A NEW SYSTEMATIC APPROACH TO NON-EQUILIBRIUM THERMODYNAMICS

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ABSTRACT

The theory presented here is based on the following definitions and postulates:

(i) A process is defined as a set of functions \( \rho(x, t), \chi(x, t), \vartheta(x, t) \) representing the density, the motion and the (empirical) temperature.

(ii) Constitutive equations are formulated for the stress tensor \( \mathbf{t} \), the internal energy \( e \) and the heat flux \( \mathbf{q} \), such that a set \( \mathbf{t}, e, \mathbf{q} \) belongs to every process.

(iii) A thermodynamic process is defined as a process which is a solution of the equations of balance for the mass, the momentum and the energy.

(iv) (Entropy Principle) In a body \( \mathcal{B} \) there exists a scalar extensive quantity which cannot decrease in any thermodynamic process, if its flux through the surface of \( \mathcal{B} \) vanishes, and whose density \( \eta \) and flux \( \Phi \) are given by constitutive relations. This quantity is called entropy.

The ideas (i)–(iv) can be put to use to derive restrictive conditions on the constitutive relations for \( \mathbf{t}, e, \mathbf{q}, \eta \) and \( \Phi \), and these restrictions are valid for arbitrary non-equilibrium processes.

In order to obtain restrictions on \( \mathbf{t}, e \) and \( \mathbf{q} \) alone one needs further information about thermodynamic processes in a body and essentially the only processes about which useful information exists are uniform equilibrium processes. We know from experience that:

(v) There exists a uniform equilibrium in a body on whose boundary the fluxes of mass and energy vanish.

(vi) If such a body \( \mathcal{B}_T \) consists of two subbodies \( \mathcal{B}^a \) \((a = 1, 2)\) of different materials, there exists a uniform equilibrium in each of the subbodies and their temperatures are equal.

(vii) If \( E_T, H_T \) and \( V_T \) are internal energy, entropy and volume of \( \mathcal{B}_T \), and \( E^a, H^a \) and \( V^a \) the internal energies, entropies and volumes of \( \mathcal{B}^a \), then the following relations hold:

\[
\left(\frac{\partial E_T}{\partial V^1}\right)_{H TV^2} = \left(\frac{\partial E^1}{\partial V^1}\right)_{H_1} \quad \text{and} \quad \left(\frac{\partial E_T}{\partial V^2}\right)_{H TV^1} = \left(\frac{\partial E^2}{\partial V^2}\right)_{H^2}
\]

From (i)–(vii) the existence of an absolute temperature can be proved for uniform equilibrium processes, but not more generally.

The theory based on (i)–(vii) avoids any specific assumptions on the entropy and the entropy flux, in particular it avoids the customary assumptions that the flux and supply of entropy are equal to the quotients of flux and supply of internal energy and absolute temperature.

If the principles (i)–(vii) are applied to a simple heat-conducting fluid, one may obtain, apart from all the familiar results for the material, a hyperbolic
equation of heat conduction; and this is an immediate consequence of avoiding specific assumptions concerning the entropy and its flux.

1. INTRODUCTION

An evaluation of the literature on thermodynamics shows that writers in this field make some specific assumptions which are motivated by thermodynamics, whose validity or range of validity, however, is never assessed, except by intuition. Such specific assumptions are:
(i) there exists an absolute temperature in non-equilibrium,
(ii) the flux of entropy is equal to the heat flux divided by the absolute temperature,
(iii) the supply of entropy is equal to the supply of internal energy divided by the absolute temperature.
The entropy inequality based on these assumptions is used as a restrictive condition on the constitutive equations for stress, heat flux, internal energy and entropy.1

After recalling basic concepts of thermodynamics and introducing the notation in Section 2, I propose (in Section 3) an entropy principle, which is free of the specific assumptions (i) to (iii) above, and obtain restrictions on constitutive equations for arbitrary non-equilibrium processes. The method for deriving these restrictions is illustrated for simple heat conducting fluids, because these materials furnish the simplest non-trivial examples. In Section 4 I show that these restrictions, if supplemented by axioms on the behaviour of fluids in equilibrium, lead to all the restrictive conditions of linear irreversible thermodynamics and, moreover, allow for a finite speed of the propagation of heat.

