Frame Dependence, Entropy, Entropy Flux, and Wave Speeds in Mixtures of Gases

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With 3 Figures

Summary

The kinetic theory provides constitutive equations of ideal gases and it can therefore be used to confirm or reject the axioms and principles of the phenomenological constitutive theory. Thus the kinetic theory provides a limit for the validity of the principle of material frame indifference. It generalizes the laws of Fick, Fourier and Navier-Stokes and provides finite speeds of waves of concentration, temperature and shear. Moreover the theory permits the calculation of entropy and entropy flux in non-equilibrium and it confirms Onsager relations in a rotating mixture of ideal gases.

Introduction

This paper is an investigation into the kinetic theory of gases but it is intended to be read by researchers in the fields of continuum mechanics and thermodynamics. Four common questions are answered:

i) Is material frame indifference a valid axiom, and if not, is it approximately valid and what is its range of validity?

ii) What are the proper forms of the constitutive equations for entropy and entropy flux in non-equilibrium?

iii) What are the speeds of propagation of diffusion waves, thermal waves and shear waves? It will be recalled that the classical theories of Fick, Fourier and Navier-Stokes predict infinite speeds.

iv) What is the form of the Onsager relations for diffusion and thermal diffusion in rotating gases?

The paper documents that the principle of material frame indifference is not supported by the kinetic theory of gases. However, it also indicates that the frame dependent terms are extremely small and that they will only be noticed in very dilute gases. We show further that the same terms which violate material frame indifference also permit finite speeds of diffusion, heat conduction and shear waves. The values of these speeds are calculated. These observations use a level of description on which the entropy has non-equilibrium contributions and the entropy flux deviates from the quotient of heat flux and absolute temperature; the extra contributions are calculated.

All this is exhibited here for mixtures of an arbitrary number of one atomic gases. The plan to write this paper was conceived when the confusion about material frame indifference in the kinetic theory spread among engineers and mathematicians to the extent that the issue was distorted beyond recognition. The topic is restated properly here and it is related to other items on which the kinetic theory and common phenomenological thermodynamics are at variance.

In the early 1970's Müller [1], Edelen and McLennan [2], and Söderholm [3] demonstrated that the kinetic theory contradicts the principle of material frame indifference; in fact Chapman and Cowling [4] had already made the same observation in 1936. Truesdell [5] disagreed and Wang [6] blamed the whole effect on the approximation, even though the frame dependent terms are also present in the exact equations of transfer. In a recent paper Speziale [7] misquoted Müller's equations and confused material frame indifference with the requirement that stress and heat flux be an objective tensor and vector respectively, a fact that has never been disputed by any one.

Mixtures were chosen for a demonstration of the salient ideas about material frame indifference, because they have not been treated before under this aspect. Also, the frame dependent terms in the diffusion fluxes are clearly just the ordinary Coriolis forces and there can be no doubt that they belong where they occur. In particular, it would not make sense to attribute the frame dependence of the diffusion fluxes to the approximations of the kinetic theory.

At the same time the treatment of mixtures makes it clear that the constitutive equations of thermodynamics of mixtures are but truncated versions of the equations of balance of relative momenta of the constituents and of their fluxes of momentum and energy. The frame dependent terms occurring in the constitutive relations come from the inertial terms in the equations of balance. This observation has recently motivated Liu and Müller to reformulate Extended Irreversible Thermodynamics so as to provide a phenomenological basis for the results of the kinetic theory that are reported in the present paper, see [15].

1. Boltzmann Equation and Equations of Transfer

1.1 Basic Concepts of the Kinetic Theory

The state of a mixture of ν mon-atomic gases is characterized by the set of distribution functions

$$f_\alpha(x_i, c_i^\alpha, t), \qquad \alpha = 1, ..., \nu.$$

$f_\alpha \, dx \, dc_\alpha := f_\alpha(x_i, c_i^\alpha, t) \, dx_1 \, dx_2 \, dx_3 \, dc_1^\alpha \, dc_2^\alpha \, dc_3^\alpha$ determines the average number of α-particles of velocity c_i^α, position x_i and time t.

1.1.1 Typical Times and Lengths

For a dilute gas of 10^{17} particles per cm³ (say) we may derive the following ratios of characteristic times and lengths.

mean time of free flight $\approx 3000 \cdot$ mean duration of collision

mean free path $\qquad \approx 3000 \cdot$ range of interaction forces

At room temperature the duration of a collision is approximately 10^{-12} sec. Thus it follows that external and inertial forces can be neglected during the collision.

1.1.2 Dynamics of Binary Collision

The velocities

$$c_i{}^\alpha, \; c_i{}^{\beta 1}, \; c_i{}^{\alpha\prime}, \; c_i{}^{\beta 1\prime} \qquad 1$$

of two particles of constituent α and β before and after a collision are related by the conservation laws of momentum and energy

$$m_\alpha c_i{}^\alpha + m_\beta c_i{}^{\beta 1} = m_\alpha c_i{}^{\alpha\prime} + m_\beta c_i{}^{\beta 1\prime}$$

$$\frac{m_\alpha}{2} \, c_\alpha{}^2 + \frac{m_\beta}{2} \, (c_\beta{}^1)^2 = \frac{m_\alpha}{2} \, c_\alpha{}'^2 + \frac{m_\beta}{2} \, (c_\beta{}^{1\prime})^2 \tag{1.1}$$

because the effect of the external forces on the outcome of the collision is negligible as we saw in Section 1.1.1.

1.1.3 Boltzmann Equation

The distribution function $f_\alpha(x_i, c_i{}^\alpha, t)$ obeys the Boltzmann equation

$$\frac{\partial f_\alpha}{\partial t} + c_i{}^\alpha \frac{\partial f_\alpha}{\partial x_i} + \left(f_i{}^\alpha + \underset{c}{i_i{}^\alpha} \right) \frac{\partial f_\alpha}{\partial c_i{}^\alpha}$$

$$= \sum_{\beta=1}^{\nu} \iiint_{-\infty}^{\infty} \int_0^{2\pi} \int_0^{\pi/2} (f_\alpha' f_\beta'^1 - f_\alpha f_\beta^1) \, \sigma_{\alpha\beta} g^{\alpha\beta} \sin\theta_{\beta\alpha} \, d\theta_{\beta\alpha} \, d\varepsilon \, dc_\beta{}^1. \tag{1.2}$$

$f_i{}^\alpha$ — specific external body force. In the sequel we shall take $f_i{}^\varkappa$ to be the same force for each constituent.

$\underset{c}{i_i{}^\alpha}$ — specific inertial force on a molecule of constituent α.

$f_\alpha, f_\beta{}^1, f_\alpha', f_\beta{}^{1\prime}$ — values of the distribution functions for the arguments $c_i{}^\alpha$, $c_i{}^{\beta 1}, c_i{}^{\alpha\prime}, c_i{}^{\beta 1\prime}$.

$\varkappa_{\beta\alpha} = \pi - 2\theta_{\beta\alpha}$ — scattering angle.

$\sigma_{\alpha\beta}$ — effective cross section for $\alpha\beta$-scattering into the solid angle element $\sin\theta_{\beta\alpha} \, d\theta_{\beta\alpha} \, d\varepsilon$.

$\boldsymbol{g}^{\alpha\beta} = \boldsymbol{c}^\alpha - \boldsymbol{c}^{\beta 1}$ — relative velocity of molecules α and β.

The inertial force $\underset{c}{i_i{}^\alpha}$ consists of the centrifugal force, the Coriolis force, the Euler force and the force of relative translation and we write

$$\underset{c}{i_i{}^\alpha} = -W_{ij}^2(x_j - b_j) + 2W_{ij}(c_j{}^\alpha - \dot{b}_j) + \dot{W}_{ij}(x_j - b_j) + \ddot{b}_i,$$

where W_{ij} is the matrix of angular velocity of the observer frame with respect to an inertial frame, and b_i is the radius vector between the origins of the two frames. W_{ij} is an antisymmetric matrix.

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[1] The index 1 on $c_i{}^\beta$ and $c_i{}^{\beta\prime}$ is redundant, if the colliding particles belong to different constituents, but it must be written, because it serves to distinguish the two particles when they belong to one constituent, or when a single gas is considered.

1.1.4 Maxwellian Molecules

The form of the cross section as a function of the relative speed $g^{\alpha\beta}$ and of the scattering angle depends on the interatomic potential. If this potential is a repulsive potential inversely proportional to the fourth power of the interatomic distance, the product $\sigma_{\alpha\beta}g^{\alpha\beta} =: f_{\alpha\beta}$ is a function of $\theta_{\alpha\beta}$ alone. This is the case of the Maxwellian molecules for which manipulations with the collision integral in (1.2) are considerably simplified.

It is expected that the choice of a particular interaction potential does not influence the equations qualitatively; in particular we shall therefore expect general validity of the results below, even though they were calculated for Maxwellian molecules.

1.1.5 Moments $m^\alpha_{i_1 \ldots i_N}$ and $M^\alpha_{i_1 \ldots i_N}$ for the Constituents

The definition of the distribution function f_α implies that

$$\bar{\psi}_\alpha{}^\alpha = \frac{m_\alpha}{\varrho_\alpha} \int \psi_\alpha f_\alpha \, dc_\alpha \tag{1.3}$$

is the local mean value of a function $\psi_\alpha(x_i, c_i^\alpha, t)$. In particular for $\psi_\alpha = c_i{}^\alpha$ we identify $\bar{\psi}_\alpha = v_i{}^\alpha$ as the (macroscopic) velocity of constituent α.

The peculiar velocity $C_i{}^\alpha$ of a molecule is defined as

$$C_i{}^\alpha := c_i{}^\alpha - v_i{}^\alpha. \tag{1.4}$$

The components $c_i{}^\alpha$ and $C_i{}^\alpha$ are used to define moments $m^\alpha_{i_1 \ldots i_N}$ and central moments $M^\alpha_{i_1 \ldots i_N}$, viz.

$$m^\alpha_{i_1 \ldots i_N} := m_\alpha \int f_\alpha c_{i_1}^\alpha \ldots c_{i_N}^\alpha \, dc_\alpha \tag{1.5}$$

$$M^\alpha_{i_1 \ldots i_N} := m_\alpha \int f_\alpha C_{i_1}^\alpha \ldots C_{i_N}^\alpha \, dC_\alpha. \tag{1.6}$$

With (1.4) one gets the following relations between $m^\alpha_{i_1 \ldots i_N}$ and $M^\alpha_{i_1 \ldots i_N}$

$$m^\alpha_{i_1 i_2} = M^\alpha_{i_1 i_2} + \varrho_\alpha v_{i_1}^\alpha v_{i_2}^\alpha \tag{1.7.1}$$

$$m^\alpha_{i_1 i_2 i_3} = M^\alpha_{i_1 i_2 i_3} + 3 v_{(i_1}^\alpha M^\alpha_{i_2 i_3)} + \varrho_\alpha v_{i_1}^\alpha v_{i_2}^\alpha v_{i_3}^\alpha \tag{1.7.2}$$

$$m^\alpha_{i_1 i_2 i_3 i_4} = M^\alpha_{i_1 i_2 i_3 i_4} + 4 v_{(i_1}^\alpha M^\alpha_{i_2 i_3 i_4)} + b v_{(i_1}^\alpha v_{i_2}^\alpha M^\alpha_{i_3 i_4)} + \varrho_\alpha v_{i_1}^\alpha v_{i_2}^\alpha v_{i_3}^\alpha v_{i_4}^\alpha. \tag{1.7.3}$$

A round bracket enclosing N indices indicates a sum of all $N!$ permutations of these indices divided by $N!$. Later in the paper we shall also indicate antisymmetric and traceless symmetric tensors of second rank by brackets, viz.

$$A_{[ij]} = \frac{1}{2}\left(A_{ij} - A_{ji}\right) \quad \text{and} \quad A_{\langle ij \rangle} = \frac{1}{2}\left(A_{ij} + A_{ji}\right) - \frac{1}{3} A_{ll} \delta_{ij}. \tag{1.8}$$

1.1.6 Moments $m_{i_1 \ldots i_N}$ and $M_{i_1 \ldots i_N}$ for the Mixture

It will turn out in chapter 1.2.3 that

$$m_{i_1 \ldots i_N} = \sum_{\alpha=1}^\nu m^\alpha_{i_1 \ldots i_N} \tag{1.9}$$

is a proper definition for the Nth order moment of the mixture. The 0th order and the 1st order moment are

$m_0 = \varrho$ — density of the mixture,

$m_i = \varrho v_i$ — momentum density of the mixture.

v_i is called the barycentric velocity.

