

Geometric thermodynamics, non-equilibrium entropy and revision of B.D. Coleman's thermomechanics

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journals.sagepub.com/home/mms**Joe D Goddard** *Department of Mechanical and Aerospace Engineering, University of California, San Diego, San Diego, CA, USA*

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Abstract

This paper is a continuation with certain modifications of a previous work by this author involving a new theory for the continuum-mechanical entropy in non-equilibrium states. Treating internal energy as an essential coordinate in the thermomechanical state space, the theory provides a nominal *calorimetric* theory of materials with memory as an alternative to the widely accepted *thermometric* theory of Coleman which treats both entropy and temperature as “primitives” without a compelling connection to experimental measurement. Following a brief review of the previous work, involving a generally defined topology of state space for higher-gradient continua, a revision of Coleman’s theory is proposed that specifies non-equilibrium entropy as the variational extremum of a functional of the forces that define the relevant cotangent bundle of the underlying state space. As a conjecture, the optimal cycle in state space is assumed to be a non-equilibrium generalization of the classical Carnot cycle.

Keywords

Second law of thermodynamics, thermomechanical map, materials with memory, non-equilibrium entropy, recoverable work

1. Introduction

The goal of this work is to provide an extension to thermomechanics of the standard geometry of continuum mechanics, the subject of impressive expositions by Segev and Epstein [5,6]. Among the benefits of such an extension is the possibility of an enhanced treatment of the thermodynamics of defects. As a rough outline, we begin with a brief review of a previous work by Goddard [1], denoted by JG in the following, where a definition was given of the non-equilibrium entropy for continuum thermomechanics as an extension of the equilibrium entropy and temperature defined by the landmark work of Carathéodory [2], hereinafter denoted by CC.

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We then consider the differential geometry of the relevant finite-dimensional thermomechanical state space and the application to *graded* (higher-gradient) materials. Following this, we lay down what we shall call a *calorimetric* theory for the thermomechanics of materials with memory to be contrasted with what may be called the *thermometric* theory of Coleman [15] hereinafter denoted by BC.

After a brief recapitulation of the definition of nonequilibrium entropy given previously by JG, a brief treatment is given of the special case of linear viscoelasticity which has received considerable attention by others.

2. Review and extension of prior work

2.1. Generalization of CC

As generalization of the equilibrium situation where entropy is constructed from calorimetry and the equilibrium equations of state for the configurational forces that define work, the non-equilibrium entropy is derived from the history of the same configurational forces and an appropriate equilibrium temperature. Following CC, we focus on what he calls *simple systems* involving a finite set of configurational variables. This suffices to provide a pointwise description of *graded* or *higher-gradient* continua defined by a finite set of higher-spatial gradients of configurational variables. Following a recapitulation of JG with elaboration on the geometric underpinnings, a revision is proposed of Coleman's thermomechanics of materials with memory given in BC. The treatise of Day [4] provides a thorough mathematical exposition.

As synopsis of JG in a somewhat different notation, we extend Carathéodory's "simple" system at equilibrium to non-equilibrium systems determined by the past history of a finite set of variables:

$$\mathbf{z} = \{z^0, z^1, \dots, z^n\} = \{\varepsilon, \zeta\}, \text{ with } z^0 = \varepsilon, \quad (1)$$

$$\text{and } \zeta = \{z^1, z^2, \dots, z^n\}$$

which, with notation for dependence on time t suppressed, represents the thermodynamic state space $\mathcal{T}$ as an $n+1$ dimensional t -dependent manifold. In lieu of the overworked term *simple*, we henceforth employ *discrete* for systems defined by equation (1).

As in JG, we identify Carathéodory's abstract z^0 with specific internal energy ε on the grounds that this is the primary measurable quantity or observable that serves to set thermomechanics apart from classical mechanics, thereby providing the foundation for the first law of thermodynamics. Then, the remaining quantities ζ represent configurational variables that serve to define configurational working.

