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1980 J. Phys. A: Math. Gen. 13 275

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An extension of the local equilibrium hypothesis

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Received 24 November 1978, in final form 3 April 1979

Abstract. In order to extend the range of application of classical irreversible thermodynamics far from equilibrium, an extension of the Gibbs equation is presented. The new Gibbs equation is assumed to contain, besides its usual contributions, supplementary terms equal to the thermodynamic fluxes. The entropy flux and the entropy production also take more general forms than in classical non-equilibrium thermodynamics. As an illustration of the formalism, an isotropic viscous and non-isothermal two-fluid mixture is considered. The results are shown to be in agreement with the Boltzmann kinetic theory.

1. Introduction

It is well known that the classical theory of irreversible thermodynamics (De Groot and Mazur 1962, Glandsdorff and Prigogine 1971) rests on the local equilibrium hypothesis, which states that locally the Gibbs equation remains valid.

In classical fluid mechanics, the system is completely described by a kinetic variable, the velocity field v , and thermodynamic variables such as the density ρ and the temperature T . The evolution of these variables is described by the balance equations of mass, momentum and energy.

In this work, it is assumed that a knowledge of the system requires supplementary variables in addition to v , ρ and T . These supplementary variables are identified as the thermodynamic dissipative fluxes such as the heat flux, the viscous pressure flux, etc; the characteristic of these fluxes is to vanish at equilibrium. Of course, in order to determine the evolution of these extra variables in time and space, one must establish a new set of differential equations involving these new variables.

In the classical theory of irreversible thermodynamics, and in so-called rational thermodynamics, one encounters the same set of dissipative fluxes. They appear indeed in the balance equations, but they are expressed in terms of the primitive variables by means of phenomenological (classical terminology) or constitutive equations (rational thermodynamics terminology). In the classical procedure, the form of the phenomenological laws is dictated by the expression of the entropy source; in the rational approach, the constitutive equations are guessed from the start.

In the present work, all the variables—i.e. v , T , ρ and the fluxes—are put on the same level, and our goal is to determine evolution equations for all of them. The missing evolution equations for the fluxes are obtained by following the procedure of classical thermodynamics. This consists of calculating the expression for the entropy

production, which is shown to be of bilinear form in the dissipative fluxes and conjugate terms involving the time derivative of the fluxes (called thermodynamics forces). By assuming a dependence between these fluxes and forces, one obtains the required evolution relations for the fluxes.

The starting point of the whole procedure is the assumption that the entropy is not only a function of the variables at equilibrium, such as internal energy and specific volume, but also of the fluxes. Such an extension has been suggested by several authors (Müller 1967a, b, Lebon and Lambermont 1976, Israel 1976, Kranys 1977, Gyarmati 1977, Lebon 1978). The works of Müller, Lebon and Lambermont were particularly devoted to the study of simple thermofluid systems, while Israel and Kranys were interested in relativistic problems. The purpose of this paper is to give a more general description in order to make it directly applicable to a larger class of systems, such as mixtures of multicomponents fluids, either charged or not, micropolar fluids, superfluids, etc. However, in order to avoid undue lengthy mathematical expressions, we restrict our analysis to second-order developments in the fluxes.

The reasons for going beyond the classical theory of irreversible thermodynamics are the following. It is well known that this theory, which rests on the hypothesis of local equilibrium (the Gibbs equation), applies essentially to simple linear materials. A large class of materials—such as non-Newtonian fluids, viscoelastic bodies and, more generally, systems with memory—cannot be coherently described by such a formalism.

Moreover, as observed by various authors (e.g. Maxwell 1867, Cattaneo 1958, Müller 1967a), the classical theory leads to the paradox of an infinite velocity of propagation of temperature and concentration signals. To overcome this difficulty and to enlarge the domain of validity of classical thermodynamics, many theories have been proposed (Coleman 1964, Truesdell 1969, Meixner 1969, Müller 1967a,b, 1971, Green and Laws 1972, Day 1972). All of them share the common property of deviating radically from classical procedure; in particular, all these theories reject the hypothesis of local equilibrium. Our objective is to show how a slight modification of the local equilibrium statement allows a description of materials outside the linear range, while avoiding the paradox of an infinite propagation of signals.

Section 2 is devoted to a brief description of the classical theory of irreversible thermodynamics. A generalisation is presented in § 3. It concerns not only the Gibbs equation which receives supplementary terms, but also the entropy flux to which extra terms are also ascribed. The formalism proposed in § 3 is applied to an isotropic mixture of two non-charged fluids (§ 4). It is determined under which conditions the substitution of the parabolic heat conduction equation by the telegraph equation is justified.

The expressions for the generalised Gibbs equation and the entropy flux are shown to be in agreement with the kinetic theory of dilute gases.

The following notation is used.

| | |
|------------------------|--------------------------------|
| a^α | extensive state variable |
| $c^k (\sum_k c^k = 1)$ | concentration of component k |
| D | diffusion coefficient |
| D' | thermal diffusion coefficient |
| D'' | Dufour diffusion coefficient |
| f | distribution function |

| | |
|--|--|
| F^k | external force exerted on component k |
| h | specific enthalpy |
| h^k | partial specific enthalpy of component k |
| \mathbf{l} | identity tensor |
| $\mathbf{J}^k (\sum_k \mathbf{J}^k = 0)$ | flux of diffusion of component k |
| \mathbf{J}^s | entropy flux |
| k | Boltzmann constant |
| p | equilibrium thermodynamic pressure |
| p^v | viscous pressure |
| \mathbf{q} | heat flux vector |
| $q^\alpha, \mathbf{q}^\alpha, \mathbf{q}^\alpha$ | generalised thermodynamic fluxes |
| r_v | heat supply per unit volume |
| s | specific entropy |
| $s^k = T^{-1}(h^k - \mu^k)$ | specific entropy of constituent k |
| T | temperature |
| u | specific internal energy |
| v | specific volume |
| \mathbf{v} | velocity field |
| \mathbf{v}^k | velocity field of constituent k . |
| $\mathbf{V} = \frac{1}{2}[\nabla\mathbf{v} + (\nabla\mathbf{v})^T]$ | rate-of-deformation tensor |
| $\mathbf{w}^k (= \mathbf{v}^k - \mathbf{v})$ | diffusion velocity |
| X^α | generalised thermodynamic force |
| Γ^α | intensive state variable |
| λ | heat conductivity |
| μ^k | chemical potential |
| ρ | total mass density |
| $\rho^k (= \rho c^k)$ | mass density of component k |
| σ | entropy production per unit volume |
| σ^α | source term in the balance laws |
| $\boldsymbol{\sigma} (= -p\mathbf{l} + \boldsymbol{\sigma}^v)$ | symmetric stress tensor |
| $\boldsymbol{\sigma}^v (= -p^v\mathbf{l} + \widetilde{\boldsymbol{\sigma}}^v)$ | symmetric viscous stress tensor |
| $\boldsymbol{\omega}$ | peculiar velocity of a molecule |
| ∇ | nabla operator. |

A tilde denotes the deviatoric part of a tensor.