In analogy to (1.7) we define central moments $M_{i_1 \ldots i_N}$ for the mixture by

$$m_{i_1 i_2} = M_{i_1 i_2} + \varrho v_{i_1} v_{i_2} \tag{1.10.1}$$

$$m_{i_1 i_2 i_3} = M_{i_1 i_2 i_3} + 3v_{(i_1} M_{i_2 i_3)} + \varrho v_{i_1} v_{i_2} v_{i_3} \tag{1.10.2}$$

$$m_{i_1 i_2 i_3 i_4} = M_{i_1 i_2 i_3 i_4} + 4v_{(i_1} M_{i_2 i_3 i_4)} + 6v_{(i_1} v_{i_2} M_{i_3 i_4)} + \varrho v_{i_1} v_{i_2} v_{i_3} v_{i_4}. \tag{1.10.3}$$

Their relation to the central moments $M^\alpha_{i_1 \ldots i_N}$ of the constituents is given by the equations

$$M_{i_1 i_2} = \sum_{\alpha=1}^{\nu} (M^\alpha_{i_1 i_2} + \varrho_\alpha u^\alpha_{i_1} u^\alpha_{i_2}) \tag{1.11.1}$$

$$M_{i_1 i_2 i_3} = \sum_{\alpha=1}^{\nu} (M^\alpha_{i_1 i_2 i_3} + 3u^\alpha_{(i_1} M^\alpha_{i_2 i_3)} + \varrho_\alpha u^\alpha_{i_1} u^\alpha_{i_2} u^\alpha_{i_3}) \tag{1.11.2}$$

$$M_{i_1 i_2 i_3 i_4} = \sum_{\alpha=1}^{\nu} (M^\alpha_{i_1 i_2 i_3 i_4} + 4u^\alpha_{(i_1} M^\alpha_{i_2 i_3 i_4)} + 6u^\alpha_{(i_1} u^\alpha_{i_2} M^\alpha_{i_3 i_4)} + \varrho_\alpha u^\alpha_{i_1} u^\alpha_{i_2} u^\alpha_{i_3} u^\alpha_{i_4}), \tag{1.11.3}$$

where the diffusion velocities $u_i{}^\alpha := v_i{}^\alpha - v_i$ have been introduced.

1.1.7 Thermodynamic Quantities in the Kinetic Theory

The kinetic theory assumes the following definitions

M^α_{ij} — momentum flux of constituent α with respect to a frame moving with velocity v_α,

$-M^\alpha_{ij}$ — total stress tensor in the mixture,

$$p_\alpha := \frac{1}{3} M^\alpha_{ii} \text{ — pressure of constituent } \alpha, \tag{1.12.1}$$

$$\varrho_\alpha \varepsilon_\alpha := \frac{1}{2} M^\alpha_{ii} + \varrho_\alpha \beta_\alpha \text{ — density of internal energy of constituent } \alpha \text{ [2]}, \tag{1.12.2}$$

$$\varrho \varepsilon := \frac{1}{2} M_{ii} + \sum_\alpha \varrho_\alpha \beta_\alpha \text{ — density of internal energy of the mixture[2]}, \tag{1.12.3}$$

$$q_i{}^\alpha := \frac{1}{2} M^\alpha_{ijj} \text{ — heat flux of constituent } \alpha \text{ with respect to a frame moving with velocity } v_\alpha, \tag{1.12.4}$$

$$q_i = \frac{1}{2} M_{ijj} + \sum_\alpha \varrho_\alpha \beta_\alpha u_i{}^\alpha \text{ — flux of internal energy in the mixture[3]}, \tag{1.12.5}$$

$$T_\alpha := \frac{m_\alpha}{k} \frac{p_\alpha}{\varrho_\alpha} \text{ — temperature of constituent } \alpha. \tag{1.12.6}$$

[2] α_α and β_α are additive constants in the specific entropies and internal energies respectively.

[3] q_i as the flux of internal energy with respect to the barycentric frame contains the convection of internal energy with the diffusive motion; hence the terms with β_α.

In this paper we consider only the case that all constituents of a mixture have the same temperature, thus

$$T_\alpha = T = \frac{m_\alpha}{k} \frac{p_\alpha}{\varrho_\alpha}.$$ (1.12.7)

$$\eta_\alpha = -\frac{k}{\varrho_\alpha} \int f_\alpha \ln f_\alpha \, dc_\alpha + \alpha_\alpha \text{ — specific entropy of constituent } \alpha \,^2,$$ (1.13.1)

$$\eta = \sum_{\alpha=1}^{\nu} \frac{\varrho_\alpha}{\varrho} \eta_\alpha + \sum_{\alpha=1}^{\nu} \varrho_\alpha \alpha_\alpha \text{ — specific entropy of the mixture }^2,$$ (1.13.2)

$$\phi_i{}^\alpha = -k \int f_\alpha C_i{}^\alpha \ln f_\alpha \, dc_\alpha \text{ — entropy flux of constituent } \alpha,$$ (1.13.3)

$$\mu_\alpha = \varepsilon_\alpha - T\eta_\alpha + \frac{p_\alpha}{\varrho_\alpha} \text{ — chemical potential of constituent } \alpha.$$ (1.13.4)

All these quantities are objective. This means that under a change of frame represented by the Euclidean transformation $x_i^* = 0_{ij}(t) x_i + b_i(t)$ they transform according to the formulae

$$s^* = s, \qquad V_i^* = 0_{ij} V_j, \qquad T_{ij} = 0_{ik} 0_{jl} T_{kl},$$

if they are scalars, vectors and tensors respectively. $\boldsymbol{0}$ is a time dependent orthogonal matrix.

1.1.8 Equilibrium

The Maxwellian distribution

$$f_M{}^\alpha = \frac{\varrho_\alpha}{m_\alpha} \sqrt{\frac{m_\alpha}{2\pi\,kT}}^3 \, e^{-\frac{m_\alpha}{2kT}(c_i{}^\alpha - v_i)(c_i{}^\alpha - v_i)}$$ (1.14)

makes the collision integral in (1.2) vanish. (1.14) considers equilibrium as a state where all constituents have the same velocity v_i, the velocity of the mixture.

Not for all fields $\varrho_\alpha(\boldsymbol{x}, t)$, $\boldsymbol{v}(\boldsymbol{x}, t)$ and $T(\boldsymbol{x}, t)$ is the distribution $f_M{}^\alpha$ a solution of the Boltzmann e quation. That is the case, however, if these fields satisfy the following conditions

$$\frac{\partial T}{\partial x_i} = 0$$ (1.15.1)

$$\frac{\partial v_{(i}}{\partial x_{j)}} + \frac{1}{2T} \frac{\partial T}{\partial t} \delta_{ij} = 0$$ (1.15.2)

$$\frac{1}{\varrho_\alpha} \frac{\partial \varrho_\alpha}{\partial x_i} + \frac{m_\alpha}{kT} \left(\frac{\partial v_i}{\partial t} + v_j \frac{\partial v_i}{\partial x_j} \right) - \frac{m_\alpha}{kT} (f_i + i_i) = 0.$$ (1.15.3)

The inertial force i_i now contains the Coriolis force $W_{ij}(v_j - \dot{b}_j)$ on the fluid rather than on a molecule.

According to their definitions (1.12.1, 2) p_α and ε_α are always given as functions of ϱ_α and T by the equations

$$p_\alpha = \varrho_\alpha \frac{k}{m_\alpha} T \quad \text{and} \quad \varepsilon_\alpha = \frac{3}{2} \frac{k}{m_\alpha} T + \beta_\alpha.$$ (1.16)

η_α and μ_α are not function of ϱ_α and T alone, except in equilibrium where, according to (1.13.1, 4) and (1.14) we have

$$\eta_\alpha|_E = \frac{3}{2}\frac{k}{m_\alpha}\ln T - \frac{k}{m_\alpha}\ln\varrho_\alpha + \alpha_\gamma, \tag{1.17.1}$$

and

$$\mu_\alpha|_E = \frac{5}{2}\frac{k}{m_\alpha}T - \frac{3}{2}\frac{k}{m_\alpha}T\ln T + \frac{k}{m_\alpha}T\ln\varrho_\alpha + (\beta_\alpha - T\alpha_\alpha). \tag{1.17.2}$$

1.2 Equations of Transfer

1.2.1 General Equations of Transfer

Multiplying the Boltzmann Equation (1.2) with ψ_α and integrating it over c_i^α, we obtain the general equation of transfer[4]

$$\frac{\partial\overline{\varrho_\alpha\psi_\alpha}^\alpha}{\partial t} + \frac{\partial\overline{\varrho_\alpha\psi_\alpha c_i^\alpha}^\alpha}{\partial x_i} - \varrho_\alpha\overline{\left(f_i + \overset{c}{i_i^\alpha}\right)\frac{\partial\psi_\alpha}{\partial c_i^\alpha}}^\alpha \tag{1.18.1}$$

$$= \sum_{\alpha=1}^\nu m_\alpha\int(\psi_\alpha' - \psi_\alpha)\,f_\alpha f_\beta^1 f_{\alpha\beta}\sin\theta_{\beta\alpha}\,d\theta_{\beta\alpha}\,d\varepsilon\,dc_\beta^1\,dc_\alpha$$

$$= \sum_{\substack{\beta=1\\\beta\neq\alpha}}^\nu\frac{1}{2}\,m_\alpha\int(\psi_\alpha - \psi_\alpha')\,(f_\alpha'f_\beta^{1\prime} - f_\alpha f_\beta^1)\,g^{\alpha\beta}\sigma_{\beta\alpha}\sin\theta_{\beta\alpha}\,d\theta_{\beta\alpha}\,d\varepsilon\,dc_\beta^1\,dc_\alpha$$

$$+ \frac{1}{4}\,m_\alpha\int(\psi_\alpha + \psi_\alpha^1 - \psi_\alpha' - \psi_\alpha^{1\prime})\,(f_\alpha'f_\alpha^{1\prime} - f_\alpha f_\alpha^1)\,g^{\alpha\alpha}\sigma_{\alpha\alpha}\sin\theta\,d\theta\,d\varepsilon\,dc_\alpha^1\,dc_\alpha. \tag{1.18.2}$$

The right hand side of (1.18) has been written in different versions:

The first form (1.18.1) will be used to calculate the collision integrals of the moments $m_{i_1\dots i_N}^\alpha$, whereas the expression (1.18.2) is suitable for considerations concerning the entropy production.

1.2.2 Collision Integrals

With $\psi_\alpha = c_{i_1}^\alpha\dots c_{i_N}^\alpha$ the integrals on the right hand side of (1.18) become

$$\mathscr{C}_{i_1\dots i_N}^{\alpha\beta} = m_\alpha\int(c_{i_1}^{\alpha\prime}\dots c_{i_N}^{\alpha\prime} - c_{i_1}^\alpha\dots c_{i_N}^\alpha)\,f_\alpha f_\beta^1 f_{\alpha\beta}\sin\theta_{\beta\alpha}\,d\theta_{\beta\alpha}\,d\varepsilon\,dc_\beta^1\,dc_\alpha.$$

Chapman and Cowling [4] describe a method for the calculation of these integrals.

Only a few collision integrals are of interest in this paper. These are listed below for Maxwellian molecules.

$$N = 0:\qquad\qquad \mathscr{C}^{\alpha\beta} = 0 \tag{1.19}$$

$$N = 1:\qquad\qquad \sum_{\beta=1}^\nu\mathscr{C}_i^{\alpha\beta} = \sum_{\beta=1}^{\nu-1}\overset{(1)}{R}_{\alpha\beta}(u_i^\beta - u_i^\nu) \tag{1.20.1}$$

$$\sum_{\alpha\beta=1}^\nu\mathscr{C}_i^{\alpha\beta} = 0 \qquad\qquad. \tag{1.20.2}$$

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[4] Derivation of the right hand sides see Chapman and Cowling [4, p. 64, 65].

