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Relativistic Boltzmann equation and relativistic irreversible thermodynamics

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Abstract. — The covariant Boltzmann equation for a relativistic gas mixture is used to formulate a theory of relativistic irreversible thermodynamics. The modified moment method is applied to derive various evolution equations for macroscopic variables from the covariant Boltzmann equation. The method rigorously yields the entropy differential which is not an exact differential if the system is away from equilibrium. Therefore, an extended Gibbs relation does not hold valid for the entropy density in contrast to the usual surmise taken in extended irreversible thermodynamics. However, an extended Gibbs relation-like equation holds for the compensation differential as has been shown to be the case for nonrelativistic gas mixtures in a recent work. The entropy balance equation is cast into an equivalent form in terms of a new function called the Boltzmann function. The equation is seen to be a local expression of the H theorem. Macroscopic evolution equations (i.e., generalized hydrodynamic equations) are presented for various macroscopic variables. Together with the equivalent form for the entropy balance equation, these macroscopic evolution equations form a mathematical structure for a theory of irreversible processes in relativistic monatomic gases.

1. Introduction.

The relativistic Boltzmann equation [1-6] was used to study irreversible processes in relativistic gases by some authors who employed either the Chapman-Enskog method [7] or the Maxwell-Grad moment method [8] to solve the kinetic equation. Especially, these methods were used as a means to obtain or justify a macroscopic theory [9-12] of irreversible processes in the relativistic framework [4-6]. Since the aforementioned methods do not afford an exact solution for the problem, one justifies, within the validity of the approximation used, a theoretical structure of irreversible thermodynamics one has in mind. However, the justification is not without an uneasy feeling since thermodynamics makes rigorous demands on theories of macroscopic irreversible processes occurring at all degrees of removal from equilibrium but approximate kinetic theory results can hardly be relied on for a sufficiently general and rigorous theory, especially, if the system is far from equilibrium. When one aims
to formulate a theory of irreversible processes, the question of the nature of entropy unavoidably arises, but relativistic kinetic theory has not as yet yielded a satisfactory answer to the question. The range of validity of the existing approximate relativistic thermodynamic theories depends on the answer to this question.

Recently, the modified moment method [13] for nonrelativistic Boltzmann equations has been shown to yield a rigorous answer to the question of whether the entropy differential for irreversible processes is exact or not. The answer turns out to be that it is not exact if the system is away from equilibrium. In this paper we aim to show that the same answer remains valid even for relativistic gases of finite masses that can be described by a relativistic Boltzmann equation.

2. Relativistic kinetic equation and balance equations.

We assume an $r$ component mixture of nonequilibrium relativistic monatomic gases of finite masses. The case of massless particles is excluded in this theory and will be discussed elsewhere [14]. It is well established that for such a mixture the singlet distribution function $f_i(x, p_i)$ obeys the covariant Boltzmann equation [1-6]:

$$ p_i^\mu \partial_\mu f_i(x, p_i) = \sum_{i', j} C(f_i, f_j) $$

(2.1)

where $x = (ct, \mathbf{r})$, $p_i = (cp_i^0, \mathbf{p}_i)$ with $p_i^0 = (p_i^2 + m_i^2 c^2)^{1/2}$, and the collision integral is given by the formula

$$ C(f_i, f_j) = G_{ij} \int d^3 \mathbf{p}_j d^3 \mathbf{p}_j^* \ d^3 \mathbf{p}_j^* \ W_{ij}(p_i, p_j | p_i^*, p_j^*) $$

$$ \times \left[ f_i^*(x, p_i^*) f_j^*(x, p_j^*) - f_i(x, p_i) f_j(x, p_j) \right], $$

(2.2)

with $d^3 \mathbf{p}_j = d^3 \mathbf{p}_j/p_i^0$, $d^3 \mathbf{p}_j^* = d^3 \mathbf{p}_j^*/p_j^0$, etc. and $W_{ij}(p_i, p_j | p_i^*, p_j^*)$ denoting the rate of transition from the initial state $(p_i, p_j)$ to $(p_i^*, p_j^*)$ as a result of a collision between particles $i$ and $j$. The factor $G_{ij} = 1 - \delta_{ij}/2$ insures that the final state is not counted twice. The asterisk denotes the post-collision value. Note that the subscripts $i$ and $j$ play a dual role of labelling a species and a particle of that species. The transition rate $W_{ij}(p_i, p_j | p_i^*, p_j^*)$ is a scalar under Lorentz transformation and obeys the microscopic reversibility [6].

