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On the definition of temperature outside equilibrium

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Abstract. Non-equilibrium temperature is defined independently of the characteristics of any particular substance. The relation defining absolute non-equilibrium temperature is shown to be similar to the definition of absolute equilibrium temperature proposed by Kelvin. No *a priori* empirical non-equilibrium temperature is introduced. Moreover, for the particular case of an elastic body, a unique non-equilibrium entropy is shown to exist.

1. Introduction

Recently, increasing attention has been paid to the problem of defining a non-equilibrium entropy and a non-equilibrium temperature (Meixner 1966a, b, 1968, 1970, De Groot and Mazur 1962, Stuart *et al* 1970, Truesdell 1968, Müller 1971a, b, Green and Laws 1972).

It has long been recognized that physical concepts must be defined independently of a particular substance. Thus although a device often used to measure force is a spring, one cannot use such a device to define force.

Similarly Kelvin, see Zemanski (1957), recognized that a thermometer cannot be used to define temperature. This led him to define equilibrium temperature by means of a Carnot engine, the measurement being independent of a particular substance.

In § 2, it is shown that by means of a somewhat modified Carnot engine, absolute non-equilibrium temperature can be defined. Kelvin's demonstration is based on the assumption that no entropy production occurs in the body whose temperature is to be determined. In the present work this restriction is relaxed.

In § 3, it is shown that a unique non-equilibrium entropy exists for an elastic body.

2. The non-equilibrium temperature

For simplicity, we limit the following considerations to heat conduction only; thus no displacements occur. The extension to thermoelasticity in which displacements take place or to a fluid is straightforward.

Consider an isolated system which may consist of a number of interacting bodies in diathermal contact. The isolated system could, for example, be composed of a number of rigid bodies with different temperatures. Henceforth we shall refer to the isolated system as the body. The object is to determine the instantaneous non-equilibrium temperature at any point of the body.

The analysis is based on the assumption that locally, the rate of change of entropy per unit volume s_v is given by

$$\dot{s}_v = \frac{\dot{u}_v}{\theta(u_v, \alpha^\gamma)} + \sum_{i=1}^p \beta^i(u_v, \alpha^\gamma) \dot{\alpha}^i \quad (2.1)$$

where u_v is the internal energy per unit volume, and $\alpha^1, \dots, \alpha^p$ are other independent variables which we do not need to know explicitly for the purpose of this work; θ and the β^i are functions of some or all the independent variables; a superscript dot means the derivative with respect to the time.

The definition (2.1) of \dot{s}_v is more general than the commonly used expression based on the local equilibrium hypothesis. According to that theory the α^i would not be present in the case of heat conduction. Following Bataille and Kestin (1975), Atkin *et al* (1975), Lebon and Lambermont (1976), and others, the entropy outside equilibrium may depend, not only on u_v , but also on other state variables, such as the heat flux vector.

On the other hand, Meixner (1966a, b) assumes that in general (2.1) is not integrable, i.e. there does not exist an unique function between s_v , u_v and the α^i . But, as can be easily checked, this has no consequences in the present analysis leading to the non-equilibrium temperature definition (2.23), because the integrated form of (2.1) is not needed in that part of the analysis.

The purpose of this section is to identify θ with the non-equilibrium temperature. To do this we proceed to show that as a consequence (2.1) an absolute temperature scale exists which is independent of a particular substance.

The first law reads locally

$$\dot{u}_v = -\text{div } \mathbf{q}, \quad (2.2)$$

where \mathbf{q} is the heat flux vector.

Combining (2.1) and (2.2) yields

$$\dot{s}_v = -\text{div } \frac{\mathbf{q}}{\theta} + \mathbf{q} \cdot \text{grad } \theta^{-1} + \sum_{i=1}^p \beta^i \dot{\alpha}^i. \quad (2.3)$$

As the entropy is an extensive quantity we can always write a balance equation for it when an entropy flux vector \mathbf{J}^s is introduced:

$$\dot{s}_v = -\text{div } \mathbf{J}^s + \sigma, \quad (2.4)$$

σ is the production of entropy per unit volume. The second law expresses the fact that

$$\sigma \geq 0. \quad (2.5)$$

The entropy balance relation (2.4) differs from the Clausius–Duhem inequality because we do not accept, at this point, that \mathbf{J}^s is the heat flux vector divided by the temperature.

