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Classical Axiomatics with Extension to Nonequilibrium Thermodynamics[1]

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An attempt is made to reorganize the axiomatics of classical thermodynamics as written by Carathéodory in 1909 and to extend it to nonequilibrium systems. The three thermodynamic laws are derived from axioms and the entropy appears as the constant of integration of the Pfaffian equation with a suitably chosen integrating factor. Transition to nonequilibrium systems is shown to require an extension of the phase space to include the gradients of temperature and velocity as additional coordinates. Accessible states then have to comply with a system of momentum equations and any departure from these restrictions leads to inaccessible states.

KEY WORDS: classical axiomatics; entropy; nonequilibrium systems; thermodynamics.

1. INTRODUCTION

An analysis of Carathéodory's study of the axiomatics of thermodynamics in the year 1909 [1] shows that there are many facets of thermodynamics which were not covered in that study. The present paper is an attempt to reorganize the axiomatics of classical thermodynamics and to extend it to nonequilibrium systems. From the three "axioms" which describe the physics of the thermodynamic process, we derive the three thermodynamic "laws." A classification of the latter leads to Carathéodory's concept of "inaccessible states," which is discussed in Section 5 and derived without introducing Carathéodory's Axiom 1. The corresponding Pfaffian differential equation and its solutions are the subject of Sections 6 and 7; their

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constraints on the possible constitutive equations are shown in Section 8, together with the only condition under which negative absolute temperatures may occur. This condition is due to a unique correlation between macroscopic axiomatics and Planck's characteristic function of statistical thermodynamics. The entropy is shown to appear as the constant of integration of the Pfaffian equation in Section 10, with a suitably chosen integrating factor.

Transition to nonequilibrium systems requires a reexamination of the inaccessible states and is discussed in Section 11. These states have now become functions of the temperature and velocity gradients. Up to this point, we have constructed an "axiomatic formalism," i.e., a structure of rules which is independent of the particular substance about which we desire information. Such specific information can be obtained by considering the "constitutive equations" of the bodies involved. However, constitutive equations are not part of this study.

2. THE AXIOMS

The axioms which govern the energy transfer in systems with nonuniform temperature are as follows.

2.1. Axiom 1

"Transient energy $d\varepsilon/dt$ appears in the form of heat input dq/dt as well as work input dw/dt":

$$\frac{d\varepsilon}{dt}=\frac{dq}{dt}+\frac{dw}{dt} \tag{1}$$

2.2 Axiom 2

"The energy input required to bring a body from state C_1 to state C_2 is independent of the nature of the energy chosen, and independent of the traversed intermediate states":

$$[\varepsilon]_1^2=U(C_2, C_1) \tag{2}$$

such that

$$U(C_2, C_1)=u(C_2)-u(C_1) \tag{3}$$

or, abbreviated,

$$U(C_2, C_1)=u_2-u_1 \tag{4}$$

From Eqs. (2) and (4) it follows for infinitesimal energy input that

$$\frac{d\varepsilon}{dt}=\frac{du}{dt} \tag{5}$$

and from Eqs. (5) and (1), we have

$$\frac{du}{dt}=\frac{dq}{dt}+\frac{dw}{dt} \tag{6}$$

where u is "internal energy." Both heat input and work input consist of a reversible and an irreversible part. Therefore, we write in accordance with classical transport theory [2]

$$\frac{dq}{dt}=\dot{Q}+\frac{\kappa}{\rho}\operatorname{div}(\operatorname{grad}\Theta) \tag{7}$$

and with $\mathbf{W}$ as the local velocity vector of the fluid motion,

$$\frac{dw}{dt}=-X_i\frac{dx_i}{dt}-\frac{1}{\rho}\mathbf{\Pi}\colon \operatorname{Grad}\mathbf{W} \tag{8}$$