The distribution function is normalized to the number density of the species in question:

$$ n_i(x) = \int d^3 \mathbf{p}_i f_i(x, p_i). $$

(2.3)

The particle four-flow $N_i^\mu$ and the covariant energy-momentum tensor of species $i$ are defined, respectively, by the statistical mechanical formulas

$$ N_i^\mu(x) = \langle p_i^\mu f_i(x, p_i) \rangle, $$

(2.4)

and

$$ T_i^{\mu\nu}(x) = \langle p_i^\mu p_i^\nu f_i(x, p_i) \rangle. $$

(2.5)

Here the angular brackets are the abbreviation of the integral

$$ \langle \cdot \cdot \rangle = c \int d^3 \mathbf{p}_i/p_i^0 = c \int d^3 \mathbf{p}_i... $$
Then, the total number four-vector \( N^\mu \) and total energy-momentum tensor \( T^{\mu \nu} \) are given, respectively, by the sum of the species components over all species: \( N^\mu = \sum_i N_i^\mu \) and \( T^{\mu \nu} = \sum_i T_i^{\mu \nu} \).

The entropy four-flow may be also defined in covariant form

\[
S^\mu (x) = \sum_i S_i^\mu (x) = - \sum_i k_B \left\{ p_i^\mu \left[ \ln f_i (x, p_i) - 1 \right] f_i (x, p_i) \right\}
\]

for the whole system of the mixture in question. We will later return to this important quantity to discuss its consequences for irreversible thermodynamics.

Following Eckart [15], we define the hydrodynamic velocity by

\[
U^\mu = cN^\mu / (N^\nu N_\nu)^{1/2}
\]

This may be put into the form

\[
U^\mu = \rho^{-1} N^\mu
\]

where \( \rho \) is the hydrodynamic number density defined by

\[
\rho = \sum_i \rho_i = \sum_i c^{-2} N_i^\mu U_\mu = c^{-2} N^\mu U_\mu .
\]

These formulas imply that \( \rho (x) = n(x)(1 - u^2/c^2)^{1/2} \) and \( U^\mu = (c, u)(1 - u^2/c^2)^{-1/2} \).

Various relevant macroscopic variables such as energy density, heat flux, etc., can be defined in covariant form with the help of the hydrodynamic four-velocity just defined. The scalar internal energy density \( E_i \) of species \( i \) is given in terms of the internal energy \( \mathcal{E} \), per particle or in terms of the energy-momentum tensor by

\[
E_i = \rho_i \mathcal{E}_i = c^{-2} U_\mu T_i^\mu U_\nu .
\]

The total internal energy density will be denoted by \( E = \sum_i E_i \). With the definition of the projector \( \Delta_i^{\mu \nu} = - g^{\mu \nu} + c^{-2} U^\mu U^\nu \), \( g^{\mu \nu} \) being the metric tensor, the heat flux \( Q_i^{\mu} \) and diffusion flux \( J_i^{\mu} \) are defined by

\[
Q_i^{\mu} = - U_\nu T_i^{\nu \sigma} \Delta_\sigma^{\mu} ,
\]

\[
J_i^{\mu} = N_i^{\mu} - c_i N^\mu ,
\]

where \( c_i \) is the number fraction defined by

\[
c_i = \rho_i / \rho .
\]

We will find it more convenient to use a new heat flux defined by

\[
Q_i^{\mu} = Q_i^{\mu} - h_i J_i^{\mu}
\]

where \( h_i \) is the enthalpy per particle of species \( i \):

\[
h_i = \mathcal{E}_i + p_i v_i, \quad \text{and} \quad h = \sum_i c_i (\mathcal{E}_i + p_i v_i) = \mathcal{E} + pv .
\]
Here \( p_i \) is the hydrostatic pressure of species \( i \), \( v_i = \rho_i^{-1} \), and \( v = \rho^{-1} \) The heat fluxes of different species sum up to the total heat flux \( Q^\mu \cdot Q^\nu = \sum Q_i^\mu \). The stress tensor \( P_{i}^{\mu \nu} \) is defined as

\[
P_{i}^{\mu \nu} = \Delta_{\alpha}^{\mu} T_{i}^{\alpha \tau} \Delta_{\tau}^{\nu}.
\] (2.16)