In a recently published paper I have developed the method, which is presented here, for a relativistic fluid.

2. THERMODYNAMIC PROCESSES

The objective of thermodynamics is to determine the future development of the density ρ, the motion \( \chi_k \) and the (empirical) temperature \( \theta \) of a body \( B \). For this one employs the equations of balance of mass, momentum and energy:

\[
\left( \frac{\partial \rho}{\partial t} \right) = (\rho v_k)_k = 0 \\
\left( \frac{\partial \rho v_i}{\partial t} \right) + (\rho v_i v_k - t_{ik})_k = 0 \\
\left( \frac{\partial \rho e}{\partial t} \right) + (\rho e v_k + q_k)_k = t_{ik}v_{i,k} 
\]

(2.1)

together with the constitutive relations for the stress \( t_{ik} \), the heat flux \( q_i \), and the specific internal energy \( e \) for a simple heat-conducting fluid:

\[
t_{ik} = t_{ik}(\rho, \theta, \theta, \theta) \\
q_i = q_i(\rho, \theta, \theta, \theta) \quad \theta \equiv (\partial \theta/\partial t) + v_k \theta_k \\
e = e(\rho, \theta, \theta, \theta) 
\]

(2.2)

* Throughout this paper I shall use the customary cartesian tensor notation.
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The equations 2.1 form a complete set of differential equations for the determination of the unknown fields $\rho$, $\chi_k$ and $\theta$ from initial and boundary conditions.

In writing the constitutive relations 2.2 I have made use of the principle of equipresence and I also wish to use the principle of objectivity according to which the constitutive functions are isotropic tensor, vector or scalar functions with respect to the Euclidean group of transformations. These same principles will be applied to the constitutive relations for the entropy flux $\Phi_i$ and the specific entropy $\eta$ [see equations (3.2)].

A solution of the set 2.1 and 2.2 of differential equations will be called a thermodynamic process.

3. THE ENTROPY PRINCIPLE

The entropy principle assumed here reads: In every body there exists an extensive quantity, the entropy, with a non-negative production:

$$\frac{\partial \rho \eta}{\partial t} + (\rho \eta \delta_k + \Phi_k)_k \geq 0 \quad (3.1)$$

where $\Phi_i$ and $\eta$ are given by constitutive relations:

$$\eta = \eta(\rho, \theta, \theta_k, \theta)$$
$$\Phi_k = \Phi_k(\rho, \theta, \theta_k, \theta) \quad (3.2)$$

and the entropy inequality 3.1 holds for every thermodynamic process. This entropy principle will now be employed to derive restrictive conditions on the constitutive functions for $t_{ik}$, $q_i$, $\epsilon$, $\eta$ and $\Phi_i, \eta$.

I shall make use of a theorem in the theory of partial differential equations which states that, in general, there exists an analytical solution of a system like 2.1, 2.2 for arbitrary analytical initial conditions. If the above assertion about the entropy is true, the entropy inequality, which may be written in the form

$$(\eta + \rho \frac{\partial \eta}{\partial \rho}) \frac{\partial \rho}{\partial t} + \rho \frac{\partial \eta}{\partial \theta} \frac{\partial \eta}{\partial \theta} + \rho \frac{\partial \eta}{\partial \theta_k} \frac{\partial v_i}{\partial t} + \rho \frac{\partial \theta_k}{\partial \theta} \frac{\partial v_i}{\partial t} + \rho \frac{\partial \theta_k}{\partial \theta_k} \frac{\partial \theta_i}{\partial t} + \left[ \left( \frac{\partial \eta}{\partial \theta_k} + \frac{\partial \theta_k}{\partial \theta} \right) \frac{\partial \theta_i}{\partial t} + \left( \frac{\partial \eta}{\partial \theta_k} + \frac{\partial \theta_k}{\partial \theta} \right) \frac{\partial \theta_i}{\partial t} \right] \frac{\partial v_i}{\partial t} + \rho \frac{\partial \theta_k}{\partial \theta} \frac{\partial \theta_i}{\partial t}$$

must hold for all such solutions of initial value problems and, in particular, for arbitrary values of

$$\rho_{,i} \left( \frac{\partial \theta}{\partial t} \right)_i, \theta_{,ik}, v_{i,k} \quad (3.3)$$

at one point at the initial time.