$N = 2:$
(trace)
$$\sum_{\beta=1}^{\nu} \mathscr{C}_{ii}^{\alpha\beta} = \sum_{\beta=1}^{\nu} 2v_i{}^{\alpha}\mathscr{C}_i{}^{\alpha\beta} + \frac{1}{m_{\alpha}} \sum_{\beta\gamma\varepsilon=1}^{\nu} \overset{(2)}{\overline{R}}{}_{\alpha\beta}^{\gamma\varepsilon} u_i{}^{\gamma} u_i{}^{\varepsilon} \qquad (1.21.1)$$

$$\sum_{\alpha\beta=1}^{\nu} \mathscr{C}_{ii}^{\alpha\beta} = 0 \qquad (1.21.2)$$

$N = 2:$
(traceless part)
$$\begin{aligned}
\sum_{\beta=1}^{\nu} \mathscr{C}_{\langle ij\rangle}^{\alpha\beta} &= \sum_{\beta=1}^{\nu} \left(v_{\langle i}^{\alpha}\mathscr{C}_{j\rangle}^{\alpha\beta} + v_{\langle j}^{\alpha}\mathscr{C}_{i\rangle}^{\alpha\beta} \right) \\
&\quad + \frac{\varrho_{\alpha}}{m_{\alpha}} \sum_{\beta=1}^{\nu} \overset{(2)}{R}{}_{\alpha\beta} M_{\langle ij\rangle}^{\beta} + \frac{1}{m_{\alpha}} \sum_{\beta\gamma\varepsilon=1}^{\nu} \overset{(2)}{R}{}_{\alpha\beta}^{\gamma\varepsilon} u_{\langle i}^{\gamma} u_{j\rangle}^{\varepsilon} \qquad ^5
\end{aligned} \qquad (1.22)$$

$N = 3:$
(contracted)
$$\begin{aligned}
\sum_{\beta=1}^{\nu} \mathscr{C}_{ijj}^{\alpha\beta} &= \sum_{\beta=1}^{\nu} \left\{ 3v_{\langle j}^{\alpha}\mathscr{C}_{ij\rangle}^{\alpha\beta} - 3v_{\langle i}^{\alpha}v_j^{\alpha}\mathscr{C}_{j\rangle}^{\alpha\beta} + \frac{3}{\varrho_{\alpha}} M_{\langle ij}^{\alpha}\mathscr{C}_{j\rangle}^{\alpha\beta} \right\} \\
&\quad + \frac{\varrho_{\alpha}}{m_{\alpha}{}^2} \sum_{\beta=1}^{\nu} \overset{(3)}{R}{}_{\alpha\beta} M_{ijj}^{\beta} + \frac{\varrho_{\alpha}}{m_{\alpha}{}^2} \sum_{\beta\varepsilon=1}^{\nu} \overset{(3)}{R}{}_{\alpha\beta}^{\varepsilon} M_{\langle ij\rangle}^{\beta} u_j{}^{\varepsilon} \\
&\quad + \frac{1}{m_{\alpha}{}^2} \sum_{\beta\gamma\delta\varepsilon=1}^{\nu} \overset{(3)}{R}{}_{\alpha\beta}^{\gamma\delta\varepsilon} u_i{}^{\gamma} u_j{}^{\delta} u_j{}^{\varepsilon}.
\end{aligned} \qquad (1.23)$$

The matrices R whose definitions can be found in the appendix are functions of the partial densities $\varrho_1, \dots, \varrho_{\nu}$. $\overset{(1)}{R}{}_{\alpha\beta}$, $\overset{(2)}{\overline{R}}{}_{\alpha\beta}^{\gamma\varepsilon}$, $\overset{(2)}{R}{}_{\alpha\beta}$, $\overset{(2)}{R}{}_{\alpha\beta}^{\gamma\varepsilon}$ and $\overset{(3)}{R}{}_{\alpha\beta}$ are symmetric in α, β, whereas $\overset{(3)}{R}{}_{\alpha\beta}^{\varepsilon}$ and $\overset{(3)}{R}{}_{\alpha\beta}^{\gamma\delta\varepsilon}$ are antisymmetric in α, β.

1.2.3 Equations of Transfer for the Partial Moments $m_{i_1 \dots i_N}^{\alpha}$ and for Moments $m_{i_1 \dots i_N}$ of the Mixture

For $\psi_{\alpha} = c_{i_1}^{\alpha} \dots c_{i_N}^{\alpha}$ Eq. (1.18) becomes

$$\begin{aligned}
&\frac{\partial m_{i_1 \dots i_N}^{\alpha}}{\partial t} + \frac{\partial m_{n i_1 \dots i_N}^{\alpha}}{\partial x_n} - N m_{(i_1 \dots i_{N-1}}^{\alpha}(z_{i_N)} + f_{i_N)}) \\
&\quad - 2N m_{n(i_1 \dots i_{N-1}}^{\alpha} W_{i_N)n} = \sum_{\beta=1}^{\nu} \mathscr{C}_{i_1 \dots i_N}^{\alpha\beta},
\end{aligned} \qquad (1.24)$$

where it was necessary to split the inertial force $\underset{c}{i_i{}^{\alpha}}$ into two parts.

$$\underset{c}{i_i{}^{\alpha}} = z_i + 2W_{in} c_n{}^{\alpha},$$

i.e. into a part independent of the velocities $c_n{}^{\alpha}$ and a part depending on $c_n{}^{\alpha}$.

The sum over all α of (1.24) gives

$$\begin{aligned}
&\frac{\partial m_{i_1 \dots i_N}}{\partial t} + \frac{\partial m_{n i_1 \dots i_N}}{\partial x_n} - N m_{(i_1 \dots i_{N-1}}(z_{i_N)} + f_{i_N)}) \\
&\quad - 2m_{n(i_1 \dots i_{N-1}} W_{i_N)n} = \sum_{\alpha\beta=1}^{\nu} \mathscr{C}_{i_1 \dots i_N}^{\alpha\beta},
\end{aligned} \qquad (1.25)$$

where the definition (1.9) has been used.

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⁵ For the bracket notation see (1.8).

As an example we evaluate the Eqs. (1.24) and (1.25) for the case $N = 1$.

$$\frac{\partial \varrho_\alpha v_i^\alpha}{\partial t} + \frac{\partial m_{ij}^\alpha}{\partial x_j} - \varrho_\alpha(z_i + f_i) - 2W_{ij}v_j^\alpha = \sum_{\beta=1}^\nu \mathscr{C}_i^{\alpha\beta} \tag{1.26}$$

$$\frac{\partial \varrho v_i}{\partial t} + \frac{\partial m_{ij}}{\partial x_j} - \varrho(z_i + f_i) - 2W_{ij}v_j = 0. \tag{1.27}$$

We note that in (1.24) and (1.25) the two inertial terms z_i and W_{ij} appear. For the purposes of section 3.1.2 below it is appropriate to eliminate z_i and W_{ij} as far as this is possible. z_i may be eliminated from (1.24) and (1.25) by use of (1.26) and (1.27) respectively. W_{ij}, however, cannot be removed.

$$\frac{\partial m_{i_1 \ldots i_N}^\alpha}{\partial t} + \frac{\partial m_{n i_1 \ldots i_N}^\alpha}{\partial x_n} - N \frac{1}{\varrho_\alpha} m_{(i_1 \ldots i_{N-1}}^\alpha \left(\frac{\partial \varrho_\alpha v_{i_N)}^\alpha}{\partial t} + \frac{\partial m_{i_N)n}^\alpha}{\partial x_n} \right)$$
$$+ 2N(m_{(i_1 \ldots i_{N-1}}^\alpha W_{i_N)n}v_n^\alpha - m_{n(i_1 \ldots i_{N-1}}^\alpha W_{i_N)n}) \tag{1.28}$$
$$= \sum_{\beta=1}^\nu \left\{ \mathscr{C}_{i_1 \ldots i_N}^{\alpha\beta} - N \frac{1}{\varrho_\alpha} m_{(i_1 \ldots i_{N-1}}^\alpha \mathscr{C}_{i_N)}^{\alpha\beta} \right\}$$

$$\frac{\partial m_{i_1 \ldots i_N}}{\partial t} + \frac{\partial m_{n i_1 \ldots i_N}}{\partial x_n} - N \frac{1}{\varrho} m_{(i_1 \ldots i_{N-1}} \left(\frac{\partial \varrho v_{i_N)}}{\partial t} + \frac{\partial m_{i_N)n}}{\partial x_n} \right)$$
$$+ 2N(m_{(i_1 \ldots i_{N-1}} W_{i_N)n}v_n - m_{n(i_1 \ldots i_{N-1}} W_{i_N)n}) = \sum_{\alpha\beta=1}^\nu \mathscr{C}_{i_1 \ldots i_N}^{\alpha\beta}. \tag{1.29}$$

1.2.4 Equations of Balance of Masses, Momenta, Energies, Stresses and Heat Fluxes

For $N = 0$ through $N = 3$ the Eqs. (1.28), (1.29) contain the equations of balance of mass, momentum and energy of the constituents and of the mixture. These equations assume their most familiar form when we replace the moments $m_{i_1 \ldots i_N}^\alpha$ and $m_{i_1 \ldots i_N}$ by the corresponding central moments. In this way we get the following equations of balance:

$N = 0$: Conservation of the masses of constituent α and of the total mass

$$\frac{\partial \varrho_\alpha}{\partial t} + \frac{\partial \varrho_\alpha v_i^\alpha}{\partial x_i} = 0 \tag{1.30.1}$$

$$\frac{\partial \varrho}{\partial t} + \frac{\partial \varrho v_i}{\partial x_i} = 0. \tag{1.30.2}$$

$N = 1$: Balance of momentum of constituent α and conservation of total momentum

$$\frac{\partial \varrho_\alpha v_i^\alpha}{\partial t} + \frac{\partial(\varrho_\alpha v_i^\alpha v_j^\alpha + M_{ij}^\alpha)}{\partial x_j} - \varrho_\alpha(f_i + z_i + 2W_{ij}v_j^\alpha) = \sum_{\beta=1}^{\nu-1} \overset{(1)}{R}_{\alpha\beta}(u_i^\beta - u_i^\nu) \tag{1.31.1}$$

$$\frac{\partial \varrho v_i}{\partial t} + \frac{\partial(\varrho v_i v_j + M_{ij})}{\partial x_j} - \varrho(f_i + z_i + 2W_{ij}v_j) = 0. \tag{1.31.2}$$

$N = 2$: For $N = 2$ is convenient to write (1.28) and (1.29) in two parts, one for the trace and the other for the traceless part of the equation.

Trace: Balance of internal energy of constituent α and first law of thermo-dynamics.

$$\frac{\partial M_{ii}^{\alpha}}{\partial t} + \frac{\partial(M_{ii}^{\alpha}v_j^{\alpha} + M_{iij}^{\alpha})}{\partial x_j} + 2M_{ij}^{\alpha}\frac{\partial v_i^{\alpha}}{\partial x_j} = \sum_{\beta=1}^{\nu} \overset{(2)}{R}_{\alpha\beta}\varrho_{\beta}u_i^{\beta} \qquad (1.32.1)$$

$$\frac{\partial M_{ii}}{\partial t} + \frac{\partial(M_{ii}v_j + M_{iij})}{\partial x_j} + 2M_{ij}\frac{\partial v_i}{\partial \alpha_j} = 0. \qquad (1.32.2)$$

Traceless part: Balance of stress deviators of constituent α

$$\frac{\partial M_{\langle ij\rangle}^{\alpha}}{\partial t} + \frac{\partial(M_{\langle i\rangle j\rangle}^{\alpha}v_n^{\alpha} + M_{\langle ij\rangle n}^{\alpha})}{\partial x_n} + 2M_{n\langle\langle j}^{\alpha}\frac{\partial v_{i\rangle\rangle}^{\alpha}}{\partial x_n} - 4M_{n\langle\langle j}^{\alpha}W_{i\rangle\rangle n}$$
$$= \frac{\varrho_{\alpha}}{m_{\alpha}}\sum_{\beta=1}^{\nu}\overset{(2)}{R}_{\alpha\beta}M_{\langle ij\rangle}^{\beta} + \frac{1}{m_{\alpha}}\sum_{\beta\gamma\varepsilon=1}^{\nu}\overset{(2)}{R}_{\alpha\beta}^{\gamma\varepsilon}u_{\langle i}^{\gamma}u_{j\rangle}^{\varepsilon}. \qquad (1.33)$$

$N = 3$: Balance of heat fluxes of constituent α.