This may be further decomposed into the traceless symmetric part \( \Pi_{i}^{\mu \nu} \), the excess trace part \( \Delta_i \), and the hydrostatic pressure \( p_i \) of species \( i \) as follows:

\[
P_{i}^{\mu \nu} = p_i \Delta_{\alpha}^{\mu} \Delta_{\nu}^{\alpha} + \Delta_i \Delta_{\alpha}^{\mu} \Delta_{\nu}^{\alpha} + \Pi_{i}^{\mu \nu}
\] (2.17)

The traceless part is related to the viscous phenomena while the excess trace part is associated with the dilatation (or compression) of the gas. The hydrostatic pressure is defined in terms of equilibrium (or local equilibrium) energy-momentum tensor \( T_{\alpha \gamma} \cdot \)

\[
p_i = \frac{1}{3} \Delta_{\alpha \gamma} T_{\alpha \gamma}^{\mu \nu}
\] (2.18)

Then, it is easy to see that

\[
\Delta_i = \frac{1}{3} \Delta_{\alpha \gamma} P_{i}^{\mu \nu} - p_i = \frac{1}{3} \Delta_{\alpha \gamma} T_{i}^{\mu \nu} - p_i,
\] (2.19)

\[
\Pi_{i}^{\mu \nu} = P_{i}^{\mu \nu} - \frac{1}{3} \Delta_{\alpha \gamma} T_{i}^{\alpha \tau} \Delta_{\tau}^{\nu} + \Delta_i \Delta_{\alpha \gamma} \Delta_{\tau}^{\nu} + \frac{1}{3} \Delta_{\alpha \gamma} T_{i}^{\alpha \tau} \Delta_{\tau}^{\nu} - \frac{1}{3} \Delta_{\alpha \gamma} T_{i}^{\alpha \tau} \Delta_{\tau}^{\nu}
\] (2.20)

The definitions made for the energy density, heat flux, and stress tensor are equivalent to the decomposition of the energy-momentum tensor as follows:

\[
T_{i}^{\mu \nu} = c^{-2} E_i U_i^\mu U_i^\nu + c^{-2} (Q_i^\mu U_i^\nu + U_i^\mu Q_i^\nu) + P_{i}^{\mu \nu}
\] = \[
c^{-2} E_i U_i^\mu U_i^\nu + p_i \Delta_{\alpha \gamma} \Delta_{\tau}^{\nu} + c^{-2} (Q_i^\mu U_i^\nu + U_i^\mu Q_i^\nu) + \Delta_i \Delta_{\alpha \gamma} \Delta_{\tau}^{\nu} + \Delta_{\alpha \gamma} \Delta_{\tau}^{\nu} + \Pi_{i}^{\mu \nu}
\] (2.21)

The entropy density \( S(x) \) and the entropy \( \mathcal{S} \) per particle are scalars defined by:

\[
S(x) = \rho \mathcal{S}(x) = c^{-2} S^\mu U_\mu.
\] (2.22)

This is the quantity we are going to deal with in the theory of irreversible processes that will be constructed on the basis of the covariant Boltzmann equation.

The particle number and energy-momentum conservation laws are easily derived from the covariant Boltzmann equation since the particle number and energy-momentum are the invariants of the Boltzmann collision term. The particle number balance equation is

\[
\partial_\mu N^\mu(x) = 0
\] (2.23)

while the energy-momentum balance equation is

\[
\partial_\mu T^{\mu \nu}(x) = 0.
\] (2.24)

With the definitions of the operators \( D = U^\mu \partial_\mu \) and \( \nabla^\mu = - \Delta_{\alpha \gamma} \partial_\nu \), it is easy to obtain from (2.23) or (2.24) the various fluid dynamic equations as follows:

