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Extended thermodynamics of ideal gases with 14 fields

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by

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ABSTRACT. — We formulate an extended thermodynamic theory of non-relativistic gases as a theory of 14 fields, the number that occurs naturally in the corresponding relativistic theory, and one more than in the extended thermodynamics of Liu and Müller. The additional field is a scalar which represents the fourth moment of the distribution function. We derive linear field equations containing only three unknown functions of two variables and two constants, for a given equation of state. Explicit results are formulated for the classical ideal gas and for degenerate gases of the Bose and Fermi type.

RÉSUMÉ. — On formule une Thermodynamique étendue des gaz non relativistes comme théorie de 14 champs, le même nombre que celui qui apparaît naturellement dans la théorie relativiste correspondante, et un de plus que dans la Thermodynamique étendue de Liu et Müller. Le champ supplémentaire est un scalaire qui représente le quatrième moment de la fonction de distribution. On établit des équations de champ linéaires contenant seulement trois fonctions inconnues de deux variables et deux constantes, pour une équation d'état du gaz donné. On donne des résultats explicites pour le gaz idéal classique et pour des gaz de Bose et de Fermi dégénérés.

1. INTRODUCTION

In a recent paper Liu and Müller [1] have formulated extended thermo-dynamics of monatomic gases as a field theory of the 13 fields of density,

velocity, energy, stress deviator and heat flux. The theory is strongly motivated by the kinetic theory of gases. It represents an improvement over the classical Navier-Stokes Fourier theory of viscous, heat conducting gases in that it achieves full agreement with the 13 moment theory in the kinetic theory of gases.

However, the question arises whether the theory can be improved by the addition of a further field or further fields and what a suitable choice for those fields might be. In this context it is noteworthy that in relativistic thermodynamics of gases the description of the thermodynamic state by 14 fields is much more natural than the one by 13 fields. In that theory the scalar field of the pressure is added to the above-mentioned 13 fields of density, velocity, energy, stress deviator and heat flux. The relativistic theory has recently been discussed by Müller, Liu and Ruggeri [2].

In the present paper we formulate a thermodynamic theory of 14 fields in the non-relativistic context. The additional variable is a scalar which —in the kinetic theory—represents the trace of the fourth moment of the distribution function. Since this quantity has no counterpart in ordinary thermodynamics, it has not received a proper name and we shall refer to it as the « 4-moment ». The exploitation of the requirement of material frame indifference and of the entropy principle leads to linear field equations that contain only three unknown functions of two variables and two constants, provided that the thermal equation of state is given. Explicit results are formulated for the classical ideal gas and for degenerate gases of the Bose and Fermi type.

In an accompanying paper [3] Dreyer and Weiss have compared the present non-relativistic 14 field theory to the corresponding relativistic theory. They found that the present variable, the « 4-moment » is closely related to the pressure of the relativistic theory. This relation is discussed in Chapter 12.

2. FIELDS AND FIELD EQUATIONS
OF EXTENDED THERMODYNAMICS WITH 14 FIELDS

The objective of extended thermodynamics with 14 fields is the determination of the fields:

$$
\begin{aligned}
&\text{F — mass density,}\\
&\text{F}_i\text{ — momentum density,}\\
&\text{F}_{ij}\text{ — momentum flux density,}\\
&\frac{1}{2}\text{F}_{jji}\text{ — energy flux density and}\\
&\text{F}_{iijj}\text{ — « 4-moment ».}
\end{aligned}
\qquad (2.1)
$$

To reach this objective we need balance equations. These are based upon the moment equations of the kinetic gas theory ([1]), viz.
Balance of mass density

$$\frac{\partial F}{\partial t} + \frac{\partial F_i}{\partial x_i} = 0.$$

Balance of momentum density

$$\frac{\partial F_i}{\partial t} + \frac{\partial F_{ij}}{\partial x_j} = 0.$$

Balance of momentum flux density

$$\frac{\partial F_{ij}}{\partial t} + \frac{\partial F_{ijk}}{\partial x_k} = P_{\langle ij \rangle} = P_{ij} - \frac{1}{3} P_{rr} \delta_{ij}. \qquad (2.2)$$

Balance of energy flux density

$$\frac{\partial F_{jji}}{\partial t} + \frac{\partial F_{ijjk}}{\partial x_k} = P_{jji}.$$

Balance of the « 4-moment »

$$\frac{\partial F_{iijj}}{\partial t} + \frac{\partial F_{iijjk}}{\partial x_k} = P_{iijj}.$$

These equations refer to inertial frames and body forces are ignored. The $\underline{P}$'s are productions, and $P_{\langle ij \rangle}$ is traceless so that the energy $\frac{1}{2} F_{ii}$ is conserved.

The equations (2.2) are not field equations for the basic fields (2.1) yet, because additional quantities have appeared, namely

$$F_{\langle ijk \rangle}, \; F_{\langle ik \rangle jj}, \; F_{iijjk}, \; P_{\langle ij \rangle}, \; P_{jji}, \; P_{iijj}. \qquad (2.3)$$

We assume that the quantities in (2.3), generically denoted by C, are constitutive quantities that depend upon the basic fields

$$C = \mathscr{C}(F, F_i, F_{ij}, F_{jji}, F_{iijj}). \qquad (2.4)$$

Insertion of (2.4) into the balance equations (2.2) leads to a set of field equations for the fields (2.1) provided that the constitutive functions $\mathscr{C}$ are known. Every solution is called a *thermodynamic process*.

([1]) See § 2 of [1] for the notation.

3. INTRODUCTION OF NON-CONVECTIVE QUANTITIES AND A NEW FORM OF FIELD EQUATIONS

Motivated by the kinetic theory of gases we decompose the fields $\underset{\sim}{F}$ into convective and a non-convective parts as follows:

$$
\begin{aligned}
F &= \rho, \\
F_i &= \rho v_i, \\
F_{ij} &= \rho v_i v_j + p_{ij}, \\
F_{ijk} &= \rho v_i v_j v_k + 3p_{(ij}v_{k)} + p_{ijk}, \\
F_{ijjk} &= \rho v_i v_j v_j v_k + 6p_{(ij}v_j v_{k)} + 4p_{(ijk}v_{j)} + p_{ijjk}, \\
F_{iijjk} &= \rho v_i v_i v_j v_j v_k + 10p_{(ij}v_i v_j v_{k)} + 10p_{(ijk}v_i v_{j)} + 5p_{(ijjk}v_{i)} + p_{iijjk}.
\end{aligned}
\tag{3.1}
$$

We insert (3.1) into the balance equations (2.2) and get a new system of balance equations that involves only non-convective quantities:

$$
\dot{\rho} + \rho \frac{\partial v_i}{\partial x_i} = 0,
$$

$$
\rho \dot{v}_i + \frac{\partial p_{ij}}{\partial x_j} = 0,
$$

$$
\dot{p}_{ij} + p_{ij}\frac{\partial v_k}{\partial x_k} + \frac{\partial p_{ijk}}{\partial x_k} + 2p_{k(i}\frac{\partial v_{j)}}{\partial x_k} = P_{\langle ij\rangle},
$$

$$
\dot{q}_i + \frac{7}{5}q_i\frac{\partial v_k}{\partial x_k} + \frac{1}{2}\frac{\partial p_{ijjk}}{\partial x_k} + p_{\langle ijk\rangle}\frac{\partial v_j}{\partial x_k} + \frac{2}{5}q_j\frac{\partial v_j}{\partial x_i} +
\tag{3.2}
$$

$$
+ \frac{7}{5}q_j\frac{\partial v_i}{\partial x_j} - \frac{p_{ij}}{\rho}\frac{\partial p_{jk}}{\partial x_k} - \frac{1}{2}\frac{p_{jj}}{\rho}\frac{\partial p_{ik}}{\partial x_k} = P_i,
$$

$$
\dot{p}_{iijj} + p_{iijj}\frac{\partial v_k}{\partial x_k} + \frac{\partial p_{iijjk}}{\partial x_k} + 4p_{ijjk}\frac{\partial v_i}{\partial x_k} - \frac{8}{\rho}q_i\frac{\partial p_{ik}}{\partial x_k} = P,
$$

where $q_i \equiv \dfrac{1}{2}p_{jji}$ is the heat flux and

$$
P_i = \frac{1}{2}(P_{jji} - P_{\langle ij\rangle}v_j), \quad P = P_{iijj} - 4(P_{jji} - P_{\langle ij\rangle}v_j)v_i.
\tag{3.3}
$$

Now we change the variables

$$
(F, F_i, F_{ij}, F_{jji}, F_{iijj}) \quad \text{to} \quad (\rho, v_i, p_{ij}, q_i, p_{iijj})
\tag{3.4}
$$

and the constitutive quantities

$$(F_{\langle ijk \rangle}, F_{\langle ik \rangle jj}, F_{iijjk}, P_{\langle ij \rangle}, P_{jji}, P_{iijj}) \quad \text{to}$$

$$(p_{\langle ijk \rangle}, p_{\langle ik \rangle jj}, p_{iijjk}, P_{\langle ij \rangle}, P_i, P). \quad (3.5)$$

We choose $(3.4)_2$ and $(3.5)_2$ as new variables and new constitutive quantities respectively, because, apart from the velocity, all these quantities are objective.

