On the other hand, Coleman and Gurtin [7] (Theorem 7) have shown that (under the assumption of fading memory) the equilibrium heat flux vanishes when the temperature gradient vanishes, irrespective of the values of the other equilibrium histories. It is not difficult to show that if the equilibrium response in our theory is defined appropriately, then in order for our constitutive assumption to be consistent with this result we must have $J^{*}(\infty) = 0$ and $j_{0}(\infty) = 0$. These remarks should serve to motivate the hypotheses of

Corollary 3. Assume that $L_n(oo)$, $f_{(oo)}$, $J^{(oo)}$, and $2_9(oo)$ exist and are equal to zero. Then

9 L.(s) = J.(s)^T, $\hat{}_{\circ}(s) = -j_{\circ}(s)$ for every s $\hat{}$ 0.

A direct consequence of Corollary 3 is the following result: in the linear relations (23) the stress and internal energy are

independent of the history of the temperature gradient if and only if the heat flux is independent of the histories of strain and temperature.

We now lay down the following additional hypothesis:

(F) $\hat{\eta}$ has a derivative $\delta \hat{\eta}$ at ω_0 ; moreover, there <u>exist continuous functions</u> $M_1 : [0,\infty) \longrightarrow \Im$, $M_2 : [0,\infty) \longrightarrow \mathbb{R}$, <u>and</u> $m_3 : [0,\infty) \longrightarrow \mathbb{V}$ <u>such that</u>

$$\delta\hat{\eta}(\mathcal{A}^{t}) = \int_{-\infty}^{t} \underbrace{M}_{-\infty}(t-s) \cdot \dot{E}(s) \, ds + \int_{-\infty}^{t} \underbrace{M}_{2}(t-s) \cdot \dot{\mathcal{Y}}(s) \, ds + \int_{-\infty}^{t} \underbrace{M}_{-\infty}(t-s) \cdot g(s) \, ds$$
(24)

for every infinitesmal closed process $\mathcal{A}(\cdot) = [\underline{H}(\cdot), \mathcal{V}(\cdot), \underline{g}(\cdot)]$ and every $t \in \mathbb{R}$. As before, \underline{E} is the infinitesmal strain (6). If we define the free-energy ψ through

 $\psi = \varepsilon - \theta \eta,$

then it follows from (8) that

$$\psi(t) = \hat{\psi}(\mathcal{A}^{t}) = \hat{\varepsilon}(\mathcal{A}^{t}) - \theta(t)\hat{\eta}(\mathcal{A}^{t}).$$

In addition, we conclude from (B) and (F) that the functional $\hat{\psi}$: $\#(\$, \bigstar_{o}) \longrightarrow \Re$ has a derivative $\delta \hat{\psi}$ at \bigstar_{o} ; in fact,

$$\delta\hat{\psi}(\mathcal{A}^{\mathsf{t}}) = \delta\hat{e}(\mathcal{A}^{\mathsf{t}}) - \theta_{0}\delta\hat{\eta}(\mathcal{A}^{\mathsf{t}}) - \hat{\eta}(\mathcal{A}_{0})\mathcal{O}(\mathsf{t})$$
(25)

for every <u>infinitesmal</u> process $\mathcal{A}(\cdot)$.

In Coleman's thermodynamics of materials with memory [8],¹ the instantaneous derivative of the free-energy with respect to strain is the stress, the instantaneous derivative of the freeenergy with respect to temperature is the negative of the entropy, and, at an equilibrium state, the derivative with respect to each of the past histories vanishes. The following assumption is motivated by -- and is completely consistent with -- Coleman's results:

(G) for every infinitesmal closed process $\mathscr{L}(\cdot)$ and every teR,

$$\delta\hat{\psi}(\mathcal{A}^{t}) = \hat{S}(\mathcal{A}_{O}) \cdot H(t) - \hat{\eta}(\mathcal{A}_{O})^{1/2}(t).$$
 (26)

By (D), (25), and (26),

$$\delta \hat{\hat{\varepsilon}}(\mathcal{A}^{t}) = \theta_{0} \delta \hat{\eta}(\mathcal{A}^{t}),$$

and (ii) and (iv) of Corollary 2 in conjunction with (23) and (24) yield

Corollary 4. For every
$$s \ge 0$$
:
(i) $G_2(s) = -M_1(s)$,
(ii) $j_2(s) = -\theta_0 m_3(s) + constant$.

¹See also [7], where a dependence on g^t is included.

Condition (i) is the assertion that the <u>stress-temperature</u> <u>relaxation function be equal to the negative of the entropy-</u>

strain relaxation function.

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