where $\dot{Q}$ = reversible heat exchange without temperature gradients, which may be given by its own constitutive equation and is independent of the thermodynamic properties; $(\kappa/\rho)\operatorname{div}(\operatorname{grad}\Theta)\equiv$ irreversible heat transfer due to a temperature gradient ($\kappa\equiv$ thermal conductivity, $\rho\equiv$ mass density, and $\Theta\equiv$ empirical temperature); $-X_i(dx_i/dt)=d\omega/dt\equiv$ reversible work input by conservative forces X_i; and $-(1/\rho)\mathbf{\Pi}\colon\operatorname{Grad}\mathbf{W}$ = irreversible momentum transfer due to a stress $\mathbf{\Pi}$ which causes displacement gradients in the subjected solid or a velocity gradient (denoted by Grad $\mathbf{W}$) in the subjected fluid.

When we define the reversible work in Eq. (8) as

$$-X_i\frac{dx_i}{dt}=\frac{d\omega}{dt} \tag{9}$$

and the irreversible work as

$$-\frac{1}{\rho}\mathbf{\Pi}\colon\operatorname{Grad}\mathbf{W}=\frac{d\phi}{dt} \tag{10}$$

then we can state for the combined work input

$$\frac{dw}{dt}=\frac{d\omega}{dt}+\frac{d\phi}{dt} \tag{11}$$

The last term is subjected to the following axiom.

2.3. Axiom 3

"The nonequilibrium work can never be negative":

$$\frac{d\phi}{dt} \geqslant 0 \tag{12}$$

Nonequilibrium work is absent in thermostatics.

3. THE LAWS

3.1. The Zeroth Law

Equations (7), (8), and (9) show that "energy input into bodies subjected to heat exchange can occur even when all deformation coordinates are kept constant." Therefore, not only does energy input act upon the deformation coordinates, x_i, but there must exist an additional thermal coordinate, Θ, which measures how hot a body is. Θ is called the "empirical temperature."

3.2. The First Law

Equation (7) can be expressed as follows: "There exists a property of state, called 'internal energy,' whose increment during a transition from state C_1 to state C_2 is equal to the input of heat and work during that transition."

3.3. The Second Law

By applying the inequality Eq. (12) to Eq. (7), it follows that, for an adiabatic process where $dq/dt = 0$,

$$\frac{du}{dt} \geqslant \frac{d\omega}{dt} \tag{13}$$

"The rate of change of internal energy in an adiabatic process can never be less than the simultaneous rate of input of equilibrium work." This inequality is the second law of thermodynamics. It is needed in thermostatics.

4. CONSTITUTIVE EQUATIONS OF THERMOSTATICS

The independent variables of simple systems are the empirical temperature, Θ, and deformation coordinates, $x_1 \cdots x_n$.

The constitutive equations of simple systems are n thermal equations of state,

$$X_i = \hat{X}_i(\Theta, x_1 \cdots x_n) \tag{14}$$

and one caloric equation of state,

$$u = \hat{u}(\Theta, x_1 \cdots x_n) \tag{15}$$

The differential

$$du = \frac{\partial u}{\partial \Theta} d\Theta + \frac{\partial u}{\partial x_i} dx_i \tag{16}$$

is exact on account of Axiom 2, which requires that $\int_1^2 du$ is independent of the path. The equilibrium work is now given as

$$d\omega = -X_i(\Theta, x_1 \cdots x_n)\, dx_i \tag{17}$$

The balance of internal energy for the system of Eqs. (16), (17), (7), and (10) becomes

$$\frac{\partial u}{\partial \Theta} d\Theta + \frac{\partial u}{\partial x_i} dx_i = -X_i\, dx_i + \frac{\kappa}{\rho} \operatorname{div}(\operatorname{grad} \Theta) + \frac{\mathbf{\Pi}}{\rho} : \operatorname{Grad} \mathbf{W} + \dot{Q} \tag{18}$$

5. INACCESSIBLE STATES

From Eqs. (6) and (11), we obtain the energy balance

$$\frac{du}{dt} = \frac{dq}{dt} + \frac{d\omega}{dt} + \frac{d\phi}{dt} \tag{19}$$