With this choice we can write the constitutive equations in a form equivalent to (2.4), namely

$$D = \mathscr{D}(\rho, v_i, p_{ij}, q_i, p_{iijj}), \quad (3.6)$$

where D is the generic expression for any quantity of the set $(3.5)_2$.

4. THE PRINCIPLE
OF MATERIAL FRAME INDIFFERENCE

According to the principle of material frame indifference the constitutive functions $\mathscr{D}$ must have the same form in an inertial and in a non-inertial frame.

From the evaluation of this principle one can prove that the constitutive quantities cannot depend on the velocity and that the constitutive functions are isotropic functions of all remaining variables. Thus (3.6) reduces to

$$D = \tilde{\mathscr{D}}(\rho, p_{ij}, q_i, p_{iijj}), \quad (4.1)$$

and the $\tilde{\mathscr{D}}$ are isotropic functions.

5. THE DEFINITION OF EQUILIBRIUM

We define equilibrium as the process in which the 9 productions $P_{\langle ij \rangle}$, P_i, P vanish. This implies that 9 variables, or combination of variables, must vanish in equilibrium and this condition will be satisfied, if the pressure deviator $p_{\langle ij \rangle}$ and the heat flux q_i are zero, and if there is a relation between p_{iijj}, ρ and p. In equilibrium we write $p_{iijj}|_E = g(\rho, p)$ and introduce a new variable $\Delta = p_{iijj} - g(\rho, p)$ which vanishes in equilibrium. $g(\rho, p)$ is the equilibrium value of the non-convective « 4-moment » p_{iijj}.

Since there is a one-to-one correspondence between Δ and p_{iijj} we use Δ instead of p_{iijj} as variable. With that (4.1) can be written as

$$D = \hat{\mathscr{D}}(\rho, p_{ij}, q_i, \Delta). \quad (5.1)$$

6. THE ENTROPY PRINCIPLE ([2])

The entropy inequality is given by:

$$\dot{h} + h\frac{\partial v_k}{\partial x_k} + \frac{\partial \Phi_k}{\partial x_k} \geqslant 0, \tag{6.1}$$

where h is the entropy density and Φ_k the non-convective entropy flux density.

We suppose that:

i) the entropy inequality is valid for every thermodynamic process, i. e. for every solution $(\rho, v_i, p_{ij}, q_i, p_{iijj})$ of the balance equations (2.2);

ii) the entropy density h and the non-convective entropy flux density Φ_k are objective constitutive quantities. They depend on the basic fields $(\rho, v_i, p_{ij}, q_i, p_{iijj})$ and the dependence is restricted by the principle of material frame indifference.

According to the principle of material frame indifference h and Φ_k cannot depend on the velocity and must be isotropic functions of all remaining variables. We use Δ instead p_{iijj} as variable and get:

$$h = \mathrm{E}(\rho, p_{ij}, q_i, \Delta), \quad \Phi_k = \mathrm{E}_k(\rho, p_{ij}, q_i, \Delta). \tag{6.2}$$

7. GENERAL EVALUATION OF THE ENTROPY INEQUALITY WITH LAGRANGE MULTIPLIERS

We evaluate the entropy inequality by using Liu's lemma [5]: if the inequality (6.1) is valid for every thermodynamic process, then the following inequality is valid for arbitrary fields $(\rho, v_i, p_{ij}, q_i, \Delta)$:

$$
\dot{h} + h\frac{\partial v_k}{\partial x_k} + \frac{\partial \Phi_k}{\partial x_k} - \Lambda\left[\dot{\rho} + \rho\frac{\partial v_i}{\partial x_i}\right] - \Lambda_i\left[\rho\dot{v}_i + \frac{\partial p_{ij}}{\partial x_j}\right] -
$$
$$
- \Lambda_{ij}\left[\dot{p}_{ij} + p_{ij}\frac{\partial v_k}{\partial x_k} + \frac{\partial p_{\langle ijk\rangle}}{\partial x_k} + \frac{4}{5}\frac{\partial q_{(i}}{\partial x_{j)}} + \frac{2}{5}\frac{\partial q_k}{\partial x_k}\delta_{ij} + 2p_{k(i}\frac{\partial v_{j)}}{\partial x_k} - \mathrm{P}_{\langle ij\rangle}\right] -
$$
$$
- \lambda_i\left[\dot{q}_i + \frac{7}{5}q_i\frac{\partial v_k}{\partial x_k} + \frac{1}{2}\frac{\partial p_{\langle ik\rangle jj}}{\partial x_k} + \frac{1}{6}\left(\frac{\partial \Delta}{\partial x_i} + \frac{\partial g}{\partial x_i}\right) + p_{\langle ijk\rangle}\frac{\partial v_j}{\partial x_k} + \right.
$$
$$
\left. + \frac{2}{5}q_k\frac{\partial v_k}{\partial x_i} + \frac{7}{5}q_k\frac{\partial v_i}{\partial x_k} - \frac{p_{ij}}{\rho}\frac{\partial p_{jk}}{\partial x_k} - \frac{3p}{2\rho}\frac{\partial p_{ik}}{\partial x_k} - \mathrm{P}_i\right] -
$$
$$
- \lambda\left[\dot{\Delta} + \dot{g} + \frac{7}{3}(\Delta + g)\frac{\partial v_k}{\partial x_k} + \frac{\partial p_{iijjk}}{\partial x_k} + 4p_{\langle ik\rangle jj}\frac{\partial v_i}{\partial x_k} - \frac{8}{\rho}q_i\frac{\partial p_{ik}}{\partial x_k} - \mathrm{P}\right] \geqslant 0. \tag{7.1}
$$

([2]) For more details see the book of Müller [4].

The inequality (7.1) is obtained by multiplying each balance equation (2.2) with a Lagrange multiplier $(\Lambda, \Lambda_i, \Lambda_{ij}, \lambda_i, \lambda)$ and subtracting the products from the inequality (6.1).

