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Abstract. This paper proves that the maximisation of the entropy in non-equilibrium is equivalent to the exploitation of the entropy inequality in extended thermodynamics.

1. Introduction

This paper proves that the maximisation of the entropy in non-equilibrium is equivalent to the exploitation of the entropy inequality in extended thermodynamics.

A kinetic theory of a given material yields moments of the phase density f and equations of transfer for those moments. In thermodynamics one usually takes some of these moments as basic variables, namely those for which initial and boundary conditions can be prescribed. The field equations of these variables are based on the equations of transfer which, however, contain higher moments and collision rates. These additional quantities must be determined by constitutive relations.

If the phase density were known as a function of the basic variables then the constitutive quantities could also be determined in terms of their dependence on the basic variables. Explicit constitutive relations for ideal gases can be calculated in this manner.

This work has been motivated by the observation—made by Kogan [1]—that the thirteen-moment phase density of Grad [2] maximises the entropy. This is an extension to non-equilibrium processes of the Boltzmann method by which the phase density f for an ideal gas in equilibrium can be obtained by maximising the entropy under the constraints of fixed mass density ρ, momentum density ρv and internal energy density $\rho \varepsilon$. In non-equilibrium, further moments of f (e.g. pressure deviator P and heat flux q) contribute to the state of the gas. If one determines the function f that maximises the entropy for given values of $(\rho, \rho v, \rho \varepsilon, P, q)$ one obtains Grad's thirteen-moment phase density, provided that f is assumed to be a linear function of the non-equilibrium quantities P and q.

The question arises whether this may be justified, since all we do know is that there exists an entropy inequality in non-equilibrium.

In this paper we prove for a degenerate ideal gas that the exploitation of the entropy inequality—for an even more detailed description of the non-equilibrium state, e.g. by ρ, ρv, $\rho \varepsilon$, P, q and higher moments—and the maximisation of the entropy leads to the same results as follows. In the first method we choose a finite number of moments as basic variables for an ideal gas and identify the constitutive quantities. The entropy inequality implies restriction on the constitutive functions. In the second method the phase density for the same variables is calculated by the maximisation of the entropy

of a degenerate ideal gas. By use of this phase density we calculate the constitutive quantities.

It proves that all restrictions of the first method are included in the constitutive functions resulting from the second method. The theory as a whole emphasises a far-reaching parallelism between the reasoning of statistical thermodynamics and phenomenological thermodynamics. Indeed, the well known Lagrange multipliers of the statistical theory prove to be identical to the Lagrange multipliers that were utilised in the evaluation of the entropy inequality.

This paper is divided into three further sections and three appendices. In § 2 a short survey of the fundamentals and the nomenclature of the kinetic theory of ideal gases is given. In § 3 the procedure of phenomenological extended thermodynamics is described. The main part of this paper is included in § 4. The maximisation of entropy in non-equilibrium is carried out and the equivalence to the phenomenological approach is proved by use of some lemmas that are derived in appendix 1.

1.1. Notations

Throughout this paper the tensor index notation is used. A tensor $T^{(M)}$ of rank M is represented by its components $T^{(M)}_{i_1...i_M}$ with respect to a cartesian inertial frame of reference. Traces of a tensor $T^{(M)}$, e.g. $T^{(M)}_{i_1...i_{M-2}ii}$ or $T^{(M)}_{i_1...i_{M-4}jjii}$ are denoted by $T^{(M)}_{i_1...i_{M-2}}$ and $T^{(M)}_{i_1...i_{M-4}}$, respectively.

The symmetric, traceless symmetric and antisymmetric parts of $T^{(M)}$ are denoted by $T^{(M)}_{(i_1...i_M)}$, $T^{(M)}_{\langle i_1...i_M\rangle}$ and $T^{(M)}_{[i_1...i_M]}$, respectively. General symmetrisation means summing $T^{(M)}_{i_1...i_M}$ for all permutations of indices and dividing by $M!$.

2. A reminder of the kinetic theory of gases

The microstate of a monatomic ideal gas is described by the phase density $f(x, c, t)$ which gives the number density of atoms in the neighbourhood $d^3x\, d^3c$ of the phase space point $(x, c) := $ (position, velocity) at time t. The phase density obeys the Boltzmann equation

$$\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} + \dot{c}_i \frac{\partial f}{\partial c_i} = \zeta(f) \tag{2.1}$$

where ζ denotes the collision operator. In addition we impose the condition on f that

$$\lim_{|c| \to \infty} f(x, c, t) \le |P(x, c, t)| \exp(-a(x, t)c^2) \tag{2.2}$$

where P must be a polynomial in c and $a > 0$.

The moments $F^{(M)}_{i_1...i_M}$ of the phase density, the entropy density and the entropy flux φ_i are defined as

$$F^{(M)}_{i_1...i_M} := m \int c_{i_1} \ldots c_{i_M} f \, d^3c \tag{2.3}$$

$$s := -k \int [f \ln f/y \mp y(1 \pm f/y) \ln(1 \pm f/y)] \, d^3c \tag{2.4}$$

$$\varphi_i := -k \int c_i[f \ln f/y \mp y(1 \pm f/y) \ln(1 \pm f/y)] \, d^3c \tag{2.5}$$

where m is the mass of an atom. The upper and lower signs in (2.4) and (2.5) correspond to bosons and fermions, respectively. y is a constant which is given by $(2s+1)/h^3$ where s is the spin number. Boltzmann's constant is denoted by k and h is Planck's constant.

