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Autor(en): **Hutter, Kolumban / Müller, Ingo**

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On Mixtures of Relativistic Fluids

by **Kolumban Hutter**

Laboratory of Hydraulics, Hydrology and Glaciology,
Federal Institute of Technology, Zürich

and **Ingo Müller**

Institut für Theoretische Physik, Universität Düsseldorf, Düsseldorf

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Abstract. A relativistic thermodynamic theory is presented for chemically reacting simple mixtures in which each constituent has its own temperature. The field equations for particle numbers, velocities and temperatures are restricted by a general entropy principle and the principle of special relativity. It is shown how absolute temperatures for each constituent can be defined and that heat fluxes and production densities of energy-momentum are related to the gradients of temperatures and densities. The paper closes with a comparison of this theory with that of Eckart for the case of a single fluid.

1. Introduction

Relativistic thermodynamics of chemically reacting mixtures is a field theory whose objective is the determination of the fields of particle number, velocity and temperature of each constituent. The field equations are the equations of balance of particle numbers and of energy-momentum of the constituents supplemented by constitutive relations for the stress-energy-momentum tensors, for the production densities of energy-momentum and for the reaction rate densities.

Previous relativistic theories of thermodynamics of fluid mixtures use the idea of a single temperature, common to all constituents (e.g. see [1]). Such theories are formulated within the framework of linear irreversible thermodynamics and *assume* the validity of the non-relativistic Gibbs equation and a particular form for the entropy flux. When each constituent has a different temperature it is not clear how to extend the ideas of linear irreversible thermodynamics and therefore we adopt a different approach: We consider constitutive relations appropriate to a simple mixture of inviscid fluids and find restrictions on these relations by the principle of special relativity and a general entropy principle. According to this entropy principle, the entropy-entropy flux vector is a constitutive quantity and the entropy production is non-negative for every solution of the field equations. Such an entropy principle was proposed by Müller [2 or 3] and has already been applied to non-relativistic simple mixtures by Müller [4], and by Alts and Müller [5] to a single relativistic fluid.

For a subclass of simple mixtures, that is characterized by linear constitutive relations, we show how absolute temperatures can be defined for every constituent and

how these temperatures approach a common value as equilibrium is approached. We *prove* that a Gibbs equation holds for every constituent and that the entropy flux and the heat flux of each constituent are proportional to each other with the absolute temperature as factor of proportionality. Furthermore, we derive that the heat flux of a constituent is equal to a linear combination of the gradients of the absolute temperature and of the density of that constituent; as a consequence, one must conclude that in equilibrium in a gravitational field the temperature fields of the constituents are not uniform. We also show that the interaction force between one constituent and all others will in a linear theory depend linearly on the relative velocities of the constituents and, in general, on their heat fluxes. Finally, it comes out that the law of mass action in a relativistic theory contains explicitly the binding energies of the constituents.

For a single inviscid fluid we compare our results with those of Eckart's theory of a relativistic fluid. That theory was proposed in [6] and uses the ideas of linear irreversible thermodynamics. With respect to the dependence of the heat flux on the gradients of temperature and density, there is agreement between the two theories; however, in Eckart's theory the heat flux contains additional terms whose interpretation seems to require further study.

2. Equations of Balance for a Mixture of Relativistic Fluids

a. Objective and notation

We consider mixtures of ν fluid constituents and assume that each point in the body is simultaneously occupied by molecules of all constituents. Quantities relating to a constituent will carry a Greek index.

x^A with $A = 1, 2, 3, 4$ denotes the coordinates of an event in space-time, so that x^a ($a = 1, 2, 3$) are Cartesian coordinates of its spatial position and $t = x^4/c$ is the time of its occurrence. In general, capital Latin indices range over the four values 1, 2, 3, 4, while lower case Latin indices range over the three values 1, 2, 3; summation over recurring Latin indices is understood, and $f_{,A}$ denotes partial differentiation of the field f with respect to x_A .

Throughout this article the frame of reference will be a Lorentz-frame with a metric tensor of the form

$$g^{AB} = \begin{pmatrix} -1 & & & \\ & -1 & & \\ & & -1 & \\ & & & 1 \end{pmatrix}.$$

g^{AB} and its inverse g_{AB} are used to raise and lower indices in the usual manner and we define $\delta_C^A = g^{AB}g_{BC}$.

The main objective of a thermodynamic theory of mixtures of fluids is the determination of the following fields:

$$\begin{aligned} \overset{\alpha}{n}(x^A) &= \text{number density of particles of constituent } \alpha \text{ in its rest frame,} \\ \overset{\alpha}{V}^a(x^A) &= \text{velocity of constituent } \alpha, \\ \overset{\alpha}{\vartheta}(x^A) &= \text{empirical temperature of constituent } \alpha \text{ in its rest frame.} \end{aligned} \tag{2.1}$$

It is often useful to replace the velocity $\overset{\alpha}{V}^a$ by the three independent components of the four-velocity $\overset{\alpha}{U}^A$:

$$\overset{\alpha}{U}^A = \left\{ \frac{\overset{\alpha}{V}^a}{\sqrt{1 - \frac{\overset{\alpha}{V}^a \overset{\alpha}{V}^a}{c^2}}}, \frac{c}{\sqrt{1 - \frac{\overset{\alpha}{V}^a \overset{\alpha}{V}^a}{c^2}}} \right\} \text{ so that } \overset{\alpha}{U}^A \overset{\alpha}{U}_A = c^2. \quad (2.2)$$

The calculation of the fields (2.1) requires the formulation of field equations and these are commonly based upon the equation of balance of mechanics and thermodynamics which we now proceed to discuss.

b. Equations of balance

α. Balance of numbers, momenta, energies, and moments of momenta. The equations of balance of particle numbers, momentum and energy of the constituents read

$$(\overset{\alpha}{n} \overset{\alpha}{U}^A)_{,A} = \overset{\alpha}{c}, \quad \alpha = 1, 2, \dots, \nu, \quad (2.3)_1$$

$$\overset{\alpha}{T}^{AB}_{,B} = \overset{\alpha}{m}^A, \quad \alpha = 1, 2, \dots, \nu. \quad (2.3)_2$$

Here, $\overset{\alpha}{c}$ is the production density of particles of constituent α due to chemical reactions. $\overset{\alpha}{T}^{AB}$ is the stress-energy-momentum tensor of constituent α and $\overset{\alpha}{m}^A$ is the production density of momentum and energy of that constituent. More specifically we have

$$\begin{aligned} \overset{\alpha}{T}^{ab} &= \text{momentum flux of constituent } \alpha, \\ \overset{\alpha}{T}^{a4} &= c \cdot \text{momentum density of constituent } \alpha, \\ \overset{\alpha}{T}^{4b} &= 1/c \cdot \text{energy flux of constituent } \alpha, \end{aligned} \quad (2.4)$$

$$\begin{aligned} \overset{\alpha}{T}^{44} &= \text{energy density of constituent } \alpha, \\ \overset{\alpha}{m}^a &= \text{momentum production of constituent } \alpha, \\ \overset{\alpha}{m}^4 &= 1/c \cdot \text{energy production of constituent } \alpha. \end{aligned} \quad (2.5)$$

The momentum production $\overset{\alpha}{m}^a$ can also be interpreted as a force of constituent α which is due to the interaction of that constituent with all others.

The balance of energy and momentum for the mixture as a whole may be written as

$$\sum_{\alpha=1}^{\nu} \overset{\alpha}{T}^{AB}_{,B} = \sum_{\alpha=1}^{\nu} \overset{\alpha}{m}^A, \quad (2.6)$$

whence follows

$$\sum_{\alpha=1}^{\nu} \overset{\alpha}{m}^A = 0 \quad (2.7)$$

as the expression of conservation of momentum and energy.

Not all ν production densities $\overset{\alpha}{c}$ of particles are independent: Indeed, if there are

n independent chemical reactions and λ^a is the reaction rate density of the a th reaction, we have

$$c^\alpha = \sum_{a=1}^n \gamma_\alpha^a \lambda^a, \quad \alpha = 1, 2, 3, \dots, \nu, \quad (2.8)$$

where γ_α^a is the stoichiometric coefficient of constituent α in reaction a . The stoichiometric coefficients are restricted by the requirement that in every reaction the number of nucleons and the number of electrons must be conserved. Therefore,

$$\sum_{\alpha=1}^{\nu} \bar{Z}_N \gamma_\alpha^a = 0 \quad \text{and} \quad \sum_{\alpha=1}^{\nu} \bar{Z}_e \gamma_\alpha^a = 0 \quad (2.9)$$

must hold, where \bar{Z}_N and \bar{Z}_e are the number of nucleons and of electrons respectively within the molecules of constituent α . It follows from (2.8) that there are $\nu - n$ relations between the ν densities c^α and that the n reaction rate densities λ^a are the true variables governing the chemical reactions.

Multiplication of (2.3)₂ by x^D leads to a tensor equation with free indices A and D and its antisymmetric part reads after an easy calculation

$$(x^{[D} \bar{T}^{A]B})_{,B} = \bar{T}^{[AD]} + x^{[D} \bar{m}^{A] \cdot 1}$$

The quantities $x^{[d} \bar{T}^{a]4}$ are the components of moment of momentum of constituent α and $x^{[d} \bar{m}^{a]}$ are the combined torques of the interaction force. We shall assume for simplicity that in every Lorentz frame those torques are the only causes for the production of moment of momentum and this assumption is tantamount to saying that the stress-energy-momentum tensors of each constituent are symmetric:

$$\bar{T}^{[AD]} = 0. \quad (2.10)$$

β . *Balance of entropy.* Various considerations of thermostatics and of statistical mechanics suggest that the entropy of a constituent is an additive quantity just like energy and momentum. In special relativity this observation can be expressed in equations of balance of the form

$$\bar{S}_{,A}^{\alpha} = \bar{\Sigma}^{\alpha} \quad (2.11)$$

where $\bar{\Sigma}^{\alpha}$ is the density of entropy production of constituent α , while $\bar{S}^{\alpha A}$ is the entropy-entropy flux vector whose components have the following interpretation:

$$\bar{S}^{\alpha a} = \text{entropy flux of constituent } \alpha, \quad (2.12)$$

$$\bar{S}^{\alpha 4} = c \cdot \text{entropy density of constituent } \alpha.$$

The entropy balance for the mixture has the form

$$S_{,A}^A = \Sigma, \quad (2.13)$$

where S^A and Σ are the sums of $\bar{S}^{\alpha A}$ and $\bar{\Sigma}^{\alpha}$ over all α . Later we shall postulate an inequality for the entropy production density Σ of the mixture.

¹⁾ Square brackets indicate antisymmetrization.

3. Field Equations, Principle of Special Relativity, Entropy Principle

a. Constitutive equations

We recall that thermodynamics has the principal objective of calculating the fields (2.1). Clearly the equations of balance (2.3) cannot by themselves serve as field equations for that purpose, and in order to obtain field equations from (2.3) we must supplement these equations by constitutive equations which relate the quantities

$$\lambda^\alpha, \overset{\alpha}{m}^A, \overset{\alpha}{T}^{AB} \tag{3.1}$$

to the fields $\overset{\alpha}{n}$, $\overset{\alpha}{V}^a$ and $\overset{\alpha}{\vartheta}$ in a materially dependent manner. By (2.8) the reaction rate densities λ^α determine the production densities $\overset{\alpha}{c}$ of particles which occur in (2.3)₁. If in particular the constitutive equations are of the form

$$\overset{\alpha}{T}^{AB} = \overset{\alpha}{\mathbf{T}}^{AB}(\overset{\alpha}{n}; \overset{\alpha}{U}^A; \overset{\alpha}{\vartheta}; \overset{\alpha}{n}_{,A}; \overset{\alpha}{\vartheta}_{,A}); \tag{3.2}_1$$

$$\overset{\alpha}{m}^A = \overset{\alpha}{\mathbf{m}}^A(\overset{\beta}{n}; \overset{\beta}{U}^A; \overset{\beta}{\vartheta}; \overset{\beta}{n}_{,A}; \overset{\beta}{\vartheta}_{,A}); \quad \beta = 1, 2, \dots, \nu; \tag{3.2}_2$$

$$\lambda^\alpha = \overset{\alpha}{\lambda}(\overset{\beta}{n}; \overset{\beta}{U}^A; \overset{\beta}{\vartheta}; \overset{\beta}{n}_{,A}; \overset{\beta}{\vartheta}_{,A}); \quad \beta = 1, 2, \dots, \nu; \tag{3.2}_3$$

we call the material a *simple mixture of inviscid fluids*.