* Tacit use has already been made in 2.2 of the principle of objectivity, because only objective quantities were admitted in the set of variables.
Of course, 3.3 contains also the derivatives $\partial \rho/\partial t$, $\partial \vartheta_i/\partial t$ and $\partial^2 \vartheta/\partial t^2$, but these are related to the quantities 3.4 by the system 2.1 and 2.2 of differential equations:

$$\frac{\partial \vartheta}{\partial t} = -(\rho v_k)_{,k}$$

$$\frac{\partial \vartheta_i}{\partial t} = -v_k v_{i,k} + \frac{1}{\rho} t_{ik,k}$$

$$\frac{\partial^2 \vartheta}{\partial t^2} = \left( v_k v_{i,k} - \frac{1}{\rho} t_{ik,k} \right) \vartheta_i + \frac{1}{(\partial \vartheta_k/\partial \vartheta)} \left( -\vartheta_k \varepsilon_{,k} + \frac{1}{\rho} t_{ik} v_{i,k} - \frac{1}{\rho} q_{k,k} \right)$$

$$+ \frac{\partial \varepsilon}{\partial \rho} (\rho v_k)_{,k} - \frac{\partial \varepsilon}{\partial \vartheta} \frac{\partial \vartheta}{\partial t} - \frac{\partial \varepsilon}{\partial \vartheta} \frac{\partial \vartheta_k}{\partial t}$$

I insert 2.2 in 3.5, carry out all differentiations and then eliminate $\partial \rho/\partial t$, $\partial \vartheta_i/\partial t$ and $\partial^2 \vartheta/\partial t^2$ from 3.3 and 3.5 thus obtaining an inequality which is explicitly linear in the derivatives 3.4; these, however, are arbitrary (except for the obvious symmetry of $\vartheta_{ik}$) and therefore the inequality could easily be violated unless their factors vanish. Therefore the entropy principle requires the following restrictions on the constitutive relations 2.2 and 3.2:

$$\frac{\partial \Phi_i}{\partial \rho} + \Lambda \frac{\partial q_i}{\partial \rho} = 0$$

$$\frac{\partial \Phi_i}{\partial \vartheta} + \frac{\partial \Phi_k}{\partial \vartheta_i} + \Lambda \left( \frac{\partial q_i}{\partial \vartheta_k} + \frac{\partial q_k}{\partial \vartheta_i} \right) = 0$$

$$\frac{\partial \Phi_i}{\partial q_i} + \Lambda \frac{\partial \vartheta_i}{\partial q_i} + \rho \left( \frac{\partial \eta}{\partial \vartheta_k} + \Lambda \frac{\partial \varepsilon_i}{\partial \vartheta_k} \right) = 0$$

$$-\rho^2 \left( \frac{\partial \eta}{\partial \rho} + \Lambda \frac{\partial \varepsilon}{\partial \rho} \right) \vartheta_{ik} - \Lambda t_{ik} + \left( \frac{\partial \Phi_k}{\partial \vartheta} + \Lambda \frac{\partial q_k}{\partial \vartheta} \right) \vartheta_i = 0$$

$$\left( \frac{\partial \eta}{\partial \vartheta} + \Lambda \frac{\partial \varepsilon}{\partial \vartheta} \right) \vartheta + \frac{1}{\rho} \left( \frac{\partial \Phi_k}{\partial \vartheta} + \Lambda \frac{\partial q_k}{\partial \vartheta} \right) \vartheta_k \geq 0$$

where $\Lambda$ is defined by

$$\Lambda = -\left( \frac{\partial \eta}{\partial \vartheta} \right) \left( \frac{\partial \varepsilon}{\partial \vartheta} \right)^{-1}$$