The Boltzmann equation yields the so-called equation of transfer and the entropy inequality

$$\frac{\partial F^{(M')}_{i_1 \dots i_{M'}}}{\partial t} + \frac{\partial F^{(M'+1)}_{i_1 \dots i_{M'} k}}{\partial x_k} = S^{(M')}_{i_1 \dots i_{M'}} \dagger \tag{2.6}$$

$$\frac{\partial s}{\partial t} + \frac{\partial \varphi_i}{\partial x_i} \geq 0 \tag{2.7}$$

$S^{(M')}_{i_1 \dots i_{M'}}$ denotes the collision rate of the M'th moment

$$S^{(M')}_{i_1 \dots i_{M'}} := m \int c_{i_1} \dots i_{M'} \zeta(f) \, d^3 c. \tag{2.8}$$

The first thirteen moments have physical significance because the following interpretations hold:

$$
\begin{aligned}
F^{(0)}_i &:= \rho & &\text{mass density} \\
F^{(1)}_i &:= \rho v_i & &\text{momentum density} \\
F^{(2)}_{ij} &:= \rho v_i v_j + P_{ij} & &\text{momentum flux} \\
F^{(3)}_i &:= \rho(\varepsilon + \tfrac{1}{2} v^2) v_i + q_i + P_{ij} v_j & &\text{energy flux.}
\end{aligned}
\tag{2.9}
$$

We have decomposed $F^{(2)}_{ij}$ and $F^{(3)}_i$ into convective parts and the non-convective quantities: pressure tensor P_{ij}, internal energy density $\rho\varepsilon$ and heat flux q_i. The pressure tensor is usually decomposed as

$$P_{ij} = P_{\langle ij \rangle} + p\delta_{ij} \qquad \text{with} \qquad p := \tfrac{1}{3} P_{ii} = \tfrac{2}{3} \rho\varepsilon \tag{2.10}$$

where $P_{\langle ij \rangle}$ denotes the pressure deviator and p is the pressure.

These quantities are directly related to the so-called central moments of f formed with the excess velocity $C := c - v$:

$$m^{(M')}_{i_1 \dots i_{M'}} := m \int C_{i_1} \dots C_{i_{M'}} f \, d^3 C. \tag{2.11}$$

It follows that we have

$$m^{(0)} = \rho \qquad m^{(1)}_i = 0 \qquad m^{(2)}_{\langle ij \rangle} = P_{\langle ij \rangle} \qquad m^{(2)} = 2\rho\varepsilon \qquad m^{(3)}_i = 2q_i. \tag{2.12}$$

Furthermore the equations of transfer for the momentum and the other central moments are

$$\frac{\partial \rho v_i}{\partial t} + \frac{\partial}{\partial x_j} (\rho v_i v_j + P_{ij}) = 0 \tag{2.13}$$

$$\frac{\partial m^{(M')}_{i_1 \dots i_{M'}}}{\partial t} + \frac{\partial}{\partial x_j} (m^{(M')}_{i_1 \dots i_{M'}} v_j + m^{(M'+1)}_{i_1 \dots i_{M'} j}) - \frac{M'}{\rho} m^{(M'-1)}_{(i_1 \dots i_{M'-1}} \frac{\partial P_{i_{M'}) j}}{\partial x_j}$$

$$+ M' m^{(M')}_{j(i_1 \dots i_{M'-1}} \frac{\partial v_{i_{M'})}}{\partial x_j} = S^{(M')}_{i_1 \dots i_{M'}} \tag{2.14}$$

where $S^{(M')}_{i_1 \dots i_{M'}}$ is the collision rate of the central moments.

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† External forces have been ignored.

For more details the reader is referred to the many textbooks on kinetic theory, such as Chapman and Cowling [3].

3. Thermodynamics

3.1. The thermodynamic state of a gas

Thermodynamics restricts itself to the determination of some lower moments of f. This is possible because in a process close to equilibrium only a few moments are needed to describe that process satisfactorily.

Definition. A thermodynamic process in a gas is said to be of grade N if the first N moments are needed for its description. The set of necessary variables for the description of the process of grade N is called the state of the gas and is denoted by

$$Z_N = (m^{(0)}, \rho v_{i_1}, m^{(2)}_{i_1 i_2}, \ldots, m^{(M)}_{i_1 \ldots i_M}) \tag{3.1}$$

consisting of all N components of the first M moments.

Remarks. For example, an equilibrium state of a gas is a process of grade 5 and its state is given by

$$Z_5 = (\rho, \rho v_i, \rho \varepsilon). \tag{3.2}$$

All processes for $N > 5$ are non-equilibrium processes. The decision about the appropriate N for a given thermodynamic process has to be made empirically.

3.2. Thermodynamics of processes of grade N

The general purpose of thermodynamics is the determination of processes of grade N. The set of variables is given by (3.1) and the necessary field equations are based on the corresponding N equations of transfer (2.14) and (2.15). Inspection of these equations of transfer reveals that we are confronted with a closure problem, because they contain the unknown fluxes $m^{(M+1)}_{i_1 \ldots i_{M+1}}$ and the collision rates $S^{(M')}_{i_1 \ldots i_{M'}}$ ($M' = 3, 4, \ldots, M$). This closure problem is solved in thermodynamics by the following assumption.