The entropy-entropy flux vectors $\overset{\alpha}{S}^A$ in a simple mixture of inviscid fluids are also assumed to be given by a constitutive equation of the same type as $\overset{\alpha}{T}^{AB}$:

$$\overset{\alpha}{S}^A = \overset{\alpha}{\mathbf{S}}^A(\overset{\alpha}{n}; \overset{\alpha}{U}^A; \overset{\alpha}{\vartheta}; \overset{\alpha}{n}_{,A}; \overset{\alpha}{\vartheta}_{,A}). \tag{3.2}_4$$

The class of materials characterized by equations of the type (3.2) is special in two respects as follows:

(i) The stress-energy-momentum tensor and the entropy-entropy flux vector of constituent α depend on the particle number, velocity and temperature of that constituent only. It is with reference to this property that we speak of *simple* mixtures. Interaction between the constituents of a simple mixture is thus effected only by the production densities $\overset{\alpha}{m}^A$ and by the reaction rate densities λ^α which may both depend on all particle numbers, velocities and temperatures.

(ii) Velocity gradients are not included among the independent variables in (3.2) and this implies that viscous effects are ignored.

In classical theories of simple mixtures density gradients would be absent from the list of variables in (3.2) (e.g. see Ref. [7], p. 186). In a relativistic theory, however, these variables play an important role which will become clear later.

When the constitutive equations (3.2)_{1,2,3} are introduced into the equations of balance (2.3), one obtains a set of field equations for the determination of the fields $\overset{\alpha}{n}(x^A)$, $\overset{\alpha}{V}^a(x^A)$, $\overset{\alpha}{\vartheta}(x^A)$ and every solution of these equations is called a *thermodynamic process* in a simple mixture of inviscid fluids.

If the constitutive functions in (3.2) were known, the problem of finding thermodynamic processes subject to certain initial and boundary values would be entirely

mathematical. However, for no material are these functions known and therefore most thermodynamicists attempt to exploit general physical principles which impose restrictions on the constitutive functions. The main principles of this type are the *principle of special relativity* and the *entropy principle* which we now proceed to discuss.

b. Transformation properties and the principle of special relativity

The transition from one Lorentz frame to another one is effected by the transformation $\bar{x}^A = L_B^A x^B$ with

$$L_B^A = \begin{pmatrix} \mathcal{O}_c^a & 0 \\ 0 & 1 \end{pmatrix} \left(\begin{array}{c|c} \delta_b^c - \frac{V^c V_b}{c^2} \left(\frac{1}{\sqrt{1 - V^2/c^2}} - 1 \right) & -\frac{1}{c} \frac{V^b}{\sqrt{1 - V^2/c^2}} \\ \hline \frac{1}{c} \frac{V^b}{\sqrt{1 - V^2/c^2}} & \frac{1}{\sqrt{1 - V^2/c^2}} \end{array} \right)$$

where \mathcal{O}_c^a is an orthogonal matrix, V^c are the components of the relative velocity of the two frames, and V is the magnitude of that velocity.

\bar{n}^α and $\bar{\vartheta}^\alpha$ are by definition scalars with respect to these Lorentz transformations while \bar{U}^A are vectors. It is assumed that $\bar{T}^{\alpha AB}$, \bar{m}^A , \bar{S}^A , $\bar{\lambda}^a$ and $\bar{\Sigma}^\alpha$ are tensors, vectors and scalars respectively so that we have

$$\bar{T}^{\alpha AB} = L_C^A L_D^B \bar{T}^{\alpha CD}; \quad \bar{m}^A = L_C^A \bar{m}^C; \quad \bar{S}^A = L_C^A \bar{S}^C; \quad \bar{\lambda}^a = \lambda^a; \quad \bar{\Sigma}^\alpha = \Sigma^\alpha. \tag{3.3}$$

Clearly, with these transformation properties, the equations of balance (2.3) and (2.11) retain their forms in every Lorentz frame.

However, the principle of special relativity requires that the *field equations* – and not merely the equations of balance – retain their forms and therefore the constitutive functions $\bar{T}^{\alpha AB}$, \bar{m}^A and $\bar{\lambda}^a$ must be the same ones in every Lorentz frame. We postulate the same invariance for the constitutive functions \bar{S}^A of the entropy-entropy flux vectors.

Thus the principle of special relativity combined with the transformation properties (3.3)₁₋₄ implies that the constitutive functions be *isotropic* tensorial, vectorial and scalar functions with respect to the transformations L_B^A , i.e. that the following conditions hold

$$\begin{aligned} \bar{T}^{\alpha CD}(\bar{n}^\alpha; L_C^A \bar{U}^C; \bar{\vartheta}^\alpha; L_C^A \bar{n}_{,C}^\alpha; L_C^A \bar{\vartheta}_{,C}^\alpha) &= L_A^C L_B^D \bar{T}^{\alpha AB}(\bar{n}^\alpha; \bar{U}^A; \bar{\vartheta}^\alpha; \bar{n}_{,A}^\alpha; \bar{\vartheta}_{,A}^\alpha); \\ \bar{S}^C(\text{---}) &= L_A^C \bar{S}^A(\text{---}); \\ \bar{m}^C(\bar{n}^\beta; L_C^A \bar{U}^C; \bar{\vartheta}^\beta; L_C^A \bar{n}_{,C}^\beta; L_C^A \bar{\vartheta}_{,C}^\beta) &= L_A^C \bar{m}^A(\bar{n}^\beta; \bar{U}^A; \bar{\vartheta}^\beta; \bar{n}_{,A}^\beta; \bar{\vartheta}_{,A}^\beta); \\ \bar{\lambda}^a(\text{---}) &= \lambda^a(\text{---}). \end{aligned} \tag{3.4}$$

These conditions must be satisfied identically in the matrices L_B^A and that requirement leads to important restrictions on the constitutive functions. Such restrictions are best expressed, in our opinion, in terms of the variables

$$\dot{n}^\alpha \equiv \dot{U}^A n_{,A}^\alpha; \quad \dot{n}^{\perp A} \equiv \dot{\Delta}^{AB} n_{,B}^\alpha; \tag{3.5}$$

and

$$\dot{\vartheta}^\alpha \equiv \dot{U}^A \vartheta_{,A}^\alpha; \quad \dot{\vartheta}^{\perp A} \equiv \dot{\Delta}^{AB} \vartheta_{,B}^\alpha,$$

rather than in terms of $n_{,A}^\alpha$ and $\vartheta_{,A}^\alpha$. In (3.5) $\dot{\Delta}^{AB}$ is a projection operator defined as

$$\dot{\Delta}^{AB} = g^{AB} - \frac{1}{c^2} \dot{U}^A \dot{U}^B \quad \text{so that} \quad \dot{\Delta}^{AB} \dot{U}_B \equiv 0. \tag{3.6}$$

In terms of the new variables (3.5) the representations implied by (3.4) read, since \dot{T}^{AB} was assumed symmetric

$$\begin{aligned} \dot{T}^{AB} = & -\dot{p}g^{AB} + \frac{1}{c^2} (\dot{n}^\alpha \dot{m}^\alpha c^2 + \dot{n}^\alpha \dot{\epsilon} + \dot{p}) \dot{U}^A \dot{U}^B + \frac{\dot{\tau}}{c^2} (\dot{U}^A \dot{n}^{\perp B} + \dot{U}^B \dot{n}^{\perp A}) \\ & + \frac{\dot{\kappa}}{c^2} (\dot{U}^A \dot{\vartheta}^{\perp B} + \dot{U}^B \dot{\vartheta}^{\perp A}) - \dot{O} \dot{n}^{\perp A} \dot{n}^{\perp B} - \dot{P} (\dot{n}^{\perp A} \dot{\vartheta}^{\perp B} + \dot{n}^{\perp B} \dot{\vartheta}^{\perp A}) - \dot{Q} \dot{\vartheta}^{\perp A} \dot{\vartheta}^{\perp B}; \end{aligned} \tag{3.7}_1$$

$$\dot{S}^A = \dot{n}^\alpha \dot{\eta} \dot{U}^A + \dot{s}_2 \dot{n}^{\perp A} + \dot{s}_3 \dot{\vartheta}^{\perp A}; \tag{3.7}_2$$

$$\dot{m}^A = \sum_{\beta=1}^v \dot{m}_1^{\alpha\beta} \dot{U}^A + \sum_{\beta=1}^v \dot{m}_2^{\alpha\beta} \dot{n}^{\perp A} + \sum_{\beta=1}^v \dot{m}_3^{\alpha\beta} \dot{\vartheta}^{\perp A} \tag{3.7}_3$$

and the scalars $\dot{m}_1^{\alpha\beta}$, $\dot{m}_2^{\alpha\beta}$, $\dot{m}_3^{\alpha\beta}$ as well as the reaction rate densities λ^α may depend on the scalar variables

$$\begin{aligned} & \dot{U}^A \dot{U}_A; \quad \dot{U}^A \dot{n}_A^\beta; \quad \dot{U}^A \dot{\vartheta}_A^\beta; \\ \dot{n}^\alpha; \dot{\vartheta}^\alpha; \dot{n}^\alpha; \dot{\vartheta}^\alpha; & \dot{n}^{\perp A} \dot{U}_A; \quad \dot{n}^{\perp A} \dot{n}_A^\beta; \quad \dot{n}^{\perp A} \dot{\vartheta}_A^\beta; \\ & \dot{\vartheta}^{\perp A} \dot{U}_A; \quad \dot{\vartheta}^{\perp A} \dot{n}_A^\beta; \quad \dot{\vartheta}^{\perp A} \dot{\vartheta}_A^\beta. \end{aligned} \tag{3.8}$$

It must be noted that the first line and the first column in the matrix scheme of (3.8) do not give rise to variables, if $\alpha = \beta$ because $\dot{U}^A \dot{U}_A = c^2$, while $\dot{U}^A \dot{n}_A^\alpha \equiv 0$ and $\dot{U}^A \dot{\vartheta}_A^\alpha \equiv 0$. The scalar variables in (3.7)_{1,2} may depend on the scalar variables

$$\dot{n}^\alpha; \dot{\vartheta}^\alpha; \dot{n}^\alpha; \dot{\vartheta}^\alpha; \quad \dot{G} \equiv \dot{\vartheta}^{\perp A} \dot{\vartheta}_A^\alpha; \quad \dot{H} \equiv \dot{n}^{\perp A} \dot{n}_A^\alpha; \quad \dot{I} \equiv \dot{\vartheta}^{\perp A} \dot{\vartheta}_A^\alpha; \tag{3.9}$$

the coefficients \dot{p} and $\dot{n}^\alpha \dot{m}^\alpha c^2 + \dot{n}^\alpha \dot{\epsilon}$ in (3.7)₁ denote the pressure and the energy density of constituent α in its rest frame and $\dot{n}^\alpha \dot{m}^\alpha$ is the density of rest mass. $\dot{n}^\alpha \dot{\eta}$ in (3.7)₂ denotes the entropy density of constituent α in its rest frame.