The conditions 3.6, 3.7 hold for all thermodynamic processes in a simple heat conducting fluid, they represent relations between the constitutive functions $t_{ik}$, $q_k$, $\varepsilon$, $\eta$, $\Phi_i$ and, if $\eta$ and $\Phi_i$ were known explicitly, we should have here what we are interested in, namely restrictions on the constitutive functions $t_{ik}$, $q_k$ and $\varepsilon$ alone. However, $\eta$ and $\Phi_i$ are not known explicitly and it is therefore necessary that the conditions 3.6, 3.7 be supplemented by axioms which express experience with processes in simple heat conducting fluids. Unfortunately observational methods are such that useful information
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can only be had for time-independent processes and indeed only for particularly simple time-independent processes.

4. PROPERTIES IN UNIFORM EQUILIBRIUM

Let us first consider a body \( \mathcal{B} \), consisting of a simple heat-conducting fluid, on whose boundary the normal components of the heat flux and of the velocity vanish (in the appropriate frame). Experience then leads to the formulation of the following axiom:
(a) There exists a uniform and time-independent process in \( \mathcal{B} \), which I shall call a uniform equilibrium or, briefly, an equilibrium for the purposes of this paper.

Let us now consider a body \( \mathcal{B}_T \) consisting of two subbodies \( \mathcal{B}^\alpha (\alpha = 1, 2) \) of different simple heat-conducting fluids and let the normal components of the heat flux and the velocity vanish on the boundary of \( \mathcal{B}_T \), whereas only the vanishing of the normal velocity is required on the boundaries of \( \mathcal{B}^\alpha \).

Experience shows that:
(b) there exists an equilibrium in the bodies \( \mathcal{B}^\alpha \) and the temperature is uniform throughout \( \mathcal{B}_T \).

With (a) and (b) the energy \( E_T \) and the entropy \( H_T \) of \( \mathcal{B}_T \) in equilibrium may depend on the temperature \( \theta \) and the volumes \( V^1 \) and \( V^2 \), whereas the energies \( E^1, E^2 \) and the entropies \( H^1, H^2 \) may depend on \( \theta, V^1 \) (for \( \alpha = 1 \)) and \( \theta, V^2 \) (for \( \alpha = 2 \)). Therefore \( E_T \) can be written as \( E_T(H_T, V^1, V^2) \) and \( E^\alpha (\theta, V^\alpha) \) and for these functions the following relations are postulated:

\[
\frac{\partial E_T}{\partial V^1} = \left( \frac{\partial E^1}{\partial V^1} \right)_{H_T, V^2} \quad \text{and} \quad \frac{\partial E_T}{\partial V^2} = \left( \frac{\partial E^2}{\partial V^2} \right)_{H_T, V^1}
\]

This last postulate is usually motivated by the form of the energy equation in a 'quasistatic and adiabatic process'.

I shall now use these axioms to obtain information about \( \Delta E \) (i.e. \( \Delta \) in equilibrium).

In equilibrium the entropy production \( \Sigma \), which is the LHS of 3.7, assumes its minimum value namely zero and a necessary condition for this is

\[
\frac{\partial \Sigma}{\partial \theta} \bigg|_E = 0 \quad \text{or} \quad \frac{\partial \eta}{\partial \theta} = - \Delta \frac{\partial E}{\partial \theta} \bigg|_E
\]

All conditions 3.6 are identically satisfied in equilibrium except the last one which shows that \( t_{ik} \bigg|_E \) has the form \( t_{ik} \bigg|_E = - p \bigg|_E \delta_{ik} \) and that

\[
\frac{\partial \eta}{\partial \rho} = - \Delta \left( \frac{\partial E}{\partial \rho} - \frac{p}{\rho^2} \bigg|_E \right)
\]

\( p \bigg|_E \) is called the pressure in equilibrium.