Assumption. The unknown quantities are functions of the state Z_N. They are given by constitutive equations of the form

$$m^{(M+1)}_{i_1 \ldots i_{M+1}} = \hat{m}^{(M+1)}_{i_1 \ldots i_{M+1}}(Z_N) \qquad S^{(M')}_{i_1 \ldots i_{M'}} = \hat{S}^{(M')}_{i_1 \ldots i_{M'}}(Z_N) \qquad M' = 3, 4, \ldots, M. \tag{3.3}$$

By use of (3.3) we can eliminate the unknown fluxes and collision rates in (2.15) and obtain a set of field equations for the N basic fields provided the constitutive functions $\hat{m}^{(M+1)}_{i_1 \ldots i_{M+1}}$ and $\hat{S}^{(M')}_{i_1 \ldots i_{M'}}$ are known.

Remark. We have selected the special case that the state contains the full moments up to a given order M which we shall proceed to investigate. There are, however, alternatives and in fact the most common cases of $N = 13$ and $N = 14$ provide such alternatives. For a discussion of this point see appendix 2. After this remark we continue with (3.1) and (3.3).

The generality of the constitutive equations (3.3) is restricted by two principles.

It follows from the *principle of Galilean invariance* that the constitutive quantities cannot depend on the velocity v, and moreover that principle states that the constitutive functions must be isotropic ones.

The *entropy principle* states [4] that the entropy density and the non-convective entropy flux are constitutive quantities given by

$$s = \hat{s}(Z_N) \qquad \Phi_i = \hat{\Phi}_i(Z_N) \tag{3.4}$$

and that s and Φ_i obey the entropy inequality

$$\frac{\partial s}{\partial t} + \frac{\partial}{\partial x_i}(sv_i + \Phi_i) \geq 0 \tag{3.5}$$

for all solutions of the field equations.

Note that (3.5) need not hold for all fields $m^{(0)}, m_{i_1}^{(1)}, \ldots, m_{i_1 \ldots i_M}^{(M)}$ but only for those which satisfy the field equations. The field equations are therefore to be considered as constraints. One can dispose of these constraints by use of Lagrange multipliers as introduced by Liu [5] who proved the following proposition.

Proposition. If (3.5) holds only for solutions of the field equations then the following inequality holds for arbitrary fields:

$$\frac{\partial s}{\partial t} + \frac{\partial}{\partial x_i}(sv_i + \Phi_i) - \Lambda_i^v\left(\frac{\partial v_i}{\partial t} + \frac{\partial}{\partial x_j}(\rho v_i v_j + P_{ij})\right)$$

$$- \sum_{\substack{M'=0 \\ M' \neq 1}}^{M} \Lambda_{i_1 \ldots i_M}^{(M')} \left(\frac{\partial m_{i_1 \ldots i_M}^{(M')}}{\partial t} + \frac{\partial}{\partial x_j}(m_{i_1 \ldots i_M}^{(M')} v_j + m_{i_1 \ldots i_M j}^{(M'+1)})\right)$$

$$- \frac{M'}{\rho} m_{i_1 \ldots i_{M'-1}}^{(M'-1)} \frac{\partial m_{i_M j}^{(2)}}{\partial x_j} + M' m_{j(i_1 \ldots i_{M'-1}}^{(M')} \frac{\partial v_{i_M)}}{\partial x_j} - S_{i_1 \ldots i_M}^{(M')}\right) \geq 0. \tag{3.6}$$

The Lagrange multipliers Λ_i^v, $\Lambda_{i_1 \ldots i_M}^{(M')}$ may be functions of Z_N.

The evaluation of an inequality of the type (3.6) has been carried out by Liu and Müller [6]. It has transpired that the following relations must hold because otherwise (3.6) could be violated:

$$ds = \sum_{M'=0}^{M} \Lambda_{i_1 \ldots i_M}^{(M')} dm_{i_1 \ldots i_M}^{(M')} \tag{3.7}$$

$$d\Phi_j = \sum_{M'=2}^{M} \Lambda_{i_1 \ldots i_M}^{(M')} dm_{i_1 \ldots i_M j}^{(M'+1)} - \sum_{M'=3}^{M} \frac{M'}{\rho} \Lambda_{i_1 \ldots i_M}^{(M')} m_{(i_1 \ldots i_{M'-1}}^{(M'+1)} \delta_{i_M)i} dm_{ij}^{(2)} \tag{3.8}$$

$$s = \Lambda^{(0)} \rho + \sum_{M'=2}^{M} (1 + \tfrac{1}{3} M') \Lambda_{i_1 \ldots i_M}^{(M')} m_{i_1 \ldots i_M}^{(M')} \tag{3.9}$$

$$\sum_{M'=2}^{M} M' \Lambda_{i_1 \ldots i_M}^{(M')} \delta_{i_M(j} m_{i)i_1 \ldots i_{M'-1}}^{(M')} = 0 \tag{3.10}$$

$$\sum_{M'=2}^{M} M' \Lambda_{i_1 \ldots i_M}^{(M')} \delta_{i_M[j} m_{i]i_1 \ldots i_{M'-1}}^{(M')} = 0 \tag{3.11}$$

$$\Lambda_i^v = 0 \tag{3.12}$$

Remark. The conditions (3.7)-(3.12) represent all restrictions imposed by the entropy inequality upon the constitutive functions except for a residual inequality which restricts the collision rates. Those restrictions, however, do not interest us here.