The energy flux $c \cdot \dot{T}^{4b}$ and the flux of entropy S^b of constituent α in its rest frame

will be denoted by \hat{q}^b and $\hat{\phi}^b$ respectively and, according to (3.7)_{1,2} these fluxes read

$$\hat{q}^b = g^{ba}(\kappa^{\hat{\alpha}}_{,a} + \tau^{\hat{\alpha}}_{,a}); \quad \hat{\phi}^b = g^{ba}(s_2^{\hat{\alpha}}_{,a} + s_3^{\hat{\alpha}}_{,a}); \quad (3.10)$$

for brevity in future arguments we call \hat{q}^a and $\hat{\phi}^a$ the *heat flux* and the *non-convective flux of entropy* respectively of constituent α .

c. Entropy principle

We recall the equation of balance of entropy (2.17) and postulate that the entropy production density Σ be non-negative for every thermodynamic process. Thus the entropy inequality

$$S_{,A}^A \geq 0 \quad (3.11)$$

must hold for every thermodynamic process, i.e. for all solutions of the field equations that result from a combination of the constitutive equations (3.2) with the equations of balance (2.3).

A general entropy principle of this type was proposed by Müller [2] in a non-relativistic context and was used by Alts and Müller [5] in a relativistic theory of a single inviscid fluid. This principle was also applied by Müller [4 and 8] for the formulation of non-relativistic thermodynamic theories of mixtures.

We recall that we rely upon the entropy principle for the derivation of restrictive conditions on the constitutive functions. Now, the key for the evaluation of the inequality (3.11) is the statement that this inequality must hold for all thermodynamic processes. In other words: the fields $\hat{n}^{\alpha}(x^A)$, $\hat{\vartheta}^{\alpha}(x^A)$ and $\hat{V}^a(x^A)$ for which (3.11) must hold are constrained by the requirement that they be solutions of the field equations. Liu [9] has shown how one can get rid of these constraints: He showed that the new inequality

$$S_{,A}^A - \sum_{\alpha=1}^v \Lambda^{(\alpha)} [(\hat{n}^{\alpha} \hat{U}^A)_{,A} - \hat{c}] - \sum_{\alpha=1}^v \Lambda_A^{(\alpha)} [\hat{T}_{,B}^{AB} - \hat{m}^A] - \sum_{\alpha=1}^v \Lambda_A^{(\alpha)} [\hat{U}_B^{\alpha} \hat{U}_{,A}^B] \geq 0 \quad (3.12)$$

must hold for *all analytic fields* $\hat{n}^{\alpha}(x^A)$, $\hat{U}^c(x^A)$, $\hat{\vartheta}^{\alpha}(x^A)$. The quantities

$$\Lambda^{(\alpha)}, \Lambda_A^{(\alpha)}, \Lambda^A$$

are called Lagrange multipliers by Liu and, according to his proof, may be functions of all variables in (3.2). Inspection of (3.12) shows how this inequality has been formed: Each field equation has been multiplied by a Lagrange factor and subtracted from the $S_{,A}^A$ in the original inequality (3.11). One feature of (3.12) deserves a remark: In (3.7) the four-velocities \hat{U}^A take the role of the velocity variable but, since $\hat{U}^A \hat{U}_A = c^2$, only three components of \hat{U}^A are independent, so that the equation $\hat{U}_A^{\alpha} \hat{U}_{,B}^{\alpha} = 0$ in addition to the field equations serves as a constraint on the fields $\hat{n}^{\alpha}(x^A)$, $\hat{U}^c(x^A)$, $\hat{\vartheta}^{\alpha}(x^A)$. The term with the Lagrange multiplier in (3.12) takes care of that additional constraint.

We shall now turn to the evaluation of the inequality (3.12).

4. Consequences of the Entropy Principle, Linear Constitutive Equations and Equilibrium

a. General consequences of the entropy principle

When the constitutive relations (3.2)_{1,4} for $\overset{\alpha}{T}{}^{AB}$ and $\overset{\alpha}{S}{}^A$ are introduced into the inequality (3.12) and when all indicated differentiations are performed, what emerges is an inequality whose left hand side is linear in the quantities

$$\overset{\alpha}{n}{}_{,AB}; \overset{\alpha}{\vartheta}{}_{,AB}; \overset{\alpha}{U}{}^E{}_{,B}. \tag{4.1}$$

Since the inequality must hold for all analytic fields $\overset{\alpha}{n}$, $\overset{\alpha}{\vartheta}$, $\overset{\alpha}{U}{}^A$, it must in particular hold for arbitrary values of the derivatives (4.1) in one event. Thus the terms with these derivatives must not contribute to the inequality or else that relation could be violated. This argument leads to the following conditions²⁾

$$\frac{\partial \overset{\alpha}{S}{}^{(B}}{\partial \overset{\alpha}{n}{}_{,E)}} - \overset{(\alpha)}{\Lambda}{}_A \frac{\partial \overset{\alpha}{T}{}^{A(B}}{\partial \overset{\alpha}{n}{}_{,E)}} = 0; \tag{4.2)_1}$$

$$\frac{\partial \overset{\alpha}{S}{}^{(B}}{\partial \overset{\alpha}{\vartheta}{}_{,E)}} - \overset{(\alpha)}{\Lambda}{}_A \frac{\partial \overset{\alpha}{T}{}^{A(B}}{\partial \overset{\alpha}{\vartheta}{}_{,E)}} = 0; \tag{4.2)_2}$$

$$\frac{\partial \overset{\alpha}{S}{}^B}{\partial \overset{\alpha}{U}{}^E} - \overset{(\alpha)}{\Lambda}{}_A \frac{\partial \overset{\alpha}{T}{}^{AB}}{\partial \overset{\alpha}{U}{}^E} - \overset{(\alpha)}{\Lambda} \overset{\alpha}{n} \delta_E^B - \overset{(\alpha)}{\Lambda}{}^B \overset{\alpha}{U}{}_E = 0. \tag{4.2)_3}$$

There remains the inequality

$$\sum_{\alpha=1}^v \left\{ \frac{\partial \overset{\alpha}{S}{}^B}{\partial \overset{\alpha}{n}} - \overset{(\alpha)}{\Lambda} \frac{\partial \overset{\alpha}{T}{}^{AB}}{\partial \overset{\alpha}{n}} - \overset{(\alpha)}{\Lambda} \overset{\alpha}{U}{}^B \right\} \overset{\alpha}{n}{}_{,B} + \sum_{\alpha=1}^v \left\{ \frac{\partial \overset{\alpha}{S}{}^B}{\partial \overset{\alpha}{\vartheta}} - \overset{(\alpha)}{\Lambda} \frac{\partial \overset{\alpha}{T}{}^{AB}}{\partial \overset{\alpha}{\vartheta}} \right\} \overset{\alpha}{\vartheta}{}_{,B} + \sum_{\alpha=1}^v \left\{ \overset{(\alpha)}{\Lambda} c^{\alpha} + \overset{(\alpha)}{\Lambda}{}_A \overset{\alpha}{m}{}^A \right\} \geq 0. \tag{4.3}$$

Some of the relations (4.2) may be used to calculate the Lagrange multipliers. Thus, multiplication of (4.2)₃ by $\overset{\beta}{\Delta}{}^{EF}$ results in a tensor equation whose trace implies

$$\overset{(\alpha)}{\Lambda} = \frac{1}{3 \overset{\alpha}{n}} \left(\frac{\partial \overset{\alpha}{S}{}^B}{\partial \overset{\alpha}{U}{}^E} - \overset{(\alpha)}{\Lambda}{}_A \frac{\partial \overset{\alpha}{T}{}^{AB}}{\partial \overset{\alpha}{U}{}^E} \right) \overset{\alpha}{\Delta}{}^E{}_B.$$

When this is put back into (4.2)₃ and when that equation is multiplied by $\overset{\alpha}{U}{}^E$ one gets

$$\overset{(\alpha)}{\Lambda}{}^B = \frac{1}{c^2} \left\{ \left(\frac{\partial \overset{\alpha}{S}{}^B}{\partial \overset{\alpha}{U}{}^E} - \overset{(\alpha)}{\Lambda} \frac{\partial \overset{\alpha}{T}{}^{AB}}{\partial \overset{\alpha}{U}{}^E} \right) \overset{\alpha}{U}{}^E - \frac{1}{3} \left(\frac{\partial \overset{\alpha}{S}{}^C}{\partial \overset{\alpha}{U}{}^E} - \overset{(\alpha)}{\Lambda}{}_A \frac{\partial \overset{\alpha}{T}{}^{AC}}{\partial \overset{\alpha}{U}{}^E} \right) \overset{\alpha}{\Delta}{}^E{}_C \overset{\alpha}{U}{}^B \right\}.$$

Therefore equation (4.2)₃ becomes

$$\left(\frac{\partial \overset{\alpha}{S}{}^C}{\partial \overset{\alpha}{U}{}^E} - \overset{(\alpha)}{\Lambda}{}_A \frac{\partial \overset{\alpha}{T}{}^{AB}}{\partial \overset{\alpha}{U}{}^E} \right) (\delta_C^B \overset{\alpha}{\Delta}{}^{EF} - \frac{1}{3} \overset{\alpha}{\Delta}{}^E{}_C \overset{\alpha}{\Delta}{}^{BF}) = 0. \tag{4.4}$$

²⁾ Round indices indicate symmetrization.

We proceed to study the equations (4.2)_{1,2} and (4.4): First of all, (4.2)₁ implies that $\overset{(\alpha)}{\Lambda}_A$ depends on $\overset{\alpha}{n}$, $\overset{\alpha}{U}^A$, $\overset{\alpha}{\vartheta}$, $\overset{\alpha}{n}_{,A}$, $\overset{\alpha}{\vartheta}_{,A}$ only and is an isotropic function of these variables so that it has a representation of the form

$$\overset{(\alpha)}{\Lambda}_A = \overset{\alpha}{\Lambda} \overset{\alpha}{U}_A + \overset{\alpha}{\Lambda}_2 \overset{\alpha}{n}_A^\perp + \overset{\alpha}{\Lambda}_3 \overset{\alpha}{\vartheta}_A^\perp, \tag{4.5}$$

where $\overset{\alpha}{\Lambda}$, $\overset{\alpha}{\Lambda}_2$ and $\overset{\alpha}{\Lambda}_3$ are scalar functions of the scalar variables (3.9). Next we introduce the representations (3.7)_{1,2} and (4.5) into the equations (4.2)_{1,2} and (4.4) and, since these equations must be satisfied identically in $\overset{\alpha}{U}_A$, $\overset{\alpha}{n}_{,A}$, $\overset{\alpha}{\vartheta}_{,A}$, we obtain a great number of conditions on the scalar functions in (3.7)_{1,2} and (4.5). The determination of these conditions is long and tedious, even though it is straightforward and we just give the results: The coefficients $\overset{\alpha}{\Lambda}_2$ and $\overset{\alpha}{\Lambda}_3$ in (4.5) turn out to be related to $\overset{\alpha}{\Lambda}$ by the equations

$$\begin{aligned} \overset{\alpha}{\Lambda}_2 &= \overset{\alpha}{R}_2 \overset{\alpha}{\Lambda}, \quad \text{where} \quad \overset{\alpha}{R}_2 = \frac{\overset{\alpha}{\tau} + \overset{\alpha}{O} \overset{\alpha}{\dot{n}} + \overset{\alpha}{P} \overset{\alpha}{\dot{\vartheta}}}{\overset{\alpha}{n} m c^2 + \overset{\alpha}{n} \overset{\alpha}{\epsilon} + \overset{\alpha}{p} - (1/c^2)(\overset{\alpha}{\tau} \overset{\alpha}{\dot{n}} + \overset{\alpha}{\kappa} \overset{\alpha}{\dot{\vartheta}})} \\ \overset{\alpha}{\Lambda}_3 &= \overset{\alpha}{R}_3 \overset{\alpha}{\Lambda}, \quad \text{where} \quad \overset{\alpha}{R}_3 = \frac{\overset{\alpha}{\kappa} + \overset{\alpha}{P} \overset{\alpha}{\dot{n}} + \overset{\alpha}{Q} \overset{\alpha}{\dot{\vartheta}}}{\overset{\alpha}{n} m c^2 + \overset{\alpha}{n} \overset{\alpha}{\epsilon} + \overset{\alpha}{p} - (1/c^2)(\overset{\alpha}{\tau} \overset{\alpha}{\dot{n}} + \overset{\alpha}{\kappa} \overset{\alpha}{\dot{\vartheta}})} \end{aligned} \tag{4.6}$$

so that by now of all the Lagrange multipliers, that we introduced, only ν are undetermined, one for each constituent, namely $\overset{\alpha}{\Lambda} \equiv (1/c^2) \overset{(\alpha)}{\Lambda}_A \overset{\alpha}{U}^A$.