Writing the balance Eq. (19) in the form

$$\frac{dB}{dt} = 0 \tag{20}$$

gives, according to Eqs. (6) and (11),

$$\frac{dB}{dt} \equiv \frac{du}{dt} - \frac{d\omega}{dt} - \frac{d\phi}{dt} - \frac{dq}{dt} = 0 \tag{21}$$

By describing all derivatives in Eq. (21), we describe a distinct thermodynamic path. All points whose coordinates coincide with Eq. (21) represent accessible states. All points whose coordinates are outside the

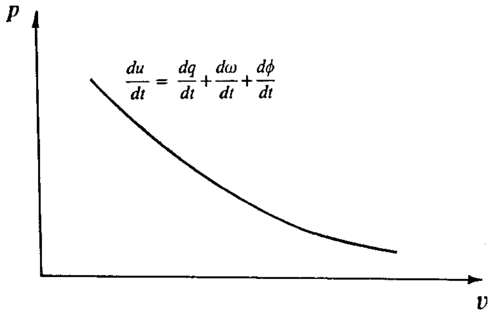

Fig. 1. Characteristic p–v diagram.

prescribed curve are the "inaccessible states" as far as a chosen integral is concerned. Figure 1 shows that situation for a two-dimensional example: only points on the chosen curve are accessible points; all other points do not represent Eq. (21) and are inaccessible.

It can be seen that fewer coordinates suffice to describe the inaccessible points than those which describe the region of accessibility. In 1909, Carathéodory proved that the energy balance equation, Eq. (21), can be integrated only for such cases where inaccessible states surround any arbitrary point P. The thermodynamic properties of such "systems with inaccessible states" are now examined. The principle named above is "Carathéodory's principle."

The general energy balance Eq. (21), with $dq/dt \neq 0$, $d\phi/dt \neq 0$, has no inaccessible points. It can, therefore, not be integrated to yield a specific path in the diagram of the state properties. However, by introducing the limits $dq/dt \to 0$, and $d\phi/dt \to 0$, we obtain from Eq. (21) the energy balance of a reversible, adiabatic process:

$$\lim_{dq/dt,\, d\phi/dt \to 0} \left(\frac{dB}{dt}\right) \equiv \frac{du}{dt} - \frac{d\omega}{dt} = 0 \tag{22}$$

or, from Eqs. (16) and (17),

$$\frac{\partial u}{\partial \Theta}\, d\Theta + \left(\frac{\partial u}{\partial x_i} + X_i\right) dx_i = 0 \tag{23}$$

This inexact Pfaffian differential equation no longer contains the time as a primitive variable. It interrelates those $(n+1)$ displacements $d\Theta$, dx_i in the $(n+1)$-dimensional property space which result in a reversible adiabatic process. When Eq. (23) is integrable, i.e., when an integrating factor exists, then all permissible displacements originating in a point $P'(\Theta', x'_1 \cdots x'_n)$

are located on an n-dimensional surface σ' through the point P' in the $(n+1)$-dimensional property space.

We now examine the properties of the Pfaffian equation, regardless of its inaccessibility conditions. In that way, we obtain numerous, time-independent solutions of thermodynamic relations.

6. THE INTEGRABILITY CONDITIONS

According to the theory of the Pfaffian equations, Eq. (23) is integrable, if the following $(n/2)$ integrability conditions are satisfied for unspecified constitutive Eqs. (14) and (15):

$$\frac{\partial u}{\partial \Theta}\left(\frac{\partial X_l}{\partial x_k}-\frac{\partial X_k}{\partial x_l}\right)-\left(\frac{\partial u}{\partial x_k}+X_k\right)\frac{\partial X_l}{\partial \Theta}+\left(\frac{\partial u}{\partial x_l}+X_l\right)\frac{\partial X_k}{\partial \Theta}=0 \qquad (24)$$

Not knowing the constitutive equations, the decision whether or not Eq. (24) is satisfied must be based on Carathéodory's principle:

> If a Pfaffian equation is given, and if it is known that in every region surrounding an arbitrary point P there are points which cannot be reached along curves satisfying that equation, then that equation must necessarily possess an integrating factor which converts it to an exact differential equation.