2.2. Differential geometry

The standard continuum-mechanical map or "placement" of material points $\mathbf{X} \in \mathbb{R}^3$ into spatial points $\mathbf{x} \in \mathbb{R}^3$, with kinematics devoid of energetics, may be regarded as thermodynamically incomplete. A more complete picture is provided by the augmented map in Figure 1 and the characterization *geometric thermodynamics* of Carathéodory's theory by Frankel [9]. Under the transformation from internal energy to equilibrium temperature θ one may if desired replace $\{\varepsilon, \mathcal{E}\}$ by $\{\theta, \Theta\}$ in the figure and the discussion immediately following.

It seems plausible to interpret time-dependent ξ and φ , respectively, as the thermomechanical *states* and *processes* of Coleman and Owen [15] and Coleman et al. [16] with certain functionals of φ defining their *actions*. We recall that these concepts provide the foundation for their mathematical proof of the existence of non-equilibrium entropy. While mathematically rigorous, their treatment does not explicitly relate the non-equilibrium entropy to non-equilibrium forces as advocated by the present author. However, their analysis does consider the possibility of materials having only approximate cycles, which may place a restriction on certain of the present results.

As for the first law of thermodynamics, the incremental heat dq received by the system on any infinitesimal trajectory is given by the Pfaffian differential form, i.e., one-form, involving configurational forces

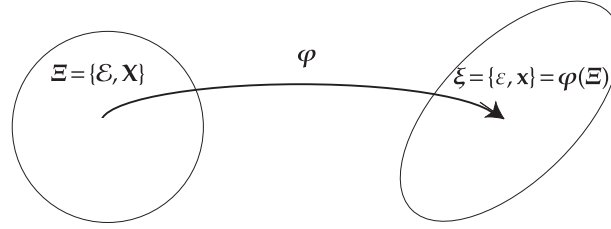


Figure 1. Thermomechanical map.

$f_i(\mathbf{z})$, $i = 1, 2, \dots, n$, and providing the first law (or energy balance (usually taken as axiomatic):

$$dq = d\varepsilon + \bar{d}w = \mathbf{h} \cdot d\mathbf{z} = \sum_{i=0}^n h_i(\mathbf{z}) dz^i, \quad (2)$$

$$\text{with } \bar{d}w = \mathbf{f} \cdot d\boldsymbol{\zeta} = \sum_{i=1}^n f_i(\mathbf{z}) dz^i, \text{ and } \mathbf{h} = \{1, \mathbf{f}\},$$

where we adopt the conventional *active* definition of incremental work $\bar{d}w$ and where the notation of exterior calculus is obtained by omitting the symbol $\bar{d}$ for infinitesimals. As done for internal energy ε in equation (2), we adopt lower case Greek for various specific (per unit mass) extensive thermodynamic properties.

Thus, the first law of thermodynamics is tantamount to the definition of incremental heat in terms of the cotangent vector $\mathbf{h}$ representing the differential form $d\varepsilon + \bar{d}w$. This determines the equivalence of heat and work in the case of constant ε or of heat and internal energy in the case of constant $\boldsymbol{\zeta}$.

We recall that CC interprets the condition $\bar{d}q = 0$ in terms of *adiabatic inaccessibility*, which serves to define a foliation (of co-dimension 1) [7–9] of equilibrium state space into hypersurfaces of constant entropy $\eta(\mathbf{z})$. As pointed out in JG, these represent local holonomic constraints on the energy balance, with scalar temperature θ representing Lagrange multiplier as force of constraint (which seems to be anticipated by the “force of heat” of Clausius [10] and Delphenich [11]). Thus, the inaccessibility of CC is simply a restriction to local hyper-surfaces of constant entropy, reflecting the time-worn mantra that adiabatic and reversible implies isentropic.