Comparing (2.3) and (2.4) identifies \mathbf{J}^s and σ as

$$\mathbf{J}^s = \mathbf{q} / \theta \quad (2.6)$$

and

$$\sigma = \mathbf{q} \cdot \text{grad } \theta^{-1} + \sum_{i=1}^p \beta^i \dot{\alpha}^i. \quad (2.7)$$

As is well known, Kelvin defined equilibrium temperature by considering a Carnot engine which subtracts heat reversibly from the body whose temperature is to be determined. During the cycle the energy is partly converted into work, the remaining part being rejected to a reference temperature reservoir.

To define an absolute non-equilibrium temperature scale, subtract during a time interval Δt_c , by means of an engine (see figure 1), a small quantity of heat ΔQ_1 from the body at the location where the temperature is to be determined. Unlike Kelvin we cannot employ a Carnot engine because during the contact time Δt_c that the heat is subtracted, the temperature may be varying rapidly in the body. Consequently an irreversible process will generally be set up in the engine. During the irreversible non-isothermal process path A-B, shown in figure 2, the engine absorbs heat ΔQ_1 continuously ($\dot{Q}_1 < 0$) from the body. At B the engine is uncoupled. The rest of the cycle is selected to correspond with a Carnot cycle.

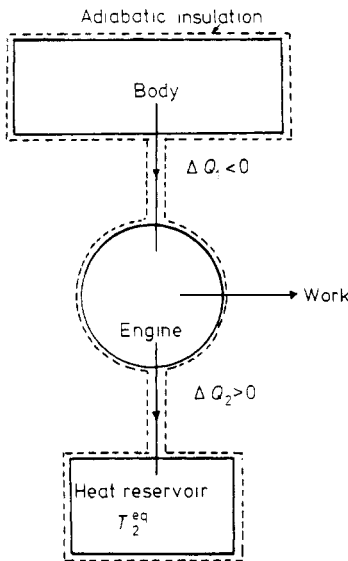


Figure 1.

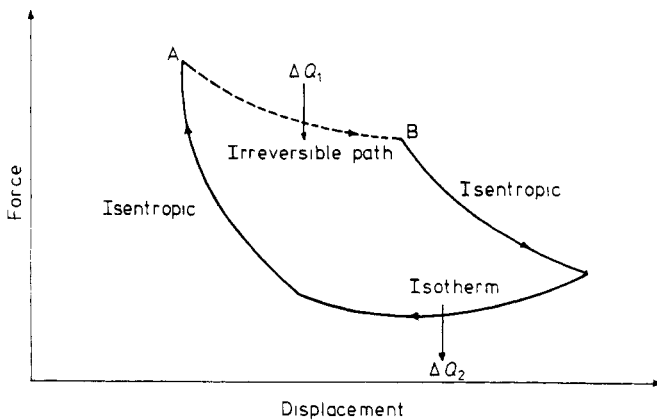


Figure 2.

During this reversible part of the cycle, the engine delivers an amount of work ΔW and exchanges an amount of heat ΔQ_2 with the reservoir at, say, the triple point of water T_2^{eq} ; ΔQ is counted as positive when heat is absorbed by the body or the reservoir. Therefore, ΔQ_1 is negative, because heat is rejected by the body while $\Delta Q_2 > 0$ when heat flows into the heat reservoir. With Kelvin, we select the reference equilibrium temperature to be $T_2^{\text{eq}} = 273.16 \text{ K}$.

In Kelvin's (formal) experiment, the state of the engine at the initial contact with the body, corresponding with point A in figure 2, is such that thermal equilibrium exists with the body whose temperature is to be determined.

Similarly we suppose that the equilibrium state of the engine at point A is such that the entropy production in the engine is, during the subsequential process, a continuous function of the time.

As the entropy change of the motor taken through the cycle is zero, the rate of entropy change of the whole system consisting of the body, the engine and the reservoir in the cycle time Δt is

$$\Delta S = \Delta S_{\text{body}} + \Delta S_{\text{reservoir}}. \quad (2.8)$$

The change of entropy of the system is necessarily equal to the entropy production in it. As there is no entropy production in the reservoir, it follows that for the cycle

$$\Delta S = \int_{\Delta t} \int_{V_B} \sigma_B dV dt + \int_{\Delta t} \int_{V_E} \sigma_E dV dt > 0 \quad (2.9)$$

where σ_B and σ_E are the entropy production per unit volume respectively inside the body with volume V_B and inside the motor with volume V_E .

In what follows use is made of the well established definition of equilibrium entropy and equilibrium temperature as defined by Kelvin.