For the coefficients $\overset{\alpha}{s}_2$ and $\overset{\alpha}{s}_3$ in the representation of the entropy-entropy flux vector we get

$$\begin{aligned} \overset{\alpha}{s}_2 &= \overset{\alpha}{\Lambda} (\overset{\alpha}{\tau} - \overset{\alpha}{R}_2 (\overset{\alpha}{O} \overset{\alpha}{H} + \overset{\alpha}{P} \overset{\alpha}{I}) - \overset{\alpha}{R}_3 (\overset{\alpha}{O} \overset{\alpha}{I} + \overset{\alpha}{P} \overset{\alpha}{G})), \\ \overset{\alpha}{s}_3 &= \overset{\alpha}{\Lambda} (\overset{\alpha}{\kappa} - \overset{\alpha}{R}_2 (\overset{\alpha}{Q} \overset{\alpha}{I} + \overset{\alpha}{P} \overset{\alpha}{H}) - \overset{\alpha}{R}_3 (\overset{\alpha}{Q} \overset{\alpha}{G} + \overset{\alpha}{P} \overset{\alpha}{I})). \end{aligned} \tag{4.7}$$

From these two equations and (3.10) we conclude that the non-convective flux of entropy and the heat flux are not proportional in general, although they are in a linear theory as we shall soon see.

Further, we have equations for the derivatives of $\overset{\alpha}{s}_2$, $\overset{\alpha}{s}_3$, $\overset{\alpha}{n} \overset{\alpha}{\eta}$ with respect to $\overset{\alpha}{\dot{n}}$, $\overset{\alpha}{\dot{\vartheta}}$, $\overset{\alpha}{G}$, $\overset{\alpha}{H}$ and $\overset{\alpha}{I}$. These derivatives imply a great number of integrability conditions which must be satisfied by the functions $\overset{\alpha}{p}$, $\overset{\alpha}{\epsilon}$, $\overset{\alpha}{\tau}$, $\overset{\alpha}{\kappa}$, $\overset{\alpha}{O}$, $\overset{\alpha}{P}$ and $\overset{\alpha}{Q}$, but such conditions are complicated and little suggestive; moreover, we shall not need them in the remainder of this paper and therefore we delete them.

Indeed, from here on we shall restrict the attention to the consideration of constitutive equations that are linear in $\overset{\alpha}{n}_{,A}$, $\overset{\alpha}{\vartheta}_{,A}$ and velocity differences $\overset{\alpha}{U}^A - \overset{\beta}{U}^A$.

b. Linear constitutive equations and further evaluation of the entropy inequality

When non-linear terms in the derivatives $\dot{n}_{,A}^\alpha, \dot{\vartheta}_{,A}^\alpha$ and in $\dot{U}^A - \dot{U}^A$ are neglected, the coefficients \dot{O}, \dot{P} and \dot{Q} in (3.7)₁ must be set equal to zero, while the equations (3.7)_{2,3} are formally unchanged. Thus we have

$$\begin{aligned} \dot{T}^{AB} = & -\dot{p}g^{AB} + \frac{1}{c^2}(\dot{n}m c^2 + \dot{n}\epsilon + \dot{p})\dot{U}^A\dot{U}^B + \frac{\dot{\tau}}{c^2}(\dot{U}^A\dot{n}^{\perp B} + \dot{U}^B\dot{n}^{\perp A}) \\ & + \frac{\dot{\kappa}}{c^2}(\dot{U}^A\dot{\vartheta}^{\perp B} + \dot{U}^B\dot{\vartheta}^{\perp A}); \end{aligned} \tag{4.8}$$

$$\dot{S}^A = \dot{n}^\alpha \eta \dot{U}^A + \dot{s}_2 \dot{n}^{\perp A} + \dot{s}_3 \dot{\vartheta}^{\perp A};$$

$$\dot{m}^A = \sum_{\beta=1}^v \dot{m}_1^{\alpha\beta} \dot{U}^A + \sum_{\beta=1}^v \dot{m}_2^{\alpha\beta} \dot{n}^{\perp A} + \sum_{\beta=1}^v \dot{m}_3^{\alpha\beta} \dot{\vartheta}^{\perp A}.$$

Moreover, in a linear theory we must require that

\dot{p}, ϵ, η are functions of $\dot{n}, \dot{\vartheta}$, and linear functions of $\dot{\dot{n}}, \dot{\dot{\vartheta}}$

$\dot{\tau}, \dot{\kappa}, \dot{s}_2, \dot{s}_3$ are functions of $\dot{n}, \dot{\vartheta}$,

\dot{m}_2, \dot{m}_3 are functions of $\dot{n}, \dot{\vartheta}$, (4.9)

\dot{m}_1, λ^a are functions of $\dot{n}, \dot{\vartheta}$ and linear functions of $\dot{\dot{n}}, \dot{\dot{\vartheta}}$
and $\dot{U}_A(\dot{U}^A - \dot{U}^A)$.

Although from here on we shall only consider the linear constitutive relations characterized by (4.8) and (4.9), we shall not recognize this in the notation so as not to overburden the formulae with indices. Note that a dependence of the scalars in (4.9) on $\dot{n}^{\perp A} \dot{n}_A^\perp, \dot{n}^{\perp A} \dot{\vartheta}_A^\perp, \dot{\vartheta}^{\perp A} \dot{\vartheta}_A^\perp$ would give rise to non-linear terms and so would a dependence on

$$\dot{U}^A \dot{n}_A^\perp \equiv (\dot{U}^A - \dot{U}^A) \dot{n}_A^\perp \quad \text{and} \quad \dot{U}^A \dot{\vartheta}_A^\perp \equiv (\dot{U}^A - \dot{U}^A) \dot{\vartheta}_A^\perp.$$

Also, with $\dot{O}, \dot{P}, \dot{Q}$ all being zero, the equations (4.7) read

$$\dot{s}_2 = \dot{\Lambda} \dot{\tau} \quad \text{and} \quad \dot{s}_3 = \dot{\Lambda} \dot{\kappa}, \tag{4.9}$$

whence follows that $\dot{\Lambda}$ can only depend on \dot{n} and $\dot{\vartheta}$. The equations (3.10) and (4.9) combine to give a relation between the heat flux and the non-convective entropy flux, viz.

$$\hat{\phi}^a = \dot{\Lambda} \hat{q}^a. \tag{4.10}$$

We shall now proceed to evaluate the inequality (4.3). When $\dot{\Lambda}, \dot{\Lambda}$ from (4.4) and (4.5) and \dot{S}^B, \dot{T}^{AB} and \dot{m}^A from (4.8) are inserted into (4.3), it is easily appreciated that

the left hand side of that inequality reads

$$\begin{aligned}
 & \sum_{\alpha=1}^{\nu} \dot{n}^{\alpha} \left[\frac{\partial \dot{\eta}^{\alpha}}{\partial \dot{n}^{\alpha}} - \dot{\Lambda} \left(\frac{\partial \dot{\epsilon}^{\alpha}}{\partial \dot{n}^{\alpha}} - \frac{\dot{\pi}^{\alpha}}{\dot{n}^{\alpha 2}} \right) \right] \dot{n}^{\alpha} + \sum_{\alpha=1}^{\nu} \dot{n}^{\alpha} \left(\frac{\partial \dot{\eta}^{\alpha}}{\partial \dot{\vartheta}^{\alpha}} - \dot{\Lambda} \frac{\partial \dot{\epsilon}^{\alpha}}{\partial \dot{\vartheta}^{\alpha}} \right) \dot{\vartheta}^{\alpha} \\
 & + \sum_{\alpha, \beta=1}^{\nu} \left(\begin{array}{cc} \left[\left(\frac{\alpha}{\tau} \frac{\partial \dot{\Lambda}}{\partial \dot{n}^{\alpha}} + \frac{\alpha}{\dot{\Lambda}} \frac{\partial \dot{p}^{\alpha}}{\partial \dot{n}^{\alpha}} \right) \delta_{\alpha\beta} + \frac{\alpha}{\dot{\Lambda}} m_2^{\alpha\beta} \right] & \frac{1}{2} B^{\alpha\beta} \\ \frac{1}{2} B^{\beta\alpha} & \left[\left(\frac{\alpha}{\kappa} \frac{\partial \dot{\Lambda}}{\partial \dot{\vartheta}^{\alpha}} + \frac{\alpha}{\dot{\Lambda}} \frac{\partial \dot{p}^{\alpha}}{\partial \dot{\vartheta}^{\alpha}} \right) \delta_{\alpha\beta} + \frac{\alpha}{\dot{\Lambda}} m_3^{\alpha\beta} \right] \end{array} \right) \\
 & \times \begin{pmatrix} \dot{n}^{\beta \perp A} \\ \dot{\vartheta}^{\beta \perp A} \end{pmatrix}, \begin{pmatrix} \dot{n}^{\alpha \perp A} \\ \dot{\vartheta}^{\alpha \perp A} \end{pmatrix} + \sum_{\alpha, \beta=1}^{\nu} [\dot{\Lambda} m_1^{\alpha\beta} + \dot{\Lambda} m_2^{\beta\alpha}] \dot{n}^{\perp A} \dot{U}_A^{\beta} + \sum_{\alpha, \beta=1}^{\nu} [\dot{\Lambda} m_1^{\alpha\beta} + \dot{\Lambda} m_3^{\beta\alpha}] \dot{\vartheta}^{\perp A} \dot{U}_A^{\beta} \\
 & + \sum_{\alpha, \beta=1}^{\nu} \dot{\Lambda} m_1^{\alpha\beta} \dot{U}^A \dot{U}_A^{\beta} + \sum_{\alpha=1}^{\nu} \left[\dot{\eta}^{\alpha} + \dot{\Lambda} \left(\dot{m} c^2 + \dot{\epsilon}^{\alpha} + \frac{\dot{\pi}^{\alpha}}{\dot{n}^{\alpha}} \right) \right] \sum_{a=1}^n \gamma_a^{\alpha} \lambda^a \geq 0, \quad (4.11)
 \end{aligned}$$

where for brevity we have defined

$$B^{\alpha\beta} = \left[\left(\frac{\alpha}{\kappa} \frac{\partial \dot{\Lambda}}{\partial \dot{n}^{\alpha}} + \frac{\alpha}{\dot{\Lambda}} \frac{\partial \dot{p}^{\alpha}}{\partial \dot{n}^{\alpha}} + \frac{\alpha}{\tau} \frac{\partial \dot{\Lambda}}{\partial \dot{\vartheta}^{\alpha}} + \frac{\alpha}{\dot{\Lambda}} \frac{\partial \dot{p}^{\alpha}}{\partial \dot{\vartheta}^{\alpha}} \right) \delta_{\alpha\beta} + \frac{\beta}{\dot{\Lambda}} m_2^{\beta\alpha} + \frac{\alpha}{\dot{\Lambda}} m_3^{\alpha\beta} \right] \quad (4.12)_1$$

and

$$\dot{\pi}^{\alpha} = \dot{p}^{\alpha} + \frac{4}{3c^2} \frac{(\dot{\tau} \dot{n}^{\perp A} + \dot{\kappa} \dot{\vartheta}^{\perp A})(\dot{\tau} \dot{n}_A^{\perp} + \dot{\kappa} \dot{\vartheta}_A^{\perp})}{\dot{n}^{\alpha} \dot{m} c^2 + \dot{n}^{\alpha} \dot{\epsilon} + \dot{p}^{\alpha}}. \quad (4.12)_2$$