Before one can extract the desired restrictions from (3.7)-(3.12) upon the constitutive functions all Lagrange multipliers must be eliminated. This is a long cumbersome procedure which Liu and Müller [6] and Kremer [7] have illustrated for the thirteen-moment and the fourteen-moment cases, respectively.

  Having concluded the derivation of the phenomenological restrictions on the constitutive relations we now proceed to find the corresponding restrictions implied by the statistical method.

4. Maximisation of the entropy in non-equilibrium

4.1. Phase density for a process of grade N

The statistical analogue to the thermodynamic description by the state Z_N is an assumption that the dependence of f on x and t is in fact a dependence on $Z_N(x, t)$:

$$f = f(x, c, t) = \hat{f}(Z_N(x, t), c) \tag{4.1}$$

where (4.1) denotes the phase density of a thermodynamic process of grade N.

  If $\hat{f}$ were known explicitly we could calculate those moments of f which are regarded as constitutive quantities in thermodynamics. In addition we should be able to calculate the collision rates. The determination of $\hat{f}$ makes use of the following assumption.

Assumption. The phase density $\hat{f}$ is the one which maximises the entropy (2.4).

4.2. Scope of this section

We shall proceed from the above assumption to calculate $\hat{f}$ by maximising s under the constraints of constant values of Z_N. Lagrange multipliers λ will take care of these constraints in the maximisation procedure and will appear in $\hat{f}$.

  Once $\hat{f}$ has been determined we shall show that the quantities

$$m^{(M')}_{i_1 \dots i_{M'}} = m \int C_{i_1} \dots C_{i_{M'}} f \, d^3C \qquad M' = 0, 1, \dots, M+1 \tag{4.2}$$

$$s = -k \int [f \ln f/y \mp y(1 \pm f/y) \ln(1 \pm f/y)] \, d^3C \tag{4.3}$$

$$\Phi_i = -k \int C_i [f \ln f/y \mp y(1 \pm f/y) \ln(1 \pm f/y)] \, d^3C \tag{4.4}$$

calculated with this $\hat{f}$ satisfy the same equations as the thermodynamic variables and constitutive quanties $m^{(M+1)}$, s and Φ and the thermodynamic Lagrange multipliers $\Lambda^{(M')}$, namely (3.7)-(3.11).

  It will thus become clear that the above assumption was a good one in the sense that the maximisation of the statistical entropy leads to the same results as the exploitation of the thermodynamic entropy inequality.

It will turn out that the statistical approach yields more information than the thermodynamic one. In this paper, however, we concentrate on the results common to both methods. The full exploitation of the knowledge of $\hat{f}$ will be described in a forthcoming paper by Dreyer and Strehlow [8].

4.3. Maximisation of the entropy under constraints

We are looking for the phase density that maximises the entropy under the constraints of given values of

$$m_{i_1\ldots i_{M'}}^{(M')} = m \int C_{i_1} \ldots C_{i_{M'}} f \, \mathrm{d}^3 C \qquad M' = 0, 1, 2, \ldots, M. \tag{4.5}$$

We can get rid of these constraints by introducing Lagrange multipliers $\lambda_{i_1\ldots i_{M'}}^{(M')}$. Therefore

$$G := s - \sum_{M'=0}^{M} \lambda_{i_1\ldots i_{M'}}^{(M')} \left(m \int C_{i_1} \ldots C_{i_{M'}} f \, \mathrm{d}^3 C - m_{i_1\ldots i_{M'}}^{(M')} \right) \tag{4.6}$$

has to be maximised without constraints. The necessary condition for a maximum of G is $\partial G/\partial f = 0$ and with s given by (4.3) that condition becomes

$$\ln \hat{f}/y - \ln(1 \pm f/y) = -\Sigma \tag{4.7}$$

or

$$\hat{f} = y/\exp(\Sigma \mp 1) \tag{4.8}$$

where Σ is defined as

$$\Sigma := \frac{m}{k} \sum_{M'=0}^{M} \lambda_{i_1\ldots i_{M'}}^{(M')} C_{i_1} \ldots C_{i_{M'}}. \tag{4.9}$$

The constraints (4.5) are linear functionals of f so that the sufficient condition for a maximum is simply given by

$$\frac{\partial}{\partial f^2} [-f \ln f/y \pm y(1 \pm f/y) \ln(1 \pm f/y)] < 0. \tag{4.10}$$

One can easily show that

$$\frac{\partial^2}{\partial f^2} [-f \ln f/y \pm y(1 \pm f/y) \ln(1 \pm f/y)] = - \begin{cases} \dfrac{1}{f/y} - \dfrac{1}{1+f/y} & \text{for bosons} \\[3mm] \dfrac{1}{f/y} + \dfrac{1}{1-f/y} & \text{for fermions} \end{cases} \tag{4.11}$$

holds. This is always smaller than zero for the Bose case, as well as for the Fermi case where one has to take into account that $f/y \le 1$.