**Equation of continuity**:

\[
D \rho = - \rho \nabla_\mu U^\mu
\] (2.25)
Density fraction balance equation: For systems without a chemical reaction

\[ \rho Dc_i = - \partial_{\mu} J_i^{\mu} \] (2.26)

Momentum balance equation:

\[ c^{-2} \hbar p D U^\mu = \nabla^\mu p + \Delta_{i}^{\sigma} \partial_{\sigma} \tilde{P}^{\sigma \nu} + c^{-2} (\Delta_{i}^{\mu} D Q^\nu - Q^\mu \nabla_{\nu} U^\nu - Q^\nu \nabla_{\nu} U^\mu) \] (2.27)

where

\[ \tilde{P}^{\sigma \nu} = \sum_{i} \left( \Delta_{i}^{\sigma \nu} + \Pi_{i}^{\sigma \nu} \right) = \Delta \Delta^{\sigma \nu} + \Pi^{\sigma \nu} \] (2.28)

Energy balance equation:

\[ \rho D \mathcal{E} = - \nabla_{\mu} q^\mu - \nabla_{\mu} U^\mu + \tilde{P}^{\mu \nu} \nabla_{\nu} U_{\mu} + 2 c^{-2} q_{\mu} U_{\mu} . \] (2.29)

These equations and the flux evolution equations presented later, together with the entropy balance equation, form a set of evolution equations in the theory of irreversible processes presented in this work.

3. Flux evolution equations.

The various balance equations derived earlier contain macroscopic variables such as the stress tensor, heat flux and diffusion fluxes, etc. which require their own evolution equations. We can derive them from the kinetic equation. To this end, we first define a tensor \( \psi_{i}^{(a)} \mu \nu \ldots \ell \sigma \) as the average of its molecular expression \( p_{i}^{\sigma} h_{i}^{(a) \mu \nu \ldots \ell} \).

\[ \psi_{i}^{(a)} \mu \nu \ldots \ell \sigma = \langle p_{i}^{\sigma} h_{i}^{(a) \mu \nu \ldots \ell} f_{i}(x, p_{i}) \rangle \] (3.1)

where \( h_{i}^{(a) \mu \nu \ldots \ell} \) is the \( a \)-th element of a set of molecular moments in terms of which the distribution function may be expanded. The leading moments relevant to physical applications of the theory developed here are:

\[
\begin{align*}
\psi_{i}^{(1)} \mu \nu &= c^{2} (U_{\lambda} p_{i}^{\lambda})^{-1} \left( \Delta_{\mu}^{\sigma} \Delta_{\nu}^{\tau} - \frac{1}{3} \Delta_{\sigma \tau} \Delta_{\mu \nu} \right) p_{i}^{\sigma} p_{i}^{\tau} , \\
\psi_{i}^{(2)} \mu &= \frac{1}{3} c^{2} (U_{\lambda} p_{i}^{\lambda})^{-1} \Delta_{\mu \nu} p_{i}^{\sigma} p_{i}^{\rho} - p_{i}^{\sigma} p_{i}^{\rho} , \\
\psi_{i}^{(3)} \mu &= - c^{2} (U_{\lambda} p_{i}^{\lambda})^{-1} \{ \Delta_{\mu}^{\sigma} p_{i}^{\rho} U_{\nu} + a_{i} \Delta_{\mu \nu} \} \\
\psi_{i}^{(4)} \mu &= c^{2} (U_{\lambda} p_{i}^{\lambda})^{-1} \{ p_{i}^{\mu} - c^{-2} (U_{\lambda} p_{i}^{\lambda}) U_{\mu} \}
\end{align*}
\] (3.2a, 3.2b, 3.2c, 3.2d)

where

\[ a_{i} = \Delta_{\mu}^{\sigma} \Delta_{\nu}^{\rho} \langle p_{i}^{\rho} p_{i}^{\sigma} f_{i} \rangle g_{\mu \nu} [\Delta_{\mu}^{\sigma} \Delta_{\nu}^{\rho} \langle h_{i}^{\sigma} p_{i}^{\rho} (p_{i}^{\lambda} U_{\lambda})^{-1} \rangle g_{\mu \nu}]^{-1} \] (3.2e)

These moments tend to the nonrelativistic moments appearing in the nonrelativistic kinetic theory [13]. They are constructed by means of the Schmidt orthogonalization method such that they, when averaged, give rise to physically relevant variables. We also note that \( a_{i} \rightarrow 1 \) as \( u/c \rightarrow 0 \).