The equations 4.1 and 4.2 can be combined to

\[
d\eta = - \Delta \left( \frac{\partial E}{\partial \theta} \bigg|_E d\theta - \Delta \left( \frac{\partial E}{\partial \rho} \bigg|_E - \frac{p}{\rho^2} \right) d\rho \right)
\]
or, when $\eta|_E$ is considered as a function of $\varepsilon|_E$ and $\rho$

$$d\eta|_E = -\Lambda|_E \left( d\varepsilon|_E + p|_E d\left(\frac{1}{\rho}\right) \right)$$  \hspace{1cm} (4.4)

or, finally, by multiplying by the mass $M$ of $\mathcal{B}$ and introducing the internal energy $E$ and entropy $H$ of $\mathcal{B}$ in equilibrium:

$$dH = -\Lambda|_E (dE + p dV)$$  \hspace{1cm} (4.5)

Let us now consider a process between two equilibria characterized by $(E, V)$ and $(E + dE, V + dV)$ such that $dE + pdV \neq 0$; if such a process occurs without exchange of entropy through the surface of $\mathcal{B}$, $dH$ is positive and hence, from 4.5, $\Lambda|_E$ cannot be zero. If it is further assumed that $dH$ is finite, then $\Lambda|_E$ must also be finite and, since the initial equilibrium $(E, V)$ is arbitrary, $\Lambda|_E$ must either be a positive valued or a negative valued function.

Let us now consider the situation to which axiom (b) above applies: Both subbodies $\mathcal{B}^\alpha$ are in equilibrium, so that 4.5 holds for both:

$$dE^\alpha = -\frac{1}{\Lambda^\alpha|_E} dH^\alpha - p^\alpha dV^\alpha$$  \hspace{1cm} (4.6)

and thus we have for the energy $E = E^1 + E^2$ of $\mathcal{B}_T$

$$dE_T = -\frac{1}{\Lambda^1|_E} dH^1 - \frac{1}{\Lambda^2|_E} dH^2 - p^1 dV^1 - p^2 dV^2$$  \hspace{1cm} (4.7)

This seems to suggest that $E_T$ depends on the four variables $H^1, H^2, V^1, V^2$; however, $E_T$ as well as $H_T$, the entropy of $\mathcal{B}_T$, depend on the common temperature $\theta$ of $\mathcal{B}(\alpha = 1, 2)$ and on $V^1, V^2$ so that we may write

$$dE_T(H_T, V^1, V^2) = \frac{\partial E_T(H_T, V^1, V^2)}{\partial H_T} dH_T + \frac{\partial E_T(H_T, V^1, V^2)}{\partial V^1} dV^1 + \frac{\partial E_T(H_T, V^1, V^2)}{\partial V^2} dV^2$$  \hspace{1cm} (4.8)

and with $dH_T = dH^1 + dH^2$ and axiom (c) we conclude by comparing 4.8 and 4.7:

$$\frac{\partial E_T(H_T, V^1, V^2)}{\partial H_T} = -\frac{1}{\Lambda^\alpha|_E} \quad (\alpha = 1, 2)$$  \hspace{1cm} (4.9)

The LHS of 4.9 may be considered to be a function of $\theta, V^1, V^2$ whereas the RHS could only depend on $\theta, V^1$ (for $\alpha = 1$) or on $\theta, V^2$ (for $\alpha = 2$). Hence $\Lambda^\alpha|_E$ cannot depend on $V^\alpha$ at all and we have

$$\Lambda^1|_E = \Lambda^2|_E \equiv \Lambda|_E \equiv -\frac{1}{T(\theta)}$$  \hspace{1cm} (4.10)

or, in words, $\Lambda|_E$ is a universal function of the temperature alone, its negative reciprocal $T$ is called the absolute temperature.

Since $\Lambda|_E$ is finite and non-vanishing, so is $T$, and by one single experiment with any simple heat-conducting fluid we may determine its sign: The
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Absolute temperature \( T \) is positive. Combining 4.10 and 4.5 we obtain the Gibbs equation

\[
dH = (1/T)(dE + p\ dV)
\]

(4.11)