4.4. Conclusions

Once $\hat{f}$ has been determined by (4.8) we may introduce it into the expressions (4.2)–(4.4) to obtain the moments, the entropy density and the entropy flux.

Proposition.

$$m_{i_1\ldots i_{M'}}^{(M')} = m \int C_{i_1}\ldots C_{i_{M'}} \hat{f}\, d^3 C \qquad M' = 0, 1, \ldots, M+1 \tag{4.12}$$

$$s = \sum_{M'=0}^{M} \lambda_{i_1\ldots i_{M'}}^{(M')} m_{i_1\ldots i_{M'}}^{(M')} \pm ky \int \ln(1 \pm \hat{f}/y)\, d^3 C \tag{4.13a}$$

or

$$s = \lambda^{(0)}\rho + \sum_{M'=2}^{M} (1 + \tfrac{1}{3}M')\lambda_{i_1\ldots i_{M'}}^{(M')} m_{i_1\ldots i_{M'}}^{(M')} \tag{4.13b}$$

and

$$\Phi_j = \sum_{M'=0}^{M} \lambda_{i_1\ldots i_{M'}}^{(M')} m_{i_1\ldots i_{M'}j}^{(M'+1)} \pm ky \int C_j \ln(1 \pm \hat{f}/y)\, d^3 C \tag{4.14a}$$

or

$$\Phi_j = \sum_{M'=1}^{M} \lambda_{i_1\ldots i_{M'}}^{(M')}(m_{i_1\ldots i_{M'}j}^{(M'+1)} + \tfrac{1}{2}M' m_{(i_1\ldots i_{M'-1}}^{(M')}\delta_{i_{M'})j}). \tag{4.14b}$$

Proof. Equations (4.13a) and (4.14a) require the use of $\ln f/y - \ln(1 \pm f/y) = -\Sigma$ (see (4.7)). The validity of the transition between (4.13a), (4.14a) and (4.13b), (4.14b) is proved in appendix 1 by use of the requirement (2.2) (lemma (A1.13) and (A1.14)).

Among equations (4.12) the first N may in principle be used to calculate the Lagrange multipliers and the remaining ones determine the constitutive quantities $m^{(M+1)}$. This can only be done in an approximate manner. A special case is described in [6].

4.5. Comparison with thermodynamics

For a comparison of the results (4.12)-(4.14) of the maximisation procedure and the results (3.7)-(3.11) of thermodynamics we need to calculate ds and $d\Phi_j$.

Proposition.

$$ds = \sum_{M'=2}^{M} \lambda_{i_1\ldots i_{M'}}^{(M')}\, dm_{i_1\ldots i_{M'}}^{(M')} \tag{4.15}$$

$$d\Phi_j = \sum_{M'=2}^{M} \lambda_{i_1\ldots i_{M'}}^{(M')}\, dm_{i_1\ldots i_{M'}j}^{(M'+1)} - \sum_{M'=3}^{M} \frac{M'}{\rho}\lambda_{i_1\ldots i_{M'}}^{(M')} m_{(i_1\ldots i_{M'-1}}^{(M'+1)}\delta_{i_{M'})j}\, dm_{ij}^{(2)}. \tag{4.16}$$

Proof. We form the total differential of s, given by (4.13a), and after replacing $d\int \ln(1 \pm f/y)\, d^3 C$ by lemma (A1.1) we end up with (4.15). Equation (4.16) is proved as follows. We form the total differential of Φ_j, given by (4.14a), and after replacing $d\int C_j \ln(1 \pm f/y)\, d^3 C$ by lemma (A1.2) we have

$$d\Phi_j = \sum_{M'=0}^{M} \lambda_{i_1\ldots i_{M'}}^{(M')}\, dm_{i_1\ldots i_{M'}j}^{(M'+1)} \tag{4.17}$$

or with $m_i^{(1)} = 0$

$$d\Phi_j = \lambda_i^{(1)}\, dm_{ij}^{(2)} + \sum_{M'=2}^{M} \lambda_{i_1\ldots i_{M'}}^{(M')}\, dm_{i_1\ldots i_{M'}j}^{(M'+1)}. \tag{4.18}$$

Finally, by use of lemma (A1.15), we can express $\lambda_i^{(1)}$ by the other Lagrange multipliers and obtain (4.16).

Inspection of (4.15) and (4.16) shows that these formulae are formally identical to the relations (3.7) and (3.8) of thermodynamics. The remaining equations (3.9), (3.19) and (3.11) also have their statistical counterparts. Thus s, given by (4.13b), compares with (3.9). The traceless symmetric part and the antisymmetric part of (A1.13) that occurred in the proof of (4.13b) are analogous to the thermodynamic equations (3.10) and (3.11). For easy reference we rewrite the three equations (4.13b), (A1.13) (traceless symmetric part) and (A1.13) (antisymmetric part) here:

$$s = \lambda^{(0)} \rho + \sum_{M'=2}^{M} (1 + \tfrac{1}{3} M') \lambda_{i_1 \ldots i_{M'}}^{(M')} m_{i_1 \ldots i_{M'}}^{(M')} \tag{4.19}$$

$$\sum_{M'=2}^{M} M' \lambda_{i_1 \ldots i_{M'}}^{(M')} \delta_{i_{M'} (j} m_{i)i_1 \ldots i_{M'-1}}^{(M')} = 0 \tag{4.20}$$

$$\sum_{M'=2}^{M} M' \lambda_{i_1 \ldots i_{M'}}^{(M')} \delta_{i_{M'} [j} m_{i]i_1 \ldots i_{M'-1}}^{(M')} = 0. \tag{4.21}$$

The full set of equations (4.17)–(4.21) is completely analogous to the set (3.7)–(3.11) of thermodynamics. Some of equations (3.7)–(3.11) are used in thermodynamics to determine the Lagrange multipliers $\Lambda^{(M')}$. Similarly the corresponding equations in the set (4.17)–(4.21) may be used to determine the Lagrange multipliers $\lambda^{(M')}$.