We then define macroscopic moments \( \Phi_{i}^{(a) \mu \nu \ldots \ell} \), which are tensors of various ranks, by taking contraction of \( \psi_{i}^{(a) \mu \nu \ldots \ell} \) with \( U_{\sigma} \).

\[ \Phi_{i}^{(a) \mu \nu \ldots \ell} = c^{-2} U_{\sigma} \psi_{i}^{(a) \mu \nu \ldots \ell} \sigma \] (3.3)
It is then easy to show, by using the definitions of $\Pi_i^{\mu \nu}$ etc. that
\[
\Phi_i^{(1)}{\mu \nu} = \Pi_i^{\mu \nu}; \quad \Phi_i^{(2)} = \Delta_i; \quad \Phi_i^{(3)}{\mu} = Q_i{\mu}; \quad \Phi_i^{(4)}{\mu} = J_i^{\mu}; \quad \text{etc.}
\]  
(3.4)

Thus, we are treating $\psi_i^{(a)}{\mu \nu} \cdot \ell_\sigma$ as a component of a four-tensor and macroscopic moments $\Phi_i^{(a)}{\mu \nu} \cdot \ell$ are their contractions with the hydrodynamic four-velocity in the sense similar to the scalars such as the density, entropy density, etc. This way, they are put on the equal conceptual footing to the conserved variables and the entropy density to which they are related as will be shown later. The evolution equation for $\psi_i^{(a)}{\mu \nu} \cdot \ell_\sigma$ is easily derived from the covariant Boltzmann equation:
\[
\partial_\sigma \psi_i^{(a)}{\mu \nu} \cdot \ell_\sigma = \langle p_i^{\nu} \partial_\sigma h_i^{(a)}{\mu \nu} \cdot \ell f_i(x, p_i) \rangle + A_i^{(a)}{\mu \nu} \cdot \ell
\]  
(3.5)

where
\[
A_i^{(a)}{\mu \nu} \cdot \ell = \sum_{j=1}^{4} \langle h_i^{(a)}{\mu \nu} \cdot \ell C(f_i, f_j) \rangle.
\]  
(3.6)

With the definition of $\Phi_i^{(a)}{\mu \nu} \cdot \ell$ as $\Phi_i^{(a)}{\mu \nu} \cdot \ell$ per particle,
\[
\Phi_i^{(a)}{\mu \nu} \cdot \ell = \rho \Phi_i^{(a)}{\mu \nu} \cdot \ell
\]  
(3.7)

and by making use of $U^\mu \nabla_\mu = 0$, we obtain
\[
\rho D \Phi_i^{(a)}{\mu \nu} \cdot \ell = Z_i^{(a)}{\mu \nu} \cdot \ell + A_i^{(a)}{\mu \nu} \cdot \ell
\]  
(3.8)

where the kinematic term $Z_i^{(a)}{\mu \nu} \cdot \ell$ is given by
\[
Z_i^{(a)}{\mu \nu} \cdot \ell = \langle p_i^{\nu} \partial_\sigma h_i^{(a)}{\mu \nu} \cdot \ell f_i(x, p_i) \rangle + \partial_\sigma (\Delta_i^{(a)} \psi_i^{(a)}{\mu \nu} \cdot \ell_\sigma) .
\]  
(3.9)

This statistical mechanical formula may be worked out more explicitly, but it is not necessary to do so at this point since our immediate interest does not lie in the relativistic theory of transport processes. See table I for their explicit formulas. We emphasize that the evolution equations (3.8) are coupled to the momentum, energy and concentration balance equation introduced earlier. As in the nonrelativistic theory this set of equations is open and therefore must be suitably closed by means of a closure relation. When the set is thus closed, it provides relativistic generalized hydrodynamic equations consisting of (2.25)-(2.29) and (3.8) with the number of moments limited to a finite value by a suitable closure. The moment evolution equation (3.8) can be easily shown to tend to the nonrelativistic counterpart in the limit of $c \rightarrow \infty$. The nonrelativistic limit of (3.8) is quite clear from table I for $Z_i^{(a)}$ in which the relativistic effect terms are easily discernable. The manner in which the moments $(\Phi_i^{(a)})$ are defined in this work is significantly different from the one in the conventional moment method [5] and as a consequence their evolution equations are accordingly different.