Taking θ to be the empirical absolute temperature of thermodynamics, with (as axiom) $\theta > 0$, ensures the positivity of $(\partial\eta/\partial\varepsilon)_{\boldsymbol{\zeta}} = 1/\theta$ and the invertibility of $\eta(\varepsilon, \boldsymbol{\zeta})$, with inverse function $\hat{\varepsilon}(\eta, \boldsymbol{\zeta})$. Following the contemporary literature [12,13], we refer to these as *caloric equations of state*. Then, with independent variables $\hat{\mathbf{z}} = \{\eta, \boldsymbol{\zeta}\}$ the first law of thermodynamics reduces to the general Gibbsian [14] relation

$$d\hat{\varepsilon} = \theta d\eta - \hat{\mathbf{f}} \cdot d\boldsymbol{\zeta}, \quad \theta = \partial_{\eta}\hat{\varepsilon}, \quad \hat{\mathbf{f}} = -\partial_{\boldsymbol{\zeta}}\hat{\varepsilon} \quad (3)$$

Here as in the following, we employ the common notation $\partial_{\mathfrak{X}} = \partial/\partial\mathfrak{X}$ for independent variables $\mathfrak{X}$.

Referring the reader to JG for a discussion of the various extremum principles that serve to establish equilibrium and the associated stability for discrete thermomechanical systems, we turn next to the case of continuous systems. We note in passing that the above relations give the equilibrium temperature θ as function of energy and configuration, say, $\theta_{\text{eq}}(\varepsilon, \boldsymbol{\zeta})$ which is essential to the revision considered below of Coleman’s [3] thermomechanics in order to achieve what is proposed here as a more acceptable form.

3. Graded continua

The adjective *graded*¹ is employed here as alternative to “higher-gradient” often used to denote thermo-mechanical continua in which the constitutive equations involve a finite number n of spatial gradients. This representation which involves a finite set of state variables may be regarded as a weakly emergent form of fully non-local effects. For the purposes of the present discussion, we set aside gradients $\partial_{\mathbf{x}}^k$,

so that the relevant tangent and cotangent spaces now become, respectively, elements of the spatial *jet bundle* [5,6,17] J_n and its cotangent J_n^* , with $J_1 = T\varphi$, the tangent space representing simple materials.

3.1. The simple continuum

With reference to Figure 1, the infinitesimal generalised displacement field $d\xi = d\varphi = \{d\varepsilon, d\mathbf{x}\}$ defines the tangent space $T\varphi$, to the configuration space at the configuration φ and the internal energy balance for the standard (Coleman-Noll) *simple continuum* is derived from an element $\mathbf{f}$ of the cotangent space $T^*\varphi$, such that

$$\rho \dot{\varepsilon} = -\text{div} \mathbf{q} - \mathbf{f} \cdot \dot{\zeta}, \quad \text{where } \zeta = \partial_{\mathbf{X}} \mathbf{x}, \quad (\dot{\cdot}) = (\partial_t)_{\mathbf{X}}, \quad (4)$$

where $\partial_{\mathbf{X}} \mathbf{x}$ is the deformation gradient, $(\dot{\cdot}) = \partial_t(\cdot)_{\mathbf{X}}$ is the standard material time derivative, $\mathbf{q}$ is heat flux², and $-\mathbf{f}$ is Piola stress. Thus, we have that

$$\bar{d}q := -\text{div} \mathbf{q} \, dt / \rho = d\varepsilon + \bar{d}w, \quad \text{with } \bar{d}w = \mathbf{f} \cdot d\zeta / \rho \quad (5)$$

at each spatial point $\mathbf{x}$. Hence, a *simple continuum* is but a pointwise realization of Carathéodory's discrete system, while the entire body $\mathcal{B}$, an infinite collection of discrete systems, evidently does not represent a discrete system unless homogeneous. A more general treatment including fully non-local effects would require an analysis in function space, taking us well beyond the scope of the present article.

Generalizing the simple material, the full 16-dimensional tangent space is represented by abstract vector

$$\{\partial_{\mathcal{E}} \varepsilon, \partial_{\mathbf{X}} \varepsilon, \partial_{\mathcal{E}} \mathbf{x}, \partial_{\mathbf{X}} \mathbf{x}\} \quad (6)$$

Roughly speaking, the terms $\partial_{\mathcal{E}} \varepsilon$ and $\partial_{\mathbf{X}} \varepsilon$ serve to represent, respectively, energy input at a fixed material point, involving change $\varepsilon - \mathcal{E}$, and deformation at fixed initial energy; whereas $\partial_{\mathbf{X}} \varepsilon$ and $\partial_{\mathcal{E}} \mathbf{x}$ can capture, respectively, spatial energy gradients and thermally driven spatial displacements.