The only equation of interest among the balance equations for M_{ijk}^{α} is the one for the trace M_{ijj}^{α} since the other components have no interpretation in thermodynamics.

$$\frac{\partial M_{ijj}^{\alpha}}{\partial t} + \frac{\partial(M_{ijj}^{\alpha}v_n^{\alpha} + M_{ijjn}^{\alpha})}{\partial x_n} + 3M_{n\langle ij}^{\alpha}\frac{\partial v_{j\rangle}^{\alpha}}{\partial x_n} - \frac{3}{\varrho_{\alpha}}M_{\langle ij}^{\alpha}\frac{\partial M_{j\rangle n}^{\alpha}}{\partial x_n} - 2M_{njj}^{\alpha}W_{in}$$
$$= \frac{\varrho_{\alpha}}{m_{\alpha}^2}\sum_{\beta=1}^{\nu}\overset{(3)}{R}_{\alpha\beta}M_{ijj}^{\beta} + \frac{\varrho_{\alpha}}{m_{\alpha}^2}\sum_{\beta\varepsilon=1}^{\nu}\overset{(3)}{R}_{\alpha\beta}^{\varepsilon}u_i^{\varepsilon}M_{\langle ij\rangle}^{\beta} + \frac{1}{m_{\alpha}^2}\sum_{\beta\gamma\delta\varepsilon=1}^{\nu}\overset{(3)}{R}_{\alpha\beta}^{\gamma\delta\varepsilon}u_i^{\gamma}u_j^{\delta}u_j^{\varepsilon}. \qquad (1.34)$$

To obtain the relation (1.34) in the form given we have used the lower order equations of transfer (1.30), (1.32) and (1.33). Equations corresponding to (1.33) and (1.34) for the mixture are not needed.

1.2.5 Equations of Balance of Entropies of the Constituents and Entropy of the Mixture

If we choose for ψ_{α} the expression $-\dfrac{k}{m_{\alpha}}\ln f_{\alpha}$ and insert it into (1.18.2) we get

$$\frac{\partial \varrho_{\alpha}\eta_{\alpha}}{\partial t} + \frac{\partial(\varrho_{\alpha}\eta_{\alpha}v_i^{\alpha} + \phi_i^{\alpha})}{\partial x_i}$$
$$= \sum_{\substack{\beta=1\\\beta\neq\alpha}}^{\nu}\frac{1}{2}\,k\int\ln\frac{f_{\alpha}'}{f_{\alpha}}\,(f_{\alpha}'f_{\beta}^{1\prime} - f_{\alpha}f_{\beta}^1)\,g^{\alpha\beta}\sigma_{\beta\alpha}\sin\theta_{\beta\alpha}\,d\theta_{\beta\alpha}\,d\varepsilon\,dc_{\beta}^1\,dc_{\alpha} \qquad (1.35)$$
$$+ \frac{1}{4}\,k\int\ln\frac{f_{\alpha}'f_{\alpha}^{1\prime}}{f_{\alpha}f_{\alpha}^1}\,(f_{\alpha}'f_{\alpha}^{1\prime} - f_{\alpha}f_{\alpha}^1)\,g^{\alpha\alpha}\sigma_{\alpha\beta}\sin\theta\,d\theta\,d\varepsilon\,dc_{\alpha}^1\,dc_{\alpha},$$

with the quantities η_{α} and ϕ_i^{α} defined in (1.13.1) and (1.13.3). This equation represents the equation of balance of entropies of constituent α.

The total entropy balance for the mixture results from summing (1.35) over all α.

$$\frac{\partial\varrho\eta}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho\eta v_i + \sum_{\alpha=1}^{\nu}(\varrho_{\alpha}\eta_{\alpha}u_i^{\alpha} + \phi_i^{\alpha})\right) = \sigma, \qquad (1.36)$$

where inspection of the production term

$$\sigma = \sum_{\substack{\alpha\beta=1 \\ \alpha>\beta}}^{\nu} \frac{1}{2} k \int \ln \frac{f_\alpha{}' f_\beta{}^{1\prime}}{f_\alpha f_\beta{}^1} \left(f_\alpha{}' f_\beta{}^{1\prime} - f_\alpha f_\beta{}^{1\prime}\right) g^{\alpha\beta} \sigma_{\beta\alpha} \sin\theta_{\beta\alpha} \, d\theta_{\beta\alpha} \, d\varepsilon \, dc_\beta{}^1 \, dc_\alpha$$

$$+ \sum_{\alpha=1}^{\nu} \frac{1}{4} k \int \ln \frac{f_\alpha{}' f_\alpha{}^{1\prime}}{f_\alpha f_\alpha{}^1} \left(f_\alpha{}' f_\alpha{}^{1\prime} - f_\alpha f_\alpha{}^1\right) g^{\alpha\alpha} \sigma_{\alpha\alpha} \sin\theta \, d\theta \, d\varepsilon \, dc_\alpha{}^1 \, dc_\alpha \tag{1.37}$$

shows that σ is a positive quantity representing the entropy production in the mixture. This fact supports the view that η in (1.13.2) indeed represents the entropy.

From (1.36) it follows that

$$\phi_i = \sum_{\alpha=1}^{\nu} \left(\phi_i{}^\alpha + \varrho_\alpha \eta_\alpha u_i{}^\alpha\right) \tag{1.38}$$

must be defined as flux of entropy for the mixture.

In view of the discussion among thermodynamicists as to whether or not an entropy exists in non-equilibrium it is worthwhile to emphasize that the kinetic theory exhibits such an entropy.

2. Closure of Equations of Transfer and Thermodynamic Limit

2.1 Closure of Equations of Transfer

The equations of transfer (1.28) and (1.29) together with the collision integrals (1.19) through (1.23) form a system of differential equations for the moments $m_{i_1 \dots i_N}^\alpha$ and $m_{i_1 \dots i_N}$. However, in an equation of order N the moments $m_{i_1 \dots i_{N+1}}^\alpha$, $m_{i_1 \dots i_{N+1}}$ occur which are of order $N + 1$. One might calculate these higher order moments from the equations of transfer of the following order, but there appear moments of even higher order in those. Thus it happens that at no stage we have a closed system of equations and we shall proceed to describe possibilities for a closure.

In all cases the closure proceeds by "cutting off" equations of balance for higher moments. In the remaining equations the highest moments are approximated in terms of lower ones. In the following two sections this procedure is illustrated for two cases: Mixture of Eulerian Gases and Extended Irreversible Thermodynamics of Mixtures. In the first case we retain $4\nu + 1$ equations and in the second case we retain $12\nu + 1$ equations.

2.1.1 Mixture of Eulerian Gases. A Closed System of $4\nu + 1$ Equations

The easiest method of closure places the cut behind the first $4\nu + 1$ equations viz. (1.30), (1.31) and (1.32.2). It proceeds by calculating the highest moments M_{ij}^α and M_{ijj} from the Maxwellian equilibrium distribution (1.14). Thus the procedure provides a closed system of equations for the determination of ϱ_α, v_i^α, and T.

Of course, this method is very rough, but we present the results in order to have a comparison with a more accurate technique described in the next section.

For M_{ij}^α and M_{ijj} we obtain with the Maxwellian distribution (1.14)

$$M_{ij}^\alpha = \varrho_\alpha \frac{kT}{m_\alpha}\, \delta_{ij}, \tag{2.1.1}$$

$$M_{ij} = \sum_{\alpha=1}^{\nu} \left(\varrho_\alpha \frac{kT}{m_\alpha}\, \delta_{ij} + \varrho_\alpha u_i^\alpha u_j^\alpha \right), \tag{2.1.2}$$

$$M_{iij} = \sum_{\alpha=1}^{\nu} \left(5\varrho_\alpha \frac{kT}{m_\alpha}\, u_i^\alpha + \varrho_\alpha u_\alpha^{\,2} u_i^\alpha \right). \tag{2.1.3}$$

Insertion of these results into (1.31) and (1.32.2) closes the system of equations. It can be rewritten in the following form in which the Eqs. (1.16) and (1.17.2) for p_α, ε_α and μ_α have been used for the benefit of those who are familiar with the equations of macroscopic mixture theories.

$N = 0$:

$$\frac{dc_\alpha}{dt} + \frac{1}{\varrho}\, \frac{\partial \varrho_\alpha u_i^\alpha}{\partial x_i} = 0, \qquad \alpha = 1, \ldots, \nu - 1 \tag{2.2.1}$$

$$\frac{\partial \varrho}{\partial t} + \frac{\partial \varrho v_i}{\partial x_i} = 0. \tag{2.2.2}$$

$N = 1$:

$$\left[\delta_{ij} \frac{d}{dt} + \frac{\partial v_i}{\partial x_j} - 2 W_{ij} \right] (u_i^\alpha - u_i^\nu) + u_j^\alpha \frac{\partial u_i^\alpha}{\partial x_j} - u_j^\nu \frac{\partial u_i^\nu}{\partial x_j}$$

$$+ \left\{ T \frac{\partial \dfrac{\mu^\alpha - \mu^\nu}{T}}{\partial x_i} - T \left(\varepsilon_\alpha + \frac{p_\alpha}{\varrho_\alpha} - \varepsilon_\nu - \frac{p_\nu}{\varrho_\nu} \right) \frac{\partial \dfrac{1}{T}}{\partial x_i} \right\} = \sum_{\beta=1}^{\nu-1} \overset{(1)}{\bar{R}}_{\alpha\beta} \varrho_\beta u_i^\beta, \tag{2.3.1}$$

$$\alpha = 1, \ldots, \nu - 1$$

$$\frac{\partial \varrho v_i}{\partial t} + \frac{\partial \left(\varrho v_i v_j + \sum\limits_{\alpha=1}^{\nu} (p_\alpha \delta_{ij} + \varrho_\alpha u_i^\alpha u_j^\alpha) \right)}{\partial x_j} - \varrho(f_i + z_i + 2 W_{ij} v_j) = 0. \tag{2.3.2}$$

$N = 2$: (trace, mixture)

$$\frac{\partial \sum\limits_{\alpha=1}^{\nu} \varrho_\alpha \left(\varepsilon_\alpha + \frac{1}{2}\, u_\alpha^{\,2} \right)}{\partial t} + \frac{\partial \sum\limits_{\alpha=1}^{\nu} \left(\varrho_\alpha \left(\varepsilon_\alpha + \frac{1}{2}\, u_\alpha^{\,2} \right) v_n + \varrho_\alpha \left(\varepsilon_\alpha + \frac{1}{2}\, u_\alpha^{\,2} + \frac{p_\alpha}{\varrho_\alpha} \right) u_n^\alpha \right)}{\partial x_n}$$

$$+ \sum_{\alpha=1}^{\nu} (p_\alpha \delta_{ij} + \varrho_\alpha u_i^\alpha u_j^\alpha) \frac{\partial v_i}{\partial x_j} = 0. \tag{2.4}$$

$c_\alpha := \dfrac{\varrho_\alpha}{\varrho}$ denotes the concentration of constituent α, $\overset{(1)}{\bar{R}}_{\alpha\beta} := \sum\limits_{\gamma\varepsilon=1}^{\nu-1} r_{\alpha\gamma} \overset{(1)}{R}_{\gamma\varepsilon} r_{\varepsilon\beta}$ and $r_{\alpha\beta} := \dfrac{\delta_{\alpha\beta}}{\varrho_\beta} + \dfrac{1}{\varrho_\nu}$ are symmetric matrices depending on the partial densities $\varrho_1, \ldots, \varrho_\nu$. $\dfrac{d}{dt} = \dfrac{\partial}{\partial t} + v_i \dfrac{\partial}{\partial x_i}$ stands for the material time derivative with respect to the barycentric motion.

The balance Eqs. (2.2) for the masses are unaffected by the closure procedure.