Insertion of the constitutive relations (5.1) and (6.2) into the inequality (7.1) leads to a inequality that is explicitly linear in the derivatives

$$\dot{v}_i, \dot{\rho}, \dot{p}_{ij}, \dot{q}_i, \dot{\Delta}, \frac{\partial v_i}{\partial x_j}, \frac{\partial \rho}{\partial x_i}, \frac{\partial p_{ij}}{\partial x_k}, \frac{\partial q_i}{\partial x_j}, \frac{\partial \Delta}{\partial x_i}. \tag{7.2}$$

The derivatives (7.2) are arbitrary, since the fields ρ, v_i, p_{ij}, q_i, Δ are, and the inequality (7.1) could thus be violated unless the coefficients of these derivatives were zero. This implies

$$\Lambda_i = 0, \quad \frac{\partial h}{\partial \rho} = \Lambda + \lambda \frac{\partial g}{\partial \rho}, \quad \frac{\partial h}{\partial p_{ij}} = \Lambda_{ij} + \lambda \frac{\partial g}{\partial p_{ij}}, \quad \frac{\partial h}{\partial q_i} = \lambda_i, \quad \frac{\partial h}{\partial \Delta} = \lambda. \tag{7.3}$$

$$h\delta_{ij} = \left[\rho\Lambda + \Lambda_{rs}p_{rs} + \frac{7}{5}\lambda_r q_r + \frac{7}{3}\lambda(\Delta + g) \right]\delta_{ij} +$$

$$+ 2\Lambda_{ik}p_{jk} + \frac{2}{5}q_i\lambda_j + \frac{7}{5}q_j\lambda_i + \lambda_r p_{\langle rij \rangle} + 4\lambda p_{\langle ij \rangle rr}. \tag{7.4}$$

$$\frac{\partial \Phi_k}{\partial \rho} = \Lambda_{rs}\frac{\partial p_{\langle rsk \rangle}}{\partial \rho} + \frac{1}{2}\lambda_r \frac{\partial p_{\langle rk \rangle ss}}{\partial \rho} + \lambda \frac{\partial p_{rrssk}}{\partial \rho} + \frac{1}{6}\lambda_k \frac{\partial g}{\partial \rho},$$

$$\frac{\partial \Phi_k}{\partial p_{ij}} = \Lambda_{rs}\frac{\partial p_{\langle rsk \rangle}}{\partial p_{ij}} + \frac{1}{2}\lambda_r \frac{\partial p_{\langle rk \rangle ss}}{\partial p_{ij}} + \lambda \frac{\partial p_{rrssk}}{\partial p_{ij}} + \frac{1}{6}\lambda_k \frac{\partial g}{\partial p_{ij}} -$$

$$- \lambda_r \frac{p_{r(i}}{\rho}\delta_{j)k} - \frac{3p}{2\rho}\lambda_{(i}\delta_{j)k} - \frac{8}{\rho}\lambda q_{(i}\delta_{j)k}, \tag{7.5}$$

$$\frac{\partial \Phi_k}{\partial q_i} = \Lambda_{rs}\frac{\partial p_{\langle rsk \rangle}}{\partial q_i} + \frac{1}{2}\lambda_r \frac{\partial p_{\langle rk \rangle ss}}{\partial q_i} + \lambda \frac{\partial p_{rrssk}}{\partial q_i} + \frac{4}{5}\Lambda_{ik} + \frac{2}{5}\Lambda_{rr}\delta_{ij},$$

$$\frac{\partial \Phi_k}{\partial \Delta} = \Lambda_{rs}\frac{\partial p_{\langle rsk \rangle}}{\partial \Delta} + \frac{1}{2}\lambda_r \frac{\partial p_{\langle rk \rangle ss}}{\partial \Delta} + \lambda \frac{\partial p_{rrssk}}{\partial \Delta} + \frac{1}{6}\lambda_k.$$

There remains the residual inequality:

$$\Sigma = \Lambda_{ij}P_{\langle ij \rangle} + \lambda_i P_i + \lambda P \geqslant 0. \tag{7.6}$$

8. THE REPRESENTATION
OF THE CONSTITUTIVE QUANTITIES

We are interested in processes near to equilibrium and, for this reason, we suppose that the constitutive equations for

$$\{ p_{\langle ijk \rangle}, p_{\langle ij \rangle kk}, p_{iijjk}, P_{\langle ij \rangle}, P_i, P \}$$

are linear in the variables $\{ p_{\langle ij \rangle}, q_i, \Delta \}$.

On the other hand, we read off from $(7.5)_1$ that $\dfrac{\partial \Phi_k}{\partial \rho}$ has a term given by

$$\frac{1}{2}\lambda_r \frac{\partial p_{\langle rk \rangle ss}}{\partial \rho} + \frac{1}{6}\lambda_k \frac{\partial g}{\partial \rho} = \frac{1}{2}\frac{\partial h}{\partial q_r}\frac{\partial p_{\langle rk \rangle ss}}{\partial \rho} + \frac{1}{6}\frac{\partial h}{\partial q_k}\frac{\partial g}{\partial \rho}. \tag{8.1}$$

In (8.1) we have used the relation $(7.3)_4$. $\dfrac{\partial p_{\langle rk \rangle ss}}{\partial \rho}$ has terms of first order in the variables $\{ p_{\langle ij \rangle}, q_i, \Delta \}$, while $\dfrac{\partial g}{\partial \rho}$ has terms of zero order. But $\dfrac{\partial h}{\partial q_r}$ starts with a first order term so that $\dfrac{\partial h}{\partial q_r}\dfrac{\partial p_{\langle rk \rangle ss}}{\partial \rho}$ starts out with a second order term. For $(7.5)_1$ to make sense as a restriction for the coefficients of $p_{\langle rk \rangle ss}$ we must therefore know Φ_k including second order terms. The same then holds for the last term in (8.1), viz. $\dfrac{\partial h}{\partial q_r}\dfrac{\partial g}{\partial \rho}$, which implies that third order terms must be included in the representation of h.

Therefore we write the representations as follows:

$$p_{\langle ijk \rangle} = 0, \qquad p_{\langle ik \rangle jj} = \gamma_0 p_{\langle ik \rangle}, \quad p_{rrssk} = \nu_0 q_k,$$

$$P_{\langle ij \rangle} = \sigma_0 p_{\langle ij \rangle}, \qquad P_i = \tau_1 q_i, \qquad P = \zeta_1 \Delta,$$

$$h = h_0 + h_1 \Delta + h_2 \Delta^2 + h_3 \Delta^3 + (h_4 + h_5 \Delta) p_{\langle rs \rangle} p_{\langle rs \rangle} + \tag{8.2}$$

$$+ (h_6 + h_7 \Delta) q_r q_r + h_8 p_{\langle rs \rangle} p_{\langle sk \rangle} p_{\langle kr \rangle} + h_9 p_{\langle rs \rangle} q_r q_s,$$

$$\Phi_k = (\varphi_1 + \varphi_2 \Delta) q_k + \varphi_3 p_{\langle kr \rangle} q_r.$$

The coefficients γ_0 through φ_3 depend on the density ρ and pressure $p \equiv p_{ii}/3$; their form is restricted by the conditions (7.3) through (7.6).

9. SUMMARY OF THE CONSEQUENCES OF THE ENTROPY INEQUALITY AND OF THE REPRESENTATIONS

The exploitation of the conditions (7.3) through (7.6) is presented in some detail in the appendix. Here we list only some intermediate results and the final form of the representations (8.2).

At some stage (see (A.15)) we obtain the equation

$$d\left(\frac{h_0}{\rho}\right) = \frac{2}{3}\frac{\partial h_0}{\partial p}\left(d\varepsilon - \frac{p}{\rho^2}d\rho\right), \tag{9.1}$$

which implies that $\dfrac{2}{3}\dfrac{\partial h_0}{\partial p}$ is *the* integrating factor of the Pfaffian form

$\left(d\varepsilon - \dfrac{p}{\rho^2}d\rho\right)$ whose integral is the specific entropy $\eta_0 = \dfrac{h_0}{\rho}$. We conclude by reference to well-known result of equilibrium thermodynamics that $\dfrac{2}{3}\dfrac{\partial h_0}{\partial p}$ equals the reciprocal of the absolute temperature

$$\frac{1}{T} = \frac{2}{3}\frac{\partial h_0}{\partial p}.\tag{9.2}$$

This relation permits a change of variables from the pair (ρ, p) to the pair (ρ, T). Thus p and $\varepsilon = \dfrac{3p}{2\rho}$ become functions of ρ and T and (9.1) reads

$$d\eta_0 = \frac{1}{T}\left\{\left(\frac{\partial\varepsilon}{\partial T}\right)_\rho dT + \left[\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T - \frac{p}{\rho^2}\right]d\rho\right\},\tag{9.3}$$

which implies the integrability condition (A.17) whose general solution reads

$$p = T^{5/2}F(z)\qquad\text{with}\qquad z = \frac{\rho}{T^{3/2}},\tag{9.4}$$

where F is an arbitrary function. Equation (9.4) represents the general form of the thermal equation of state whose explicit form must be taken from statistical mechanics of ideal gases.