A dot over a symbol denotes the material time derivative.

A superscript 'T' means transposition.

2. The classical theory of non-equilibrium thermodynamics

In classical non-equilibrium thermodynamics, the basic hypothesis is the local equilibrium hypothesis. It states that locally the energy depends on the same set of variables as in equilibrium and, in particular, that the Gibbs equation

$$\dot{u} = T\dot{s} + \sum_{\alpha=1}^n \Gamma^{\alpha} \dot{a}^{\alpha} \quad (2.1)$$

remains locally valid. Γ^{α} represents intensive variables such as the pressure p , the chemical potential μ^k , etc. a^{α} represents extensive state variables, such as the specific volume v , the concentration c^k , etc. n is the number of state variables which, besides s , are necessary to specify univocally the state of the system. All the quantities refer to unit mass.

The set of variables a^{α} obey balance equations whose general form is

$$\rho \dot{a}^{\alpha} = -\nabla \cdot \mathbf{q}^{\alpha} + \sigma^{\alpha} \quad (\alpha = 1, \dots, n). \quad (2.2)$$

\mathbf{q}^{α} is a vectorial flux associated with the variable a^{α} , and σ^{α} is a source term. If, for instance, a^{α} represents the specific volume, $-\mathbf{q}^{\alpha}$ must be identified with the velocity vector \mathbf{v} , while σ^{α} is zero. By identification of a^{α} with the internal energy u , one obtains the energy balance law

$$\rho \dot{u} = -\text{div } \mathbf{q} + \sigma^u, \quad (2.3)$$

where \mathbf{q} is the heat flux and σ^u the source of internal energy. The balance equation for entropy is of particular importance and is expressed as

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

where \mathbf{J}^s is the entropy flux and σ the entropy production per unit volume. In the presence of an internal heat supply, (2.4) is assumed to include a supplementary term of the form r_v/T .

A straightforward calculation (De Groot and Mazur 1962) shows that the entropy flux and the entropy production are respectively given by

$$\mathbf{J}^s = T^{-1} \left(\mathbf{q} - \sum_1^n \Gamma^{\alpha} \mathbf{q}^{\alpha} \right) \quad (2.5)$$

and

$$\sigma = \mathbf{q} \cdot \text{grad } T^{-1} - \sum_1^n \mathbf{q}^{\alpha} \cdot \nabla (\Gamma^{\alpha} T^{-1}) + T^{-1} \sigma^u - T^{-1} \sum_1^n \Gamma^{\alpha} \sigma^{\alpha}. \quad (2.6)$$

By putting

$$\Gamma^0 = -1, \quad \mathbf{q}^0 = \mathbf{q}, \quad \sigma^0 = \sigma^u, \quad (2.7)$$

(2.5) and (2.6) take a more compact form, namely

$$\mathbf{J}^s = -T^{-1} \sum_0^n \Gamma^{\alpha} \mathbf{q}^{\alpha}, \quad (2.8)$$

$$\sigma = -\sum_0^n \mathbf{q}^\alpha \cdot \text{grad} (\Gamma^\alpha T^{-1}) - T^{-1} \sum_0^n \Gamma^\alpha \sigma^\alpha. \quad (2.9)$$

It appears that σ takes the form of a bilinear expression in the fluxes and conjugate terms (called thermodynamic forces):

$$\sigma = \sum_0^m q^\alpha X^\alpha + \sum_0^n \mathbf{q}^\alpha \cdot \mathbf{X}^\alpha + \sum_0^l \mathbf{q}^\alpha : \mathbf{X}^\alpha. \quad (2.10)$$

q^α , \mathbf{q}^α , \mathbf{q}^α denote respectively the scalar, vectorial and second-order tensorial fluxes, while X^α , \mathbf{X}^α and \mathbf{X}^α are the conjugate forces. Further, by denoting by J^α the set q^α , \mathbf{q}^α , \mathbf{q}^α and by \mathbf{X}^α the set X^α , \mathbf{X}^α , \mathbf{X}^α , the above expression reduces to

$$\sigma = \sum_\alpha J^\alpha \mathbf{X}^\alpha. \quad (2.11)$$

At equilibrium, the J^α 's as well as the \mathbf{X}^α 's vanish identically.

It is known experimentally that the fluxes are functions of the forces, i.e.

$$J^\alpha = J^\alpha(\mathbf{X}^\gamma). \quad (2.12)$$

Relations between fluxes and forces are termed phenomenological laws. Not too far from equilibrium, the fluxes are linear functions of the forces,

$$J^\alpha = \sum_\gamma L^{\alpha\gamma} \mathbf{X}^\gamma, \quad (2.13)$$

where the phenomenological coefficients $L^{\alpha\gamma}$ obey the Onsager–Casimir reciprocal relations

$$L^{\alpha\gamma} = \pm L^{\gamma\alpha}. \quad (2.14)$$

It is generally admitted that the above results are valid in the vicinity of equilibrium. Far from equilibrium, it is clear that Gibbs equation as well as linear phenomenological laws are no longer acceptable. In the next section, an extension of the above results to cover more general situations is proposed.

3. A generalised Gibbs equation

In classical theory, it is supposed that the entropy s is a function of the energy u and some extensive variables a^α which are non-zero at equilibrium. Now, we make the assumption that s depends, in addition, on the thermodynamic fluxes J^γ :

$$s = s(u, a^\alpha, J^\gamma). \quad (3.1)$$

The quantities u , a^α and J^γ are those appearing in the field equations of mass, momentum and energy and are consequently well defined. However, a difficulty is raised with the definition of entropy far from equilibrium. This problem has been widely debated in recent years (see e.g. Gal-Or 1974, Domingos *et al* 1974), and up to now has not received a definite answer. As soon as the hypothesis of local equilibrium is relaxed, the existence of a macroscopic entropy which should be a function of the macroscopic variables has been questioned (Domingos *et al* 1974, ch V). In the present

work, we take for granted the existence, outside equilibrium, of an entropy function whose production is positive definite. We also undertake to recover the results of classical thermodynamics in the local equilibrium range.

The existence of an entropy far from equilibrium has been postulated in most of the theories of continuum thermodynamics (Coleman 1964, Müller 1971, Green and Laws 1972, Nemat-Nasser 1975). A justification of this attitude can be found in the kinetic theory of gases and in statistical theory, wherein the existence of a non-equilibrium entropy is also merely accepted.