The Eqs. (2.2.1) through (2.4) form a closed system of differential equations for the $4\nu + 1$ fields

$$\varrho,\ c_1,\ ...,\ c_{\nu-1},\ v_i,\ u_i{}^1,\ ...\ u_i{}^{\nu-1},\ T$$

in an ideal gas.

2.1.2 Grad's Distribution. A Closed System of $12\nu + 1$ Equations (Extended Irreversible Thermodynamics [10])

A method of closure somewhat more elaborate places the cut behind the first $12\nu + 1$ equations, viz. (1.30), (1.31) and (1.32.2) (1.33), (1.34). It proceeds by calculating the highest moments M_{ijn}^α and M_{ijjn}^α from a Grad distribution, by which M_{ijn}^α and M_{ijjn}^α are related to moments of lower order.

The Grad distribution represents the beginning of an expansion of f_α in terms of Hermite polynomials (see [8], [9]). The expansion starts from an equilibrium state. It reads

$$f_G{}^\alpha = f_M{}^\alpha(1 + \varphi), \tag{2.5}$$

where φ abbreviates the expression

$$\begin{aligned}
\varphi = {}&-\frac{1}{2}\frac{m_\alpha}{kT}\,u_\alpha{}^2 + \frac{1}{2\varrho_\alpha}\left(\frac{m_\alpha}{kT}\right)^2 M_{\langle ij\rangle}^\alpha G_i{}^\alpha G_j{}^\alpha + \frac{1}{2}\left(\frac{m_\alpha}{kT}\right)^2 u_i{}^\alpha u_j{}^\alpha G_i{}^\alpha G_j{}^\alpha \\
&+ \frac{1}{2}\frac{m_\alpha}{kT}\left(7 - \frac{m_\alpha}{kT}\,G_\alpha{}^2\right)u_i{}^\alpha G_i{}^\alpha - \frac{1}{2\varrho_\alpha}\left(\frac{m_\alpha}{kT}\right)^2 Z_i{}^\alpha G_i{}^\alpha\left(1 - \frac{1}{5}\frac{m_\alpha}{kT}\,G_\alpha{}^2\right).
\end{aligned} \tag{2.6}$$

$G_i{}^\alpha$ and $Z_i{}^\alpha$ in (2.6) are defined by $G_i{}^\alpha := c_i{}^\alpha - v_i{}^\alpha$ and

$$Z_i{}^\alpha := M_{ijj}^\alpha + 2M_{\langle ij\rangle}^\alpha u_j{}^\alpha + 5\varrho_\alpha\frac{kT}{m_\alpha}\,u_i{}^\alpha + \varrho_\alpha u_i{}^\alpha u_\alpha{}^2. \tag{2.7}$$

From now on all terms of quadratic or higher order in the quantities $u_i{}^\alpha$, $M_{\langle ij\rangle}^\alpha$, $\dfrac{\partial v_{\langle i}}{\partial x_{j\rangle}}$, M_{ijj}^α which all vanish in an equilibrium state described by (1.14) are dropped. This is admissible in the neighbourhood of equilibrium. Note that $\dfrac{\partial v_{[i}}{\partial x_{j]}}$, the antisymmetric part of the velocity gradient, need not vanish in equilibrium, nor does $\dfrac{\partial v_l}{\partial x_l}$ necessarily vanish. With (2.5), (2.6) we get for the higher order moments

$$M_{ijn}^\alpha = \frac{3}{5}\,M_{ll\langle i}^\alpha\delta_{jn\rangle} \tag{2.8.1}$$

$$M_{ijjn}^\alpha = 5\varrho_\alpha\left(\frac{kT}{m_\alpha}\right)^2\delta_{in} + 7\frac{kT}{m_\alpha}\,M_{\langle in\rangle}^\alpha. \tag{2.8.2}$$

Insertion of these into (1.33) and (1.34) closes the system of equations which then reads

$N = 0$:

$$\frac{dc_\alpha}{dt} + \frac{1}{\varrho}\frac{\partial\varrho_\alpha u_i{}^\alpha}{\partial x_i} = 0, \qquad \alpha = 1, ..., \nu - 1 \tag{2.9.1}$$

$$\frac{\partial\varrho}{\partial t} + \frac{\partial\varrho v_i}{\partial x_i} = 0. \tag{2.9.2}$$

$N = 1$:

$$\left\{ T \frac{\partial \frac{\mu^\alpha - \mu^\nu}{T}}{\partial x_i} - T \left(\varepsilon_\alpha + \frac{p_\alpha}{\varrho_\alpha} - \left(\varepsilon_\nu + \frac{p_\nu}{\varrho_\nu} \right) \right) \frac{\partial \frac{1}{T}}{\partial x_i} \right\}$$

$$+ \left\{ \delta_{ij} \frac{d}{dt} + \frac{\partial v_{[i}}{\partial x_{j]}} - 2 W_{ij} \right\} (u_i{}^\alpha - u_i{}^\nu) + \frac{1}{3} (u_i{}^\alpha - u_i{}^\nu) \frac{\partial v_l}{\partial x_l} \qquad (2.10.1)$$

$$+ \frac{1}{\varrho_\alpha} \frac{\partial M^\alpha_{\langle ij \rangle}}{\partial x_j} - \frac{1}{\varrho_\nu} \frac{\partial M^\nu_{\langle ij \rangle}}{\partial x_j} = \sum_{\beta=1}^{\nu-1} \overset{(1)}{\overline{R}}_{\alpha\beta\varrho\beta} u_i{}^\beta$$

$$\frac{\partial \varrho v_i}{\partial t} + \frac{\partial \left(\varrho v_i v_j + \sum_{\alpha=1}^\nu (p_\alpha \delta_{ij} + M^\alpha_{\langle ij \rangle}) \right)}{d x_j} - \varrho(f_i + z_i + 2 W_{ij} v_j) = 0. \qquad (2.10.2)$$

$N = 2$: (trace, mixture)

$$\frac{\partial \sum\limits_{\alpha=1}^\nu \varrho_\alpha \varepsilon_\alpha}{\partial t} + \frac{\partial \left(\sum\limits_{\alpha=1}^\nu \left(\varrho_\alpha \varepsilon_\alpha v_n + \varrho_\alpha \left(\varepsilon_\alpha + \frac{p_\alpha}{\varrho_\alpha} \right) u_n{}^\alpha + \frac{1}{2} M^\alpha_{njj} \right) \right)}{\partial x_n}$$

$$+ \sum_{\alpha=1}^\nu (p_\alpha \delta_{jn} + M^\alpha_{\langle jn \rangle}) \frac{\partial v_j}{\partial x_n} = 0. \qquad (2.11)$$

$N = 2$: (traceless part, constituent α)

$$\frac{\varrho_\alpha}{m_\alpha} \left\{ 2kT \left(\frac{\partial v^\alpha_{\langle i}}{\partial x_{j \rangle}} - \frac{1}{3} \frac{\partial v_l{}^\alpha}{\partial x_l} \delta_{ij} \right) \right\}$$

$$+ \left\{ \delta_{in} \delta_{jm} \frac{d}{dt} + \delta_{jm} \left(\frac{\partial v_{[i}}{\partial x_{n]}} - 2 W_{in} \right) + \delta_{im} \left(\frac{\partial v_{[j}}{\partial x_{n]}} - 2 W_{jn} \right) \right\} M^\alpha_{\langle nm \rangle} \qquad (2.12)$$

$$+ \frac{5}{3} M^\alpha_{\langle ij \rangle} \frac{\partial v_n}{\partial x_n} + \frac{2}{5} \frac{\partial M^\alpha_{ll \langle i}}{\partial x_{j \rangle}} = \frac{\varrho_\alpha}{m_\alpha} \sum_{\beta=1}^\nu \overset{(2)}{R}_{\alpha\beta} M^\beta_{\langle ij \rangle}.$$

$N = 3$: (contracted, constituent α)

$$\frac{\varrho_\alpha}{m_\alpha{}^2} \left\{ -5 k^2 T^3 \frac{\partial \frac{1}{T}}{\partial x_i} \right\} + \left\{ \delta_{in} \frac{d}{dt} + \frac{\partial v_{[i}}{\partial x_{n]}} - 2 W_{in} \right\} M^\alpha_{njj}$$

$$+ 2 M^\alpha_{ijj} \frac{\partial v_n}{\partial x_n} + 5 \frac{k}{m_\alpha} M^\alpha_{\langle in \rangle} \frac{\partial T}{\partial x_n} + 2 \frac{kT}{m_\alpha} \frac{\partial M^\alpha_{\langle in \rangle}}{\partial x_n} \qquad (2.13)$$

$$- \frac{2}{\varrho_\alpha} M^\alpha_{\langle in \rangle} \frac{kT}{m_\alpha} \frac{\partial \varrho_\alpha}{\partial x_n} = \frac{\varrho_\alpha}{m_\alpha{}^2} \sum_{\beta=1}^\nu \overset{(3)}{R}_{\alpha\beta} M^\beta_{ijj}.$$

The balance Eqs. (2.9), (2.10) and (2.11) for the masses and momenta of the constituents and for the energy of the mixture are unaffected by the closure procedure.

The Eqs. (2.9) through (2.13) represent a closed system of differential equations for the $12\nu + 1$ fields

$$\varrho, c_1, \ldots c_{\nu-1}, v_i, u_i{}^1, \ldots u_i{}^{\nu-1}, T, M^\alpha_{\langle ij \rangle}, M^\alpha_{ijj} \qquad (2.14)$$

in an ideal gas.

For a single fluid a phenomenological theory with stress and heat flux as variables was formulated in [10] and called Extended Linear Irreversible Thermodynamics. The equations of that theory are similar to (2.9) through (2.13) and they predicted finite speeds for all waves. This is also true for the present system of equations was we proceed to show.

2.1.3 Finite Speeds for Diffusion, Shear Waves and Heat Conduction

The aim of this section is to investigate the propagation speeds of disturbances of concentration, temperature and velocity. For this purpose we consider special cases in order to uncouple the system of differential Eqs. (2.9) through (2.13) so that we may deal with separate equations for c_α, u_i^α, T. These equations will prove to be of hyperbolis type having wave solutions with finite speeds.

Diffusion

Here we consider the special case of a binary mixture with

$$\varrho = \text{const.}, \quad v_i = 0, \quad M^\alpha_{\langle ij\rangle} = 0, \quad T = \text{const.}, \quad W_{ij} = 0. \qquad (2.15)$$

Moreover we neglect terms which are non-linear in u_i^α and derivatives of ϱ_α and μ_α.

We eliminate the diffusion velocities between (2.9.1) and (2.10.1) and obtain an equation for c_1 alone, viz.

$$-\frac{\varrho^2}{\varrho_1\varrho_2}\frac{\partial^2 c_1}{\partial t^2} + \frac{\partial(\mu^2 - \mu^1)}{\partial c_1}\frac{\partial^2 c_1}{\partial x_i\,\partial x_i} + \overset{(1)}{R}_{11}\varrho\,\frac{\partial c_1}{\partial t} = 0. \qquad (2.16)$$

Since, by (1.17.2), $\dfrac{\partial(\mu^2 - \mu^1)}{\partial c_1} > 0$ this equation is of hyperbolic type and predicts the propagation of disturbances of c_1 with the maximum speed

$$V_c = \sqrt{\frac{\varrho_1\varrho_2}{\varrho^2}\frac{\partial(\mu^2 - \mu^1)}{\partial c_1}}.$$

Shear Waves

For a single gas with

$$\varrho = \text{const.}, \quad T = \text{const.}, \quad M_{ijj} = 0, \quad W_{ij} = 0,$$
$$z_i = 0, \quad f_i = 0, \quad v_i = \big(v(y), 0, 0\big) \qquad (2.17)$$

we neglect terms non-linear in $M_{\langle ij\rangle}$ and v_i and eliminate $M_{\langle ij\rangle}$ between (2.10.2) and (2.12), thus obtaining another hyperbolic equation

$$-\frac{\partial^2 v}{\partial t^2} + \frac{kT}{m}\frac{\partial^2 v}{\partial y^2} + \frac{\varrho}{m}\overset{(2)}{R}\,\frac{\partial v}{\partial t} = 0. \qquad (2.18)$$

This equation describes the propagation of shear waves with the maximum speed

$$V_v = \sqrt{\frac{kT}{m}}.$$

Heat Waves

For a single fluid with

$$\varrho = \text{const.}, \qquad v_i = 0, \qquad W_{ij} = 0, \qquad M_{\langle ij \rangle} = 0 \qquad (2.19)$$

the Eqs. (2.11) and (2.13) may be combined to form a hyperbolic differential equation for T by elimination of M_{ijj}.

$$-\frac{\partial^2 T}{\partial t^2} + \frac{5}{3}\frac{k}{m}T\frac{\partial^2 T}{\partial x_i \partial x_i} + \frac{\varrho}{m^2}\overset{(3)}{R}\frac{\partial T}{\partial t} = 0. \qquad (2.20)$$

In (2.20) products of gradients of T have been neglected. This equation describes the propagation of a heat wave with the maximum speed

$$V_T = \sqrt{\frac{5}{3}\frac{kT}{m}}.$$

A careful analysis of the coupled system (2.9) through (2.13) also shows finite speeds of diffusion, shear waves and heat waves. The above Eqs. (2.16), (2.18) and (2.20) are merely supposed to illustrate this point and for this illustration we have enforced uncoupled equations by the assumptions (2.15), (2.17), (2.19) that would be quite impossible to realize in a gas.