It requires considerable study of (4.11) to see that further conclusions can most easily be drawn from this inequality, when a change of variables is made: Indeed, we shall now replace $\dot{\vartheta}^{\perp A}$ by the quantity

$$\dot{q}^A = \dot{\tau} \dot{n}^{\perp A} + \dot{\kappa} \dot{\vartheta}^{\perp A}, \quad (4.13)$$

whose first three components, by (3.10), in the rest frame of constituent α are the heat flux of that constituent. It is then easily confirmed that (4.11) assumes the following form:

$$\begin{aligned}
 & \sum_{\alpha=1}^{\nu} \dot{n}^{\alpha} \left[\frac{\partial \dot{\eta}^{\alpha}}{\partial \dot{n}^{\alpha}} - \dot{\Lambda} \left(\frac{\partial \dot{\epsilon}^{\alpha}}{\partial \dot{n}^{\alpha}} - \frac{\dot{\pi}^{\alpha}}{\dot{n}^{\alpha 2}} \right) \right] \dot{n}^{\alpha} + \sum_{\alpha=1}^{\nu} \dot{n}^{\alpha} \left(\frac{\partial \dot{\eta}^{\alpha}}{\partial \dot{\vartheta}^{\alpha}} - \dot{\Lambda} \frac{\partial \dot{\epsilon}^{\alpha}}{\partial \dot{\vartheta}^{\alpha}} \right) \dot{\vartheta}^{\alpha} \\
 & + \sum_{\alpha, \beta=1}^{\nu} \left(\begin{array}{cc} 0 & \widehat{\frac{1}{2} B^{\alpha\beta}} \\ \frac{1}{2} \widehat{B}^{\beta\alpha} & \frac{1}{\dot{\kappa} \dot{\kappa}} \left[\left(\frac{\alpha}{\kappa} \frac{\partial \dot{\Lambda}}{\partial \dot{\vartheta}^{\alpha}} + \frac{\alpha}{\dot{\Lambda}} \frac{\partial \dot{p}^{\alpha}}{\partial \dot{\vartheta}^{\alpha}} \right) \delta_{\alpha\beta} + \frac{\alpha}{\dot{\Lambda}} m_3^{\alpha\beta} \right] \end{array} \right) \begin{pmatrix} \dot{n}^{\beta \perp A} \\ \dot{q}^{\beta A} \end{pmatrix}, \begin{pmatrix} \dot{n}^{\alpha \perp A} \\ \dot{q}^{\alpha A} \end{pmatrix} \\
 & + \sum_{\alpha, \beta=1}^{\nu} \dot{\Lambda} \left(m_2^{\beta\alpha} - \frac{\alpha}{\dot{\kappa}} m_3^{\beta\alpha} \right) \dot{n}^{\perp A} \dot{U}^B + \sum_{\alpha, \beta=1}^{\nu} \frac{1}{\dot{\kappa}} \left(\frac{\alpha}{\dot{\Lambda}} m_1^{\alpha\beta} + \frac{\beta}{\dot{\Lambda}} m_3^{\beta\alpha} \right) \dot{q}^A \dot{U}_A^{\beta} \\
 & + \sum_{\alpha, \beta=1}^{\nu} \dot{\Lambda} m_1^{\alpha\beta} \dot{U}^A \dot{U}_A^{\beta} + \sum_{\alpha=1}^{\nu} \left[\dot{\eta}^{\alpha} - \dot{\Lambda} \left(\dot{m} c^2 + \dot{\epsilon}^{\alpha} + \frac{\dot{\pi}^{\alpha}}{\dot{n}^{\alpha}} \right) \right] \sum_{a=1}^n \gamma_a^{\alpha} \lambda^a \geq 0, \quad (4.14)
 \end{aligned}$$

where $\hat{B}^{\alpha\beta}$ stands for

$$\hat{B}^{\alpha\beta} = \frac{1}{\beta} \left[\left(\kappa \frac{\partial \Lambda}{\partial n} + \frac{\Lambda}{3} \frac{\partial p}{\partial n} - \frac{\Lambda}{\tau} \frac{\partial \Lambda}{\partial \vartheta} - \frac{\Lambda}{2} \frac{\partial p}{\partial \vartheta} \right) \delta_{\alpha\beta} + \left(\frac{\beta}{3} m_2 - \frac{\beta}{2} m_3 \right) \right].$$

Inspection of (4.14) shows that the left hand side of that inequality is linear in $n^{\perp A}$; on the other hand the inequality must hold for arbitrary values of $n^{\perp A}$ and therefore we have

$$\sum_{\beta=1}^v \frac{1}{\beta} \left[\left(\kappa \frac{\partial \Lambda}{\partial n} + \frac{\Lambda}{3} \frac{\partial p}{\partial n} - \frac{\Lambda}{\tau} \frac{\partial \Lambda}{\partial \vartheta} - \frac{\Lambda}{2} \frac{\partial p}{\partial \vartheta} \right) \delta_{\alpha\beta} + \left(\frac{\beta}{3} m_2 - \frac{\beta}{2} m_3 \right) \right] \Delta_{AB} q^{\beta B} + \sum_{\beta=1}^v \frac{\beta}{\Lambda} \left(m_2 - \frac{\tau}{\kappa} m_3 \right) \Delta_{AB} U^{\beta B} = 0.$$

This equation must hold for any $q^{\beta B}$ and $U^{\beta B}$, whence we conclude

$$m_2 = \frac{\tau}{\kappa} m_3 \quad \text{and} \quad \kappa \frac{\partial \Lambda}{\partial n} - \frac{\Lambda}{\tau} \frac{\partial \Lambda}{\partial \vartheta} + \frac{\Lambda}{3} \frac{\partial p}{\partial n} - \frac{\Lambda}{2} \frac{\partial p}{\partial \vartheta} = 0. \tag{4.15}$$

Equation (4.15)₁ shows that the vector $\overset{\alpha}{m}_A$ has the form

$$\overset{\alpha}{m}_A = \sum_{\beta=1}^v \overset{\alpha\beta}{m}_1 U_A^{\beta} + \sum_{\beta=1}^v \frac{\overset{\alpha\beta}{m}_3}{\kappa} q_A^{\beta}, \tag{4.16}$$

so that, if all constituents are at rest, there is an interaction force $\overset{\alpha}{m}_a$ due to the heat fluxes of the constituents, unless all coefficients $\overset{\alpha\beta}{m}_3$ are zero. Equation (4.15)₂ will be evaluated later (see equation (5.2)₂).

The residual entropy inequality reads

$$\begin{aligned} & \sum_{\alpha=1}^v \overset{\alpha}{n} \left[\frac{\partial \overset{\alpha}{\eta}}{\partial \overset{\alpha}{n}} + \frac{\Lambda}{\alpha} \left(\frac{\partial \overset{\alpha}{\epsilon}}{\partial \overset{\alpha}{n}} - \frac{\overset{\alpha}{\pi}}{\overset{\alpha}{n}^2} \right) \overset{\alpha}{\dot{n}} + \sum_{\alpha=1}^v \overset{\alpha}{n} \left(\frac{\partial \overset{\alpha}{\eta}}{\partial \overset{\alpha}{\vartheta}} - \frac{\Lambda}{\alpha} \frac{\partial \overset{\alpha}{\epsilon}}{\partial \overset{\alpha}{\vartheta}} \right) \overset{\alpha}{\dot{\vartheta}} \right. \\ & + \left[\left(\kappa \frac{\partial \Lambda}{\partial \vartheta} + \frac{\Lambda}{3} \frac{\partial p}{\partial \vartheta} \right) \delta_{\alpha\beta} + \frac{\overset{\alpha\beta}{m}_3}{\kappa} \right] \frac{q^A q_A}{\kappa} + \sum_{\alpha,\beta=1}^v \left(\frac{\overset{\alpha\beta}{m}_1}{3} + \frac{\overset{\alpha\beta}{m}_3}{\Lambda} \right) \frac{q^A}{\kappa} U_A^{\beta} \\ & \left. + \sum_{\alpha,\beta=1}^v \frac{\overset{\alpha\beta}{m}_1}{\Lambda} U^A U_A^{\beta} + \sum_{\alpha=1}^v \left[\overset{\alpha}{\eta} - \frac{\Lambda}{\alpha} \left(\overset{\alpha}{m} c^2 + \overset{\alpha}{\epsilon} + \frac{\overset{\alpha}{\pi}}{\overset{\alpha}{n}} \right) \right] \sum_{\alpha=1}^n \gamma_{\alpha}^{\alpha} \lambda^{\alpha} \geq 0. \tag{4.17} \end{aligned}$$

The left hand side of this inequality is the entropy production and we shall now proceed to draw conclusions from it for the equilibrium values of constitutive functions.

c. Equilibrium and equilibrium properties

Equilibrium is characterized as a process, in which the number densities, velocities and temperatures of all constituents are time-independent, so that $\overset{\alpha}{\dot{n}} = \overset{\alpha}{U}^A \overset{\alpha}{n}_{,A} = 0$,

$\dot{\vartheta} = \dot{U}^A \dot{\vartheta}_{,A} = 0$ and $\dot{U}^A \dot{U}_{,A}^B = 0$, and in which the reaction rate densities λ^a vanish as well as the heat fluxes \dot{q}^b of all constituents.

Since \dot{q}^b is zero in equilibrium, (4.16) shows that $\dot{m}_A|_E = \sum_{\beta=1}^{\nu} \dot{m}_1^{\alpha\beta} \dot{U}_A|_E$ holds³⁾ and furthermore that the equations of balance of particle number, momentum and energy of constituent α read in the rest frame of that constituent

$$\begin{aligned} \hat{U}^a_{,a}|_E &= 0; \\ -\hat{p}_{,a}|_E &= \sum_{\beta=1}^{\nu} \dot{m}_1^{\alpha\beta} \hat{U}_a|_E, \quad \text{where} \quad \hat{U}_a = 0; \\ 0 &= \sum_{\beta=1}^{\nu} \dot{m}_1^{\alpha\beta} \hat{U}^4|_E \end{aligned} \tag{4.18}$$

The number balance (4.18)₁ shows that only isochoric motions are possible in equilibrium and the energy balance (4.18)₃, written in an arbitrary Lorentz frame rather than the rest frame of constituent α , reads

$$\sum_{\beta=1}^{\nu} \dot{m}_1^{\alpha\beta} \dot{U}_A \dot{U}^A|_E = 0. \tag{4.19}$$

By (2.11) we have $\sum_{\alpha,\beta=1}^{\nu} \dot{m}_1^{\alpha\beta} \dot{U}_A \dot{U}^A = 0$ and therefore (4.19) are $\nu - 1$ equilibrium conditions.

Inspection of the inequality (4.17) shows that its left hand side, the entropy production Σ , assumes its minimum, namely zero, in equilibrium. Σ is a function of $\dot{n}, \dot{\vartheta}, \dot{U}^a, \dot{n}, \dot{\vartheta}, \dot{n}_a^\perp$ and \dot{q}_a ⁴⁾; alternatively, assuming that the Jacobians

$$\left| \frac{\partial \lambda^a}{\partial \dot{n}} \right| (\alpha, a = 1, 2, \dots, n) \quad \text{and} \quad \left| \frac{\partial \sum_{\beta=1}^{\nu} \dot{m}_1^{\alpha\beta} \dot{U}^A \dot{U}_A}{\partial \dot{\vartheta}} \right| (\alpha, \gamma = 1, 2, \dots, \nu - 1)$$

do not vanish, we may write

$$\begin{aligned} \Sigma &= \Sigma \left(\lambda^a, \dot{n}, \dots, \dot{n}, \left(\sum_{\beta=1}^{\nu} \dot{m}_1^{\alpha\beta} \dot{U}^A \dot{U}_A \right), \dot{\vartheta}, \dot{U}^a, \dot{n}, \dot{\vartheta}, \dot{n}_a^\perp, \dot{\vartheta}_a^\perp \right) \\ \Sigma|_E &= \Sigma(0, \dot{n}, \dots, \dot{n}, 0, \dot{\vartheta}, \dot{U}^a, 0, 0, 0, 0). \end{aligned} \tag{4.20}$$

Of necessity then, we must have the following conditions

$$\frac{\partial \Sigma}{\partial X^\Delta} \Big|_E = 0, \tag{4.21}$$

³⁾ The index E denotes equilibrium and the hat denotes the rest frame of constituent α .
⁴⁾ Note that $\dot{n}_a^\perp, \dot{q}_a$ and \dot{U}^4 are not among the variables, because they can be determined from the identities $\dot{U}_A \dot{n}^{\perp A} = 0, \dot{U}_A \dot{q}_A = 0$ and $\dot{U}_A \dot{U}^A = c^2$.

where X^Δ stands for any one of the quantities λ^a ($a = 1, 2, \dots, n$), $\sum_{\beta=1}^{\nu} m_1^{\alpha\beta} \dot{U}_A^\alpha \dot{U}^{\beta A}$ ($\alpha = 1, 2, \dots, \nu - 1$), $\dot{q}^a, \dot{n}, \dot{\vartheta}$ ($\alpha = 1, 2, \dots, \nu$).