Of course, instead of using the entropy s as dependent variable as in (3.1) and u as an independent quantity, it is equivalent to interchange the roles of the entropy and the energy and to reformulate (3.1) as

$$u = u(s, a^\alpha, J^\gamma). \quad (3.2)$$

The principle of material indifference (Truesdell and Noll 1965) requires that the J^γ 's transform like objective scalars. If this is not the case, adequate combinations of the J^γ 's meeting this criterion will be selected.

Defining a new state parameter A^γ by

$$(\partial u / \partial J^\gamma)_{s, a^\alpha, J^{\gamma'}} = A^\gamma \quad (\gamma' \neq \gamma), \quad (3.3)$$

the generalised Gibbs equation reads as

$$\dot{u} = T\dot{s} + \sum_\alpha \Gamma^\alpha \dot{a}^\alpha + \sum_\gamma A^\gamma \dot{J}^\gamma. \quad (3.4)$$

A^γ and J^γ are tensorial quantities of the same order; in particular, J^0 will be identified with the heat flux \mathbf{q} . From (3.4), it is clear that T , Γ^α and A^α , which are defined by

$$T = (\partial u / \partial s)_{a^\alpha, J^\gamma}, \quad \Gamma^\alpha = (\partial u / \partial a^\alpha)_{s, J^\gamma, a^{\alpha'}} \quad (\alpha' \neq \alpha)$$

and (3.3), are functions of the whole set of variables s , a^α and J^γ .

At this point, an additional assumption is introduced by which the supplementary variables contribute also to the entropy flux:

$$\mathbf{J}^s = \mathbf{J}^s(q^\gamma, \mathbf{q}^\gamma, \mathbf{q}^\gamma). \quad (3.5)$$

In the linear approximation, the above expression can be written simply as

$$\mathbf{J}^s = \sum_0^m \mathbf{L}^\gamma q^\gamma + \sum_0^n \mathbf{L}^\gamma \cdot \mathbf{q}^\gamma + \sum_0^l \mathbf{L}^\gamma \cdot \mathbf{q}^\gamma$$

wherein the coefficients \mathbf{L}^γ , \mathbf{L}^γ , \mathbf{L}^γ are functions of the intensive variables Γ^α and T .

Let us now give (3.5) some particular forms valid for *isotropic systems*. In order to avoid unduly lengthy mathematical expressions, we assume that only one symmetric second-order tensorial flux \mathbf{q} is involved. According to the representation theorems (Truesdell and Noll 1965), one obtains for \mathbf{J}^s

$$\mathbf{J}^s = \sum_0^n (\phi_0^\gamma \mathbf{I} + \phi_1^\gamma \mathbf{q} + \phi_2^\gamma \mathbf{q} \cdot \mathbf{q}) \cdot \mathbf{q}^\gamma, \quad (3.6)$$

wherein ϕ_i ($i = 0, 1, 2$) are scalar functions of the intensive variables T and Γ^α , the scalar fluxes q^γ and the invariants of \mathbf{q}^γ and \mathbf{q} , namely $\text{tr } \mathbf{q}$, $\text{tr}(\mathbf{q})^2$, $\text{tr}(\mathbf{q})^3$, $\mathbf{q}^\alpha \cdot \mathbf{q}^\beta$, $\mathbf{q}^\alpha \cdot \mathbf{q} \cdot \mathbf{q}^\beta$, $\mathbf{q}^\alpha \cdot (\mathbf{q})^2 \cdot \mathbf{q}^\beta$.

Up to the second order of approximation in the fluxes, the entropy flux reads as

$$\mathbf{J}^s = \sum_0^n \phi_0^\gamma(\Gamma^\alpha, q^\beta, \text{tr } \mathbf{q}) \mathbf{q}^\gamma + \sum_0^n \phi_1^\gamma(\Gamma^\alpha) \mathbf{q} \cdot \mathbf{q}^\gamma. \quad (3.7)$$

An equivalent expression is

$$\mathbf{J}^s = -T^{-1} \sum_0^n \Gamma^\gamma \mathbf{q}^\gamma + \sum_0^n \left[\left(\sum_0^m \phi_{00}^\beta(\Gamma^\alpha) q^\beta + \phi_{01}(\Gamma^\alpha) \text{tr } \mathbf{q} \right) \mathbf{1} + \phi_1^\gamma(\Gamma^\alpha) \mathbf{q} \right] \cdot \mathbf{q}^\gamma. \quad (3.8)$$

In the linear range, (3.8) reduces to the classical form

$$\mathbf{J}^s = -T^{-1} \sum_0^n \Gamma^\gamma \mathbf{q}^\gamma. \quad (3.9)$$

Clearly (3.8) represents the simplest and most natural generalisation of (3.9) and will, from now on, be used throughout this work. For printing convenience, the next more compact expression will be used instead of (3.8), namely

$$\mathbf{J}^s = -T^{-1} \sum_\gamma \Gamma^\gamma \mathbf{q}^\gamma + \sum_{\gamma, \beta} b^{\gamma\beta} J^\gamma J^\beta. \quad (3.10)$$

J^γ and J^β may, of course, be of completely different tensorial character.

As an illustration, let us derive the expression for the entropy flux for a one-component viscous fluid. The thermodynamic fluxes are the heat flux vector, the viscous pressure p^v and the deviatoric stress tensor σ^v , so that

$$\mathbf{J}^s = \mathbf{J}^s(p^v, \mathbf{q}, \widetilde{\sigma}^v). \quad (3.11)$$

Up to second order, the entropy flux reads, according to (3.8),

$$\mathbf{J}^s = -T^{-1} \mathbf{q} + \phi_0(T, p) p^v \mathbf{q} + \phi_1(T, p) \widetilde{\sigma}^v \cdot \mathbf{q}. \quad (3.12)$$

We now return to the general formalism. The next step is the derivation of the entropy production and the rate of change of the fluxes.