In this context it is instructive to look back upon the case of a mixture of Eulerian gases which was described by the Eqs. (2.2) through (2.4) in Section 2.1.1. In that case the differential equation for the concentration c_1 turns out to be identical to (2.16). Thus we have finite wave speed of diffusion in Eulerian gases. However, since in those gases $M_{\langle ij \rangle}^\alpha = 0$, $M_{ijj}^\alpha = 0$ it is not possible to have shear waves or heat waves.

2.1.4 Discussion of Complexity of System. Thermodynamic Limit

It is true that, by (2.9) through (2.13) we have an explicit set of field equations for the $12\nu + 1$ variables ϱ_α, v_i^α, T, $M_{\langle ij \rangle}^\alpha$, M_{ijj}^α. The set of equations is hyperbolic and yields finite speeds as we have seen. However, it represents a more elaborate theory than thermodynamics, because thermodynamics is a field theory of only the $\nu + 4$ fields ϱ_α, v_i, and T[6]. In view of the difficulties of defining boundary values for $M_{\langle ij \rangle}^\alpha$ and M_{ijj}^α in the extended theory, and in view of the difficulties of solving the Eqs. (2.9) through (2.13), we wish to go back to thermodynamics proper. This may be done by relying on the balance laws (2.9), (2.10.2) and (2.11) and by making them into field equations for ϱ_α, v_i, and T by means of the formulation of constitutive equations for the diffusion fluxes $\varrho_\alpha u_i^\alpha$, the partial stress deviators $M_{\langle ij \rangle}^\alpha$ and the partial heat fluxes $\frac{1}{2}M_{ijj}^\alpha$. Such constitutive equations relate $\varrho_\alpha u_i^\alpha$, $M_{\langle ij \rangle}^\alpha$, M_{ijj}^α to the fields of ϱ_α, v_i, and T.

---

[6] Linear irreversible thermodynamics as described in [11] and [12] conforms exactly to this description. In contrast to this, rational thermodynamics of mixtures is a theory of the $4\nu + 1$ fields ϱ_α, v_i^α, and T based on the Eqs. (2.9) through (2.11), and it formulates constitutive relations for $M_{\langle ij \rangle}^\alpha$ and $\sum_{\alpha=1}^{\nu} M_{ijj}^\alpha$ (see [13]).

The formulation of constitutive equations in the kinetic theory is based upon the equations of transfer (2.10.1), (2.12) and (2.13) and makes use of an iterative scheme which we proceed to describe.

2.2 Iteration within the Closed System of 12ν + 1 Equations

2.2.1 Description of Iteration and First and Second Iterates

We construct thermodynamic constitutive equations for $\varrho_\alpha u_i^\alpha$, $M^\alpha_{\langle ij\rangle}$ and M^α_{ijj} from the Eqs. (2.10.1), (2.12), and (2.13) by an iteration as follows:

On the left hand side of (2.10.1), (2.12), and (2.13) we calculate all moments by use of the Maxwellian distribution (1.14) and thus obtain a first iterate each for $\varrho_\alpha u_i^\alpha$, $M^\alpha_{\langle ij\rangle}$, and M^α_{ijj}:

$$\overset{(1)}{\varrho_\alpha u_i^\alpha} = \sum_{\beta=1}^{\nu} \overset{(1)}{(\overline{R}^{-1})}_{\alpha\beta} \left\{ T\, \frac{\partial \frac{\mu^\beta}{T}}{\partial x_i} - T\left(\varepsilon_\beta + \frac{p_\beta}{\varrho_\beta}\right) \frac{\partial \frac{1}{T}}{\partial x_i} \right\} \tag{2.21.1}$$

$$\overset{(1)}{M^\alpha_{\langle ij\rangle}} = \sum_{\beta=1}^{\nu} \overset{(2)}{(\overline{R}^{-1})}_{\alpha\beta} \left\{ 2kT \left(\frac{\partial v_{\langle i}}{\partial x_{j\rangle}} - \frac{1}{3}\frac{\partial v_l}{\partial x_l}\,\delta_{ij} \right) \right\} \quad (\alpha = 1, \ldots, \nu) \tag{2.21.2}$$

$$\overset{(1)}{M^\alpha_{ijj}} = \sum_{\beta=1}^{\nu} \overset{(3)}{(\overline{R}^{-1})}_{\alpha\beta} \left\{ -5k^2T^3\, \frac{\partial \frac{1}{T}}{\partial x_i} \right\} \quad (\alpha = 1, \ldots, \nu). \tag{2.21.3}$$

By (1.12.5) and (1.11.2) we have $q_i = \sum_{\alpha=1}^{\nu} \left(\frac{1}{2} M^\alpha_{ijj} + \frac{5}{2}\,\varrho_\alpha\,\frac{kT}{m_\alpha}\,u_i^\alpha + \varrho_\alpha\beta_\alpha u_i^\alpha \right)$ in the present linear theory. Hence the first iterate for the flux of internal energy of the mixture reads

$$\overset{(1)}{q_i} = \sum_{\alpha\beta=1}^{\nu} \overset{(1)}{(\overline{R}^{-1})}_{\alpha\beta} \left(\frac{5}{2}\,\frac{kT}{m_\alpha} + \beta_\alpha \right) T\, \frac{\partial \frac{\mu^\beta}{T}}{\partial x_i} + \overset{(1)}{\varkappa}\, \frac{\partial \frac{1}{T}}{\partial \partial_i}, \tag{2.21.4}$$

where $\overset{(1)}{\varkappa}$ abbreviates the expression

$$\overset{(1)}{\varkappa} := -\sum_{\alpha\beta=1}^{\nu} T \left(\overset{(3)}{(\overline{R}^{-1})}_{\alpha\beta}\, \frac{5}{2}\,(kT)^2 + \overset{(1)}{(\overline{R}^{-1})}_{\alpha\beta} \left(\varepsilon_\alpha + \frac{p_\alpha}{\varrho_\alpha}\right)\left(\varepsilon_\beta + \frac{p_\beta}{\varrho_\beta}\right) \right).$$

In (2.21.1) the original matrix $\overset{(1)}{(\overline{R}^{-1})}_{\alpha\beta}$ of $(\nu-1)^2$ elements was enlarged to contain a νth line and row, viz.

$$\overset{(1)}{(\overline{R}^{-1})}_{\nu\beta} := -\sum_{\gamma=1}^{\nu-1} \overset{(1)}{(\overline{R}^{-1})}_{\gamma\beta} \qquad (\beta = 1, \ldots, \nu-1)$$

and

$$\overset{(1)}{(\overline{R}^{-1})}_{\alpha\nu} := -\sum_{\beta=1}^{\nu-1} \overset{(1)}{(\overline{R}^{-1})}_{\alpha\beta} \qquad (\alpha = 1, \ldots, \nu). \tag{2.22}$$

Thus Eq. (2.21.1) is valid for all α from 1 through ν.

The next step proceeds by inserting the first iterates (2.21) of the moments into the left hand sides of (2.10.1), (2.12), and (2.13). Thus we get second iterates

for $\varrho_\alpha u_i{}^\alpha$, $M^\alpha_{\langle ij\rangle}$ and M^α_{ijj}. For easy notation we define the abbreviations

$$A_i{}^\alpha = \left\{ T \frac{\partial \frac{\mu^\alpha}{T}}{\partial x_i} - T \left(\varepsilon^\alpha + \frac{n^\alpha}{\varrho_\alpha} \right) \frac{\partial \frac{1}{T}}{\partial x_i} \right\}$$

$$E_{ij} = \frac{\partial v_{\langle i}}{\partial x_{j\rangle}} - \frac{1}{3} \frac{\partial v_l}{\partial x_l} \delta_{ij}$$

$$E = \frac{\partial v_n}{\partial x_n}$$

and obtain

$$\varrho_\alpha \overset{(2)}{u}_i{}^\alpha = \sum_{\beta=1}^\nu \overset{(1)}{\bar{R}}{}^{-1}_{\alpha\beta} \left[A_i{}^\beta + \left\{ \delta_{ij} \frac{d}{dt} + \frac{\partial v_{[i}}{\partial x_{j]}} - 2W_{ij} \right\} \frac{1}{\varrho_\beta} \sum_{\beta=1}^\nu (\overset{(1)}{\bar{R}}{}^{-1})_{\beta\gamma} A_j{}^\gamma \right.$$
$$\left. + \frac{1}{3} E \frac{1}{\varrho_\beta} \sum_{\gamma=1}^\nu (\overset{(1)}{\bar{R}}{}^{-1})_{\beta\gamma} A_i{}^\gamma + \frac{1}{\varrho_\beta} \frac{\partial}{\partial x_j} \left(\sum_{\gamma=1}^\nu \overset{(1)}{\bar{R}}{}^{-1}_{\beta\gamma} 2kT E_{ij} \right) \right], \tag{2.23.1}$$

$$\overset{(2)}{M}^\alpha_{\langle ij\rangle} = \sum_{\beta=1}^\nu (\overset{(2)}{R}{}^{-1})_{\alpha\beta} \left[\left\{ 2kT E_{ij} + 2kT \frac{\partial}{\partial x_{\langle j}} \left(\sum_{\gamma=1}^\nu \frac{1}{\varrho_\beta} (\overset{(1)}{\bar{R}}{}^{-1})_{\beta\gamma} A^\alpha_{i\rangle} \right) \right\} \right.$$
$$+ \frac{m_\beta}{\varrho_\beta} \left\{ \delta_{in}\delta_{jm} \frac{d}{dt} + \delta_{im} \left(\frac{\partial v_{[j}}{\partial x_{n]}} - 2W_{jn} \right) + \delta_{jm} \left(\frac{\partial v_{[i}}{\partial x_{n]}} - 2W_{in} \right) \right\}$$
$$\cdot \sum_{\gamma=1}^\nu (\overset{(2)}{R}{}^{-1})_{\beta\gamma} 2kT E_{ij} + \frac{5}{3} E \sum_{\gamma=1}^\nu \frac{m_\beta}{\varrho_\beta} (\overset{(2)}{R}{}^{-1})_{\beta\gamma} 2kT E_{ij} \tag{2.23.2}$$
$$\left. - \frac{2}{5} \frac{m_\beta}{\varrho_\beta} \frac{\partial}{\partial x_{\langle j}} \left(\sum_{\gamma=1}^\nu (\overset{(3)}{R}{}^{-1})_{\beta\gamma} 5k^2 T^3 \frac{\partial \frac{1}{T}}{\partial x_{i\rangle}} \right) \right],$$

$$\overset{(2)}{M}^\alpha_{ijj} = \sum_{\beta=1}^\nu (\overset{(3)}{R}{}^{-1})_{\alpha\beta} \left[\left[\left\{ -5k^2 T^3 \frac{\partial \frac{1}{T}}{\partial x_i} \right\} + \left\{ \delta_{in} \frac{d}{dt} + \frac{\partial v_{[i}}{\partial x_{n]}} - 2W_{in} \right\} \right. \right.$$
$$\cdot \frac{m_\beta{}^2}{\varrho_\beta} \sum_{\gamma=1}^\nu (\overset{(3)}{R}{}^{-1})_{\beta\gamma} \left(-5k^2 T^3 \frac{\partial \frac{1}{T}}{\partial x_n} \right)$$
$$+ \frac{m_\beta{}^2}{\varrho_\beta} \left\{ 2E \sum_{\gamma=1}^\nu (\overset{(3)}{R}{}^{-1})_{\beta\gamma} \left(-5k^2 T^3 \frac{\partial \frac{1}{T}}{\partial x_i} \right) \right.$$
$$+ \frac{2kT}{m_\beta} \frac{\partial}{\partial x_n} \left(\sum_{\gamma=1}^\nu (\overset{(2)}{R}{}^{-1})_{\beta\gamma} 2kT E_{in} \right) + 5 \sum_{\gamma=1}^\nu (\overset{(2)}{R}{}^{-1})_{\beta\gamma} 2kT E_{in} \frac{k}{m_\beta} \frac{\partial T}{\partial x_n} \tag{2.23.3}$$
$$\left. \left. \left. - \frac{2}{\varrho_\beta} \frac{kT}{m_\beta} \sum_{\gamma=1}^\nu (\overset{(2)}{R}{}^{-1})_{\beta\gamma} 2kT E_{in} \frac{\partial \varrho_\beta}{\partial x_n} \right\} \right] \right].$$

The flux of internal energy of the mixture is calculated in this step just as it was done in the first step; in the present case q_i (or rather $\overset{(2)}{q}_i$) is given by a very long expression which we do not list here. Later, in Section 3.2.2 a truncated form of this expression will be discussed.