Further evaluation of the conditions (7.3)-(7.6) gives the explicit form of the constitutive relations (8.2) in terms of the function F(z), viz. (see (A.5), (A.18)$_{2,3}$, (A.19) and (A.23) through (A.30))

$$p_{\langle ik\rangle jj} = \gamma_0 p_{\langle ik\rangle},$$

$$p_{rrssk} = \left\{\frac{2}{3}\left(\frac{\partial g}{\partial T}\bigg/\frac{\partial p}{\partial T}\right) - \frac{1}{15pT}\left(\gamma_0 - \frac{5p}{\rho}\right)^{-1}\frac{1}{h_2}\right\}q_k,$$

$$h = \left[\frac{3}{2}\int\left(\frac{F'}{z} - \frac{5}{3}\frac{F}{z^2}\right)dz + a_1\right]\rho + h_2\Delta^2 - \frac{1}{4pT}p_{\langle rs\rangle}p_{\langle rs\rangle} - \\ -\frac{2}{5pT}\left(\gamma_0 - \frac{5p}{\rho}\right)^{-1}q_r q_r,\tag{9.5}$$

$$\Phi_k = \left[\frac{1}{T} - \frac{2\Delta}{15pT}\left(\gamma_0 - \frac{5p}{\rho}\right)^{-1}\right]q_k - \frac{2}{5pT}p_{\langle kr\rangle}q_r,$$

where:

$$\gamma_0 = \frac{7T}{F}\left(\int \frac{FF'}{z}\,dz + a_2\right),$$

$$g = 15T^{7/2}\left(\int \frac{FF'}{z}\,dz + a_2\right),$$

$$h_2^{-1} = T^{11/2}\int\left\{30F\left[\frac{7}{F}\left(\int\frac{FF'}{z}\,dz+a_2\right)-\frac{5F}{z}\right]\left[\left(\frac{7\left(\int\frac{FF'}{z}\,dz+a_2\right)-3FF'}{F-3F'z/5}\right)' - \right.\right.$$

$$\left.\left. -\frac{4F'}{z}\right]\right\}dz + a_3T^{11/2}, \quad (9.6)$$

a_1, a_2 and a_3 are constants of integration.

We conclude from (9.5) and (9.6) that all coefficients in the representations $(8.2)_{2,3,7,8}$ have been reduced to the thermal equation, or rather to the function $F\left(\dfrac{\rho}{T^{3/2}}\right)$ which characterizes the thermal equation of state. It is true though that three constants have also appeared of which a_1 is the additive entropy constant.

Furthermore, the residual inequality implies

$$\sigma_0 \leqslant 0, \quad \tau_1\left(\gamma_0 - \frac{5p}{\rho}\right)^{-1} \leqslant 0, \quad h_2\zeta_1 \geqslant 0. \quad (9.7)$$

10. SPECIFIC RESULTS

10.1 Thermal equations of state for ideal gases.

In statistical mechanics the thermal equation of state of a monatomic ideal gas is given by (see Huang [6])

$$p = \frac{2k}{3m}\frac{T^{5/2}}{A_\pm}I_4^\pm(\alpha) \quad \text{with} \quad I_2^\pm(\alpha) = A_\pm\frac{\rho}{T^{3/2}}. \quad (10.1)$$

$I_n^+(\alpha)$ is an integral defined by

$$I_n^\pm(\alpha) = \int_0^\infty \frac{x^n dx}{e^{(x^2+\alpha)} \pm 1} \quad (10.2)$$

where the $\pm$ signs refer to Fermi and Bose gases respectively. $A_\pm$ is a

constant which is different for Fermions and Bosons. The integrals $I_n^{\pm}$ satisfy the recurrence formula

$$\frac{dI_n^{\pm}(\alpha)}{d\alpha} = -\frac{n-1}{2} I_{n-2}^{\pm}(\alpha).$$ (10.3)

Comparison of (10.1) with the general expression (9.4) of the thermal equation of state shows that the function $F(z)$ is given by

$$F(z) = \frac{2k}{3m} \frac{1}{A_{\pm}} I_4^{\pm}(\alpha) \quad \text{with} \quad I_2^{\pm}(\alpha) = A_{\pm} z.$$ (10.4)

In general, α cannot be eliminated between $(10.1)_{1,2}$ or $(10.4)_{1,2}$ to give the thermal equation of state $p = \hat{p}(\rho, T)$ or the form of $F(z)$. However, there are three limiting cases in which this can be done. These are the cases of the classical ideal gas and of the strongly degenerate Bose and Fermi gases which are characterized by

 i) classical ideal gas: $\alpha \gg 1$

$$p = \frac{k}{m} \rho T \quad \text{i. e.} \quad F(z) = \frac{k}{m} z,$$ (10.5)

 ii) strongly degenerate Fermi gas: $\alpha \ll -1$

$$p = v_F \rho^{5/3} \quad \text{i. e.} \quad F(z) = v_F z^{5/3},$$ (10.6)

 iii) strongly degenerate Bose gas: $\alpha \gtrsim 0$

$$p = v_B T^{5/2} \quad \text{i. e.} \quad F(z) = v_B.$$ (10.7)

New constants v_F and v_B have been introduced in (10.6) and (10.7) by the definitions

$$v_F = \frac{2k}{5m} (3A_+)^{2/3} \quad \text{and} \quad v_B = \frac{2k}{3m} \frac{1}{A_-} I_4^-(0).$$ (10.8)

Corresponding to the three limiting cases (10.5) through (10.7) we have:

 i) classical ideal gas:

$$I_n^{\pm}(\alpha) = \frac{n-1}{2} I_{n-2}^{\pm}(\alpha), \qquad I_2^{\pm}(\alpha) = \frac{\pi^{1/2}}{4} e^{-\alpha} = A_{\pm} \frac{\rho}{T^{3/2}},$$ (10.9)

 ii) strongly degenerate Fermi gas:

$$I_n^+(\alpha) = \frac{1}{(n+1)} (-\alpha)^{\frac{n+1}{2}}, \quad I_2^+(\alpha) = \frac{1}{3}(-\alpha)^{3/2} = A_+ \frac{\rho}{T^{3/2}},$$ (10.10)

iii) strongly degenerate Bose gas:

$$I_0^-(0) = \infty, \quad I_2^-(0) \simeq 1.16, \quad I_4^-(0) \simeq 0.89,$$
$$I_6^-(0) \simeq 1.87, \quad I_8^-(0) \simeq 6.13. \quad (10.11)$$

Knowing F(z) in general, by (10.4), we can now proceed to write the conditions (9.5) in a specific form:

10.2 The results for $F(z) = (2k/3m)(I_4^\pm(\alpha)/A_\pm)$.

For F(z) given by (10.4), the equations (9.6) assumes the forms

$$\gamma_0 = \frac{14}{5}\frac{k}{m}\frac{I_6^\pm(\alpha)}{I_4^\pm(\alpha)}T + \frac{21}{2}\frac{m}{k}\frac{A_\pm}{I_4^\pm(\alpha)}a_2 T,$$

$$g = 4\left(\frac{k}{m}\right)^2\frac{I_6^\pm(\alpha)}{A_\pm}T^{7/2} + 15a_2 T^{7/2},$$

$$h_2^{-1} = a_3 T^{11/2} + T^{11/2}\left\{-144\left(\frac{k}{m}\right)^3\frac{1}{A_\pm}I_8^\pm(\alpha) + \frac{560}{3}\left(\frac{k}{m}\right)^3\frac{1}{A_\pm}\frac{I_6^\pm(\alpha)I_4^\pm(\alpha)}{I_2^\pm(\alpha)} + \right.$$

$$+ \left[210a_2 + 20\left(\frac{k}{m}\right)^2\frac{1}{A_\pm}\left(\frac{14}{5}I_6^\pm(\alpha) - \frac{10}{3}\frac{(I_4^\pm(\alpha))^2}{I_2^\pm(\alpha)}\right)\right]\left[\frac{14}{5}\frac{k}{m}\frac{I_6^\pm(\alpha)}{I_4^\pm(\alpha)} + \right.$$

$$\left.+ \frac{21}{2}\frac{m}{k}\frac{A_\pm a_2}{I_4^\pm(\alpha)} - 6\frac{k}{m}\frac{I_2^\pm(\alpha)}{I_0^\pm(\alpha)}\right]\left[1 - \frac{9}{5}\frac{(I_2^\pm(\alpha))^2}{I_0^\pm(\alpha)I_4^\pm(\alpha)}\right]^{-1} +$$

$$\left.+ \frac{k}{m}a_2\left(1\,890\alpha + 700\frac{I_4^\pm(\alpha)}{I_2^\pm(\alpha)}\right)\right\}. \quad (10.12)$$