We exploit the derivatives with respect to \dot{q}^a first and obtain (note that $\dot{q}^4 \dot{U}_4^\alpha = -\dot{q}^a \dot{U}_a^\alpha$)

$$\frac{1}{\kappa} \sum_{\beta=1}^{\nu} (\overset{\alpha}{\Lambda} m_1^{\alpha\beta} + \overset{\alpha}{\Lambda} m_3^{\alpha\beta}) \left(\dot{U}_a^\beta - \dot{U}_a^\alpha \frac{\dot{U}_4^\beta}{\dot{U}_4^\alpha} \right) \Big|_E = 0.$$

Excluding the possibility that the matrix of coefficients of this linear system is singular, we thus conclude

$$(\dot{V}^\beta - \dot{V}^\alpha) \Big|_E = 0,$$

i.e. in equilibrium the *velocities of all constituents are equal*. Because of this property, (4.19) can be written as

$$\sum_{\beta=1}^{\nu} m_1^{\alpha\beta} \Big|_E = 0, \tag{4.22}$$

and the momentum balance (4.18)₂ reads

$$\hat{p}_{,a} \Big|_E = 0;$$

together with $\hat{q}^a \Big|_E = 0$ this equation implies that $\dot{\vartheta}$ and \dot{n} are uniform in equilibrium, but of course this holds only when there are no external forces acting on the constituent α .

Since $\sum_{\alpha,\beta=1}^{\nu} m_1^{\alpha\beta} \dot{U}_A^\alpha \dot{U}^{\beta A} = 0$ holds, the next to the last term on the left hand side of (4.17) can be written as $\sum_{\alpha=1}^{\nu-1} (\overset{\alpha}{\Lambda} - \overset{\nu}{\Lambda}) (\sum_{\beta=1}^{\nu} m_1^{\alpha\beta} \dot{U}_A^\alpha \dot{U}^{\beta A})$ and (4.21) with $X^\Delta = (\sum_{\beta=1}^{\nu} m_1^{\alpha\beta} \dot{U}_A^\alpha \dot{U}^{\beta A})$ implies

$$\overset{\alpha}{\Lambda} \Big|_E = \overset{\nu}{\Lambda} \Big|_E. \tag{4.23}$$

Thus all $\overset{\alpha}{\Lambda}$'s have the same equilibrium value. Since $\overset{\alpha}{\Lambda}$ is a function of $\dot{n}, \dot{\vartheta}$, equation (4.23) shows that $\dot{\vartheta}$ is determined by $\dot{\vartheta}, \dot{n}$ and \dot{n} in equilibrium; later we shall strengthen this statement by showing that $\dot{\vartheta}$ alone determines $\dot{\vartheta}$ in equilibrium.

The conditions that follow from (4.21) for $X^\Delta = \dot{n}$ and $X^\Delta = \dot{\vartheta}$ are

$$\frac{\partial \overset{\alpha}{\eta}}{\partial \dot{n}} \Big|_E = \overset{\alpha}{\Lambda} \Big|_E \left(\frac{\partial \overset{\alpha}{\epsilon}}{\partial \dot{n}} \Big|_E - \frac{\overset{\alpha}{p}}{\dot{n}^2} \Big|_E \right) \quad \text{and} \quad \frac{\partial \overset{\alpha}{\eta}}{\partial \dot{\vartheta}} \Big|_E = \overset{\alpha}{\Lambda} \Big|_E \frac{\partial \overset{\alpha}{\epsilon}}{\partial \dot{\vartheta}} \Big|_E \tag{4.24}$$

and these will be discussed in the next chapter.

Finally we can choose $X^\Delta = \lambda^a$ in (4.21) and obtain, using (4.12)₂

$$\sum_{\alpha=1}^{\nu} \left(\overset{\alpha}{\eta} - \overset{\alpha}{\Lambda} \left(\overset{\alpha}{m} c^2 + \overset{\alpha}{\epsilon} + \frac{\overset{\alpha}{p}}{\dot{n}} \right) \right) \Big|_E \gamma_\alpha^a = 0, \tag{4.25}$$

which is the *law of mass action* in a form appropriate for the simple mixtures of relativistic fluid that we are considering here. We shall come back to this relation in Section 5.c.

We shall now turn to an interpretation and elaboration of the results of this chapter.

5. Absolute Temperatures, Heat Fluxes, Law of Mass Action, Diffusion and Temperature Relaxation

a. Absolute temperatures and the Gibbs equation

α . The functions $\overset{\alpha}{\Lambda}(\overset{\alpha}{n}, \overset{\alpha}{\vartheta})$. The equations (4.24) are conditions on the functions $\overset{\alpha}{\eta}(\overset{\alpha}{n}, \overset{\alpha}{\vartheta}, \overset{\alpha}{\dot{n}}, \overset{\alpha}{\dot{\vartheta}})$ and $\overset{\alpha}{\epsilon}(\overset{\alpha}{n}, \overset{\alpha}{\vartheta}, \overset{\alpha}{\dot{n}}, \overset{\alpha}{\dot{\vartheta}})$ which – in a simple mixture – are specific entropy and specific internal energy of constituent α , even if no other constituent is present. In the relations (4.24) we may therefore regard $\overset{\alpha}{n}$ and $\overset{\alpha}{\vartheta}$ as independent variables even in equilibrium and write e.g.

$$\left. \frac{\partial \overset{\alpha}{\eta}}{\partial \overset{\alpha}{n}} \right|_E = \frac{\partial \overset{\alpha}{\eta}}{\partial \overset{\alpha}{n}} \quad \text{or} \quad \left. \frac{\partial \overset{\alpha}{\epsilon}}{\partial \overset{\alpha}{\vartheta}} \right|_E = \frac{\partial \overset{\alpha}{\epsilon}}{\partial \overset{\alpha}{\vartheta}},$$

where $\overset{\alpha}{\eta}|_E = \overset{\alpha}{\eta}(\overset{\alpha}{n}, \overset{\alpha}{\vartheta}, 0, 0)$ and $\overset{\alpha}{\epsilon}|_E = \overset{\alpha}{\epsilon}(\overset{\alpha}{n}, \overset{\alpha}{\vartheta}, 0, 0)$. Thus the relations (4.24) may be combined to read

$$d\overset{\alpha}{\eta}|_E = \overset{\alpha}{\Lambda}(\overset{\alpha}{n}, \overset{\alpha}{\vartheta}) \left[\frac{\partial \overset{\alpha}{\epsilon}|_E}{\partial \overset{\alpha}{\vartheta}} d\overset{\alpha}{\vartheta} + \left(\frac{\partial \overset{\alpha}{\epsilon}|_E}{\partial \overset{\alpha}{n}} - \frac{\overset{\alpha}{p}|_E}{\overset{\alpha}{n}^2} \right) d\overset{\alpha}{n} \right]. \quad (5.1)$$

We see that $\overset{\alpha}{\Lambda}$ is an integrating factor of the expression $[d\overset{\alpha}{\epsilon}|_E - (\overset{\alpha}{p}|_E/\overset{\alpha}{n}^2)d\overset{\alpha}{n}]$ and therefore $\overset{\alpha}{\Lambda}$ must satisfy the following integrability condition for $\overset{\alpha}{\eta}|_E$

$$\frac{\partial \overset{\alpha}{\epsilon}|_E}{\partial \overset{\alpha}{\vartheta}} \frac{\partial \ln \overset{\alpha}{\Lambda}}{\partial \overset{\alpha}{n}} - \left(\frac{\partial \overset{\alpha}{\epsilon}|_E}{\partial \overset{\alpha}{n}} - \frac{\overset{\alpha}{p}|_E}{\overset{\alpha}{n}^2} \right) \frac{\partial \ln \overset{\alpha}{\Lambda}}{\partial \overset{\alpha}{\vartheta}} = \frac{-1}{\overset{\alpha}{n}^2} \frac{\partial \overset{\alpha}{p}|_E}{\partial \overset{\alpha}{\vartheta}}. \quad (5.2)_1$$

Similarly, we may consider equation (4.15)₂ as an equation for constituent α alone which, in equilibrium, has independent variables $\overset{\alpha}{n}$ and $\overset{\alpha}{\vartheta}$:

$$\overset{\alpha}{\kappa} \frac{\partial \ln \overset{\alpha}{\Lambda}}{\partial \overset{\alpha}{n}} - \overset{\alpha}{\tau} \frac{\partial \ln \overset{\alpha}{\Lambda}}{\partial \overset{\alpha}{\vartheta}} = \frac{\overset{\alpha}{\tau} \frac{\partial \overset{\alpha}{p}|_E}{\partial \overset{\alpha}{\vartheta}} - \overset{\alpha}{\kappa} \frac{\partial \overset{\alpha}{p}|_E}{\partial \overset{\alpha}{n}}}{\overset{\alpha}{n} \overset{\alpha}{m} c^2 + \overset{\alpha}{n} \overset{\alpha}{\epsilon}|_E + \overset{\alpha}{p}|_E} \quad (5.2)_2$$

The equations (5.2) form a linear system from which the derivatives $\partial \ln \overset{\alpha}{\Lambda} / \partial \overset{\alpha}{n}$ and

$\partial \ln \overset{\alpha}{\Lambda} / \partial \overset{\alpha}{\vartheta}$ can be calculated:

$$\frac{\partial \ln \overset{\alpha}{\Lambda}}{\partial \overset{\alpha}{n}} = \frac{1}{\overset{\alpha}{n} \overset{\alpha}{m} c^2 + \overset{\alpha}{n} \overset{\alpha}{\epsilon}|_E + \overset{\alpha}{p}|_E} \left(\frac{\overset{\alpha}{\tau}}{\overset{\alpha}{\vartheta}} \frac{\partial \overset{\alpha}{p}|_E}{\partial \overset{\alpha}{\vartheta}} - \frac{\overset{\alpha}{\kappa}}{\overset{\alpha}{n}} \frac{\partial \overset{\alpha}{p}|_E}{\partial \overset{\alpha}{n}} \right) \left(\frac{\partial \overset{\alpha}{\epsilon}|_E}{\partial \overset{\alpha}{n}} - \frac{\overset{\alpha}{p}|_E}{\overset{\alpha}{n}^2} \right) - \frac{\overset{\alpha}{\tau}}{\overset{\alpha}{n}^2} \frac{\partial \overset{\alpha}{p}|_E}{\partial \overset{\alpha}{\vartheta}},$$

$$- \frac{\overset{\alpha}{\kappa}}{\overset{\alpha}{n}} \left(\frac{\partial \overset{\alpha}{\epsilon}|_E}{\partial \overset{\alpha}{n}} - \frac{\overset{\alpha}{p}|_E}{\overset{\alpha}{n}^2} \right) + \frac{\overset{\alpha}{\tau}}{\overset{\alpha}{n}} \frac{\partial \overset{\alpha}{\epsilon}|_E}{\partial \overset{\alpha}{\vartheta}} \tag{5.3}$$

$$\frac{\partial \ln \overset{\alpha}{\Lambda}}{\partial \overset{\alpha}{\vartheta}} = \frac{1}{\overset{\alpha}{n} \overset{\alpha}{m} c^2 + \overset{\alpha}{n} \overset{\alpha}{\epsilon}|_E + \overset{\alpha}{p}|_E} \left(\frac{\overset{\alpha}{\tau}}{\overset{\alpha}{\vartheta}} \frac{\partial \overset{\alpha}{p}|_E}{\partial \overset{\alpha}{\vartheta}} - \frac{\overset{\alpha}{\kappa}}{\overset{\alpha}{n}} \frac{\partial \overset{\alpha}{p}|_E}{\partial \overset{\alpha}{n}} \right) \frac{\partial \overset{\alpha}{\epsilon}|_E}{\partial \overset{\alpha}{\vartheta}} - \frac{\overset{\alpha}{\kappa}}{\overset{\alpha}{n}^2} \frac{\partial \overset{\alpha}{p}|_E}{\partial \overset{\alpha}{\vartheta}}$$

$$- \frac{\overset{\alpha}{\kappa}}{\overset{\alpha}{n}} \left(\frac{\partial \overset{\alpha}{\epsilon}|_E}{\partial \overset{\alpha}{n}} - \frac{\overset{\alpha}{p}|_E}{\overset{\alpha}{n}^2} \right) + \frac{\overset{\alpha}{\tau}}{\overset{\alpha}{n}} \frac{\partial \overset{\alpha}{\epsilon}|_E}{\partial \overset{\alpha}{\vartheta}}$$

The equations (5.3) embrace our knowledge about the functions $\overset{\alpha}{\Lambda}(\overset{\alpha}{n}, \overset{\alpha}{\vartheta})$ so far. In the next subsection we shall show that $\partial \overset{\alpha}{\Lambda} / \partial \overset{\alpha}{n}$ must vanish and shall draw further conclusions from that.