The corresponding element $\mathbf{h}$ of the cotangent space $T^*\varphi$, a generalized force (JG) represented by the last member of equation (2), defines the associated energetics by means of constitutive relations that generally involve coupling between variables.

We focus here on effects associated with spatial gradients arising from material gradients $\partial_{\mathbf{X}}$ and assume that gradients of ε represent heating effects and not mechanical power. Then, the abstract state vector

$$\mathbf{z} = \{\epsilon, \zeta\}, \quad \text{where } \epsilon = \{\varepsilon, \partial_{\mathbf{X}} \varepsilon\} \text{ \& } \zeta = \{\mathbf{x}, \partial_{\mathbf{X}} \mathbf{x}\} \quad (7)$$

represents the energetics of the conventional (Coleman-Noll) *simple continuum*. We assume translation invariance, neglecting external body forces, so that the leading component $\mathbf{x}$ of ζ can be ignored.

3.2. Higher gradients

Here, the relevant independent coordinates are obtained by replacing $\partial_{\mathbf{X}}$ in equation (7) by a series of terms $\partial_{\mathbf{X}}^k$, $k = 1, 2, \dots, n$ with the state vector now being

$$\begin{aligned} \mathbf{z} &= \{\epsilon, \zeta\}, \quad \text{with } \epsilon = \{\varepsilon, \partial_{\mathbf{X}} \varepsilon, \dots, \partial_{\mathbf{X}}^n \varepsilon\}, \\ &\text{and } \zeta = \{\partial_{\mathbf{X}} \mathbf{x}, \dots, \partial_{\mathbf{X}}^n \mathbf{x}\}, \end{aligned} \quad (8)$$

and this presumably covers higher-gradient effects in heat flux and stress.

The configurational power or working is once more given by equation (4) with

$$\mathbf{f} \cdot \dot{\zeta} = \sum_{k=1}^n \mathbf{f}_k \cdot \dot{\mathbf{z}}^{(k)}, \quad \text{with } \mathbf{z}^{(k)} = \partial_{\mathbf{X}}^k \varphi, \quad (\dot{\cdot}) = (\partial_t)_{\mathbf{X}}, \quad (9)$$

where $\mathbf{q}$ again denotes heat flux, and $-\mathbf{f}_k$ a generalized Piola stress, all depending generally on the history $\mathbf{z}^{(k)}(t')$ for $-\infty < t' \leq t$, $k = 1 : n$. This corresponds to the local differential form equation (5). It is once more evident that the entire body $\mathcal{B}$ does not represent Carathéodory's discrete system.

3.3. Remark on approximation

While the graded material may be regarded as arising from a local polynomial approximation to a smooth map φ , one can obtain a more general approximation in terms of a given finite functional basis $\varphi^{(m)}(\Xi)$ with, e.g.

$$\begin{aligned} \varphi(\Xi) &\approx \sum_m p_m \varphi^{(m)}(\Xi), \text{ and } \mathbf{z} = \sum_m p_m \mathbf{z}^{(m)}, \\ \text{with } \mathbf{z}^{(m)} &= \partial_{\mathbf{X}} \varphi^{(m)}(\Xi), \end{aligned} \quad (10)$$

where the finite set of coefficients p_m depend on the history of the $\mathbf{z}^{(m)}$. This could prove useful for variational methods relevant to the following discussion devoted to non-equilibrium states.

4. Non-equilibrium entropy

We recall that the postulate of JG, based on the notion of extremal recoverable work, takes on the general form for a system of given mass:

For a given energy and configuration, the difference between equilibrium entropy η_{eq} and the non-equilibrium entropy η is given by $\eta_{eq} - \eta = w_{\max}/\theta$ where $w_{\max}$ is the maximum work that could be obtained by heat exchange with a reservoir at the equilibrium temperature θ .

This leads to a variational principle for the determination of η .