By (9.5)$_3$ the specific entropy in equilibrium is given by:

$$\eta_0 = \frac{k}{m}\alpha + \frac{5}{3}\frac{k}{m}\frac{I_4^\pm(\alpha)}{I_2^\pm(\alpha)} + a_1. \quad (10.13)$$

On the other hand, the value of v_0 follows from equations (A.30) and (10.12)

$$v_0 = \frac{-T}{10}\left[a_3 - 144\left(\frac{k}{m}\right)^3\frac{1}{A_\pm}I_8^\pm(\alpha) + \frac{560}{3}\left(\frac{k}{m}\right)^3\frac{1}{A_\pm}\frac{I_6^\pm(\alpha)I_4^\pm(\alpha)}{I_2^\pm(\alpha)} + \right.$$

$$\left.+ \frac{k}{m}a_2\left(1\,890\alpha + 700\frac{I_4^\pm(\alpha)}{I_2^\pm(\alpha)}\right)\right]\left[\frac{21}{2}a_2 + \left(\frac{k}{m}\right)^2\frac{1}{A_\pm}\left(\frac{14}{5}I_6^\pm(\alpha) - \frac{10}{3}\frac{(I_4^\pm(\alpha))^2}{I_2^\pm(\alpha)}\right)\right]^{-1},$$

$$(10.14)$$

10.3 The classical ideal gas.

Insertion of (10.9) into the equations (10.12) through (10.14) gives the values γ_0, g, h_2, η_0 and v_0 for a classical ideal gas:

$$\gamma_0 = 7\frac{k}{m}T + 7\frac{m}{k}\frac{T^{5/2}}{\rho}a_2,$$

$$g = 15\left(\frac{k}{m}\right)^2 T^2\rho + 15a_2 T^{7/2},$$

$$h_2^{-1} = -240\left(\frac{k}{m}\right)^3\rho T^4 + 105\frac{k}{m}a_2 T^{11/2}\left[18\ln\frac{T^{3/2}}{\rho} + 35\left(\frac{m}{k}\right)^2 a_2\frac{T^{3/2}}{\rho}\right] +$$

$$+\left[a_3 + 4\,200\frac{k}{m}a_2\left(\frac{9}{20}\ln\frac{\pi^{1/2}}{4A_\pm} + 1\right)\right]T^{11/2}, \tag{10.15}$$

$$\eta_0 = \frac{k}{m}\left[\ln\frac{T^{3/2}}{\rho} + \frac{5}{2} + \ln\frac{\pi^{1/2}}{4A_\pm} + \frac{m}{k}a_1\right],$$

$$v_0 = \left\{28\frac{k}{m}T - 63\left(\frac{m}{k}\right)\frac{T^{5/2}}{\rho}a_2\ln\frac{T^{3/2}}{\rho} - \left(\frac{m}{k}\right)^2\frac{T^{5/2}}{\rho}\left[\frac{a_3}{30} + \right.\right.$$

$$\left.\left. + 35\frac{k}{m}a_2\left(\frac{9}{5}\ln\frac{\pi^{1/2}}{4A_\pm} + 1\right)\right]\right\}\left[1 + \frac{7}{2}a_2\left(\frac{m}{k}\right)^2\frac{T^{3/2}}{\rho}\right].$$

There is a strong suspicion that the constants a_2 and a_3 are both zero, because in the kinetic theory of gases these constants do not appear. It is therefore appropriate to write down the final results for classical ideal gases without those constants. The results are obtained by insertion of (10.15) into the equations (9.5).

$$p_{\langle ik\rangle jj} = 7\frac{k}{m}Tp_{\langle ik\rangle},$$

$$p_{rrssk} = 28\frac{k}{m}Tq_k,$$

$$h = \frac{k}{m}\left[\ln\frac{T^{3/2}}{\rho} + \frac{5}{2} + \ln\frac{\pi^{1/2}}{4A_\pm} + \frac{m}{k}a_1\right]\rho - \frac{m^3}{240k^3\rho T^4}\Delta^2 -$$

$$-\frac{1}{4pT}p_{\langle rs\rangle}p_{\langle rs\rangle} - \frac{m}{5kpT^2}q_r q_r, \tag{10.16}$$

$$\Phi_k = \left(\frac{1}{T} - \frac{m}{15kpT^2}\Delta\right)q_k - \frac{2}{5pT}p_{\langle kr\rangle}q_r,$$

$$g = 15\left(\frac{k}{m}\right)^2\rho T^2.$$

10.4 Strongly degenerate Fermi gas.

For a strongly degenerate Fermi gas insertion of (10.10) into the equations (10.12) through (10.14) leads to

$$\gamma_0 = 5v_F\rho^{2/3} + 7\frac{a_2 T^{7/2}}{v_F\rho^{5/3}},$$

$$g = \frac{75}{7}v_F^2\rho^{7/3} + 15a_2 T^{7/2},$$

$$h_2 = 0,$$

$$\eta_0 = a_1,$$

$$v_0 = 35\,v_F\rho^{2/3} - \frac{a_3}{105a_2}\,T.$$

(10.17)

Hence, the constitutive equations for a strongly degenerate Fermi gas are given by insertion of (10.17) into the equations (9.5)

$$p_{\langle ik\rangle jj} = \left(5v_F\rho^{2/3} + 7\frac{a_2 T^{7/2}}{v_F\rho^{5/3}}\right)p_{\langle ik\rangle},$$

$$p_{rrssk} = \left(35v_F\rho^{2/3} - \frac{a_3}{105a_2}\,T\right)q_k,$$

$$h = a_1\rho - \frac{1}{4v_F\rho^{5/3}T}p_{\langle rs\rangle}p_{\langle rs\rangle} - \frac{2}{35a_2 T^{9/2}}q_r q_r,$$

(10.18)

$$\Phi_k = \left(\frac{1}{T} - \frac{2\Delta}{105a_2 T^{9/2}}\right)q_k - \frac{2}{5v_F\rho^{5/3}T}p_{\langle kr\rangle}q_r,$$

$$g = \frac{75}{7}v_F^2\rho^{7/3} + 15a_2 T^{7/2}.$$

10.5 Strongly degenerate Bose gas.

The results for a strongly degenerate Bose gas follow by the substitution of the values (10.11) into the equations (10.12) through (10.14)

$$\gamma_0 = \left(5.88\frac{k}{m} + 7\frac{a_2}{v_B}\right)T,$$

$$g = \left(12.59\frac{k}{m}v_B + 15a_2\right)T^{7/2},$$

$$h_2^{-1} = \left[a_3 + 1\,470\frac{a_2^2}{v_B}\left(1 + 1.68\frac{k}{m}\frac{v_B}{a_2}\right) - 449.48\left(\frac{k}{m}\right)^2 v_B\right]T^{11/2},$$

(10.19)

$$\eta_0 = 1.29\frac{k}{m} + a_1,$$

$$v_0 = \frac{T}{105}\left[1\,032.33\left(\frac{k}{m}\right)^2 v_B - 539.67\frac{k}{m}a_2 - a_3\right]\left[a_2 + 0.47\frac{k}{m}v_B\right]^{-1},$$