Since the two sets of equations are identical so are the Lagrange multipliers $\Lambda^{(M')}$ and $\lambda^{(M')}$.

The proof of the identity of the statistical and thermodynamic Lagrange multipliers was one of the objectives of this paper.

This identity of Lagrange multipliers does not mean that thermodynamics and statistical mechanics obtain the same *number* of results. In fact, statistical mechanics obtains more results than thermodynamics.

In particular equations (4.12) do not come out in thermodynamics. N of these equations may be used to calculate the Lagrange multipliers and the remaining ones furnish the constitutive functions $m^{(M+1)}$. Once the Lagrange multipliers and $\hat{m}^{(M+1)}$ are known we can use (4.13b) and (4.14b) to calculate s and Φ. (Note that in thermodynamics we can only calculate the derivates of $m^{(M+1)}$ and Φ.)

Appendix 1. Some useful lemmas

The proof of (4.15)–(4.21) is easily performed by the following lemmas.

Lemma.

$$d \int \ln(1 \pm f/y) \, d^3C = \mp \frac{1}{yk} \sum_{M'=0}^{M} m_{i_1 \ldots i_{M'}}^{(M')} \, d\lambda_{i_1 \ldots i_{M'}}^{(M')} \tag{A1.1}$$

$$d \int C_j \ln(1 \pm f/y) \, d^3C = \mp \frac{1}{yk} \sum_{M'=0}^{M} m_{i_1 \ldots i_{M'} j}^{(M'+1)} \, d\lambda_{i_1 \ldots i_{M'}}^{(M')}. \tag{A1.2}$$

Proof. The integral $\int \ln(1 \pm f/y) \, d^3C$ is a function of the N Lagrange multipliers, so

we can write

$$d \int \ln(1 \pm f/y) \, d^3C = \mp \frac{1}{y} \int f \, d\Sigma \, d^3C = \mp \frac{m}{yk} \sum_{M'=0}^{M} d\lambda_{i_1 \ldots i_{M'}}^{(M')} \int C_{i_1} \ldots C_{i_M} f \, d^3C$$

$$= \mp \frac{1}{yk} \sum_{M'=0}^{M} m_{i_1 \ldots i_{M'}}^{(M')} \, d\lambda_{i_1 \ldots i_{M'}}^{(M')}. \tag{A1.3}$$

(A1.2) is proved in an analogous manner.

Lemma.

$$\delta_{ij} \int \ln(1 \pm f/y) \, d^3C \mp \frac{1}{y} \int C_1 \frac{\partial \Sigma}{\partial C_j} f \, d^3C = 0 \tag{A1.4}$$

$$2 \int C_i \ln(1 \pm f/y) \, d^3C \mp \frac{1}{y} \int C^2 \frac{\partial \Sigma}{\partial C_i} f \, d^3C = 0 \tag{A1.5}$$

$$M' m_{(i_1 \ldots i_{M'-1})}^{(M'-1)} \delta_{i_{M'})i} + k \int \frac{\partial \Sigma}{\partial C_i} \frac{\partial f}{\partial \lambda_{i_1 \ldots i_{M'}}^{(M')}} \, d^3C = 0. \tag{A1.6}$$

Proof. We have imposed the condition on f that it must vanish sufficiently strongly in the limit $c \to \pm\infty$ (see (2.2)). Relations (A1.6) are based on this fact. Consequently we have

$$0 = \int \frac{\partial C_i \ln(1 \pm f/y)}{\partial C_j} = \delta_{ij} \int \ln(1 \pm f/y) \, d^3C + \int C_i \frac{\partial \ln(1 \pm f/y)}{\partial C_j} \, d^3C. \tag{A1.7}$$

By use of

$$\frac{\partial \ln(1 \pm f/y)}{\partial C_j} = -\frac{\partial \ln(1 \mp \exp -\Sigma)}{\partial C_j} = \mp \frac{1}{y} \frac{\partial \Sigma}{\partial C_j} f \tag{A1.8}$$

then (A1.4) is proved and (A1.5) follows in an analogous manner.
   In order to prove (A1.6) we start with

$$0 = \int \frac{\partial C_{i_1} \ldots C_{i_M} f}{\partial C_i} \, d^3C = \int (C_{i_2} \ldots C_{i_M} \delta_{i_1 i} + C_{i_1} C_{i_3} \ldots C_{i_M} \delta_{i_2 i} + \ldots) f \, d^3C$$

$$+ \int C_{i_1} \ldots C_{i_M} \frac{\partial f}{\partial C_i} \, d^3C. \tag{A1.9}$$