4.1. Discrete systems

As a simplified and amended version of that in JG, η is determined from the extremum given by the variation of a functional of $\mathbf{z} = \{\epsilon, \zeta\}$ defined in equation (8):

$$\begin{aligned} w_{\max}(t) &= (\eta_{eq} - \eta)\theta = \psi - \psi_{eq} = \mathfrak{W}\{\mathbf{z}(\overset{t}{\underset{-\infty}{t'}})\} \\ &= \max_{\mathbf{z}(s), s > t} \int_t^\infty \mathbf{f}(s) \cdot d\zeta(s), \text{ with } \psi = \epsilon - \theta\eta \quad , \\ \mathbf{f}(s) &= \mathfrak{F}\{\mathbf{z}(\overset{s}{\underset{-\infty}{t'}})\}, \text{ and } \lim_{s \rightarrow \infty} \mathbf{z}(s) = \mathbf{z}(t) \end{aligned} \quad (11)$$

where the last relation corresponds to the closed connection of Day [4], whose definition of non-equilibrium entropy of the standare simple material with memory is presumably subsumed by the present treatment.

As pointed out in JG equation (11) provides a constructive definition of entropy and dissipation, which as pointed out above we denote as *calorimetric*, to distinguish it from the celebrated *thermometric* version of BC in which θ replaces ϵ and entropy is regarded as a primitive. Although Coleman's theory might be enhanced by taking θ to be the equilibrium temperature at given energy and configuration, it would still fail to connect entropy explicitly to the history of forces, regarded here as a natural generalization of the equilibrium construct, in which entropy is inferred from equilibrium equations of state.

5. Thermometric theory

We recall that Coleman recognizes in BC the possibility of theories involving various independent variables based on certain assumptions as to the invertibility of transformations between histories. Thus,

unburdened by the present concerns for observability, he proposes in §12 of BC our $\mathbf{z} = \{\varepsilon, \partial_{\mathbf{x}}\mathbf{x}\}$ as independent variables for simple materials, appealing to the transformation from the history of his empirical temperature to the history of ε (cf. §5.5 of Day [4]). While ostensibly more general it is in our view less defensible than the proposal above to set the empirical temperature equal to the equilibrium temperature θ and employ the invertible equilibrium relation between θ and ε .

Hence, with the above in mind for a discrete system representing a material point in a graded continuum, we take:

$$\begin{aligned} \mathbf{z} = \{\boldsymbol{\epsilon}, \zeta\} &\Rightarrow \tilde{\mathbf{z}} = \{\boldsymbol{\vartheta}, \zeta\}, \text{ with } \mathbf{f}(s) := \mathfrak{F}\{\mathbf{z}(\frac{s}{t'})\} \\ &= \tilde{\mathfrak{F}}\{\tilde{\mathbf{z}}(\frac{s}{t'})\} =: \tilde{\mathbf{f}}(s), \text{ \& } \boldsymbol{\vartheta} = \{\theta, \partial_{\mathbf{x}}\theta, \dots, \partial_{\mathbf{x}}^n\theta\}, \end{aligned} \quad (12)$$

such that the variational problem for determination of nonequilibrium entropy becomes

$$\begin{aligned} (\eta_{eq} - \eta)\theta &= \psi - \psi_{eq} = \tilde{\mathfrak{W}}\{\tilde{\mathbf{z}}(\frac{t}{t'})\} \\ &= \max_{\tilde{\mathbf{z}}(s), s > t} \int_t^\infty \tilde{\mathbf{f}}(s) \cdot d\zeta(s), \text{ with } \lim_{s \rightarrow \infty} \tilde{\mathbf{z}}(s) = \tilde{\mathbf{z}}(t) \end{aligned} \quad (13)$$