Eliminate \dot{u} between the energy balance (2.3) and the generalised Gibbs equation (3.4). After use of expression (3.10) of the entropy flux, one obtains the relation

$$\begin{aligned} \rho \dot{s} = & -\nabla \cdot \left(-T^{-1} \sum_\alpha \Gamma^\alpha \mathbf{q}^\alpha + \sum_{\gamma, \beta} b^{\gamma\beta} J^\gamma J^\beta \right) - \sum_\alpha \mathbf{q}^\alpha \cdot \nabla(\Gamma^\alpha T^{-1}) - \sum_\alpha \Gamma^\alpha T^{-1} \sigma^\alpha \\ & - \rho T^{-1} \sum_\gamma A^\gamma j^\gamma + \sum_{\gamma, \beta} b^{\gamma\beta} J^\beta \nabla J^\gamma + \sum_{\gamma, \beta} J^\gamma J^\beta \nabla b^{\gamma\beta}. \end{aligned} \quad (3.13)$$

The second, third, fourth and fifth terms represent the entropy production, which can be expressed by

$$\sigma = \sigma^{(1)} + \sigma^{(2)} \geq 0. \quad (3.14)$$

$\sigma^{(1)}$ is the classical contribution (2.9), while $\sigma^{(2)}$ arises from the extra terms and is given by

$$\sigma^{(2)} = -\rho T^{-1} \sum_\gamma A^\gamma j^\gamma + \sum_{\gamma, \beta} b^{\gamma\beta} J^\beta \nabla J^\gamma + \sum_{\gamma, \beta} J^\gamma J^\beta \nabla b^{\gamma\beta}. \quad (3.15)$$

For a second-order analysis, it is sufficient to assume that the A^γ 's are linear functions of the J^β 's:

$$\rho T^{-1} A^\gamma = \sum_\beta c^{\gamma\beta}(T, \Gamma^\alpha) J^\beta. \quad (3.16)$$

Substitution of (3.16) in (3.15) yields, at the second order of approximation,

$$\sigma^{(2)} = \sum_{\beta} J^{\beta} \sum_{\gamma} (-c^{\gamma\beta} j^{\gamma} + b^{\beta\gamma} \nabla J^{\gamma} + J^{\gamma} \nabla b^{\gamma\beta}) = \sum_{\beta} J^{\beta} X^{\beta(2)}, \quad (3.17)$$

where $X^{\beta(2)}$ represents the terms between parentheses and will be termed the generalised thermodynamic force. Contrary to the thermodynamic forces $X^{\beta(1)}$ appearing in the classical theory, $X^{\beta(2)}$ depends not only on the J^{α} 's but also on their time and space derivatives. Gathering the results (2.13) and (3.17) one obtains

$$\sigma = \sum_{\beta} J^{\beta} X^{\beta} \geq 0,$$

with

$$X^{\beta} = X^{\beta(1)} + X^{\beta(2)}. \quad (3.18)$$

The entropy production still appears as a bilinear form in generalised fluxes J^{β} and forces X^{β} . As confirmed by experiment and kinetic theory, the fluxes depend generally on the forces:

$$J^{\beta} = J^{\beta}(X^{\gamma}). \quad (3.19)$$

In the linear approximation, the phenomenological equations (3.19) reduce to

$$J^{\beta} = \sum_{\gamma} L^{\beta\gamma} X^{\gamma}. \quad (3.20)$$

Restrictions on the sign of the phenomenological coefficients are derived by substitution of (3.19) in the positive definite entropy production.

It must be pointed out that the $X^{\beta(2)}$'s contain time derivatives such as $\dot{\mathbf{q}}$ and $\dot{\mathbf{q}}$ which are not objective. If objective equations are needed, it is necessary to replace the non-objective derivatives by objective derivatives, such as the co-rotational time derivative, defined by

$$\mathbf{q}^* = \dot{\mathbf{q}} + \mathbf{W} \cdot \mathbf{q}, \quad \mathbf{q}^* = \dot{\mathbf{q}} + \mathbf{W} \cdot \mathbf{q} - \mathbf{q} \cdot \mathbf{W},$$

where \mathbf{W} is the skew-symmetric spin tensor.

4. An example: the two-component mixture

In order to illustrate the above treatment, let us consider an isotropic mixture of two chemically inert fluids.

4.1. The classical linear situation

In the classical linear theory of irreversible thermodynamics (De Groot and Mazur 1962), the Gibbs equation is given by

$$\dot{u} = T\dot{s} - p\dot{v} + \sum_{k=1}^2 \mu^k \dot{c}^k, \quad (4.1)$$

while the entropy flux and the entropy production are respectively

$$\mathbf{J}^s = T^{-1} \mathbf{q}' + \sum_{k=1}^2 s^k \mathbf{J}^k, \tag{4.2}$$

$$\sigma = \mathbf{q}' \cdot \nabla T^{-1} - T^{-1} \sum_{k=1}^2 \mathbf{J}^k \cdot [T(\nabla \mu^k)_T - \mathbf{F}^k] + T^{-1} \widetilde{\boldsymbol{\sigma}}^v : \dot{\mathbf{V}} - T^{-1} p^v \nabla \cdot \mathbf{v}. \tag{4.3}$$

In (4.2) and (4.3), one has introduced a new heat flux \mathbf{q}' defined by

$$\mathbf{q}' = \mathbf{q} - \sum_{k=1}^2 h^k \mathbf{J}^k. \tag{4.4}$$

Index T affecting $(\nabla \mu^k)$ indicates that the corresponding quantity has to be calculated at constant temperature.

Setting $\bar{\mu} = \mu^1 - \mu^2$, the corresponding linear phenomenological laws are

$$\mathbf{q}' = -L^{qq} T^{-2} \nabla T - L^{q1} T^{-1} [(\nabla \bar{\mu})_T - (\mathbf{F}^1 - \mathbf{F}^2)], \tag{4.5}$$

$$\mathbf{J}^1 = (-\mathbf{J}^2) = -L^{1q} T^{-2} \nabla T - L^{11} T^{-1} [(\nabla \bar{\mu})_T - (\mathbf{F}^1 - \mathbf{F}^2)], \tag{4.6}$$

$$p^v = -L^{pp} T^{-1} \nabla \cdot \mathbf{v}, \tag{4.7}$$

$$\widetilde{\boldsymbol{\sigma}}^v = L^{vv} T^{-1} \dot{\mathbf{V}}. \tag{4.8}$$

The phenomenological coefficients are linked to the usual transport coefficients by

$$L^{qq} = \lambda T^{-2}, \quad L^{q1} = \rho c^1 c^2 T^{-2} D'', \quad L^{1q} = \rho c^1 c^2 T^{-2} D',$$

$$L^{11} = \rho c_2 T D / (\partial u_1 / \partial c_1)_{p, T},$$

$$L^{pp} = \eta_v T, \quad L^{vv} = 2\eta T.$$

The Onsager reciprocity relation ($L^{1q} = L^{q1}$) implies the equality of the diffusion coefficients D' and D'' .