Hence, it follows from (9.5) and (10.19) the constitutive equations for a strongly degenerate Bose gas

$$p_{\langle ik\rangle jj} = \left(5.88\frac{k}{m} + 7\frac{a_2}{v_B}\right)Tp_{\langle ik\rangle},$$

$$p_{rrssk} = \frac{T}{105}\left[1032.33\left(\frac{k}{m}\right)^2 v_B - 539.67\frac{k}{m}a_2 - a_3\right]\left[a_2 + 0.47\frac{k}{m}v_B\right]^{-1}q_k,$$

$$h = \frac{k}{m}\left(1.29 + \frac{m}{k}a_1\right)\rho + T^{-11/2}\left[a_3 + 1470\frac{a_2^2}{v_B}\left(1 + 1.68\frac{k}{m}\frac{v_B}{a_2}\right) - \right.$$

$$\left. - 449.48\left(\frac{k}{m}\right)^2 v_B\right]^{-1}\Delta^2 - \frac{1}{4v_B T^{7/2}}p_{\langle rs\rangle}p_{\langle rs\rangle} - $$

$$- \frac{2}{5v_B T^{9/2}}\left(3.32\frac{k}{m} + 7\frac{a_2}{v_B}\right)^{-1}q_r q_r,$$

$$\Phi_k = \left[\frac{1}{T} - \frac{2\Delta}{15v_B T^{9/2}}\left(3.32\frac{k}{m} + 7\frac{a_2}{v_B}\right)^{-1}\right]q_k - \frac{2}{5v_B T^{7/2}}p_{\langle kr\rangle}q_r,$$

$$g = \left(12.59\frac{k}{m}v_B + 15a_2\right)T^{7/2}. \tag{10.20}$$

11. THE TRANSITION
TO ORDINARY THERMODYNAMICS

As we have seen in (10.16) for a classical ideal gas the coefficients of the constitutive relations for

$$p_{\langle ij\rangle rr}, \quad p_{rrssk}, \quad h, \quad \Phi_k \quad \text{and} \quad g$$

are all explicitly known from the preceding thermodynamic argument. This leaves only the coefficients σ_0, τ_1 and ζ_1 undetermined in the list of equations (8.2). We shall now see how σ_0 and τ_1 can be related to measurable quantities.

The transition from extended thermodynamics to ordinary thermodynamics proceeds by an iterative scheme that has been described in [1]. In the step of this scheme the equilibrium values of p_{ij}, q_i and p_{iijj} are introduced on the left hand sides of the equations $(3.2)_{3,4,5}$ and the resulting

equations are solved for $p_{\langle ij \rangle}$, q_i and Δ that occur on their right hand sides. Thus one obtains first iterates which read

$$\overset{(1)}{p}_{\langle ij \rangle} = 2\frac{p}{\sigma_0}\frac{\partial v_{\langle i}}{\partial x_{j \rangle}}, \quad \overset{(1)}{q}_i = \frac{5p}{2T\tau_1}\left(\gamma_0 - \frac{5p}{\rho}\right)\frac{\partial T}{\partial x_i}, \quad \overset{(1)}{\Delta} = 0. \quad (11.1)$$

The first two of these equations easily recognized as the constitutive equations of Navier-Stokes and Fourier in ordinary thermodynamics. Therefor the coefficients are related to the shear viscosity μ and the heat conductivity K according to the equations

$$\mu = -\frac{p}{\sigma_0}, \quad K = -\frac{5p}{2T\tau_1}\left(\gamma_0 - \frac{5p}{\rho}\right). \quad (11.2)$$

In particular for a classical ideal gas we have by $(10.15)_1$, if the constant a_2 is taken to be zero.

$$\mu = -\frac{k\rho T}{m\sigma_0}, \quad K = -\frac{5k^2\rho T}{m^2\tau_1}. \quad (11.3)$$

Since μ and K are measurable, the equations (11.3) may be used to calculate σ_0 and τ_1.

Second iterates for $p_{\langle ij \rangle}$, q_i and Δ are obtained by introducing the first iterates (11.1) into the left hand side of the equations $(3.2)_{3,4,5}$ and again solving for $p_{\langle ij \rangle}$, q_i and Δ. We carry this out only for Δ, because for this quantity the second iterative step gives the leading term, since $\overset{(1)}{\Delta}$ vanishes. We obtain

$$\overset{(2)}{\Delta} = \frac{1}{\zeta_1}\left\{-8\left(\frac{k}{m}\right)\left[\frac{\partial}{\partial x_i}\left(KT\frac{\partial T}{\partial x_i}\right) + 2\mu T\frac{\partial v_{\langle i}}{\partial x_{j \rangle}}\frac{\partial v_{\langle i}}{\partial x_{j \rangle}}\right] + \right.$$
$$\left. + 4K\frac{\partial T}{\partial x_i}\left[\frac{2}{\rho}\frac{\partial p}{\partial x_i} - 5\frac{k}{m}\frac{\partial T}{\partial x_i}\right] - \frac{16}{\rho}K\frac{\partial T}{\partial x_i}\frac{\partial}{\partial x_j}\left(\mu\frac{\partial v_{\langle i}}{\partial x_{j \rangle}}\right)\right\}. \quad (11.4)$$

This would be the constitutive relation for Δ in ordinary thermodynamics, if indeed that quantity were considered. Note that Δ, according to (11.4) is related to second gradients of v_i and T.

12. ON THE STATUS OF THE « 4-MOMENT » p_{iijj}

One aspect of the variable p_{iijj}, introduced in this paper, is implicit in equation $(11.1)_3$ which states that the first iterate of Δ vanishes. It is because of that that Δ does not play a role in ordinary thermodynamics, where as a rule the constitutive quantities are functions of ρ, v_i and T and their first order spatial derivatives. Equation (11.4) shows however, that the leading terms in Δ contain second order derivatives.

Another aspect of the variable Δ reveals itself in a relativistic theory. It was proved by Dreyer and Weiss [3] that the « 4-moment » p_{iijj} of the present paper corresponds to the combination

$$8c^2\left[(e - nmc^2) - 3p/2\right] \tag{12.1}$$

in relativistic thermodynamics. e is the energy density and n the particle number density. In particular the non-equilibrium part Δ of p_{iijj} corresponds to the non-equilibrium part of (12.1) which is equal to $-12c^2\pi$, where π is the dynamic pressure, i.e. the non-equilibrium contribution to the pressure. Thus we have

$$\pi = -\frac{1}{12c^2}\Delta, \tag{12.2}$$

and it follows that the dynamic pressure in a gas is a relativistically small quantity.

APPENDIX

A.1 CONSEQUENCES FROM THE ENTROPY INEQUALITY AND REPRESENTATIONS

The Lagrange multipliers follow by insertion of the representation of h $(8.2)_7$ into (7.3):

$$\lambda = h_1 + 2h_2\Delta + 3h_3\Delta^2 + h_5 p_{\langle rs \rangle}p_{\langle rs \rangle} + h_7 q_r q_r,$$

$$\lambda_i = 2(h_6 + h_7\Delta)q_i + 2h_9 p_{\langle ir \rangle}q_r,$$

$$\Lambda_{ii} = \left(\frac{\partial h_0}{\partial p} - h_1\frac{\partial g}{\partial p}\right) + \left(\frac{\partial h_1}{\partial p} - 2h_2\frac{\partial g}{\partial p}\right)\Delta + \left(\frac{\partial h_2}{\partial p} - 3h_3\frac{\partial g}{\partial p}\right)\Delta^2 +$$

$$+ \left(\frac{\partial h_4}{\partial p} - h_5\frac{\partial g}{\partial p}\right)p_{\langle rs \rangle}p_{\langle rs \rangle} + \left(\frac{\partial h_6}{\partial p} - h_7\frac{\partial g}{\partial p}\right)q_r q_r, \tag{A.1}$$

$$\Lambda_{\langle ij \rangle} = 2(h_4 + h_5\Delta)p_{\langle ij \rangle} + 3h_8 p_{\langle r \langle i}p_{\langle j \rangle r \rangle} + h_9 q_{\langle i}q_{j \rangle},$$

$$\Lambda = \left(\frac{\partial h_0}{\partial \rho} - h_1\frac{\partial g}{\partial \rho}\right) + \left(\frac{\partial h_1}{\partial \rho} - 2h_2\frac{\partial g}{\partial \rho}\right)\Delta + \left(\frac{\partial h_2}{\partial \rho} - 3h_3\frac{\partial g}{\partial \rho}\right)\Delta^2 +$$

$$+ \left(\frac{\partial h_4}{\partial \rho} - h_5\frac{\partial g}{\partial \rho}\right)p_{\langle rs \rangle}p_{\langle rs \rangle} + \left(\frac{\partial h_6}{\partial \rho} - h_7\frac{\partial g}{\partial \rho}\right)q_r q_r.$$