Both the first and second iterates (2.21) and (2.23) are equations of the general form of the constitutive equations of thermodynamics. That is to say that the diffusion fluxes, the stresses and the heat flux are related to the thermodynamic fields ϱ_α, v_i and T. Some properties of flux constitutive relations will be discussed in the next chapter.

2.2.2 Critique of Iterative Scheme

The iterative scheme described above is akin to the Maxwellian iteration which has been used to construct constitutive relations for stress and heat flux in single fluids by Ikenberry and Truesdell [14]. This Maxwellian iteration does not use the Grad distribution rather it works on the exact equations of transfer for moments and more and more equations are drawn into the scheme as the iteration progresses. In this respect the Maxwellian iteration is more systematic than the one presented here. However, the present method is simple and it yields all terms of qualitative significance which we wish to discuss here.

We recall that the closed system (2.9) through (2.13) furnished finite speeds for diffusion, shear waves and heat conduction. The iteration destroys this feature; indeed, if the constitutive relations (2.21), or (2.23) are introduced into the equations of balance (2.9) through (2.11) we obtain a set of parabolic equations which predicts infinite speeds. This feature is common to all iterative schemes that lead to thermodynamic constitutive relations, in particular, the Maxwellian iteration and the Chapman-Enskog method share this deficiency.

3. Implications on Thermodynamics

3.1 Results of First Step of Iteration

3.1.1 Laws of Fick, Navier-Stokes and Fourier

The results of the first iterative step (2.21.1, 2, 4) represent the phenomenological equations of Fick (generalized) for diffusion, of Navier-Stokes for stress and of Fourier (generalized) for heat flux.

We can identify the following phenomenological quantities:

matrix of diffusion coefficients: $(\overset{(1)}{R}{}^{-1})_{\alpha\beta}\, T$

heat conductivity: $-\sum\limits_{\alpha\beta=1}^{\nu} T\left((\overset{(3)}{R}{}^{-1})_{\alpha\beta}\frac{5}{2}\,(kT)^2 + (\overset{(1)}{R}{}^{-1})_{\alpha\beta}\left(\varepsilon_\alpha + \frac{p_\alpha}{\varrho_\alpha}\right)\left(\varepsilon_\beta + \frac{p_\beta}{\varrho_\beta}\right)\right)$

thermo-diffusion coefficient: $-T \sum\limits_{\beta=1}^{\nu}\left(\varepsilon_\beta + \frac{p_\beta}{\varrho_\beta}\right)(\overset{(1)}{R}{}^{-1})_{\alpha\beta}$

diffusion-thermo coefficient: $-T \sum\limits_{\alpha=1}^{\nu}\left(\varepsilon_\alpha + \frac{p_\alpha}{\varrho_\alpha}\right)(\overset{(1)}{R}{}^{-1})_{\alpha\beta}$

viscosity of constituent α: $2kT \sum\limits_{\beta=1}^{\nu} (\overset{(2)}{R}{}^{-1})_{\alpha\beta}$.

The Eqs. (2.21.1, 2, 4) are of the form that linear irreversible thermodynamics assumes for the constitutive relations of diffusion fluxes, stress deviators, and heat flux.

3.1.2 Material Frame Indifference, Onsager Relations and Infinite Speeds

Frame Indifference

The principle of material objectivity requires that the constitutive functions for the diffusion fluxes, stress and heat flux are independent of the frame of reference. This is indeed the case for the results of the first iterative step, since no terms depending on the observer frame appear in (2.21).

Onsager Relations for Diffusion and Thermal Diffusion

The Eqs. (2.21.1, 4) may be slightly rewritten such that they assume the form

$$
\begin{bmatrix} \varrho_\alpha \overset{(1)}{u_i}{}^\alpha \\[2em] \overset{(1)}{q_i} \end{bmatrix} = \begin{bmatrix} -T(\overset{(1)}{\overline{R}}{}^{-1})_{\alpha\beta} & -T\sum_{\beta=1}^{\nu}\left(\varepsilon_\beta + \frac{p_\beta}{\varrho_\beta}\right)(\overset{(1)}{\overline{R}}{}^{-1})_{\alpha\beta} \\[2em] -T\sum_{\alpha=1}^{\nu}\left(\varepsilon_\alpha + \frac{p_\alpha}{\varrho_\alpha}\right)(\overset{(1)}{\overline{R}}{}^{-1})_{\alpha\beta} & \overset{(1)}{\varkappa} \end{bmatrix} \begin{bmatrix} -\dfrac{\partial \dfrac{\mu^\beta - \mu^\nu}{T}}{\partial x_i} \\[2em] \dfrac{\partial \dfrac{1}{T}}{\partial x_i} \end{bmatrix}.
$$

$$(3.1)$$

Inspection of $\overset{(1)}{R}_{\alpha\beta}$ in (A.1) and of the definition of $(\overset{(1)}{\overline{R}})_{\alpha\beta}$ below (2.4) shows that the matrix of coefficients in (3.1) is symmetric. This symmetry is known as the Onsager reciprocity relation for heat conduction and diffusion. Thus in particular, the kinetic theory confirms that the thermo-diffusion coefficients are equal to the diffusion-thermo coefficients.

Infinite Speeds

Elimination of $\varrho_1 \overset{(1)}{u_i}{}^1$ between the constitutive relation (2.21.1) and the mass balance (2.9.1) yields the equation

$$
\frac{dc_1}{dt} + \frac{1}{\varrho}\,\frac{\partial(\mu^1 - \mu^2)}{\partial c_1}\,(\overset{(1)}{\overline{R}}{}^{-1})_{11}\,\frac{\partial^2 c_1}{\partial x_i\,\partial x_i} = 0 \tag{3.2}
$$

for a binary mixture of constant temperature. This is a parabolic differential equation for the concentration c_1, which predicts an infinite speed of diffusion. This confirms the earlier remark that the iteration has led to a set of parabolic equations.

3.2 Results of Second Step of Iteration

3.2.1 Frame Dependent Constitutive Relations for Diffusion, Stress and Heat Conduction

The results of the second iterative step are contained in the Eqs. (2.23) which relate the diffusion fluxes, the heat fluxes and the stress to the thermodynamic fields ϱ_α, $v_i{}^\alpha$, and T. Inspection of (2.23) shows that the constitutive functions

are frame dependent, because they contain the matrix W_{ij} of angular velocity of the frame. Thus the kinetic theory contradicts the principle of material frame indifference.

In particular, the relation (2.23.1) between $\varrho_\alpha u_i{}^\alpha$ and $\dfrac{\partial}{\partial x_i}\left(\dfrac{\mu^\alpha}{T}\right)$ is different in an inertial frame and in a non-inertial one, because W_{ij} vanishes in one and is non-zero in the other one.

In order to anticipate misunderstanding we note that both sides of all Eqs. (2.23) are objective vectors and tensors. It is true that e.g.

$$\delta_{ij}\,\frac{dA_j{}^\gamma}{dt},\quad \frac{\partial v_{[i}}{\partial x_{j]}}A_j{}^\gamma,\quad \text{and}\quad 2W_{ij}A_j{}^\gamma \tag{3.3}$$

are not objective vectors, but the sum of these three expressions forms an objective vector. Similarly the operators in the curly brackets of (2.23.2, 3) form an objective tensor and vector respectively.

The physical root of the frame dependence of (2.23) becomes particularly obvious for a binary mixture in rigid rotation with a constant angular velocity about the same axis about which the frame rotates. We consider a constant and uniform field of temperature and stationary fields of densities and chemical potentials such that ϱ_α and μ_α at a point depend only on its distance from the axis of rotation. In this special case (2.23.1) assumes the simple form

$$\varrho_1\overset{(2)}{u_i}{}^1 = (\overset{(1)}{\bar{R}}{}^{-1})_{11}\left[\delta_{ij} + 2\,\frac{\varrho}{\varrho_1\varrho_2}\,(\overset{(1)}{\bar{R}}{}^{-1})_{11}\left(\frac{\partial v_{[i}}{\partial x_{j]}} - W_{ij}\right)\right]\frac{\partial(\mu^1 - \mu^2)}{\partial x_j}. \tag{3.4}$$

In order to interpret this formula suggestively let us consider the above special case for a gas at rest between two coaxial circular cylinders as shown in Fig. 1, μ stands for $\mu^1 - \mu^2$. In order to maintain the prescribed rotational velocity field the two constituents must move in opposite directions. Stationarity will be ensured by proper boundary conditions on the two cylinders. Let us focus the attention upon a small volume element of which a blow-up is shown in Fig. 2 and 3. The element has dimensions of the order of magnitude of the mean free path. Fig. 2 refers to the case when the gas it at rest in an inertial frame.
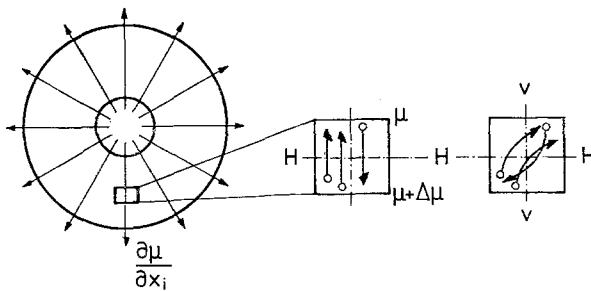

Fig. 1   Fig. 2   Fig. 3

With the indicated direction of $\frac{\partial \mu}{\partial x_i}$ there will be more molecules of constituent
1 on the lower side of the volume element than on the upper one. Consequently
within the element more molecules are flying upwards than downwards as
indicated in Fig. 2. As a consequence there is a net mass flux of constituent 1
in the upward direction, i.e. opposite to $\frac{\partial \mu}{\partial x_i}$. This is in fact what Eq. (3.4) describes
for the case of an inertial frame where $W_{ij} = 0$ holds.

The situation is changed when the cylinders are taken to a non-inertial
frame. We establish the same field of $\frac{\partial \mu}{\partial x_i}$ as before and have again a surplus
of molecules of constituent 1 at the lower side of the volume element depicted
now in Fig. 3.[7] Again more particles are moving upwards than downwards but
their paths between collisions are now curved by the Coriolis force as shown
in Fig. 3. Consequently there is now still a net mass flux across the plane $H-H$,
but in addition there is a net mass flux across the plane $V-V$, i.e. in the
direction perpendicular to $\frac{\partial \mu}{\partial x_i}$ and to the angular velocity just as predicted by
Eq. (3.4).