6. Linear viscoelasticity

We consider a general version of the classical Boltzmann–Volterra form employed in modern treatments of linear viscoelasticity [4,18–21], for which Del Piero and Deseri [20] offer a comprehensive analysis of various free energies. For easier interpretation, and in order to connect to the existing literature, we restrict ourselves to *energetically simple materials*, i.e., materials without dependence of force on gradients of energy. Thus, we take $\boldsymbol{\epsilon} = \varepsilon$ in the linear force-displacement relation:

$$\begin{aligned} \mathbf{f}(s) &= \int_{-\infty}^s \mathbf{M}(\varepsilon', s - s') \mathbf{v}(s') ds', , \\ \text{i.e. } f_i(s) &= \int_{-\infty}^s M_{ij}(\varepsilon'_k, s - s') v^j(s') ds', \\ \text{with } \varepsilon' &= \varepsilon(s') \text{ and } \mathbf{v} := \dot{\zeta}, \end{aligned} \quad (14)$$

where $\mathbf{M}(\varepsilon, \sigma) = 0$ for $\sigma < 0$, is a tensorial modulus depending smoothly on its arguments for $\sigma > 0$. Also, the integral is to be interpreted as Riemann–Stieltjes, with $\mathbf{v}(u) du = d\zeta(u)$ for discontinuous changes in $\zeta(u)$.

Hence, the work to be maximized is given by the quadratic form

$$\begin{aligned} w_t &= \int_t^\infty \int_{-\infty}^s v^i(s) M_{ij}(\varepsilon'_k, s - s') v^j(s') ds' ds \\ &= \int_t^\infty \int_{-\infty}^s \mathbf{v}(s) \cdot \mathbf{M}(\varepsilon', s - s') \mathbf{v}(s') ds' ds \\ &= \int_{-\infty}^\infty \int_{-\infty}^\infty \mathbf{v}(s) \cdot \mathbf{L}_t(s, s') \mathbf{v}(s') ds' ds, \text{ where } , \\ \mathbf{L}_t(s, s') &= \frac{1}{2} [\mathbf{K}_t(s, s') + \mathbf{K}_t^*(s', s)] = \mathbf{L}_t^*(s', s), \\ \text{with } \mathbf{K}_t(s, s') &= H(s - t) H(s - s') \mathbf{M}(\varepsilon', |s - s'|) \end{aligned} \quad (15)$$

where asterisk denotes the adjoint or matrix transpose and H denotes the Heaviside step function, employed here to achieve a certain symmetry.

Noting that $\delta_t\{\varepsilon(u), \mathbf{v}(u)\} := H(u-t)\delta\{\varepsilon(u), \mathbf{v}(u)\}$ represents the restriction of a variation to the domain $u > t$, the stationarity of equation (15) with respect to $\delta_t\{\varepsilon(u), \mathbf{v}(u)\}$ implies that

$$\int_t^\infty \int_{-\infty}^\infty \delta \mathbf{v}(s) \cdot \mathbf{L}_t(s, s') \mathbf{v}(s') \, ds' \, ds = 0, \quad (16)$$

and that

$$\int_t^\infty \int_t^s \mathbf{v}(s) \cdot [\delta \varepsilon(s') \cdot \mathbf{N}_t(s, s')] \mathbf{v}(s') \, ds' \, ds = 0, \quad (17)$$

where

$$\mathbf{N}_t(s, s') = \partial_\varepsilon \mathbf{M}(\varepsilon', s - s') := \partial_\varepsilon \mathbf{M}(\varepsilon, s - s')|_{\varepsilon=\varepsilon'}$$

These relations lead to the further conditions for $s > t$

$$\begin{aligned} & \int_{-\infty}^\infty [H(s - s') \mathbf{M}(\varepsilon(s'), s - s') \\ & + H(s' - s) \mathbf{M}^*(\varepsilon(s), s' - s)] \mathbf{v}(s') \, ds' = 0, \end{aligned} \quad (18)$$

and

$$\partial_\varepsilon \int_t^s \mathbf{v}(s) \cdot \mathbf{M}(\varepsilon(s'), s - s') \mathbf{v}(s') \, ds' = 0 \quad (19)$$