β. Absolute temperatures. The concept of temperature is a basic and primitive one in thermodynamics, both classically and relativistically; it gives a measure for how hot a body is and – in the present case – $\overset{\alpha}{\vartheta}$ measures the hotness of a constituent.

Now, in thermostatics and in statistical mechanics, it is common to define an *absolute temperature* T as the integrating denominator of the expression $d\epsilon - (p/n^2) dn$. Accordingly we shall define the absolute temperature $\overset{\alpha}{T}$ of constituent α as the integrating denominator of $d\overset{\alpha}{\epsilon}|_E - (\overset{\alpha}{p}|_E / \overset{\alpha}{n}^2) d\overset{\alpha}{n}$ so that, by (5.1), we have

$$\overset{\alpha}{T} \equiv \frac{1}{\overset{\alpha}{\Lambda}(\overset{\alpha}{n}, \overset{\alpha}{\vartheta})} \tag{5.4}$$

There are three good things to be said for considering the absolute temperature $\overset{\alpha}{T} = 1/\overset{\alpha}{\Lambda}$ as a possible measure of temperature of constituent α :

(i) In equilibrium, by (4.23), the absolute temperatures of all constituents are equal.

(ii) Temperatures of bodies are measured by thermometers by virtue of the assumption that the thermometric substance – when in contact with the body – has the same temperature as the body. Therefore, a quantity deserves to be called a temperature only if it is continuous across the wall of the thermometer and we shall now show that $\overset{\alpha}{\Lambda}$ indeed has that property: We take it for granted that in the wall of a thermometer there is neither production of energy nor of entropy; therefore, the normal components of the heat flux and of the non-convective entropy flux are continuous across the wall under rather general conditions which are easily satisfied here.⁵⁾ Now, let the substance within the thermometer be the single constituent β and let the body, whose temperature is to be measured, consist of the single constituent α .

⁵⁾ See Ref. [10], p. 526 for a specification of such conditions.

Then the above-mentioned continuity conditions for the heat flux and the flux of entropy read

$$\hat{q}^b e_b = \hat{q}^{\beta} e_b \quad \text{and} \quad \hat{\phi}^b e_b = \hat{\phi}^{\beta} e_b, \quad (5.5)$$

where e_b is the unit normal to the wall. According to (4.10) we have $\hat{\phi}^b = \Lambda \hat{q}^b$ for both the body and the thermometric substance and hence (5.5)_{1,2} imply

$$\Lambda^{\alpha} = \Lambda^{\beta}, \quad (5.6)$$

which shows that indeed the Λ^{α} 's may be used as temperatures.

(iii) In statistical mechanics the temperature of a body is considered to be a measure of the mean kinetic energy of its molecules. Now, all statistical relativistic theories of gases show that indeed it is the integrating factor of $(d\epsilon - (p/n^2) dn)$ that determines the mean kinetic energy of the molecules and vice versa; e.g. see Jüttner [11], or Synge [12] or the more far reaching papers by Chernikov [13].

Thus it would appear that we have made out a good case for calling $\bar{T}^{\alpha} = 1/\Lambda^{\alpha}(n^{\alpha}, \vartheta^{\alpha})$ a temperature. How then do the empirical temperatures ϑ^{α} fit into this? Obviously, from (5.4) the ϑ^{α} 's can be called temperatures only, if the Λ^{α} 's are independent of n^{α} .

Therefore we must have $\partial \Lambda^{\alpha} / \partial n^{\alpha} = 0$, and the two equations (5.3) reduce to

$$\tau^{\alpha} = -\kappa^{\alpha} \frac{1}{dT^{\alpha}/d\vartheta^{\alpha}} \cdot \frac{T^{\alpha} \frac{\partial \bar{p}|_E}{\partial n^{\alpha}}}{\bar{n}^{\alpha} m c^2 + \bar{n}^{\alpha} \epsilon|_E + \bar{p}|_E - \bar{T}^{\alpha} (\partial \bar{p}|_E / \partial T^{\alpha})} \quad (5.7)$$

and

$$\frac{d \ln \Lambda^{\alpha}}{d\vartheta^{\alpha}} = -\frac{1}{\bar{T}^{\alpha}} \frac{d\bar{T}^{\alpha}}{d\vartheta^{\alpha}} = \frac{d\bar{p}|_E/d\vartheta^{\alpha}}{\bar{n}^{\alpha} (\partial \epsilon|_E / \partial n^{\alpha}) - \bar{p}|_E}, \quad (5.8)$$

But this is only a necessary condition for the ϑ^{α} 's to be proper temperatures. We must also require that ϑ has the same value at both sides of a thermometer wall and this brings us back to the considerations under (ii) above: With $\bar{\Lambda}^{\gamma}$ being independent of \bar{n}^{γ} the equation (5.6) at the wall of a thermometer reads

$$\Lambda^{\alpha}(\vartheta^{\alpha}) = \Lambda^{\beta}(\vartheta^{\beta})$$

and, since we must have $\vartheta^{\alpha} = \vartheta^{\beta} = \vartheta$

$$\Lambda^{\alpha}(\vartheta) = \Lambda^{\beta}(\vartheta).$$

This has to hold for all ϑ . Hence, $\bar{\Lambda}^{\alpha}$ or \bar{T}^{α} is a *universal* function of ϑ^{α} , i.e. the same function for all constituents:

$$\bar{\Lambda}^{\alpha} = \Lambda(\vartheta^{\alpha}) \quad \text{or} \quad \bar{T}^{\alpha} = T(\vartheta^{\alpha}). \quad (5.9)$$

Note that $d\bar{T}^{\alpha}/d\vartheta^{\alpha}$ in (5.7), (5.8) can thus be written $dT/d\vartheta^{\alpha}$.

We can calculate the function $T(\vartheta^\alpha)$ from (5.8) by integration to within a factor of integration, if only the functions $\check{p}|_E$ and $\partial\check{\epsilon}|_E/\partial\check{n}^\alpha$ have been determined for a single material. This is no different from non-relativistic thermodynamics and with a proper choice of the factor of integration $T(\vartheta^\alpha)$ turns out to be a positive-valued, monotonically increasing function. Therefore, we may now choose \check{T} , instead of ϑ^α , as variables in the constitutive relations. By (5.4), we can then write the equation (5.1) as

$$d\check{\eta}|_E = \frac{1}{\check{T}} \left(\frac{\partial\check{\epsilon}|_E}{\partial\check{T}} d\check{T} + \left(\frac{\partial\check{\epsilon}|_E}{\partial\check{n}^\alpha} - \frac{\check{p}|_E}{\check{n}^2} \right) d\check{n}^\alpha \right) = \frac{1}{\check{T}} \left(d\check{\epsilon}|_E - \frac{\check{p}|_E}{\check{n}^2} d\check{n}^\alpha \right) \tag{5.10}$$

and this is the well-known Gibbs equation of thermostatics, written down here for constituent α .

Note that (4.23) and (5.9) imply that in equilibrium all ϑ^α 's are equal as well as all $\check{\Lambda}$'s.

b. Heat fluxes

The general constitutive equation for the heat flux of constituent α reads, according to (3.10)₁

$$\hat{q}^b = q^{ba} (\kappa \hat{\vartheta}^\alpha_{,a} + \check{\tau} \hat{n}^\alpha_{,a}).$$

We can now eliminate the coefficient $\check{\tau}$ between this relation and (5.7) and obtain

$$\hat{q}^b = q^{ba} \check{\kappa} \frac{1}{d\check{T}/d\vartheta^\alpha} \left(\hat{T}^\alpha_{,a} - \frac{\check{T}(\partial\check{p}|_E/\partial\check{n}^\alpha)}{\check{n}^\alpha \check{m}c^2 + \check{n}^\alpha \check{\epsilon}|_E + \check{p}|_E - \check{T}(\partial\check{p}|_E/\partial\check{T})} \hat{n}^\alpha_{,a} \right) \tag{5.11}$$

Equation (5.11) shows that in relativistic thermodynamics the heat flux \hat{q}^b is not proportional to the gradient of temperature $\hat{T}^\alpha_{,a}$. Indeed, the density gradient $\hat{n}^\alpha_{,a}$ also contributes to the heat flux in a manner that is determined by the functions $\check{p}|_E$ and $\check{\epsilon}|_E$.

This result recovers a result that was obtained for a single fluid by Alts and Müller [5] and it is akin – in a manner to be discussed in Chapter 6 – to a result in Eckart's theory of relativistic thermodynamics (see Ref. [6]).

The equation (5.11) implies that if the temperature is uniform, the heat flux is not zero unless the density is uniform. In other words, if a density gradient is kept up by a gravitational field the temperature field is not uniform in equilibrium.

c. The law of mass action

With $\check{\Lambda} = 1/\check{T}$ and $\check{T} = \check{T} = T$ in equilibrium the equations (4.25) read

$$\sum_{\alpha=1}^v \left(\check{m}c^2 + \check{\epsilon}|_E - T\check{\eta}|_E + \frac{\check{p}|_E}{\check{n}^\alpha} \right) \gamma_\alpha^a = 0, \quad (a = 1, 2, \dots, n). \tag{5.12}$$

This relation represents as many conditions for the particle densities \dot{n}^α as there are independent reactions. We shall now derive an alternative and more suggestive form of (4.25): The rest mass \dot{m}^α of a molecule of constituent α can be decomposed into the sum of the rest masses of all nucleons and all electrons and into the mass equivalent of the binding energy of constituent α . Thus

$$\dot{m}^\alpha = Z_N^\alpha m_N + Z_e^\alpha m_e + \frac{E_B^\alpha}{c^2} \tag{5.13}$$

where m_N and m_e are the rest masses of nucleons and electrons respectively.