This can also be written as

$$0 = M' m_{(i_1 \ldots i_{M'-1}}^{(M'-1)} \delta_{i_{M'})i} + m \int C_{i_1} \ldots C_{i_M} \frac{\partial f}{\partial C_i} \, d^3C. \tag{A1.10}$$

From

$$\frac{\partial f}{\partial C_i} = -\frac{1}{y} f^2 \exp \Sigma \frac{\partial \Sigma}{\partial C_i} \qquad \frac{\partial f}{\partial \lambda_{i_1 \ldots i_{M'}}^{(M')}} = C_{i_1} \ldots C_{i_M} \left(-\frac{1}{y} f^2 \exp \Sigma \right) \frac{m}{k} \tag{A1.11}$$

we conclude that

$$\frac{k}{m} \frac{\partial \Sigma}{\partial C_i} \frac{\partial f}{\partial \lambda_{i_1 \ldots i_{M'}}^{(M')}} = C_{i_1} \ldots C_{i_M} \frac{\partial f}{\partial C_i} \tag{A1.12}$$

holds. Now we replace the expression under the integral in (A1.10) by the left-hand side of (A1.12) and obtain (A1.6).

Although $m^{(-1)}$ is not defined, (A1.6) is valid for $M' = 0$ too, since the first integral on the right-hand side of (A1.9) does not occur for $M' = 0$.

Lemma.

$$\delta_{ij} \int \ln(1 \pm f/y) \, \mathrm{d}^3 C \mp \frac{1}{yk} \sum_{M'=2}^{M} M' \lambda_{i_1 \ldots i_M}^{(M')} m_{i(i_1 \ldots i_{M'-1}}^{(M')} \delta_{i_{M'})j} = 0 \tag{A1.13}$$

$$2 \int C_i \ln(1 \pm f/y) \, \mathrm{d}^3 C \mp \frac{1}{yk} \sum_{M'=1}^{M} M' \lambda_{i_1 \ldots i_M}^{(M')} m_{(i_1 \ldots i_{M'-1}}^{(M'+1)} \delta_{i_{M'})i} = 0 \tag{A1.14}$$

$$\rho \lambda_i^{(1)} + \sum_{M'=3}^{M} M' \lambda_{i_1 \ldots i_M}^{(M')} m_{i_1 \ldots i_{M'-1}}^{(M'-1)} \delta_{i_{M'})i} = 0. \tag{A1.15}$$

Proof. Differentiation of Σ, given by (4.9) with respect to C_i yields

$$\frac{\partial \Sigma}{\partial C_i} = \frac{m}{k} \sum_{M'=1}^{M} M' \lambda_{i_1 \ldots i_M}^{(M')} C_{(i_1} \ldots C_{i_{M'-1}} \delta_{i_{M'})i}. \tag{A1.16}$$

After replacing $\partial \Sigma / \partial C_i$ under the integrals in (A1.4) and (A1.5) by (A1.16) we obtain (A1.13) and (A1.14).

In order to prove (A1.15) we start with (A1.6) which can also be written in the form

$$M' m_{(i_1 \ldots i_{M'-1}}^{(M'-1)} \delta_{i_{M'})i} + k \frac{\partial}{\partial \lambda_{i_1 \ldots i_M}^{(M')}} \int f \frac{\partial \Sigma}{\partial C_i} \mathrm{d}^3 C - k \int f \frac{\partial^2 \Sigma}{\partial C_i \partial \lambda_{i_1 \ldots i_M}^{(M')}} \mathrm{d}^3 C = 0. \tag{A1.17}$$

Due to (A1.16) the last integral (A1.17) can be reduced to

$$k \int f \frac{\partial}{\partial \lambda_{i_1 \ldots i_M}^{(M')}} \frac{\partial \Sigma}{\partial C_i} \mathrm{d}^3 C = \sum_{N'=1} N' \frac{\partial \lambda_{j_1 \ldots j_N}^{(N')}}{\partial \lambda_{i_1 \ldots i_M}^{(M')}} m \int C_{(j_1} \ldots C_{j_{N'-1}} \delta_{j_{N'})i} f \, \mathrm{d}^3 C$$

$$= M' m_{(i_1 \ldots i_{M'-1}}^{(M'-1)} \delta_{i_{M'})i} \tag{A1.18}$$

which gives just the first term in (A1.17). Both terms cancel each other and we have

$$\frac{\partial}{\partial \lambda_{i_1 \ldots i_M}^{(M')}} \left(k \int f \frac{\partial \Sigma}{\partial C_i} \mathrm{d}^3 C \right) = 0. \tag{A1.19}$$

Now we replace $\partial \Sigma / \partial C_i$ by (A1.16) and obtain

$$\frac{\partial}{\partial \lambda_{i_1 \ldots i_M}^{(M')}} \left(\rho \lambda_i^{(1)} + \sum_{M'=3}^{M} M' \lambda_{i_1 \ldots i_M}^{(M')} m_{(i_1 \ldots i_{M'-1}}^{(M'-1)} \delta_{i_{M'})i} \right) = 0 \tag{A1.20}$$

We conclude that the term within the bracket must be independent of $\lambda_{i_1 \ldots i_M}^{(M')}$. For $\lambda_i^{(1)} = 0$ and $\lambda_{i_1 \ldots i_M}^{(M')} = 0$ $(M' = 3, 4, \ldots, M)$ that term is identically zero, whence (A1.15) is proved.