The existence of such adiabatically inaccessible states in the immediate neighborhood of every point P is guaranteed by Eq. (21), which is obtained by a limiting process imposed on the general energy balance for processes with heat input. Therefore, Carathéodory's principle is satisfied, and Eq. (23) possesses an integrating factor. The simplest case (the elastic solid) has six simultaneous equations from Eq. (24) to solve.

7. CONSTRAINTS ON THE CONSTITUTIVE EQUATIONS

Even though unspecified, the constitutive equations are subjected to severe thermodynamic constraints. This is seen when Eq. (24) is written in the form

$$\frac{\partial u}{\partial \Theta}=\left[\left(\frac{\partial u}{\partial x_k}+X_k\right)\frac{\partial X_l}{\partial \Theta}-\left(\frac{\partial u}{\partial x_l}+X_l\right)\frac{\partial X_k}{\partial \Theta}\right]\Big/\left(\frac{\partial X_l}{\partial x_k}-\frac{\partial X_k}{\partial x_l}\right) \qquad (25)$$

Whichever pair k, l is chosen for X_k, x_k, and X_l, x_l, the right-hand side must always be equal to the same function $\partial u/\partial \Theta = c_v$. This is possible only if the right-hand side has the indeterminate form 0/0. Therefore,

$$\frac{\partial X_l}{\partial x_k}=\frac{\partial X_k}{\partial x_l} \qquad (26)$$

and

$$\left(\frac{\partial u}{\partial x_k}+X_k\right)\Big/\frac{\partial X_k}{\partial \Theta}=\left(\frac{\partial u}{\partial x_l}+X_l\right)\Big/\frac{\partial X_l}{\partial \Theta} \tag{27}$$

According to Eq. (27), each ratio must be equal to a common function T,

$$\left(\frac{\partial u}{\partial x_i}+X_i\right)\Big/\frac{\partial X_i}{\partial \Theta}=T(\Theta, x_1\cdots x_n) \tag{28}$$

Therefore, the thermal and caloric equations are coupled, according to Eq. (28), by the relation

$$\frac{\partial u}{\partial x_i}=T\frac{\partial X_i}{\partial \Theta}-X_i \tag{29}$$

In order to find the function $T(\Theta, x_1\cdots x_n)$, we have to introduce Planck's "characteristic function," ψ.

8. THE CHARACTERISTIC FUNCTION

We now calculate the value of the function $(u/\Theta)_{\text{ad}}^{\text{rev}}$ along a reversible adiabatic surface through a given initial point P. For independent variables Θ and x_i we obtain from Eq. (23)

$$d\left(\frac{u}{\Theta}\right)+\frac{u}{\Theta^2}\,d\Theta+\frac{X_i}{\Theta}\,dx_i=0 \tag{30}$$

The "characteristic function," $\psi(\Theta, x_i)$ is defined as

$$d\psi=\frac{u}{\Theta^2}\,d\Theta+\frac{X_i}{\Theta}\,dx_i \tag{31}$$

such that

$$\frac{\partial \psi}{\partial \Theta}=\frac{u}{\Theta^2} \tag{32}$$

$$\frac{\partial \psi}{\partial x_i}=\frac{X_i}{\Theta} \tag{33}$$

Then

$$d\left(\frac{u}{\Theta}\right)=-d\psi \tag{34}$$

where Eq. (34) represents the change of u/Θ on a surface of reversible adiabatic process in a $[\Theta, x_i, (u/\Theta)]$ diagram.

The importance of the function $\psi(\Theta, x_i)$ lies in the fact that it can be calculated from statistical mechanics as the logarithm of the partition function, Z. For any physically defined substance, ψ is always a known function of Θ and x_i.