The exchange of the heat quantity ΔQ_2 to the reservoir at the triple point T_2^{eq} is reversible and is therefore given by

$$\Delta S_{\text{reservoir}} = \frac{\Delta Q_2}{T_2^{\text{eq}}} = \frac{\Delta Q_2}{273.16}. \quad (2.10)$$

The entropy change of the body is

$$\Delta S_{\text{body}} = \int_{\Delta t} \int_{V_B} \dot{s}_v dV dt. \quad (2.11)$$

As explained before, the body stands for a number of interacting bodies whose physical natures may differ. In that case the first integral in (2.9) is understood to stand for the sum over all interacting bodies:

$$\sum_i \int_{\Delta t} \int_{V_i} \sigma_i dV dt$$

where V_i is the volume and σ_i the entropy source strength of the i th body. Also (2.11) is understood to stand for a similar sum. For simplicity of notation those sums are not written out explicitly in the subsequent analysis.

Replacing (2.9), (2.10) and (2.11) in (2.8) yields

$$\int_{\Delta t} \int_{V_E} \sigma_E dV dt + \int_{\Delta t} \int_{V_B} \sigma_B dV dt = \int_{\Delta t} \int_{V_B} \dot{s}_v dt dV + \frac{\Delta Q_2}{273.16}. \quad (2.12)$$

Substitution of (2.3) and (2.7) into (2.12) results in

$$0 = - \int_{\Delta t} \int_{V_B} \operatorname{div} \frac{\mathbf{q}}{\theta} dV dt + \frac{\Delta Q_2}{273 \cdot 16} - \int_{\Delta t_c} \int_{V_E} \sigma_E dV dt. \quad (2.13)$$

Making use of Gauss' theorem, the first term can be written as:

$$\int_{\Delta t} \int_{V_B} \operatorname{div} \frac{\mathbf{q}}{\theta} dV dt = \int_{\Delta t_c} \int_{A_{B-E}} \frac{\mathbf{q} \cdot \mathbf{n}}{\theta} dA dt \quad (2.14)$$

where A_{B-E} denotes the small contact surface between the body and engine, \mathbf{n} is the outer normal to the body. No other contribution appears in (2.14) because the body is adiabatically isolated except for the contact point with the engine to which it is connected during the contact time interval Δt_c .

Combining (2.13) and (2.14) results in:

$$\int_{A_{B-E}} \int_{\Delta t_c} \frac{\mathbf{q} \cdot \mathbf{n}}{\theta} dA dt = \frac{\Delta Q_2}{273 \cdot 16} - \int_{\Delta t_c} \int_{V_E} \sigma_E dV dt. \quad (2.15)$$

Making use of the definition of the mean, we obtain for the left-hand side of (2.15), since heat is subtracted continuously ($\mathbf{q} \cdot \mathbf{n} > 0$) during the path A-B (figure 2):

$$\int_{A_{B-E}} \int_{\Delta t_c} \frac{\mathbf{q} \cdot \mathbf{n}}{\theta} dA dt = \frac{1}{\bar{\theta}} \int_{\Delta t_c} \int_{A_{B-E}} \mathbf{q} \cdot \mathbf{n} dA dt = -\frac{1}{\bar{\theta}} \int_{\Delta t_c} Q_1 dt = -\frac{1}{\bar{\theta}} \Delta Q_1 \quad (2.16)$$

where

$$\bar{\theta} = \theta(t_0 + \alpha \Delta t_c) \quad 0 < \alpha < 1 \quad (2.17)$$

is the mean of θ over the contact time interval $\Delta t_c = t_c - t_0$ and ΔQ_1 is the heat subtracted by the engine in that time interval.

The expression (2.15) can be derived more straightforwardly from the condition that the entropy change of the engine for the whole cycle is zero:

$$\Delta S_E = \int_{\Delta t} \int_{V_E} \dot{s}_{v,E} dV dt = 0 \quad (2.18)$$

where Δt is the cycle time.