Now we put the Lagrange multipliers (A.1) and the representation of the productions $(8.2)_{4,5,6}$ in the residual inequality (7.6) and keep only those terms that are at most quadratic in $p_{\langle ij \rangle}$, q_i and Δ.

$$\Sigma = 2h_4\sigma_0 p_{\langle rs \rangle}p_{\langle rs \rangle} + 2h_6\tau_1 q_r q_r + (h_1 + h_2\Delta)\zeta_1\Delta \geqslant 0. \tag{A.2}$$

$\Sigma = \hat{\Sigma}(\rho, p, p_{\langle ij \rangle}, q_i, \Delta)$ assumes its minimum in equilibrium, i. e.,

$$\Sigma|_{\text{E}} = \hat{\Sigma}(\rho, p, 0, 0, 0) = 0. \tag{A.3}$$

The necessary conditions for Σ to be a minimum in equilibrium are:

$$\left.\frac{\partial\Sigma}{\partial X_A}\right|_{\text{E}} = 0, \qquad \left\|\left|\frac{\partial^2\Sigma}{\partial X_A \partial X_B}\right|_{\text{E}}\right\| \text{ is non-negative definite} \tag{A.4}$$

where $X_A = \{p_{\langle ij \rangle}, q_i, \Delta\}$.

We get from (A.2) and $(A.4)_1$:

$$h_1 = 0, \tag{A.5}$$

and from (A.2) and $(A.4)_2$:

$$h_4\sigma_0 \geqslant 0, \quad h_6\tau_1 \geqslant 0, \quad h_2\zeta_1 \geqslant 0. \tag{A.6}$$

On the other hand we take the trace, the symmetric traceless part and the antisymmetric part of (7.4):

$$h = \rho\Lambda + \frac{5}{3}\Lambda_{rs}p_{rs} + 2\lambda_r q_r + \frac{7}{3}\lambda(g + \Delta),$$

$$2\Lambda_{k\langle i}p_{j\rangle k} + \lambda_r p_{\langle rij \rangle} + \frac{9}{5}\lambda_{\langle i}q_{j\rangle} + 4\lambda p_{\langle ij \rangle rr} = 0, \tag{A.7}$$

$$2\Lambda_{r[i}p_{j]r} + \lambda_{[i}q_{j]} = 0.$$

The insertion of the representation of h $(8.2)_7$ and the Lagrange multipliers $(A.1)$ into $(A.7)_1$ leads to a polynomial in $p_{\langle ij \rangle}$, q_i and Δ. This polynomial is equal to zero, so all its coefficients are equal to zero:

$$h_0 = \rho \frac{\partial h_0}{\partial \rho} + \frac{5}{3} p \frac{\partial h_0}{\partial p},$$

$$\rho \frac{\partial g}{\partial \rho} + \frac{5}{3} p \frac{\partial g}{\partial p} - \frac{7}{3} g = 0,$$

$$h_2 = \rho \frac{\partial h_2}{\partial \rho} + \frac{5}{3} p \frac{\partial h_2}{\partial p} + \frac{14}{3} h_2, \qquad (A.8)$$

$$h_4 = \rho \frac{\partial h_4}{\partial \rho} + \frac{5}{3} p \frac{\partial h_4}{\partial p} + \frac{10}{3} h_4,$$

$$h_6 = \rho \frac{\partial h_6}{\partial \rho} + \frac{5}{3} p \frac{\partial h_6}{\partial p} + 4h_6.$$

In the equation $(A.8)$, we have supposed that $h_2 \neq 0$.

In the same way we get from $(A.7)_2$ by insertion of $(A.1)$ and (8.2):

$$2h_4 + 3ph_8 = 0, \quad 6ph_4 + \frac{\partial h_0}{\partial p} = 0, \quad ph_5 + h_2 \left(2\gamma_0 - \frac{1}{3} \frac{\partial g}{\partial p} \right) = 0, \quad ph_9 + \frac{9}{5} h_6 = 0. \quad (A.9)$$

The equation $(A.7)_3$ is identically satisfied.

It remains to exploit the equations (7.5) and insertion of the representations (8.2) and the Lagrange multipliers $(A.1)$ leads to:

i) from $(7.5)_1$:

$$\frac{\partial \varphi_1}{\partial \rho} = \frac{1}{3} h_6 \frac{\partial g}{\partial \rho},$$

$$\frac{\partial \varphi_2}{\partial \rho} = 2h_2 \frac{\partial v_0}{\partial \rho} + \frac{1}{3} h_7 \frac{\partial g}{\partial \rho}, \qquad (A.10)$$

$$\frac{\partial \varphi_3}{\partial \rho} = h_6 \frac{\partial \gamma_0}{\partial \rho} + \frac{1}{3} h_9 \frac{\partial g}{\partial \rho};$$

ii) from $(7.5)_2$:

$$\frac{\partial \varphi_1}{\partial p} = h_6 \left(\frac{1}{3} \frac{\partial g}{\partial p} - \frac{5p}{\rho} \right),$$

$$\frac{\partial \varphi_2}{\partial p} = h_7 \left(\frac{1}{3} \frac{\partial g}{\partial p} - \frac{5p}{\rho} \right) + 2h_2 \left(\frac{\partial v_0}{\partial p} - \frac{8}{\rho} \right),$$

$$\frac{\partial \varphi_3}{\partial p} = h_9 \left(\frac{1}{3} \frac{\partial g}{\partial p} - \frac{5p}{\rho} \right) + h_6 \left(\frac{\partial \gamma_0}{\partial p} - \frac{2}{\rho} \right), \qquad (A.11)$$

$$\varphi_3 = h_6 \left(\gamma_0 - \frac{5p}{\rho} \right);$$

iii) from $(7.5)_3$:

$$\varphi_1 = \frac{2}{3} \frac{\partial h_0}{\partial p}, \quad \varphi_2 = 2h_2 \left(v_0 - \frac{2}{3} \frac{\partial g}{\partial p} \right), \quad \varphi_3 = \frac{8h_4}{5}; \qquad (A.12)$$

iv) from $(7.5)_4$:

$$\varphi_2 = \frac{h_6}{3}. \qquad (A.13)$$

A.2 THE IDENTIFICATION OF THE ABSOLUTE TEMPERATURE, GENERAL FORM OF THE THERMAL EQUATION OF STATE AND THE EQUILIBRIUM VALUE OF THE SPECIFIC ENTROPY

First we write

$$d\left(\frac{h_0}{\rho}\right) = \frac{\partial}{\partial\rho}\left(\frac{h_0}{\rho}\right)d\rho + \frac{\partial}{\partial p}\left(\frac{h_0}{\rho}\right)dp . \tag{A.14}$$

This equation can be written as

$$d\left(\frac{h_0}{\rho}\right) = \frac{2}{3}\frac{\partial h_0}{\partial p}\left(d\varepsilon - \frac{p}{\rho^2}d\rho\right), \tag{A.15}$$

if we use the equation $(A.8)_1$ and $3p = 2\rho\varepsilon$.