In order to evaluate the function T in Eq. (28), we obtain from Eqs. (32) and (33)

$$T(\Theta, x_1 \cdots x_n) = \left[\Theta^2 \frac{\partial}{\partial x_i}\left(\frac{\partial \psi}{\partial \Theta}\right) + \Theta \frac{\partial \psi}{\partial x_i}\right] \Bigg/ \left[\frac{\partial \psi}{\partial x_i} + \Theta \frac{\partial}{\partial \Theta}\left(\frac{\partial \psi}{\partial x_i}\right)\right] \qquad (35)$$

For nearly all substances, $\psi(\Theta, x_i)$ is a continuous function such that

$$\frac{\partial}{\partial x_i}\left(\frac{\partial \psi}{\partial \Theta}\right) = \frac{\partial}{\partial \Theta}\left(\frac{\partial \psi}{\partial x_i}\right) \qquad (36)$$

In that case, Eq. (35) yields

$$T(\Theta, x_1 \cdots x_n) = \Theta \qquad (37)$$

and if Θ is defined as positive, T is always positive.

By convention, Θ is that extrapolated temperature which is proportional to the pressure ratio observed when an ideal gas is heated in a constant-volume vessel, such that its pressure rises from p_0 to p, while p_0 is asymptotically lowered toward zero in successive experiments:

$$\Theta = 273.16 \lim_{p_0 \to 0} \left(\frac{p}{p_0}\right) \qquad (38)$$

Since p can never be negative, Θ as defined by Eq. (38) is always positive; thus, there exists an absolute zero of empirical temperature.

However, there exists an extensively discussed case where $\psi(\Theta, x_i)$ is not continuous and where the temperature jumps from $+\infty$ to $-\infty$. In the neighborhood of such points, Eq. (37) is not valid, and negative temperatures do occur.

9. THE INTEGRATING FACTOR

Multiplying Eq. (23) by the dimensionless integrating factor $M(\Theta, x_1 \cdots x_n)$ yields

$$M(\Theta, x_1 \cdots x_n) \frac{\partial u}{\partial \Theta} d\Theta + M(\Theta, x_1 \cdots x_n) \left(\frac{\partial u}{\partial x_i} + X_i\right) dx_i = 0 \qquad (39)$$

Since this is now an exact differential, the exactness conditions must be satisfied, i.e., the mixed second-order derivatives must be equal. Due to Eq. (24), this yields for every pair $i=k$, $i=l$, the $\binom{n}{2}$ exactness conditions

$$\frac{\partial M}{\partial x_k}\left(\frac{\partial u}{\partial x_l}+X_l\right)=\frac{\partial M}{\partial x_l}\left(\frac{\partial u}{\partial x_k}+X_k\right) \tag{40}$$

and for every i, the n additional exactness conditions

$$\frac{\partial}{\partial x_i}\left(M\frac{\partial u}{\partial \Theta}\right)=\frac{\partial}{\partial \Theta}\left[M\left(\frac{\partial u}{\partial x_i}+X_i\right)\right] \tag{41}$$

After canceling out the identical mixed second-order derivatives, Eq. (41) yields

$$\left(\frac{\partial M}{\partial \Theta}\right)_{x_i}\left(\frac{\partial u}{\partial x_i}+X_i\right)+M\frac{\partial X_i}{\partial \Theta}=\left(\frac{\partial M}{\partial x_i}\right)_{\Theta}\frac{\partial u}{\partial \Theta}$$

The substitution of Eq. (23) yields n simultaneous differential equations for M:

$$\left[\Theta\left(\frac{\partial M}{\partial \Theta}\right)_{x_i}+M\right]\frac{\partial X_i}{\partial \Theta}=\left(\frac{\partial M}{\partial x_i}\right)_{\Theta}\frac{\partial u}{\partial \Theta} \tag{42}$$