According to (2.4) the entropy balance equation for the motor is given by

$$\dot{s}_{v,E} = -\operatorname{div} \frac{\mathbf{q}}{\theta} + \sigma_E. \quad (2.19)$$

Substituting (2.19) into (2.18) results in

$$0 = - \int_{\Delta t} \int_{V_E} \operatorname{div} \frac{\mathbf{q}}{\theta} dV dt + \int_{\Delta t_c} \int_{V_E} \sigma_E dV dt \quad (2.20)$$

or, by Gauss' theorem

$$\int_{\Delta t} \int_{A_E} \frac{\mathbf{q} \cdot \mathbf{n}}{\theta} dA dt = \int_{\Delta t_c} \int_{V_E} \sigma_E dV dt. \quad (2.21)$$

The expression on the left-hand side is zero except during the interval of time the engine is in contact with the body and during the time interval when heat is exchanged reversibly with the reference temperature reservoir. When it is assumed that for the latter reversible part of the cycle, θ reduces to the equilibrium temperature, (2.21) is seen to reduce to (2.15). The more elaborate derivation of (2.15) presented above avoids this assumption.

Substitution of (2.16) into (2.15) yields an expression for $\bar{\theta}$ in terms of ΔQ_2 and σ_E . We observe from (2.17) that the smaller Δt_c becomes, the closer $\bar{\theta}$ approaches the value of θ . As will be shown later, for sufficiently small Δt_c the following condition holds:

$$\int_{A_{B-E}} \int_{\Delta t_c} \frac{\mathbf{q} \cdot \mathbf{n}}{\theta} dA dt \gg \int_{V_E} \int_{\Delta t_c} \sigma_E dV dt. \quad (2.22)$$

Using (2.22) in (2.15) and substitution of (2.16) results in the following expression for $\bar{\theta}$, valid for small Δt_c :

$$\theta \approx \bar{\theta} \approx -273.16 \frac{\Delta Q_1}{\Delta Q_2} \text{ K}. \quad (2.23)$$

θ is seen to depend only on the heat fluxes exchanged by the engine. As this is an independent measurement and as θ clearly has the dimension of a temperature, it is justified to call it the non-equilibrium temperature. The quantity θ has been defined whatever the nature of the working substance of the engine; it is clearly independent of the numerical values assigned to an empirical temperature scale.

Since ΔQ_1 is negative, ΔQ_2 is necessarily positive as follows from the Planck–Kelvin statement of the second law which states: ‘It is impossible to construct an engine that, operating in a cycle, will produce no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of work’. Thus the absolute non-equilibrium temperature *defined* by (2.23) is non-negative.

The expression (2.23) is seen to be identical to Kelvin’s definition of equilibrium temperature (Zemanski 1957). We have thus proved that an experiment similar to that proposed by Kelvin to define equilibrium temperature can be used to define non-equilibrium temperature.

If the relation (2.1) is integrable, i.e. if a unique entropy exists, it follows from (2.1) that

$$s_v = s_v(u_v, \alpha^{-1}, \dots, \alpha^p) \quad (2.24)$$

and that

$$\left. \frac{\partial s_v}{\partial u_v} \right|_{\alpha^i} = \frac{1}{\theta}, \quad \left. \frac{\partial s_v}{\partial \alpha^i} \right|_{u_v} = \beta^i. \quad (2.25)$$

The non-equilibrium temperature follows then in the same way as in thermostatics, the important problem remains of course the determination of the physical nature of the parameters α_i .

Proof of the relation (2.22)

Just as for the body, we do not assume that during the irreversible process occurring in the engine the local equilibrium hypothesis is valid. The expression for the entropy source strength in the engine, σ_E , will therefore be of the form (2.7). For generality let σ_E be a function of x_1, x_2, \dots, x_n , where the x_i stand for $\mathbf{q}, \dot{\alpha}_i, \dots$

Expanding σ_E in a Taylor series around the initial contact time t_0 , leads to

$$\sigma_E(t) = \sigma_E(t_0) + \left. \frac{\partial \sigma_E}{\partial t} \right|_{t_0} \Delta t + \frac{1}{2} \left. \frac{\partial^2 \sigma_E}{\partial t^2} \right|_{t_0} (\Delta t)^2 + \dots \quad (2.26)$$

where $\Delta t = t - t_0$.

Since at the initial contact time (point A, figure 2) the engine is in an equilibrium state, one has $x_1 = x_2 = \dots = x_n = 0$ and $\sigma_E(t_0) = 0$. Moreover, since by virtue of the second principle σ_E is positive definite, it follows that†

$$\left. \frac{\partial \sigma_E}{\partial t} \right|_{t_0} = 0.$$

Thus (2.26) reduces to

$$\sigma_E = \frac{1}{2} \left. \frac{\partial^2 \sigma_E}{\partial t^2} \right|_{t_0} (\Delta t)^2 + \dots \quad (2.27)$$

The Taylor expansion of the integrand in the left-hand side of (2.22) is

$$J^s \equiv \frac{\mathbf{q} \cdot \mathbf{n}}{\theta} = J^s(t_0) + \left. \frac{\partial J^s}{\partial t} \right|_{t_0} \Delta t + \frac{1}{2} \left. \frac{\partial^2 J^s}{\partial t^2} \right|_{t_0} (\Delta t)^2 + \dots \quad (2.28)$$

where $J^s(t_0) = 0$.