An analogous suggestive argument can be presented for the interpretation
of the frame dependent term in the heat fluxes (2.23.3). This argument has
been described in [1]; with respect to heat conduction the argument is
somewhat simpler, since the temperature field is not affected by the centrifugal
force and because temperature is a more plausible quantity than the chemical
potential.

While the kinetic theory thus predicts frame-dependence of the constitutive
function for diffusion fluxes, stress, and heat flux, the relevant terms are quite
small. Indeed, $\frac{\varrho}{\varrho_1 \varrho_2} (\overset{(1)}{\overline{R}}{}^{-1})_{11}$ in Eq. (3.4) (say) is of magnitude of a mean time of
free flight, whereas the components of $\frac{\partial v_{[i}}{\partial x_{j]}} - W_{ij}$ represent the frequency of
rotation of the fluid with respect to an inertial frame. Thus the frame dependent
terms have the size of the quotient

$$\frac{\text{time of free flight}}{\text{period of rotation}}$$

and this is a small ratio indeed for all feasible centrifuges.

3.2.2 Onsager Relations in a Rotating Fluid

We summarize the constitutive equations for the diffusion fluxes and for
the heat flux of the mixture and simplify them by neglecting all terms with
E_{ij} and E. Thus we obtain from (2.23.1, 3), and from the definition

---

[7] This surplus of molecules is superimposed now on the natural excess of molecules at
larger radii that is created by the centrifugal force.

$$\overset{(2)}{q_i} = \sum_{\alpha=1}^{\nu} \cdot \left(\frac{1}{2} \overset{(2)}{M_{ijj}^{\alpha}} + \left(\varepsilon_\alpha + \frac{p_\alpha}{\varrho_\alpha} \right) \varrho_\alpha \overset{(2)}{u_i^{\alpha}} \right):$$

$$\begin{bmatrix} \varrho_\alpha \overset{(2)}{u_i^{\alpha}} \\ \\ \overset{(2)}{q_i} \end{bmatrix} = \begin{bmatrix} -\sum_{\beta=1}^{\nu} (\overset{(1)}{\bar{R}^{-1}})_{\alpha\beta}\, T \left[\delta_{ij}\delta_{\beta\gamma} + O_{ij} \frac{1}{\varrho_\beta} (\overset{(1)}{\bar{R}^{-1}})_{\beta\gamma} \right] \\ \\ -\sum_{\beta=1}^{\varepsilon} (\overset{(1)}{\bar{R}^{-1}})_{\gamma\beta}\, T \left[\delta_{ij}\left(\varepsilon_\beta + \frac{p_\beta}{\varrho_\beta} \right) + \sum_{\alpha=1}^{\nu} \frac{1}{\varrho_\beta} (\overset{(1)}{\bar{R}^{-1}})_{\beta\alpha} O_{ij} \left(\varepsilon_\alpha + \frac{p_\alpha}{\varrho_\alpha} \right) \right] \end{bmatrix}$$

$$\begin{bmatrix} & -\sum_{\beta=1}^{\nu} (\overset{(1)}{\bar{R}^{-1}})_{\alpha\beta}\, T \left[\delta_{ij}\left(\varepsilon_\beta + \frac{p_\beta}{\varrho_\beta} \right) \right] \\ & + \sum_{\gamma=1}^{\nu} \frac{1}{\varrho_\beta} (\overset{(1)}{\bar{R}^{-1}})_{\beta\gamma} O_{ij} \left(\varepsilon_\gamma + \frac{p_\gamma}{\varrho_\gamma} \right) \right] \\ & \overset{(2)}{\varkappa} \end{bmatrix} \cdot \begin{bmatrix} -\dfrac{\partial \dfrac{\mu^\gamma}{T}}{\partial x_j} \\ \\ \dfrac{\partial \dfrac{1}{T}}{\partial x_j} \end{bmatrix} \qquad (3.5)$$

where O_{ij} stands for the operator $\delta_{ij} \frac{d}{dt} + \frac{\partial v_{[i}}{\partial x_{j]}} - 2W_{ij}$. The form of $\overset{(2)}{\varkappa}$ does not interest here.

We abbreviate the matrix in (3.5) by $T_{ij}^{\alpha\gamma}$ and observe by inspection that it satisfies the following symmetry relations

$$T_{ij}^{\alpha\gamma}(\boldsymbol{S}, \boldsymbol{W}) = T_{ji}^{\gamma\alpha}(-\boldsymbol{S}, -\boldsymbol{W}) \qquad (3.6)$$

where $\boldsymbol{S}$ is the antisymmetric part of the velocity gradient, often called the spin tensor. This symmetry relation confirms the Onsager reciprocity relations in the presence of axial fields, here the fields of spin and of the angular velocity of the frame.

3.3 Implications for Entropy and Entropy Flux

According to (1.13.1, 3) the kinetic theory defines the density and flux of entropy of constituent α by

$$\varrho_\alpha \eta_\alpha = -k \int f_\alpha \ln f_\alpha dc_\alpha + \varrho_\alpha a_\alpha, \qquad \varphi_i^{\alpha} = -k \int f_\alpha C_i^{\alpha} \ln f_\alpha dc_\alpha. \qquad (3.7)$$

It is important to realize that these entropic quantities are defined for arbitrary distribution functions, in particular these functions may characterize non-equilibria. In order to emphasize this fact we introduce the Grad distribution (2.5), (2.6) into the Eq. (3.7). $\ln(1 + \varphi)$ is replaced by $\varphi - \frac{\varphi^2}{2}$ and we obtain after considerable calculation

$$\eta_\alpha = \eta_\alpha|_E - \frac{1}{4} \frac{M_{\langle ij\rangle}^{\alpha} M_{\langle ij\rangle}^{\alpha}}{\varrho_\alpha p_\alpha T} - \frac{1}{20} \frac{M_{ijj}^{\alpha} M_{ikk}^{\alpha}}{p_\alpha{}^2 T}$$

$$\varphi_i^{\alpha} = \frac{M_{ijj}^{\alpha}}{2T} - \frac{1}{5} \frac{M_{\langle ij\rangle}^{\alpha} M_{jkk}^{\alpha}}{p_\alpha T}, \qquad (3.8)$$

where $\eta_\alpha|_E$ is given by (1.17.1). Always, of course, $\frac{1}{2} M_{ijj}^\alpha$ is equal to the heat flux q_α of constituent α.

The entropy and entropy flux of the mixture result from (3.8) by summation according to (1.13.2) and (1.38). Thus the entropy flux assumes the form

$$\varphi_i = \frac{q_i - \sum\limits_{\alpha=1}^\nu \varrho_\alpha \mu_\alpha u_i^\alpha}{T} - \sum\limits_{\alpha=1}^\nu \left(\frac{M_{\langle ij \rangle}^\alpha u_j^\alpha}{T} + \frac{2}{5}\, \frac{M_{\langle ij \rangle}^\alpha q_j^\alpha}{p_\alpha T} \right). \tag{3.9}$$

The first term in (3.9) is the familiar entropy flux of phenomenological thermodynamics of mixtures.

Appendix

The matrices R on the right hand sides of (1.20) through (1.23) are defined by the following expressions

$$\overset{(1)}{R}_{\alpha\beta} = \frac{4\pi Y_1^{\alpha\beta}}{m_\alpha + m_\beta}\, \varrho_\alpha \varrho_\beta - \delta_{\alpha\beta} \sum\limits_{\gamma=1}^\nu \frac{4\pi Y_1^{\alpha\gamma}}{m_\alpha + m_\beta}\, \varrho_\alpha \varrho_\gamma \tag{A.1}$$

$$\overset{(2)}{R}_{\alpha\beta}^{\gamma\varepsilon} = \frac{8\pi Y_1^{\alpha\beta}}{(m_\alpha + m_\beta)^2}\, m_\alpha m_\beta \varrho_\alpha \varrho_\beta (U_{\alpha\gamma} - U_{\beta\gamma})(U_{\alpha\varepsilon} - U_{\beta\varepsilon}) \tag{A.2}$$

$$\overset{(2)}{R}_{\alpha\beta} = \frac{4\pi m_\alpha m_\beta}{(m_\alpha + m_\beta)^2}\, (3Y_2^{\alpha\beta} - Y_1^{\alpha\beta})$$
$$+ \delta_{\alpha\beta} \sum\limits_{\gamma=1}^\nu \frac{4\pi m_\alpha \frac{\varrho_\gamma}{\varrho_\alpha}}{(m_\alpha + m_\gamma)^2}\, (3m_\gamma Y_2^{\alpha\gamma} - 3m_\gamma Y_1^{\alpha\gamma} - 2m_\alpha Y_1^{\alpha\gamma}) \tag{A.3}$$

$$\overset{(2)}{R}_{\alpha\beta}^{\gamma\varepsilon} = \frac{4\pi m_\alpha m_\beta}{(m_\alpha + m_\beta)^2}\, (3Y_2^{\alpha\beta} - Y_1^{\alpha\beta})\, \varrho_\alpha \varrho_\beta (U_{\alpha\gamma} - U_{\beta\gamma})(U_{\alpha\varepsilon} - U_{\beta\varepsilon}) \tag{A.4}$$

$$\overset{(3)}{R}_{\alpha\beta} = \frac{16\pi m_\alpha^2 m_\beta^2 Y_2^{\alpha\beta}}{(m_\alpha + m_\beta)^3} + \delta_{\alpha\beta} \sum\limits_{\gamma=1}^\nu \frac{4\pi m_\alpha^2 \frac{\varrho_\gamma}{\varrho_\alpha}}{(m_\alpha + m_\gamma)^3}$$
$$\cdot (4m_\alpha m_\gamma Y_2^{\alpha\gamma} - 4m_\alpha m_\gamma Y_1^{\alpha\gamma} - m_\gamma^2 Y_1^{\alpha\gamma} - 3m_\alpha^2 Y_1^{\alpha\gamma}) \tag{A.5}$$

$$\overset{(3)}{R}_{\alpha\beta}^\varepsilon = \left\{ -\frac{32\pi m_\alpha^2 m_\beta^2}{(m_\alpha + m_\beta)^3}\, Y_2^{\alpha\beta} + \delta_{\alpha\beta} \sum\limits_{\gamma=1}^\nu \frac{8\pi m_\alpha^2 m_\gamma \frac{\varrho_\gamma}{\varrho_\alpha}}{(m_\alpha + m_\gamma)^3} \right.$$
$$\left. \cdot [3Y_1^{\alpha\gamma}(m_\alpha + m_\gamma) + Y_2^{\alpha\gamma}(m_\alpha - 3m_\gamma)] \right\} (U_{\alpha\varepsilon} - U_{\beta\varepsilon}) \tag{A.6}$$

$$\overset{(3)}{R}_{\alpha\beta}^{\gamma\delta\varepsilon} = -\frac{16\pi m_\alpha^2 m_\beta^2 Y_1^{\alpha\beta}}{(m_\alpha + m_\beta)^3}\, \varrho_\alpha \varrho_\gamma (U_{\alpha\gamma} - U_{\beta\gamma})(U_{\alpha\delta} - U_{\beta\delta})(U_{\alpha\varepsilon} - U_{\beta\varepsilon}), \tag{A.7}$$

where $U_{\alpha\gamma}$, $Y_1^{\alpha\beta}$, and $Y_2^{\alpha\beta}$ are defined by

$$U_{\alpha\gamma} = \delta_{\alpha\gamma} - \frac{\varrho_\gamma}{\varrho_\nu}\, \delta_{\alpha\nu}$$

$$Y_1^{\alpha\beta} = \int\limits_{\theta_{\beta\alpha}=0}^{\pi/2} f_{\alpha\beta}(\theta_{\beta\alpha})\, \sin\theta_{\beta\alpha}\, \cos^2\theta_{\beta\alpha}\, d\theta_{\beta\alpha} \qquad\text{(A.8)}$$

$$Y_2^{\alpha\beta} = \int\limits_{\theta_{\beta\alpha}=0}^{\pi/2} f_{\alpha\beta}(\theta_{\beta\alpha})\, \sin\theta_{\beta\alpha}\, \cos^4\theta_{\beta\alpha}\, d\theta_{\beta\alpha}.$$

The Y's are constants depending on the strength of the interaction between particles α and β.

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