4. The H theorem, temperature and pressure.

4.1 THE H THEOREM. — The entropy balance equation can be derived from the kinetic equation. By covariantly differentiating (2.6), we obtain
\[
\partial_\mu S_i^\mu = \sigma_{\text{em}}(x)
\]  
(4.1)
Table I. — Kinematic Terms $Z_i^{(x)}$. 

**Definitions**:

\[
\left[ \nabla U \right]^{(2)}_{\mu \nu} = \frac{1}{2} \left( \nabla^\mu U^\nu + \nabla^\nu U^\mu \right) - \frac{1}{3} \Delta^\mu_{\sigma} \nabla^\nu U_{\sigma},
\]

\[
\left[ A \cdot B \right]^{(2)}_{\mu \nu} = \frac{1}{2} \left( A^\mu \sigma B^\nu_{\sigma} + A^\nu \sigma B^\mu_{\sigma} \right) - \frac{1}{3} \Delta^\mu_{\sigma} A^\sigma \tau B_{\sigma \tau}.
\]

**Kinematic Terms**:

\[
Z_i^{(1)}_{\mu \nu} = - \nabla_\sigma \psi_i^{(1)} \mu \nu \sigma - 2 \left[ \Pi_i \cdot \nabla U \right]^{(2)}_{\mu \nu} + 2 \partial_i \left[ \nabla U \right]^{(2)}_{\mu \nu} + 2 \Delta_i \left[ \nabla U \right]^{(2)}_{\mu \nu}
\]
\[- 2 c^{-2} \left( Q_i \cdot DU \right)_{\mu \nu} + \left\{ f_i p_i^\sigma p_i^\tau \left( p_i^\nu U_{\nu} \right)^{-1} \right\} \nabla_\sigma U_{\tau} \left( \Delta^\mu_{\nu} \nabla U^\nu + U^\mu \Delta^\nu_{\tau} \right)
\]
\[- \frac{1}{3} c^2 \left\{ f_i p_i^\sigma p_i^\tau p_i^\lambda \left( p_i^\nu U_{\nu} \right)^{-2} \right\} \nabla_\sigma U_{\lambda} \left( \Delta^\mu_{\nu} \nabla U^\nu - \frac{1}{3} \Delta_{\mu \nu} \Delta_{\nu \lambda} \right)
\]
\[- c^{-2} \left[ \left( P_i^\mu \nu U^\nu + P_i^\nu \mu U^\mu \right) DU_{\nu} + \left( p_i + \Delta_i \right) \left( U^\mu DU^\mu + U^\nu DU^\nu \right) \right],
\]

\[
Z_i^{(2)} = - \nabla_\mu \psi_i^{(2)} \mu \nu + \frac{2}{3} \Pi_i^{\mu \nu} \nabla U_{\mu \nu} \right) \frac{p_i}{D \ln \left( p_i, v^3 \right)} + 2 \Delta_i \nabla U^\nu - \nabla_\mu \left( J_i, p_i/p_i \right)
\]
\[+ \frac{2}{3} c^2 Q_i^\mu \Delta_{\nu \lambda} \Delta_{\nu \lambda} \left( \Delta^\mu_{\nu} \nabla U^\nu - \frac{1}{3} \Delta_{\mu \nu} \Delta_{\nu \lambda} \right),
\]