4.2. The second-order approximation

In addition to the variables s , v and c^1 , the specific energy is assumed to be a potential function of the thermodynamic fluxes:

$$u = u(s, v, c^1, \mathbf{q}', \mathbf{J}^1, p^v, \boldsymbol{\sigma}^v). \tag{4.9}$$

If one defines quantities \mathbf{A} , \mathbf{B} , \mathbf{C} and E by

$$v\mathbf{A} = \frac{\partial u}{\partial \mathbf{q}'}, \quad v\mathbf{B} = \frac{\partial u}{\partial \mathbf{J}^1}, \quad v\mathbf{C} = \frac{\partial u}{\partial \widetilde{\boldsymbol{\sigma}}^v}, \quad vE = \frac{\partial u}{\partial p^v}, \tag{4.10}$$

the generalised Gibbs equation can be rewritten as†

$$\dot{u} = T\dot{s} - p\dot{v} + \bar{\mu}\dot{c} + v\mathbf{A} \cdot \dot{\mathbf{q}}' + v\mathbf{B} \cdot \dot{\mathbf{J}} + v\mathbf{C} : \dot{\widetilde{\boldsymbol{\sigma}}}^v + vE\dot{p}^v. \tag{4.11}$$

Like T , p and $\bar{\mu}$, the new parameters \mathbf{A} , \mathbf{B} , \mathbf{C} and E are functions of the whole set of variables appearing in (4.9).

The expressions relating T , p , $\bar{\mu}$, \mathbf{A} , \mathbf{B} , \mathbf{C} and E to the variables s , v , c , \mathbf{q}' , \mathbf{J} , p^v , $\widetilde{\boldsymbol{\sigma}}^v$ are the state equations. As in classical thermodynamics, they are characteristic of the behaviour of the system and must be injected *a priori* into the theory. By expanding

† Since no confusion is possible, the superscript 1 of c and \mathbf{J} has been dropped.

them around their local equilibrium value, one obtains

$$T = T_{\text{eq}}(s, v, c) + \left(\frac{\partial T}{\partial p^v}\right)_{\text{eq}} p^v + O(2), \tag{4.12}$$

$$p = p_{\text{eq}}(s, v, c) + \left(\frac{\partial p}{\partial p^v}\right)_{\text{eq}} p^v + O(2), \tag{4.13}$$

$$\bar{\mu} = \bar{\mu}_{\text{eq}}(s, v, c) + \left(\frac{\partial \bar{\mu}}{\partial p^v}\right)_{\text{eq}} p^v + O(2), \tag{4.14}$$

$$\mathbf{A} = \left(\frac{\partial \mathbf{A}}{\partial \mathbf{q}'}\right)_{\text{eq}} \mathbf{q}' + \left(\frac{\partial \mathbf{A}}{\partial \mathbf{J}}\right)_{\text{eq}} \mathbf{J} + O(2) = 2\alpha_0(s, v, c)\mathbf{q}' + 2\alpha_2(s, v, c)\mathbf{J} + O(2), \tag{4.15}$$

$$\mathbf{B} = \left(\frac{\partial \mathbf{B}}{\partial \mathbf{q}'}\right)_{\text{eq}} \mathbf{q}' + \left(\frac{\partial \mathbf{B}}{\partial \mathbf{J}}\right)_{\text{eq}} \mathbf{J} + O(2) = 2\beta_1(s, v, c)\mathbf{q}' + 2\alpha_1(s, v, c)\mathbf{J} + O(2), \tag{4.16}$$

$$\check{\mathbf{C}} = \left(\frac{\partial \check{\mathbf{C}}}{\partial \check{\boldsymbol{\sigma}}^v}\right)_{\text{eq}} \check{\boldsymbol{\sigma}}^v + O(2) \equiv 2\alpha_4(s, v, c)\boldsymbol{\sigma}^v + O(2), \tag{4.17}$$

$$E = \left(\frac{\partial E}{\partial p^v}\right)_{\text{eq}} p^v + O(2) \equiv 2\alpha_3(s, v, c)p^v + O(2).^\dagger \tag{4.18}$$

In accordance with elementary calculus, the mixed second derivatives of u with respect to s and p^v , v and p^v , c and p^v , \mathbf{J} and \mathbf{q}' are respectively

$$\begin{aligned} \left(\frac{\partial T}{\partial p^v}\right)_{\text{eq}} &= \left(v\frac{\partial E}{\partial s}\right)_{\text{eq}} = 0, & \left(\frac{\partial p}{\partial p^v}\right)_{\text{eq}} &= \left(-\frac{\partial(vE)}{\partial v}\right)_{\text{eq}} = 0, \\ \left(\frac{\partial \bar{\mu}}{\partial p^v}\right)_{\text{eq}} &= \left(v\frac{\partial E}{\partial c}\right)_{\text{eq}} = 0, & \left(\frac{\partial \mathbf{A}}{\partial \mathbf{J}}\right)_{\text{eq}} &= \left(\frac{\partial \mathbf{B}}{\partial \mathbf{q}'}\right)_{\text{eq}}. \end{aligned} \tag{4.19}$$

The vanishing of the three first relations results from the property that, at equilibrium (i.e. for $p^v = 0$), E and its derivatives with respect to u , v and c are equal to zero; from the fourth equation follows the reciprocity relation

$$\alpha_2 = \beta_1.$$

After use of (4.15)–(4.19), the Gibbs equation (4.11) takes the form

$$\rho \dot{u} = T\rho \dot{s} - p\rho \dot{v} + \bar{\mu}\rho \dot{c} + \alpha_0 \overline{\mathbf{q}' \cdot \mathbf{q}'} + \alpha_1 \overline{\mathbf{J} \cdot \mathbf{J}} + \alpha_2 \overline{\mathbf{q}' \cdot \mathbf{J}} + \alpha_3 \overline{p^v p^v} + \alpha_4 \overline{\check{\boldsymbol{\sigma}}^v \cdot \check{\boldsymbol{\sigma}}^v}. \tag{4.20}$$

The next step is the formulation of the generalised entropy flux. By virtue of (3.6), its most general expression is

$$\mathbf{J}^s = (\phi_0 \mathbf{I} + \phi_1 \check{\boldsymbol{\sigma}}^v + \phi_2 \check{\boldsymbol{\sigma}}^v \cdot \check{\boldsymbol{\sigma}}^v) \cdot \mathbf{q}' + (\psi_0 \mathbf{I} + \psi_1 \check{\boldsymbol{\sigma}}^v + \psi_2 \check{\boldsymbol{\sigma}}^v \cdot \check{\boldsymbol{\sigma}}^v) \mathbf{J}, \tag{4.21}$$

where the ϕ_i 's and the ψ_i 's are functions of the variables s (or T), v (or p), c , p^v and the invariants of $\check{\boldsymbol{\sigma}}^v$, \mathbf{q}' and \mathbf{J} . At the second-order approximation, (4.21) reduces to

$$\mathbf{J}^s = T^{-1} \mathbf{q}' + (s^1 - s^2) \mathbf{J} + 2\phi_{00} p^v \mathbf{q}' + 2\phi_{11} \check{\boldsymbol{\sigma}}^v \cdot \mathbf{q}' + 2\psi_{00} p^v \mathbf{J} + 2\psi_{11} \check{\boldsymbol{\sigma}}^v \cdot \mathbf{J}, \tag{4.22}$$

where ϕ_{00} , ψ_{00} , ϕ_{11} and ψ_{11} are functions of the variables s (or T), v (or p) and c . The

[†] Observe the absence in (4.18) of a term independent of p^v . This is justified by the local equilibrium hypothesis which implies stability. Indeed, since u is a minimum at the local equilibrium value, it must necessarily be a quadratic function of the extra variables. This should not be the case if E should involve an extra term — a function of s , v and c only.

quantity $\mathbf{q}' \times \mathbf{J}$ does not appear in (4.22) since it is an axial vector while \mathbf{J}^s is a polar one. The factor two has been introduced for convenience.