5. CONDITIONS ON LINEAR CONSTITUTIVE RELATIONS

We may be inclined to consider constitutive relations which are linear in \( \vartheta \) and \( \vartheta \) as good approximations to the exact relations in the 'neighbourhood' of uniform equilibrium. The most general representations of such linear constitutive relations are:

\[
\begin{align*}
\vartheta_k^L &= -(p|_E + \rho|_E \varrho^k) \delta_{ik} \\
q_k^L &= -\kappa|_E \varrho_k \\
\varepsilon^L &= \varepsilon|_E + \varepsilon|_E \varrho \\
\Phi^L_i &= \varphi|_E \varrho_{i,i} \\
\eta^L &= \eta|_E + \eta|_E \varrho
\end{align*}
\]

(5.1)

where all coefficients \( p|_E, \rho|_E, \kappa|_E, \varepsilon|_E, \varphi|_E, \eta|_E \) and \( \eta|_E \) may depend on \( \rho \) and \( \varrho \).

If the relations 5.1 and the linear representation of \( A \) (see 4.10)

\[
A = -\frac{1}{T} + A|_E \varrho
\]

(5.2)

are introduced in the equations 3.6, 3.8, they yield the following restrictions on the coefficients:

\[
\begin{align*}
\frac{\partial \varrho|_E}{\partial \vartheta} &= \frac{1}{T} \frac{\partial \varepsilon|_E}{\partial \vartheta}, \\
\varrho|_E &= \frac{1}{T} \varepsilon|_E, \\
\varphi|_E &= -\kappa|_E \\
\frac{\partial \varrho}{\partial \rho} &= \frac{1}{T} \left( \frac{\partial \varepsilon|_E}{\partial \rho} - \frac{p|_E}{\rho^2} \right), \\
\Phi^L_i &= \frac{q^L_i}{T}
\end{align*}
\]

(5.3)

While 5.3.1, 2 have already been discussed in Section 4, 5.3.4 states a new result: The linear entropy flux is equal to the linear heat flux divided by the absolute temperature:

\[
\Phi^L_i = \frac{q^L_i}{T}
\]

(5.4)

This relation, however, does not hold in a non-linear theory in general, although that is commonly assumed in thermodynamic theories.

If the linear relations 5.1 are introduced into the residual inequality 3.7 we obtain after some straightforward calculation and by use of the previous results 5.3

\[
\varepsilon|_E \leq \frac{T^2}{dT/d\vartheta} A|_E \frac{\partial \varepsilon|_E}{\partial \vartheta} + \kappa|_E \frac{dT}{d\vartheta} \geq 0
\]

(5.5)
If, as is usually done, the empirical temperature \( \theta \) is chosen to be identical to the absolute temperature, \( \kappa \) states the well known result that the heat conductivity is non-negative.

6. THE LINEAR EQUATION OF HEAT CONDUCTION

We might be content in this presentation of a new approach to the old subject of non-equilibrium thermodynamics to derive assumptions and results of the established theories on that subject and show their limitations. In this sense, if there were no other result than the derivation of the Gibbs equation 4.11, of the inequality 5.5 on \( \kappa \), and of the linear relation 5.4 between the fluxes of entropy and heat, we should still have been able to compose a list of all the assumptions and axioms that lead to these results in a manner which allows us to appreciate their validity.

There is, however, a bonus, even for such a singularly simple material as the simple heat-conducting fluid considered here: When we introduce 5.12 into 2.13 and consider a process with \( \rho \) time-independent and uniform and \( \theta |_{\rho} \equiv 0 \), we find in a linear theory the following form of the linear differential equation of heat conduction

\[
\left( \frac{\partial \varepsilon |_{\theta}}{\partial \theta} \right) \frac{\partial \theta}{\partial t} + \varepsilon_{\theta} \frac{\partial^2 \theta}{\partial t^2} = \kappa |_{\theta} \Delta \theta
\]

Provided that \( \varepsilon_{\theta} |_{\theta} > 0 \), this is a hyperbolic differential equation which implies a finite speed for the propagation of disturbances in temperature; and the fact that the theory presented here allows for this finite speed gives it a marked advantage over other thermodynamic theories which predict infinite speed. Of course, I cannot prove here that indeed \( \varepsilon_{\theta} |_{\theta} > 0 \) holds; what we can conclude from 5.5 is that \( \varepsilon_{\theta} |_{\theta} \) may be positive.

REFERENCES