The relations (18) and (19) can be cast into forms involving the null space of linear differential operators in $D = \partial_s$ involving translations $\exp(\pm D\sigma)$. Thus, equation (18) becomes

$$\begin{aligned} \mathbf{S}(s, D) \mathbf{v}(s) &= 0, \\ \text{where} \\ \mathbf{S}(s, D) &= \int_0^\infty [e^{-D\sigma} \mathbf{M}(\varepsilon(s), \sigma) + \mathbf{M}^*(\varepsilon(s), \sigma) e^{D\sigma}] \, d\sigma \end{aligned} \quad (20)$$

...

while equation (19) can be written as

$$\begin{aligned} \mathbf{v}(s) \cdot \mathbf{P}_t(s, D) \mathbf{v}(s) &= 0 \\ \text{where } \mathbf{P}_t(s, D) &= \int_0^{s-t} e^{-D\sigma} \partial_\varepsilon \mathbf{M}(\varepsilon(s), \sigma) \, d\sigma \end{aligned} \quad (21)$$

6.1. Constant energy or temperature

Whenever internal energy is constant, such that heating is balanced by working, the relation (20) with $\varepsilon = \text{const.}$ is the sole restriction on ζ . If we further impose the symmetry (self-adjointness) $\mathbf{M} = \mathbf{M}^*$ deemed essential by previous works [20] this relation reduces to the form

$$\left\{ \int_0^\infty \mathbf{M}(\sigma) \cosh(\sigma D) \, d\sigma \right\} \mathbf{v}(s) = 0, \quad (22)$$

where we suppress notation for dependence on the constant ε . Note that when $\mathbf{v}$ is a sum of exponentials D is replaced by a constant for each term in sum and the integral equation (22) reduces to an algebraic form. In particular, the Fourier-space version of equation (22) is

$$\int_{-\infty}^{\infty} \hat{\mathbf{M}}(\omega) \hat{\mathbf{v}}(\omega) d\omega = 0,$$

where

$$\hat{\mathbf{v}}(\omega) = \int_{-\infty}^{\infty} e^{i\omega\sigma} \mathbf{v}(\sigma) d\sigma \quad (23)$$

and

$$\hat{\mathbf{M}}(\omega) = \int_0^{\infty} \cos(\omega\sigma) \mathbf{M}(\sigma) d\sigma$$

Under rather mild restrictions on $\mathbf{M}(\sigma)$ this implies that $\mathbf{v}(s) \equiv \mathbf{0}$ and, hence, that the nominal non-equilibrium entropy and free energy are identical with their equilibrium counterparts. This result, perhaps surprising at first glance, rules out adiabatic paths where work involves change in internal energy, paths whose equilibrium counterparts are essential to Carnot cycles.

A similar result applies to isothermal processes in the thermometric theory, since the restriction to constant temperature generally implies that work must be compensated by heating, once again ruling out adiabatic paths.

It is worth noting that the above findings are compatible with various phenomenological models of rubber-like “entropic” viscoelasticity based on equilibrium entropy. By the same token the free energies associated with various mathematical theories [18–20,22,23], should be regarded as equilibrium quantities based on equilibrium entropy.

The present treatment suggests that the extremum of recoverable work defining non-equilibrium entropy is achieved by a sort of non-equilibrium Carnot cycle or approximate cycle involving both diabatic and adiabatic paths. At the time of this writing, the author is unable to provide a more conclusive argument.

Acknowledgements

It is both privilege and pleasure to offer this article as tribute to a distinguished colleague, Professor Marcelo Epstein, whose work on the geometry of continuum mechanics, much of it done in collaboration with Professor Reuven Segev, stands as a monument in the field. To a certain extent it lays a modern groundwork for the classical “geometric thermodynamics” [9] of Carathéodory that inspires the present paper. At the same time, I also add my overdue tribute to the late B.D. Coleman who paved the way to a modern thermomechanical theory of materials with memory, providing not only a mathematical foundation for the classical Boltzmann-Volterra ideas but also the mathematical *lingua franca* reflected in the present article.

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Notes

1. Distinct from the contemporary “functionally graded” denoting materials with spatial property gradients.
2. In contrast to the usual representation as heat source, we attribute radiant heating to the divergence of the radiant portion of the total heat flux $\mathbf{q}$.

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