The calculation of the entropy production is classical. It consists of determining the entropy balance law by inserting the mass and energy balances into the generalised Gibbs equation. The source term takes the form

$$\sigma = \mathbf{q}' \cdot \mathbf{X}^q + \mathbf{J} \cdot \mathbf{X}^J + p^v \mathbf{X}^p + \widetilde{\boldsymbol{\sigma}}^v : \widetilde{\mathbf{X}}^v > 0, \quad (4.23)$$

where the generalised forces are given by

$$\mathbf{X}^q = -T^{-2} \nabla T - 2T^{-1} \alpha_0 \dot{\mathbf{q}}' + T^{-1} \alpha_2 \dot{\mathbf{J}} + \widetilde{\boldsymbol{\sigma}}^v \cdot \nabla \phi_{11} + 2\phi_{11} \nabla \cdot \widetilde{\boldsymbol{\sigma}}^v + p^v \nabla \phi_{00} + 2\phi_{00} \nabla p^v, \quad (4.24)$$

$$\begin{aligned} \mathbf{X}^J = T^{-1} [(\nabla \mu)_T + \mathbf{F}^2 - \mathbf{F}^1] + 2\alpha_1 T^{-2} \dot{\mathbf{J}} + \alpha_2 T^{-2} \dot{\mathbf{q}}' - \widetilde{\boldsymbol{\sigma}}^v \cdot \nabla \psi_{11} \\ - 2\psi_{11} \nabla \cdot \widetilde{\boldsymbol{\sigma}}^v - p^v \nabla \psi_{00} - 2\psi_{00} \nabla p^v, \end{aligned} \quad (4.25)$$

$$\mathbf{X}^p = -T^{-1} \nabla \cdot \mathbf{v} - 2\alpha_3 T^{-1} \dot{p}^v + 2\phi_{00} \nabla \cdot \mathbf{q}' + 2\psi_{00} \nabla \cdot \mathbf{J} + \mathbf{q}' \cdot \nabla \phi_{00} + \mathbf{J} \cdot \nabla \psi_{00}, \quad (4.26)$$

$$\widetilde{\mathbf{X}}^v = T^{-1} \widetilde{\nabla} - 2\alpha_4 T^{-1} \dot{\widetilde{\boldsymbol{\sigma}}^v} + 2\phi_{11} \langle \nabla \mathbf{q}' \rangle + 2\psi_{11} \langle \nabla \mathbf{J} \rangle + \langle \mathbf{q}' \nabla \phi_{11} \rangle + \langle \mathbf{J} \nabla \psi_{11} \rangle. \quad (4.27)$$

The brackets stand for the symmetric part of the deviatoric part of the corresponding tensor. Observe that the above forces are linear in the fluxes and in their time and spatial derivatives.

Although the \mathbf{q}' , \mathbf{J} , p^v and $\widetilde{\boldsymbol{\sigma}}^v$ transform as objective quantities, this property is not met by their conjugated forces because of the presence of the material time derivatives. This difficulty is overcome by observing that one has

$$\mathbf{q} \cdot \dot{\mathbf{q}} = \mathbf{q} \cdot \dot{\mathbf{q}}^*, \quad \mathbf{J} \cdot \dot{\mathbf{J}} = \mathbf{J} \cdot \dot{\mathbf{J}}^*, \quad \widetilde{\boldsymbol{\sigma}}^v : \dot{\widetilde{\boldsymbol{\sigma}}^v} = \widetilde{\boldsymbol{\sigma}}^v : \dot{\widetilde{\boldsymbol{\sigma}}^v}^*,$$

where the upper asterisk means the co-rotational objective time derivative. Substituting these results in expression (4.23) for the entropy production shows that expressions (4.24)–(4.27) remain unchanged by replacing the material by the co-rotational time derivative.

The final step is the establishment of the phenomenological laws. Therefore, it is assumed that the fluxes are functions of the whole set of forces, namely

$$\mathbf{q}' = \mathbf{q}'(\mathbf{X}^q, \mathbf{X}^J, \mathbf{X}^p, \widetilde{\mathbf{X}}^v), \quad (4.28)$$

with similar expressions for \mathbf{J} , p^v and $\widetilde{\boldsymbol{\sigma}}^v$.

Clearly, such phenomenological laws are evolution equations, since they involve the time derivatives of \mathbf{q}' , \mathbf{J} , p^v and $\widetilde{\boldsymbol{\sigma}}^v$ through the expressions of the generalised forces.

Since all the previous developments have been limited to second order, it is logical to formulate the set of phenomenological equations at the same order of approximation. With the representation theorem of isotropic tensors, one obtains

$$\mathbf{q}' = (\Psi_0 \mathbf{I} + \Psi_1 \widetilde{\mathbf{X}}^v) \cdot \mathbf{X}^q + (\Psi_2 \mathbf{I} + \Psi_3 \widetilde{\mathbf{X}}^v) \cdot \mathbf{X}^J + \mathbf{O}(3), \quad (4.29)$$

$$\mathbf{J} = (\Psi_4 \mathbf{I} + \Psi_5 \widetilde{\mathbf{X}}^v) \cdot \mathbf{X}^q + (\Psi_6 \mathbf{I} + \Psi_7 \widetilde{\mathbf{X}}^v) \cdot \mathbf{X}^J + \mathbf{O}(3), \quad (4.30)$$

$$p^v = \Psi_8, \quad (4.31)$$

$$\widetilde{\boldsymbol{\sigma}}^v = \Psi_9 \mathbf{I} + \Psi_{10} \widetilde{\mathbf{X}}^v + \Psi_{11} \widetilde{\mathbf{X}}^v \cdot \widetilde{\mathbf{X}}^v + \Psi_{12} \langle \mathbf{q}' \mathbf{J} + \mathbf{J} \mathbf{q}' \rangle + \Psi_{13} \langle \mathbf{q}' \mathbf{q}' \rangle + \Psi_{14} \langle \mathbf{J} \mathbf{J} \rangle. \quad (4.32)$$

The coefficients Ψ_i are functions of the scalars T , p , c , X^p and the invariants of \mathbf{X}^q , \mathbf{X}^J and $\widetilde{\mathbf{X}}^v$; they must be determined by experiment or calculated by the kinetic theory.