\[
Z_i^{(3)} = - \nabla_\nu \psi_i^{(3)} \mu \nu + \Pi_i^{\mu \nu} DU_{\nu} - \left( p_i + \Delta_i \right) DU_{\mu} - J_i^\mu v_{\nu} U_{\mu}
\]
\[+ a_i J_i^\mu U_{\mu} \nabla U_{\nu} + \left( \Delta_i \right) U^\mu DU_{\nu} + \nabla U_{\nu} - U^\mu \Pi_i^{\nu \sigma} \nabla U_{\sigma}
\]
\[+ c^2 a_i \left\{ f_i p_i^\sigma p_i^\tau \left( p_i^\nu U_{\nu} \right)^{-1} \right\} \nabla h_{\nu} - c^{-2} U^\mu Q_i^\nu DU_{\nu}
\]
\[+ c^2 \left\{ f_i p_i^\sigma p_i^\tau p_i^\lambda \left( p_i^\nu U_{\nu} \right)^{-2} \right\} a_i \nabla U_{\lambda} + \left( a_i h_{\nu} n_{\nu} - E_i \right) DU^\mu
\]
\[+ U^\nu N_i^\sigma h_{\nu} \partial_\sigma a_{\nu} + c^2 \left\{ f_i p_i^\sigma p_i^\tau p_i^\lambda \left( p_i^\nu U_{\nu} \right)^{-1} \right\} a_i \nabla U_{\lambda}
\]
\[+ c^2 \left\{ f_i p_i^\sigma p_i^\tau p_i^\lambda \left( U, p_i^\nu \right)^{-2} \right\} a_i \nabla U_{\lambda},
\]

\[
Z_i^{(4)} = - \nabla_\nu \psi_i^{(4)} \mu \nu - J_i^\nu \nabla U^\mu - \partial_\nu J_i^\mu DU_{\nu} - c^{-2} U^\mu J_i^\nu DU_{\nu}
\]
\[- c^2 \left\{ f_i p_i^\sigma p_i^\tau p_i^\lambda \left( p_i^\nu U_{\nu} \right)^{-2} \right\} \nabla_\sigma U_{\lambda}.
\]

where

\[
\sigma_{\text{ent}}(x) = - k_B \sum_{i=1}^{I} \sum_{j=1}^{I} \left\{ \ln f_i(x, p_i) C(f_i, f_j) \right\} \tag{4.2}
\]

By following the well known procedure [6] based on the symmetry properties of the transition probability $W(p, p_j | p_j^* | p_j^*)$, it is easy to show that the entropy production $\sigma_{\text{ent}}(x)$ is positive:

\[
\sigma_{\text{ent}}(x) \geq 0 \tag{4.3}
\]

with the equality applying only at equilibrium. This is the content of the H theorem. It is a statistical mechanical representation of the second law of thermodynamics. The entropy balance equation for the entropy density introduced in (2.22) can be obtained from (4.1) by using (2.23):

\[
\rho D^S = - \partial_{\mu} J_i^\mu + \sigma_{\text{ent}}(x) \tag{4.4}
\]
where

\[ J^\mu_s = S^\mu - \mathcal{J}N^\mu = S^\mu - \rho \mathcal{J}U^\mu \]  

(4.4)

Equation (4.4) may be recast into the form

\[ \rho D\mathcal{J} = - \nabla_\mu J^\mu_s + c^{-2} J^\mu_s DU^\mu + \sigma_{\text{ent}}(x). \]  

(4.6)

Various balance equations and flux evolution equations previously introduced are subject to the entropy balance equation in the sense that the entropy production \( \sigma_{\text{ent}}(x) \) must remain positive so that the second law of thermodynamics is satisfied. As it stands, the entropy balance equation provides no clue as to how this requirement of the second law is fulfilled. This point is usually clarified by using an approximate distribution function (e.g., the Chapman-Enskog solutions), but since the thermodynamic laws must be satisfied rigorously, any conclusion drawn in that respect on the basis of an approximate solution to the kinetic equation cannot be relied on if the system is removed from equilibrium by an arbitrary degree. We therefore must employ a rigorous approach. The modified moment method [13] meets this stringent billing, and we will use it in this work.