Substituting (2.27) and (2.28) into the right- and left-hand sides of (2.22) respectively and performing the time integration shows that the condition (2.22) is valid for a time interval Δt_c of such magnitude that third- and higher-order terms in Δt_c can be neglected compared to the second-order term.

3. Proof of the existence of non-equilibrium entropy for an elastic body

An elastic body is defined by the requirement that the stress tensor depends on the strain tensor and internal energy or temperature.

Consider an elastic body which is heated and undergoes large deformations. The latter are described by

$$\mathbf{x} = \mathbf{x}(\mathbf{X}, t) \quad (3.1)$$

where \mathbf{x} is the position at time t of a particle which, in some reference configuration, was located at position \mathbf{X} . This reference state is supposed to be one that is externally unstressed and at uniform temperature θ_0 .

The deformation is conveniently described by the deformation gradient \mathbf{F} defined by

$$d\mathbf{x} = \mathbf{F} \cdot d\mathbf{X} \quad \left(F_{ik} = \frac{\partial x_i}{\partial X_k} \right). \quad (3.2)$$

We shall adopt the spatial description. Following Pearson (1959) we introduce as a measure for the deformation the following Eulerian strain tensor:

$$\boldsymbol{\epsilon} = \mathbf{F}^{-1} \cdot \dot{\mathbf{F}}^{-1} - \mathbf{I} \quad \left(\epsilon_{KL} = \frac{\partial X_K}{\partial x_k} \frac{\partial X_L}{\partial x_k} - \delta_{KL} \right); \quad (3.3)$$

† For example, when σ_E is a quadratic function of two variables x_1 and x_2 then $\sigma_E = ax_1^2 + bx_2^2 + cx_1x_2$ ($a > 0, b > 0, b^2 - 4ac > 0$) whence, $\dot{\sigma}_E = 2ax_1\dot{x}_1 + 2bx_2\dot{x}_2 + c(\dot{x}_1x_2 + x_1\dot{x}_2) = 0$ for $t = t_0$.

a tilde denotes the transposed tensor while the superscript -1 indicates the inverse of a transformation. The summation convention over repeated indices applies throughout this section.

The material time derivative of $\boldsymbol{\epsilon}$ is related to the deformation rate tensor, \mathbf{d} , by

$$\frac{1}{2}\mathbf{F} \cdot \dot{\boldsymbol{\epsilon}} \cdot \tilde{\mathbf{F}} = -\mathbf{d}, \quad (3.4)$$

where a superscript dot denotes the material time derivative.

The power per unit mass due to the mechanical action of body and surface forces is

$$\dot{w} = \frac{1}{\rho} \boldsymbol{\sigma} : \mathbf{d} + \dot{\mathbf{x}} \cdot \dot{\mathbf{x}}; \quad (3.5)$$

$\boldsymbol{\sigma}$ is the Cauchy stress tensor and ρ the density, the colon stands for the double scalar product.

Using (3.4), the relation (3.5) can be written as

$$\dot{w} = \mathbf{t} : \dot{\boldsymbol{\epsilon}} + \dot{\mathbf{x}} \cdot \dot{\mathbf{x}} \quad (3.6)$$

where

$$\mathbf{t} = -\frac{1}{2\rho} \tilde{\mathbf{F}} \cdot \boldsymbol{\sigma} \cdot \mathbf{F} \quad \left(t_{KL} = -\frac{1}{2\rho} \frac{\partial x_k}{\partial X_K} \sigma_{kj} \frac{\partial x_j}{\partial X_L} \right) \quad (3.7)$$

is an Eulerian stress tensor.

Making use of (3.6), the first law of thermodynamics may be written, locally, as

$$\rho \dot{u} = -\nabla \cdot \mathbf{q} + \rho \mathbf{t} : \dot{\boldsymbol{\epsilon}} + \rho r \quad (3.8)$$

where \mathbf{q} is the heat flux vector, $\nabla \cdot \mathbf{q}$ its divergence, u the internal energy per unit mass and r the heat supply by radiation per unit mass.