The most general form of ψ_i , limited to second order, is given by

$$\begin{aligned} \Psi_i = & \Psi_i^{(0)} + \Psi_i^{(1)} \mathbf{X}^p + \Psi_i^{(2)} (\mathbf{X}^p)^2 + \psi_i^{(3)} \mathbf{X}^q \cdot \mathbf{X}^q + \Psi_i^{(4)} \mathbf{X}^J \cdot \mathbf{X}^J \\ & + \Psi_i^{(5)} \mathbf{X}^q \cdot \mathbf{X}^J + \Psi_i^{(6)} \text{tr} (\widetilde{\mathbf{X}}^v \cdot \widetilde{\mathbf{X}}^v). \end{aligned} \quad (4.33)$$

In (4.33), the $\Psi_i^{(j)}$'s depend only on the intensive variables T , p and c . Restrictions on the sign of the coefficients $\Psi_i^{(j)}$ are derived by inserting the laws (4.29)–(4.32) into the expression for the entropy production and imposing the condition that the latter quantity be positive definite.

In the linear approximation, the equations (4.29)–(4.32) become simply

$$\mathbf{q}' = \psi_0^{(0)} \mathbf{X}^q + \Psi_2^{(0)} \mathbf{X}^J, \quad (4.34)$$

$$\mathbf{J} = \Psi_4^{(0)} \mathbf{X}^q + \Psi_6^{(0)} \mathbf{X}^J, \quad (4.35)$$

$$p^v = \Psi_8^{(1)} \mathbf{X}^p, \quad (4.36)$$

$$\widetilde{\boldsymbol{\sigma}}^v = \Psi_{10}^{(0)} \widetilde{\mathbf{X}}^v. \quad (4.37)$$

These relations contain as a particular case the classical stationary expressions (4.5)–(4.8). In accordance with Onsager's reciprocity theorem, one has $\Psi_2^{(0)} = \Psi_4^{(0)}$.

4.3. A simplified problem: heat conduction in a rigid body

In the particular case of heat conduction in an isotropic rigid body ($\mathbf{J} = p^v = \widetilde{\boldsymbol{\sigma}}^v = 0$), the phenomenological law (4.29) reduces to

$$\mathbf{q} = \Psi_0 \mathbf{X}^q + \text{O}(3). \quad (4.38)$$

Identifying $\Psi_0 T^{-2}$ with λ , the heat conductivity, and using the explicit expression (4.24) of \mathbf{X}^q , one obtains, up to order two,

$$\mathbf{q} = -\lambda (\nabla T + 2 T \alpha_0 \dot{\mathbf{q}}). \quad (4.39)$$

Defining a relaxation time τ by

$$\tau = 2 T \lambda \alpha_0, \quad (4.40)$$

one recovers the Maxwell–Cattaneo form (Maxwell 1867, Cattaneo 1958) of the generalised Fourier law, namely

$$\mathbf{q} = -\lambda \nabla T - \tau \dot{\mathbf{q}}. \quad (4.41)$$

In the literature (e.g. Vernotte 1958, Chester 1963, Swenson 1978, Sieniutycz 1977), it is customary to combine (4.41) with the first law

$$\rho \dot{u} = -\nabla \cdot \mathbf{q}, \quad (4.42)$$

where

$$\dot{u} = c \dot{T}, \quad (4.43)$$

to obtain the hyperbolic heat conduction equation

$$\rho c \tau \ddot{T} + \rho c \dot{T} = \lambda \nabla \cdot \nabla T. \quad (4.44)$$

In (4.44), c denotes the specific heat which, like τ and λ , is assumed to be positive and constant.

In our opinion, this procedure is not generally justified as it mixes a relation like the Maxwell–Cattaneo law, which was obtained from a second-order Gibbs equation, with a state equation like (4.43), which is a direct consequence of the classical first-order Gibbs equation. Therefore, equation (4.44) can only be valid under some restrictions. These are obtained by determining under which conditions the generalised Gibbs equation

$$\dot{u} = T\dot{s} + v\alpha_0\mathbf{q} \cdot \dot{\mathbf{q}} \quad (4.45)$$

leads consistently to the state equation (4.43). Expression (4.45) can still be written as

$$\dot{u} = T\left(\frac{\partial s}{\partial T}\right)_q \dot{T} + T\left(\frac{\partial s}{\partial \mathbf{q}}\right)_T \cdot \dot{\mathbf{q}} + v\alpha_0\mathbf{q} \cdot \dot{\mathbf{q}}. \quad (4.46)$$

From the equality of the mixed partial derivatives of the Helmholtz free energy $u - Ts$, it is seen that

$$-\left(\frac{\partial s}{\partial \mathbf{q}}\right)_T = v\mathbf{q}\left(\frac{\partial \alpha_0}{\partial T}\right)_q.$$

Putting

$$\alpha_{,\tau} = \left(\frac{\partial \alpha_0}{\partial T}\right)_q, \quad c_q = T\left(\frac{\partial s}{\partial T}\right)_q,$$

(4.46) reads

$$\dot{u} = c_q\dot{T} + v(\alpha_0 - T\alpha_{,\tau})\mathbf{q} \cdot \dot{\mathbf{q}}.$$

This expression reduces to the usual relation (4.43) under the condition that either second-order terms are omitted or that the following relation is fulfilled:

$$\alpha_0 - T\alpha_{,\tau} = 0.$$

This implies that α_0 is proportional to T , or from the definition (4.40) of τ , that λ behaves like τ/T^2 .

4.4. Comparison with the kinetic theory

The expressions (4.20) and (4.22) of the generalised Gibbs equation and the entropy flux can be justified by the Boltzmann kinetic theory of dilute gases. This is done by expanding the distribution function f^j , associated with the component j of the mixture, around the local equilibrium value f_{eq}^j :

$$f^j = f_{\text{eq}}^j(1 + f_{(1)}^j + f_{(2)}^j + \dots) \quad (\text{Enskog development}). \quad (4.47)$$

$f_{(1)}^j$ and $f_{(2)}^j$ are respectively the first- and second-order approximation functions and are calculated in every textbook on kinetic theory. For future purpose, we need the expression of $f_{(1)}^j$ given by (Chapman and Cowling 1970)

$$f_{(1)}^j = A^j \boldsymbol{\omega}^j \cdot \nabla T + B^j \boldsymbol{\omega}^j \boldsymbol{\omega}^j : \mathbf{V} + C^j \nabla \cdot \mathbf{v} + D^j \boldsymbol{\omega}^j \cdot \mathbf{d}^j. \quad (4.48)$$

$\boldsymbol{\omega}^j$ denotes the peculiar velocity of the molecules of component j , the coefficients A^j up to D^j are scalar functions of $\boldsymbol{\omega}^j \cdot \boldsymbol{\omega}^j$, while \mathbf{d}^j stands for $\mathbf{d}^j = \rho^{-1}(\nabla p^j - \rho^j \mathbf{F}^j)$.