Thus $\dfrac{2}{3}\dfrac{\partial h_0}{\partial p}$ is *the* integrating factor of the Pfaffian form $d\varepsilon - \dfrac{p}{\rho^2}d\rho$ whose integral is the specific entropy $\eta_0 = \dfrac{h_0}{\rho}$ in equilibrium. By a well-established argument of equilibrium thermodynamics it follows therefore that $\dfrac{2}{3}\dfrac{\partial h_0}{\partial p}$ is the reciprocal of the absolute temperature T.

$$\frac{2}{3}\frac{\partial h_0}{\partial p} = \frac{1}{T} \quad \text{and therefore} \quad d\eta_0 = \frac{1}{T}\left(d\varepsilon - \frac{p}{\rho^2}d\rho\right). \tag{A.16}$$

The equation $(A.16)_1$ permits the replacement of the pair of variables (ρ, p) by the pair (ρ, T) which in many respects is preferable. Thus ε and $p = \dfrac{2}{3}\rho\varepsilon$ become functions of ρ and T and the integrability condition implied by $(A.16)_2$ reads

$$\rho\frac{\partial p}{\partial\rho} + \frac{2}{3}T\frac{\partial p}{\partial T} = \frac{5}{3}p , \tag{A.17}$$

with the solution

$$p = T^{5/2}F(z) \quad \text{where} \quad z = \frac{\rho}{T^{3/2}} . \tag{A.18}$$

This equation restricts the thermal equation of state of a gas which is thus seen to contain only a function of a single variable, namely $z = \rho/T^{3/2}$.

With the thermal equation of state (A.18) and the use of $\varepsilon = (3p/2\rho)$ we can integrate $(A.16)_2$ and obtain for equilibrium value of the specific entropy

$$\eta_0 = \frac{3}{2}\int\left(\frac{F'}{z} - \frac{5}{3}\frac{F}{z^2}\right)dz + a_1 \tag{A.19}$$

a_1 is a constant of integration and F' is the derivative of F with respect to its argument.

A.3 THE INTRODUCTION OF THE ABSOLUTE TEMPERATURE AS A VARIABLE AND THE FINAL RESULTS

Now we change the variables throughout all our conditions, that is instead of the pair (ρ, p) we use the pair (ρ, T).

By virtue of the relations

$$\left(\frac{\partial f}{\partial\rho}\right)_p = \left(\frac{\partial f}{\partial\rho}\right)_T + \left(\frac{\partial f}{\partial T}\right)_p\left(\frac{\partial T}{\partial\rho}\right)_p \quad \text{and} \quad \left(\frac{\partial f}{\partial p}\right)_\rho = \left(\frac{\partial f}{\partial T}\right)_\rho\left(\frac{\partial T}{\partial p}\right)_\rho , \tag{A.20}$$

we get alternative forms for the conditions (A.9) through (A.13).

$$h_2 = \frac{-1}{15pT}\left(\gamma_0 - \frac{5p}{\rho}\right)^{-1}\left(v_0 - \frac{2}{3}\frac{\partial g}{\partial T}\Big/\frac{\partial p}{\partial T}\right)^{-1}, \quad h_4 = \frac{-1}{4pT}, \quad h_6 = \frac{-2}{5pT}\left(\gamma_0 - \frac{5p}{\rho}\right)^{-1},$$

$$h_5 = \frac{1}{15p^2T}\left(\gamma_0 - \frac{5p}{\rho}\right)^{-1}\left(v_0 - \frac{2}{3}\frac{\partial g}{\partial T}\Big/\frac{\partial p}{\partial T}\right)^{-1}\left(2\gamma_0 - \frac{1}{3}\frac{\partial g}{\partial T}\Big/\frac{\partial p}{\partial T}\right),$$

$$h_8 = \frac{1}{6p^2T}, \quad h_9 = \frac{18}{25p^2T}\left(\gamma_0 - \frac{5p}{\rho}\right)^{-1}. \tag{A.21}$$

$$\varphi_1 = \frac{1}{T}, \quad \varphi_3 = \frac{-2}{5pT}, \quad \varphi_2 = \frac{-2}{15pT}\left(\gamma_0 - \frac{5p}{\rho}\right)^{-1} = 2h_2\left(v_0 - \frac{2}{3}\frac{\partial g}{\partial T}\Big/\frac{\partial p}{\partial T}\right). \tag{A.22}$$

$$\frac{\partial g}{\partial \rho} = \frac{15p}{\rho}\frac{\partial p}{\partial \rho}, \quad \frac{\partial g}{\partial T} = \frac{15p}{\rho}\frac{\partial p}{\partial T} + \frac{15p}{2T}\left(\gamma_0 - \frac{5p}{\rho}\right),$$

$$\frac{\partial \gamma_0}{\partial \rho} = \frac{-1}{p}\frac{\partial p}{\partial \rho}\left(\gamma_0 - \frac{7p}{\rho}\right), \quad \frac{\partial \gamma_0}{\partial T} = \frac{-1}{p}\frac{\partial p}{\partial T}\left(\gamma_0 - \frac{7p}{\rho}\right) + \frac{7}{2T}\left(\gamma_0 - \frac{5p}{\rho}\right), \tag{A.23}$$

$$\frac{\partial \varphi_2}{\partial \rho} = 2h_2\left(\frac{\partial v_0}{\partial \rho} - \frac{8}{\rho}\frac{\partial p}{\partial \rho}\right), \quad \frac{\partial \varphi_2}{\partial T} = 2h_2\left(\frac{\partial v_0}{\partial T} - \frac{8}{\rho}\frac{\partial p}{\partial T}\right) + \frac{5ph_7}{2T}\left(\gamma_0 - \frac{5p}{\rho}\right).$$

On the other hand we get from (A.8)$_{2,3}$ and (A.17)

$$\rho\frac{\partial g}{\partial \rho} + \frac{2}{3}T\frac{\partial g}{\partial T} = \frac{7}{3}g, \quad \rho\frac{\partial h_2^{-1}}{\partial \rho} + \frac{2}{3}T\frac{\partial h_2^{-1}}{\partial T} = \frac{11}{3}h_2^{-1}. \tag{A.24}$$

Integration of (A.24) gives

$$g = T^{7/2}G(z) \quad \text{and} \quad h_2^{-1} = T^{11/2}H(z), \tag{A.25}$$

where G and H are arbitrary functions of $z = \rho/T^{3/2}$. By use of (A.23)$_1$ the function G may be related to the function F(z) in the thermal equation of state and we obtain by integration:

$$g = 15T^{7/2}\left(\int\frac{FF'}{z}dz + a_2\right). \tag{A.26}$$

a_2 is a constant of integration.

Insertion of this expression for g into (A.23)$_2$ leads to the determination of γ_0

$$\gamma_0 = \frac{7T}{F}\left(\int\frac{FF'}{z}dz + a_2\right). \tag{A.27}$$

The function H in (A.25)$_2$ may be determined by insertion of (A.22)$_3$ into (A.23)$_5$ and a little calculation shows that we obtain by use of (A.26) and (A.27)

$$H' = 30F\left\{\frac{7}{F}\left(\int\frac{FF'}{z}dz + a_2\right) - \frac{5F}{z}\right\}\left\{\left(\frac{7\left(\int\frac{FF'}{z}dz + a_2\right) - 3FF'}{F - 3F'z/5}\right)' - \frac{4F'}{z}\right\}. \tag{A.28}$$

It follows that h_2^{-1} can be written as

$$h_2^{-1} = T^{11/2}\left(\int\left[30F\left\{\frac{7}{F}\left(\int\frac{FF'}{z}dz + a_2\right) - \frac{5F}{z}\right\}\left\{-\frac{4F'}{z} + \right.\right.\right.$$

$$\left.\left.\left. + \left(\frac{7\left(\int\frac{FF'}{z}dz + a_2\right) - 3FF'}{F - 3F'z/5}\right)'\right\}\right]dz + a_3\right) \tag{A.29}$$

where a_3 is a constant of integration.

The determination of v_0 follows from (A.22)$_3$ and (A.29). We get

$$v_0 = 2T \left\{ -\frac{\int\left[\quad\right]dz + a_3}{30F\left\{\frac{7}{F}\left(\int\frac{FF'}{z}dz+a_2\right)-\frac{5F}{z}\right\}} + \frac{7\left(\int\frac{FF'}{z}dz + a_2\right) - 3FF'}{F - \frac{3}{5}F'z} \right\} \quad (A.30)$$

where the bracket [ ] encloses the same integrand as in (A.29).
Finally we get from (A.6) and (A.21)$_{2,3}$

$$\sigma_0 \leqslant 0, \quad \tau_1\left(\gamma_0 - \frac{5p}{\rho}\right)^{-1} \leqslant 0, \quad h_2\zeta_1 \geqslant 0. \quad (A.31)$$

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