Appendix 2. The thirteen-moment case

Up to now we have considered the case that the state of the gas is characterised by the full moments up to a given order M and the constitutive quantities are the components of the $(M+1)$th moment.

There are, however, other possibilities to characterise a state. In particular, processes of grade $N = 13$ were treated by Grad [2] in the kinetic theory and by Liu and Müller [6] in phenomenological thermodynamics. The state is

$$Z_{13} = (m^{(0)}, \rho v_i, m_{ij}^{(2)}, m_i^{(3)}) = (\rho, \rho v_i, \rho \varepsilon, P_{\langle ij \rangle}, q_i)$$

and the constitutive quantities are

$$m_{\langle ijk \rangle}^{(3)} = \hat{m}_{\langle ijk \rangle}^{(3)}(Z_{13}) \qquad m_{ij}^{(4)} = \hat{m}_{ij}^{(4)}(Z_{13})$$
$$S_{\langle ij \rangle}^{(2)} = \hat{S}_{\langle ij \rangle}^{(2)}(Z_{13}) \qquad S_i^{(3)} = \hat{S}_i^{(3)}(Z_{13}).$$

In this case only a part of the third moment, namely $m_i^{(3)} = 2q_i$, is considered to be a variable. Consequently we only need the trace of the equation of transfer for the third moment as a basis for a field equation.

The restrictions (3.7)-(3.13) imposed by the entropy inequality were derived under the assumption that Z_N contains only full moments.

In order to treat a case like $Z_N = Z_{13}$ one has to change (3.7)-(3.13) as follows. $m_{ijk}^{(3)}$ and the corresponding Lagrange multiplier $\Lambda_{ijk}^{(3)}$ are decomposed as

$$m_{ijk}^{(3)} = m_{\langle ijk \rangle}^{(3)} + \tfrac{1}{5}(m_i^{(3)}\delta_{jk} + m_j^{(3)}\delta_{ik} + m_k^{(3)}\delta_{ij}) \tag{A2.1}$$

$$\Lambda_{ijk}^{(3)} = \Lambda_{\langle ijk \rangle}^{(3)} + \tfrac{1}{5}(\Lambda_i^{(3)}\delta_{jk} + \Lambda_j^{(3)}\delta_{ik} + \Lambda_k^{(3)}\delta_{ij}). \tag{A2.2}$$

Since the equation of transfer for $m_{\langle ijk \rangle}^{(3)}$ is no longer taken into account, $\Lambda_{ijk}^{(3)}$ in (3.7)-(3.13) has to be replaced by (A2.2) and $\Lambda_{\langle ijk \rangle}^{(3)}$ is set equal to zero. Furthermore $m_{ijk}^{(3)}$ has to be replaced by (A2.1) with $m_{\langle ijk \rangle}^{(3)} = \hat{m}_{\langle ijk \rangle}^{(3)}(Z_{13})$.

Appendix 3. Some remarks on the behaviour of f in the limit $c \to \pm\infty$

For $c \to \pm\infty$, f assumes the asymptotic form

$$f_\infty = y \exp{-\Sigma} = y \exp\left(-\sum_{M'=0}^{M} \lambda_{i_1 \dots i_{M'}}^{(M')} C_{i_1} \dots C_{i_{M'}}\right). \tag{A3.1}$$

Let us compare (A3.1) with imposed condition (2.2) on f_∞

$$f_\infty(x, C, t) \leq |P(x, C, t)| \exp(-a(x, t)C^2). \tag{A3.2}$$

If M is an even number and if the matrix $\lambda_{i_1 \dots i_M}^{(M)}$ is positive definite, then (A3.2) is satisfied.

If M is an uneven number or if the positive definiteness of $\lambda_{i_1 \dots i_M}^{(M)}$ is not guaranteed, then (A3.2) can be satisfied in the following way.

We split Σ into an equilibrium part $\lambda_0^{(0)} + \lambda_0^{(2)} C^2$ and a non-equilibrium part $\hat{\Sigma}$. $\lambda_0^{(0)}$ and $\lambda_0^{(2)}$ denote the equilibrium parts of $\lambda^{(0)}$ and $\lambda^{(2)}$, respectively. (A3.1) can now be written as

$$f_\infty = y \exp[-(\lambda_0^{(0)} + \lambda_0^{(2)} C^2)] \exp(-\hat{\Sigma}). \tag{A3.3}$$

The λ contained in $\hat{\Sigma}$ correspond to the non-equilibrium moments and in a process close to equilibrium we assume them to be small since the non-equilibrium moments are small.

Now we expand the asymptotic form of f as

$$f_\infty = y \exp(-\lambda_0^{(0)} + \lambda_0^{(2)} C^2)\left(1 + \hat{\Sigma} + \tfrac{1}{2}\hat{\Sigma}^2 + \dots\right). \tag{A3.4}$$

If we break off this expansion after some finite number of terms, then (A3.2) is satisfied.

Just this procedure is carried out in the paper by Dreyer and Strehlow [8], where the λ will be explicitly derived as functions of Z_{13} up to a second order in $P_{\langle ij \rangle}$ and q_i.

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