According to kinetic theory, the specific entropy and the entropy flux are defined by

$$\rho s = -k \sum_j \int f^j (\ln f^j - 1) d\omega^j, \quad (4.49)$$

$$\mathbf{J}^s = -k \sum_j \int \omega^j f^j (\ln f^j - 1) d\omega^j. \quad (4.50)$$

Making use of the kinetic definitions of \mathbf{J}^i , \mathbf{q}^i , p^v , $\widetilde{\boldsymbol{\sigma}}^v$ and substituting (4.48) in the above expressions of s and \mathbf{J}^s , one obtains for a two-component mixture

$$\rho s_{\text{eq}} = T^{-1} \left(\rho u + p - \sum_{j=1}^2 \mu^j \rho^j \right), \quad (4.51)$$

$$\rho s_{(1)} = 0, \quad (4.52)$$

$$\rho s_{(2)} = -T^{-1} (\alpha_0 \mathbf{q}'_{(1)} \cdot \mathbf{q}'_{(1)} + \alpha_1 \mathbf{J}_{(1)} \cdot \mathbf{J}_{(1)} + \alpha_2 \mathbf{q}'_{(1)} \cdot \mathbf{J}_{(1)} + \alpha_3 p_{(1)}^v p_{(1)}^v + \alpha_4 \widetilde{\boldsymbol{\sigma}}_{(1)}^v : \widetilde{\boldsymbol{\sigma}}_{(1)}^v), \quad (4.53)$$

and

$$\mathbf{J}_{(0)}^s = 0, \quad (4.54)$$

$$\mathbf{J}_{(1)}^s = T^{-1} (\mathbf{q}_{(1)} - \bar{\mu} \mathbf{J}_{(1)}), \quad (4.55)$$

$$\begin{aligned} \mathbf{J}_{(2)}^s = T^{-1} (\mathbf{q}_{(2)} - \bar{\mu} \mathbf{J}_{(2)}) + 2\phi_{00} p_{(1)}^v \mathbf{q}'_{(1)} + 2\Psi_{00} p_{(1)}^v \mathbf{J}_{(1)} \\ + 2\phi_{11} \widetilde{\boldsymbol{\sigma}}_{(1)}^v \cdot \mathbf{q}'_{(1)} + 2\Psi_{11} \widetilde{\boldsymbol{\sigma}}_{(1)}^v \cdot \mathbf{J}_{(1)}. \end{aligned} \quad (4.56)$$

The coefficient α_i , Ψ_{ij} and ϕ_{ij} are complicated functions of f_{eq} and ω^k (Jou 1978), while $\mathbf{q}'_{(1)}$, $\mathbf{J}_{(1)}$, $p_{(1)}^v$ and $\widetilde{\boldsymbol{\sigma}}_{(1)}^v$ are expressed by (4.5)–(4.8). For a mixture of rigid spherical molecules for which the bulk viscosity vanishes, the above coefficients take the form

$$\alpha_0 = \frac{3\rho}{5p^2} g_0, \quad \alpha_1 = \frac{3\rho}{2\rho^1(\rho - \rho^1)} g_1, \quad \alpha_2 = \frac{6\rho D'}{5\rho^1(\rho - \rho^1)} \left(\frac{g_{21}}{D} + \frac{g_{22}}{\lambda} \right), \quad \alpha_4 = \frac{g_4}{4p}$$

and

$$\phi_{11} = -\frac{1}{5pT} h_0, \quad \Psi_{11} = \frac{D'}{5DT\rho^1(\rho - \rho^1)} h_1,$$

where the g_i and h_i are polynomial functions of the partial densities of the components.

By differentiation of (4.53) with respect to time, while keeping the coefficients constant, it is seen that the presence of the extra terms in the Gibbs equation (4.11) is indeed corroborated by the kinetic theory of dilute gases. The agreement between the kinetic and the macroscopic expressions (4.56) and (4.22) of the entropy flux is also complete.

In the same way, the phenomenological laws (4.34)–(4.37) have been compared (Jou 1978) with the Burnett equations of the kinetic theory of gases (Chapman and Cowling 1970). It was seen that all the terms present in Burnett's relations are recovered in our proposed equations. The analysis is lengthy, but similar to that presented by Lebon (1978) for a one-component fluid, and will not be repeated here.

5. Conclusions

The present work is aimed at generalising the classical theory of irreversible thermodynamics outside the linear range. This objective is achieved in three steps.

Firstly, it is assumed that the internal energy (or the entropy) depends in addition to the usual variables (temperature, pressure, concentrations) on the thermodynamic fluxes, namely the heat flux, the diffusion flux, etc.

The second step consists of expressing the entropy flux as a function of the same set of thermodynamic fluxes.

In a third step, evolution equations for the extra variables are determined. The form of these differential equations is suggested by the expression for entropy production. The latter appears in a bilinear form in the fluxes and some factor involving their time derivatives, which are termed forces. The existence of such evolution relations has been confirmed empirically and theoretically by the kinetic theory of gases.

As an illustration, a two-component isotropic mixture has been considered. Explicit expressions have been derived for the generalised Gibbs equation, the entropy flux and the evolution equations for the fluxes up to the second-order approximation in the fluxes.

Our formalism clearly goes beyond the local equilibrium hypothesis, which is the keystone of the classical theories of non-equilibrium thermodynamics. It differs also from rational thermodynamics and Gyarmati's formalisms wherein the entropy flux is still taken to be equal to its classical value (2.8). Our approach also generalises Müller's (1967) work, where the analysis was limited to one-component fluids with linear phenomenological laws between fluxes and forces. Moreover, Müller kept the coefficients ϕ_{ij} in the entropy flux constant and did not take into account the objectivity principle. It must also be observed that the difficulties raised by the parabolic character of the diffusion equation is now overcome.

In our opinion, the interest of our formalism is that it reduces at the maximum the *ad hoc* hypotheses. Truly, only one fundamental assumption is needed: namely that the Gibbs equation involves extra terms in the fluxes, and the number and the nature of these fluxes are dictated by the nature of the system under consideration. Starting from this hypothesis, the proposed procedure leads naturally to the extra equations required to describe the system unequivocally by using invariance requirements and representation theorems. Moreover, nowhere are hidden variables introduced whose physical meaning is not clearly established.

The approach presented in this work is general and can be applied as well to charged systems (Jou 1978) and to micropolar media (Rubi 1979).

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