Elimination of \dot{m}^α between (5.13) and (5.12) gives, when due regard is given to (2.9),

$$\sum_{\alpha=1}^v \left[E_B^\alpha + \epsilon|_E^\alpha - T\eta|_E^\alpha + \frac{\dot{p}|_E^\alpha}{\dot{n}^\alpha} \right] \gamma_\alpha^a = 0, \quad (a = 1, 2, \dots, n) \tag{5.14}$$

and these relations represent the law of mass action in a simple mixture. Classically one gets the same form of this law, except that the binding energy does not explicitly appear there.

d. Temperature relaxation and stationary diffusion

The conditions (4.21) are not the only ones that must be satisfied, if the entropy production on the left hand side of (4.17) is to have its minimum in equilibrium and in this section we shall derive some additional ones. Let us write the entropy production as

$$\Sigma = \Sigma(\dot{n}; \dot{T}; \dot{U}^a; \dot{n}; \dot{T}; \dot{n}_a^\perp; \dot{q}_a); \tag{5.15}$$

we know from before that Σ has a minimum in equilibrium, where \dot{n}, \dot{T} and \dot{q}^a vanish, when the \dot{n} 's obey the law of mass action and when all \dot{T} 's and \dot{U}^a 's are equal. Necessary conditions, which Σ must then satisfy, include

$$\frac{\partial^2 \Sigma}{\partial \dot{q}_a^2} \Big|_E \geq 0 \quad \text{and} \quad \left\| \frac{\partial^2 \Sigma}{\partial \dot{T} \partial \dot{T}} \Big|_E \right\| \text{ positive semidefinite.} \tag{5.16}$$

$$\left\| \frac{\partial^2 \Sigma}{\partial \dot{U}_a \partial \dot{U}_a} \Big|_E \right\|$$

There are other conditions which the second derivatives of Σ with respect to the variables in (5.15) must satisfy, but they do not interest us here.

Insertion of Σ from (4.17) into (5.16)₁ gives

$$\kappa^\alpha \left(1 - \frac{T^\alpha \frac{\partial \dot{p}|_E^\alpha}{\partial T^\alpha}}{\dot{n}^\alpha m c^2 + \dot{n}^\alpha \epsilon|_E^\alpha + \dot{p}|_E^\alpha} - \frac{T^\alpha m_3^{\alpha\alpha}}{\dot{n}^\alpha m c^2 + \dot{n}^\alpha \epsilon|_E^\alpha + \dot{p}|_E^\alpha} \frac{1}{\frac{dT^\alpha}{d\vartheta^\alpha}} \right) \geq 0, \tag{5.17}$$

a relation which, in the non-relativistic limit simply states that the heat conductivity is non-negative.

The remaining conditions (5.16) read

$$\left\| \frac{\partial \sum_{\beta=1}^{\nu} \gamma^{\beta} m_1}{\partial T} \Big|_E + \frac{\partial \sum_{\beta=1}^{\nu} \delta^{\beta} m_1}{\partial T} \Big|_E \right\| \quad \text{negative semidefinite, and} \tag{5.18}$$

$$\left\| m_1^{\gamma\delta} \Big|_E + m_1^{\delta\gamma} \Big|_E \right\| \quad \text{negative semidefinite.}$$

In order to demonstrate the significance of these relations, we consider two very special processes.

First, we consider a process with uniform fields of \dot{n}^{α} , $\dot{\vartheta}^{\alpha}$ and \dot{U}_A^{α} in which moreover \dot{n}^{α} and \dot{U}_A^{α} are time independent and all \dot{U}_A^{α} are equal. Under these circumstances all λ^{α} vanish and the only relevant equations are the energy equations which in the common rest frame of the constituents read

$$\frac{\partial}{\partial t} (\dot{n}^{\alpha} m c^2 + \dot{n}^{\alpha} \epsilon) = c^2 \sum_{\beta=1}^{\nu} \alpha^{\beta} m_1.$$

Unless temperature differences are too large, we may set

$$\sum_{\beta=1}^{\nu} \alpha^{\beta} m_1 = \sum_{\beta=1}^{\nu} \alpha^{\beta} m_1 \Big|_E + \sum_{\gamma=1}^{\nu} \frac{\partial \sum_{\beta=1}^{\nu} \alpha^{\beta} m_1}{\partial T} \Big|_E (T^{\gamma} - T^{\nu})$$

and therefore the energy equations read with (4.22) and when $\dot{\epsilon}$ is independent of \dot{n}^{α}

$$\dot{n}^{\alpha} \frac{\partial \dot{\epsilon}^{\alpha}}{\partial T} \frac{\partial T}{\partial t} = \sum_{\gamma=1}^{\nu} \frac{\partial \sum_{\beta=1}^{\nu} \alpha^{\beta} m_1}{\partial T} \Big|_E (T^{\gamma} - T^{\nu}). \tag{5.19}$$

When the specific heats $\partial \dot{\epsilon}^{\alpha} / \partial T$ are positive constants, the equations (5.19) describe a *relaxation* of temperature differences, if only the matrix in (5.18)₁ is negative definite.

Next we consider time-independent diffusion: Let there be no heat fluxes and let the densities and temperatures be time independent, so that $\dot{U}^A \dot{n}_{,A}^{\alpha} = 0$ and $\dot{U}^A \dot{\vartheta}_{,A}^{\alpha} = 0$; the equations of balance of momenta then read

$$-\dot{p}_{,a}^{\alpha} = \sum_{\beta=1}^{\nu} m_1^{\alpha\beta} \dot{U}_a^{\beta}$$

and, if the right hand sides are expanded around equilibrium up to linear terms in differences of velocity $\dot{U}_a^{\gamma} - \dot{U}_a^{\nu}$, we obtain with (4.22)

$$-\dot{p}_{,a}^{\alpha} = \sum_{\gamma=1}^{\nu-1} m_1^{\alpha\gamma} \Big|_E (\dot{U}_a^{\gamma} - \dot{U}_a^{\nu}). \tag{5.20}$$

We thus see that (5.18)₂ implies that the relative velocities essentially point into a direction opposite to the pressure gradients.

6. Comparison with Eckart's Theory for a Single Fluid

All results so far hold also for a single constituent and we get the appropriate result by just dropping the Greek index on our quantities. For example, the Gibbs relation (5.10) for a single fluid reads

$$d\eta|_E = \frac{1}{T} \left(d\epsilon|_E - \frac{p|_E}{n^2} dn \right). \quad (6.1)$$

Eckart's theory of a relativistic fluid, proposed in [6], is based upon equation (6.1) and the assumption that η , ϵ and p during a process are equal to $\eta|_E$, $\epsilon|_E$ and $p|_E$. If this is so, one may write (6.1) as an equation for the rate of change of η :

$$\dot{\eta} = \frac{1}{T} \left(\dot{\epsilon} - \frac{p}{n^2} \dot{n} \right) \quad (6.2)$$

where $\dot{\eta} = U^A \eta_{,A}$ and $\dot{\epsilon} = U^A \epsilon_{,A}$. Now, the conservation laws of particle numbers and energy-momentum read

$$(nU^A)_{,A} = 0 \quad \text{and} \quad T^{AB}_{,B} = 0 \quad (6.3)$$

and T^{AB} is decomposed according to

$$T^{AB} = \frac{nm c^2 + n\epsilon}{c^2} U^A U^B + w^{AB} + \frac{1}{c^2} (q^A U^B + q^B U^A),$$

so that in the rest frame of the fluid $\hat{n}\hat{\epsilon}$ is the energy density, \hat{w}^{ab} is the negative stress and \hat{q}^a , i.e. q^a in the rest frame, is the heat flux. The conservation law of particle numbers may be written as

$$\dot{n} + nU^A_{,A} = 0 \quad (6.4)$$

and the conservation laws of momentum and energy (6.3)₂ upon multiplication by Δ_{CA} and U_A , respectively become after a simple calculation, with $\dot{U}_C \equiv U^A U_{C,A}$,

$$\left(nm + \frac{n\epsilon}{c^2} \right) \dot{U}_A + w^B_{A,B} = \frac{1}{c^2} [U_A w^{CB} U_{C,B} - q^B U_{A,B} - \Delta_{AC} (q^C U^B)_{,B}] \quad (6.5)$$

$$n\dot{\epsilon} + q^B_{,B} - w^{AB} U_{A,B} = \frac{1}{c^2} q_A \dot{U}^A. \quad (6.6)$$

If $\dot{\eta}$ and $\dot{\epsilon}$ are eliminated between (6.2), (6.4) and (6.6) one gets

$$n\dot{\eta} + \left(\frac{q^B}{T} \right)_{,B} = -\frac{1}{T^2} q^B \left(T_{,B} - \frac{T}{c^2} \dot{U}_B \right) + \frac{1}{T} (w^{AB} + p\Delta^{AB}) U_{A,B}. \quad (6.7)$$

In linear irreversible thermodynamics this equation is interpreted as the equation of balance of entropy, whose right hand side is the production of entropy which is postulated to be non-negative.

That inequality is then satisfied by linear relations between the ‘forces’ $(T_{,B} - (T/c^2)\dot{U}_B)$ and $U_{A,B}$ and the ‘fluxes’ q^B and $w^{AB} + p\Delta^{AB}$, viz

$$q^B = \tilde{\kappa}\Delta^{BA}\left(T_{,A} - \frac{T}{c^2}\dot{U}_A\right) \quad \text{where } \tilde{\kappa} \geq 0, \tag{6.8}$$

$$w^{AB} + p\Delta^{AB} = 2\mu(\Delta^{BC}U_{A,C} + \Delta^{AC}U_{,C}^B) \quad \text{where } \mu \geq 0.$$

The foregoing is a brief outline of Eckart’s theory and we proceed to compare the results of that theory with our results.

First, in restricting our attention to inviscid fluids, we have effectively set $\mu = 0$ in (6.8)₂ and any comparison therefore has to be made on the ground that in our theory we have

$$w^{AB} = -p\Delta^{AB}. \tag{6.9}$$

With regard to the heat flux we have to compare our equation (5.11) for a single fluid, viz.

$$\hat{q}^b = g^{ba}\kappa \frac{1}{dT/d\vartheta} \left(\hat{T}_{,a} - \frac{T(dp|_E/\partial n)}{nmc^2 + n\epsilon|_E + p|_E - T(\partial p|_E/dT)} \hat{n}_{,a} \right) \tag{6.10}$$

with Eckart’s equation (6.8)₁ in the rest frame, viz.

$$\hat{q}^b = g^{ba}\tilde{\kappa} \left(\hat{T}_{,a} - \frac{T}{c^2}\hat{U}_a \right). \tag{6.11}$$

Obviously therefore we must replace \hat{U}_a in (6.11). For that purpose we rely on the first three components of (6.5) in the rest frame: If we use (6.9) and ignore the non-linear term $q^b U_{,b}^a$ we get from (6.5)

$$\frac{1}{c^2}\hat{U}_a = \frac{1}{nmc^2 + n\epsilon + p} \left(\hat{p}_{,a} + \frac{1}{c^2}\frac{\partial \hat{q}_a}{\partial t} \right)$$

and elimination of $(1/c^2)\hat{U}^a$ between this relation and (6.11) gives

$$\begin{aligned} \hat{q}^b - \frac{(\tilde{\kappa}/c^2)T}{nmc^2 + n\epsilon + p} \frac{\partial \hat{q}^b}{\partial t} \\ = g^{ba}\tilde{\kappa} \left(1 - \frac{T(\partial p/\partial T)}{nmc^2 + n\epsilon + p} \right) \left(\hat{T}_{,a} - \frac{T(\partial p/\partial n)}{nmc^2 + n\epsilon + p - T(\partial p/\partial T)} \hat{n}_{,a} \right). \end{aligned} \tag{6.12}$$

Comparison of (6.10) of our theory and of (6.12) of Eckart’s theory shows agreement on the right hand sides, if only κ and $\tilde{\kappa}$ are related by

$$\kappa \frac{1}{dT/d\vartheta} = \tilde{\kappa} \left(1 - \frac{T(\partial p/\partial T)}{nmc^2 + n\epsilon + p} \right);$$

note that $\tilde{\kappa} \geq 0$ implies the inequality (5.17), if that inequality is written in a form appropriate for a single constituent. The left hand sides of (6.10) and (6.12) are not in

agreement, however. Indeed, if $T_{,a}$ and $n_{,a}$ both vanish, (6.12) implies an exponential growth of the heat flux which represents an awkward feature of Eckart's theory even though, of course, inspection shows that the term in question is extremely small.

Kluitenberg [1] has extended Eckart's ideas to mixtures of relativistic fluids. But that theory is formulated within the framework of linear irreversible thermodynamics of mixtures and there is therefore no straightforward manner in which its results can be compared with ours. A comparison of the corresponding non-relativistic theories may be found in [8].

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