For an elastic body the following constitutive relation exists

$$\mathbf{t} = \mathbf{t}(u, \boldsymbol{\epsilon}). \quad (3.9)$$

To prove the integrability of (3.8) when (3.9) is valid we make use of the following axiom proposed by Caratheodory (1909).

Axiom

Arbitrarily near to any prescribed initial state there exist states which cannot be reached from the initial state by means of an adiabatic process, reversible or irreversible.

The truth of this statement is trivial. Indeed if two adiabatic lines could intersect one could construct a closed cycle with one single isothermal line.

A reversible or irreversible engine working through this cycle would absorb heat at the temperature of the isotherm and convert it totally into work. But such a device violates the Kelvin-Planck statement of the second law.

Moreover, one has the following theorem (Sneddon 1957): If a Pfaffian differential form

$$\oint \mathfrak{d}y = \sum_{i=1}^n y_i(x_1, x_2, \dots, x_n) dx_i \quad (3.10)$$

has the property that in every arbitrarily close neighbourhood of a given point $G_0(x_1^0, \dots, x_n^0)$ there exists points $G(x_1, \dots, x_n)$ which are inaccessible from G_0 along curves for which $\oint \mathfrak{d}y = 0$, the corresponding Pfaffian differential equation $\mathfrak{d}y = 0$ is

integrable; a line drawn through the differential symbol indicates that it is not an exact differential.

Hence an integrating factor $\lambda(x_1, \dots, x_n)$ and a primitive function $\phi(x_1, \dots, x_n)$ exist such that

$$\sum_{i=1}^n \frac{1}{\lambda} y_i dx_i = d\phi. \quad (3.11)$$

It is well known that λ and ϕ are not unique; generally one can find an infinite number of combinations of integrating factors and primitives. For if Φ is an arbitrary function of ϕ , $\Phi = \Phi(\phi)$, then multiplication of (3.11) by $\partial\Phi/\partial\phi$ shows that the associated primitive of the integrating factor Φ is $(1/\lambda)\partial\Phi/\partial\phi$.

Setting

$$\rho\dot{q} = -\nabla \cdot \mathbf{q} + \rho r, \quad (3.12)$$

the relation (3.8) can be written in incremental form as

$$\delta q = du - \mathbf{t}(u, \boldsymbol{\epsilon}) : d\boldsymbol{\epsilon} \quad (3.13)$$

where δq is the increment of heat supplied to a unit mass in the time dt during the irreversible process.

The relation (3.13) is a Pfaffian form which, according to Caratheodory's axiom, is integrable. Therefore an integrating factor $\lambda(u, \boldsymbol{\epsilon})$ and a primitive $\phi(u, \boldsymbol{\epsilon})$ exist such that

$$d\phi = \frac{1}{\lambda} (du - \mathbf{t} : d\boldsymbol{\epsilon}). \quad (3.14)$$

It follows that an entropy potential which in general may be a function of the potential ϕ , can be defined.

We shall prove that we may select an integrating factor which is identical to the non-equilibrium temperature defined by (2.23). Let s be an arbitrary function of ϕ . From $s = s(\phi)$, it follows readily, by multiplying (3.14) by $ds/d\phi$ that

$$\frac{1}{\eta} = \frac{1}{\lambda} \frac{ds}{d\phi} \quad (3.15)$$

is also an integrating factor. Thus

$$ds = \frac{1}{\eta} (du - \mathbf{t} : d\boldsymbol{\epsilon}). \quad (3.16)$$

It follows from (3.16) that

$$\left. \frac{\partial s}{\partial u} \right|_{\boldsymbol{\epsilon}} = \frac{1}{\eta}. \quad (3.17)$$

Comparing this result with (2.25) shows that η is the non-equilibrium temperature θ . The entropy introduced above is thereby also unique within an arbitrary constant.

Hence we have proved the existence of the fundamental relation

$$s = s(u, \boldsymbol{\epsilon}) \quad (3.18)$$

from which the equations of state follow by differentiation:

$$\left. \frac{\partial s}{\partial u} \right|_{\epsilon} = \theta^{-1}, \quad \left. \frac{\partial s}{\partial \epsilon} \right|_{\theta} = -\frac{\mathbf{t}}{\theta}. \quad (3.19)$$

Once θ and \mathbf{t} are known as functions of u and ϵ , s can, within an arbitrary constant, be determined by integration of (3.16).

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