Since a relation between $\partial u/\partial\Theta$ and a *single* $\partial X_i/\partial\Theta$ cannot exist [see Eq. (25)], each side of Eq. (42) must be zero. Therefore, it follows that

$$\frac{\partial M}{\partial x_i}=0 \tag{43}$$

and the differential equation for the integrating factor becomes

$$\Theta\frac{dM}{d\Theta}+M=0 \tag{44}$$

According to Eq. (44), M depends on the temperature alone. Therefore, M cannot depend on any constitutive equation, i.e., M is a "universal function." Integration of Eq. (44) yields the dimensionless integrating factor

$$M=e^{-\int_{\Theta'}^{\Theta}\frac{d\Theta}{\Theta}}=\frac{\Theta'}{\Theta} \tag{45}$$

This function M, with the derivatives Eq. (43), simultaneously satisfies the set of exactness conditions Eq. (40).

When $\Theta = \Theta'$, we have $M = 1$, i.e., no integrating factor is needed. That is the case when all deformation coordinates in Eq. (23) are fixed. Thus, Θ' is the empirical temperature of a system which is subjected to heat exchange only.

10. THE THERMOSTATIC ENTROPY

Substituting in Eq. (39) the integrating factor [by means of Eq. (45) and canceling out the constant Θ'] yields the area element of the adiabatic σ surface

$$\left\{\frac{1}{\Theta}\left[\frac{\partial u}{\partial \Theta}\,d\Theta + \left(\frac{\partial u}{\partial x_i} + X_i\right)dx_i\right]\right\}_\sigma = 0 \tag{46}$$

or by virtue of Eqs. (28) and (38),

$$\left[\frac{c_{\mathrm{v}}}{\Theta}\,d\Theta + \frac{\partial X_i}{\partial \Theta}\,dx_i\right]_\sigma = 0 \tag{47}$$

Only displacements $d\Theta$, dx_i which satisfy Eq. (47) are confined to an adiabatic surface. The indefinite integral of Eq. (47) is the equation of that surface:

$$\int\left[\frac{c_{\mathrm{v}}}{\Theta}\,d\Theta + \frac{\partial X_i}{\partial \Theta}\,dx_i\right]_\sigma = s(\sigma) \tag{48}$$

where s is the constant of integration, called the "thermostatic entropy." Since such a σ surface can be constructed through any point in the property space where the constitutive Eqs. (14) and (15) are valid, the constant of integration, s, is a continuous function with continuous first-order derivatives. Therefore, Eq. (48) can be differentiated; this yields

$$ds = \frac{c_{\mathrm{v}}}{\Theta}\,d\Theta + \frac{\partial X_i}{\partial \Theta}\,dx_i \tag{49}$$

and hence

$$\left(\frac{\partial s}{\partial \Theta}\right)_{x_i} = \frac{c_{\mathrm{v}}}{\Theta}; \qquad \left(\frac{\partial s}{\partial x_i}\right)_{\Theta, x_j} = \frac{\partial X_i}{\partial \Theta}, \qquad i \neq j \tag{50}$$

Substituting Eqs. (16), (28), and (40) into Eq. (49) gives the thermostatic entropy:

$$ds = \frac{1}{\Theta}\,(du + X_i\,dx_i) \tag{51}$$

Comparing Eq. (23) with Eq. (51) shows that a transition from one surface $s = constant$ to another such surface cannot be achieved by means of a reversible, adiabatic process. For such a transition, the limit of Eq. (21) is not applicable. Therefore, that transition is either irreversible or non-adiabatic or both.

We substitute Eq. (51) into Eq. (31) in order to eliminate dx_i and obtain

$$d\psi = \frac{u}{\Theta^2}\, d\Theta + ds - \frac{du}{\Theta}$$

or, equivalently,

$$d\psi = ds - d\left(\frac{u}{\Theta}\right) \tag{52}$$

Hence,

$$\psi = s - \frac{u}{\Theta} \tag{53}$$

and from Eq. (29), it follows that

$$s = \psi + \Theta \frac{d\psi}{d\Theta} \tag{54}$$

Furthermore, from Eq. (51), we have

$$\frac{1}{\Theta} = \left(\frac{\partial s}{\partial u}\right)_{x_i} \tag{55}$$

Each thermostatic system is defined by its characteristic function ψ; from the latter, the functions u and s can be calculated. From these, the curves $s = s(u)$ are obtained; their slope is $\partial s/\partial u = 1/\Theta$, which might be either positive or negative, depending on whether the internal energy has an upper bound or not. That determines the sign of Θ.

11. THE TRANSITION TO NONEQUILIBRIUM THERMODYNAMICS

We now examine the irreversible system where heat flow and viscous dissipation are present. In that case, we have to employ the complete transport Eqs. (7) and (8). While in the reversible case, both sides of the curve in Fig. 1 are inaccessible for the Pfaffian Eq. (19), they have now become accessible. Therefore, a new search for the inaccessible states is required, in order to ensure the existence of an integrating factor for the differential Eq. (19).

We have to expect that the combination of Eqs. (6), (7), and (8) will make the internal energy a function of all independent variables, which includes the gradients:

$$u = \hat{u}(\Theta, x_i, \text{grad}\ \Theta, \text{Grad}\ \mathbf{W}) \tag{56}$$

In that case, the members of the energy balance equation become, from Eq. (21),

$$du = \frac{\partial u}{\partial \Theta} d\Theta + \frac{\partial u}{\partial x_i} dx_i + \frac{\partial u}{\partial(\nabla\Theta)} \cdot d(\nabla\Theta) + \frac{\partial u}{\partial(\nabla\mathbf{W})} : d(\nabla\mathbf{W}) \tag{57}$$

with the following contributions from Eqs. (9), (10), and (7), respectively:

$$d\omega = -X_i\, dx_i \tag{58}$$

$$d\phi = -\frac{1}{\rho}(\mathbf{\Pi}: \text{Grad}\ \mathbf{W})\, dt \tag{59}$$

$$dq = d\dot{Q} + \frac{\kappa}{\rho}(\text{div grad}\ \Theta)\, dt \tag{60}$$

Since $\dot{Q}$ in Eq. (7) is a constant heat supply, we have $d\dot{Q} = 0$. Substituting in Eq. (57) gives the energy balance for a viscous, irreversible process with heat conduction:

$$\frac{\partial u}{\partial \Theta}\frac{d\Theta}{dt} + \left(\frac{\partial u}{\partial x_i} - X_i\right)\frac{dx_i}{dt} = -\left[\frac{\partial u}{\partial\nabla\Theta} \cdot \frac{d(\nabla\Theta)}{dt} + \frac{\partial u}{\partial\nabla\mathbf{W}} : \frac{d(\nabla\mathbf{W})}{dt}\right] + \frac{\kappa}{\rho}\text{div}(\nabla\Theta) - \frac{\mathbf{\Pi}}{\rho} : \nabla\mathbf{W} \tag{61}$$

For fixed gradients, Eq. (61) reduces to Eq. (23), which is the energy balance in the absence of inaccessible states. Thus, the right-hand side of Eq. (61) provides the condition of inaccessibility for media with temperature gradients and velocity gradients. This condition can be written as

$$-\left[\frac{\partial u}{\partial\nabla\Theta} \cdot \frac{d(\nabla\Theta)}{dt} + \frac{\partial u}{\partial\nabla\mathbf{W}} : \frac{d(\nabla\mathbf{W})}{dt}\right] + \frac{\kappa}{\rho}\text{div}(\nabla\Theta) - \frac{\mathbf{\Pi}}{\rho} : \nabla\mathbf{W} = 0 \tag{62}$$

Since the gradients of temperature and velocity are independent of each other, Eq. (62) can be satisfied only when each gradient is constant, i.e., when Eq. (62) is of the trivial form $0 = 0$. This means that the gradients are actually parasitic variables which do not enter the system of thermodynamic functions. For that reason, they are already incorporated into the "enthalpy" function [3].

This is as far as we can get with Carathéodory's approach. In order to proceed further, an independent constitutive equation for $\mathbf{\Pi}$ has to be added to complete the system.

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