As a further preparation for this method, we note that the equilibrium solution to the covariant Boltzmann equation is given by the well known Jüttner function [6]

\[ f_{eq} = \exp\left[-\beta_x (\rho_{eq} U_{eq\mu} - \mu_{eq}^e)\right] \]  

(4.7)

where \( \mu_{eq}^e \) is the normalization factor which turns out to be the chemical potential, \( U_{eq} \) is the velocity at equilibrium, and \( \beta_x \) turns out to be proportional to the inverse temperature:

\[ \beta_x = 1/k_B T_e. \]  

(4.8)

This parameter \( \beta_x \) is determined by comparing the thermodynamic entropy, pressure, and internal energy with the statistical mechanical entropy \( S_e \), pressure and internal energy calculated with the equilibrium solution (4.7) of the kinetic equation by following the basic strategy of the Gibbs ensemble theory. Since the chemical potential is defined by

\[ \mu_{eq}^e/T_e = - (\partial S_e/\partial \rho_{eq}). \]  

(4.9)

in thermodynamics, the statistically derived formula for \( S_e \) indicates that the normalization factor \( \mu_{eq}^e \) is identified with the chemical potential. The ideal gas equation of state is similarly identified by

\[ p = \rho k_B T_e, \quad (v = \rho^{-1}). \]  

(4.10)

This formula is also easily derived from (2.18) when the statistical formula for \( p \) is computed with the equilibrium distribution function (4.7). Therefore, the thermodynamically defined pressure through the equation of state (4.10) is consistent with the statistical mechanical definition of \( p \). The situation thus is seen to be the same as in the nonrelativistic theory in that the kinetically and the thermodynamically defined pressure are identical.

4.2 Temperature in Relativistic Kinetic Theory. — In the nonrelativistic kinetic theory the temperature of the fluid is defined such that the following relation holds true between the internal energy and the temperature [7]:

\[ \mathcal{E} = \frac{3}{2} k_B T. \]  

(4.11)
The temperature defined in this manner is called the kinetic temperature and coincides with the thermodynamic temperature defined through the thermodynamic relation

\[ T^{-1} = \frac{\partial S_e}{\partial E}. \]  \hspace{1cm} (4.12)

However, in the relativistic theory the situation is altered significantly since if the kinetic temperature is defined by (4.11), then the temperature so defined does not agree with the thermodynamic temperature defined by means of (4.12). Nevertheless, (4.12) is consistent with (4.10). One recovers the coincidence between (4.11) and (4.12) in the limit of \( u/c \to 0 \), provided that the \( mc^2 \) term is neglected; see reference [6] for the expression for \( \sigma' \). However, it would be preferable to have the thermodynamic temperature coincide with the kinetic temperature in the relativistic theory as well, since the kinetic theory should be a molecular representation of thermodynamics underlying macroscopic processes. Here we define the kinetic temperature for a system of particles of finite masses such that it precisely coincides with the thermodynamic temperature as follows:

\[ \frac{3}{2} \rho k_B T_e = \sum_{i=1}^{N} \left( \frac{2 c^2}{i} \right)^{-1} \left\langle \left( p_i^\mu p_i^\nu U_{e\mu} U_{e\nu} - m_i^2 c^4 \right) f_{ei}(x, p_i) \right\rangle. \]  \hspace{1cm} (4.13)

This definition yields a correct nonrelativistic limit. It is still rooted basically in the idea that the temperature is a measure of kinetic energy. Since the rest mass should not be a factor in the measure, it is subtracted out in the definition. Since the integrand in (4.13) is scalar, the integral may be evaluated in the local rest frame where \( U_{e\mu} = (c, 0, 0, 0) \). Then,

\[ f_{ei} = \exp \left[ -\beta_e (cp_i^0 - \mu_i^e) \right]. \]  \hspace{1cm} (4.14)

Now, by following the well-known procedure in the Gibbs ensemble theory we can identify \( \beta_e \) by \( \beta_e = 1/k_B T_e \) as in (4.8). This also proves the coincidence of the kinetic temperature with the thermodynamic temperature, if the kinetic temperature is defined as stated in (4.13). Equation (4.13) is another way of expressing Tolman's equipartition theorem [16]. Therefore, the definition of temperature by (4.13) is seen to be based on the equipartition law. In other words, the statistical mechanical temperature may be defined by means of the equipartition theorem of Tolman, which equally holds for the classical and relativistic theories. This interpretation of the definition of temperature provides us with a universal way of defining temperature for both classical and relativistic theories: the equipartition law of Tolman.

The local rest frame version of the definition (4.13) of kinetic temperature in relativity was suggested by ter Haar and Wergeland [17], and it was later taken up by Menon and Agrawal [18], but as pointed out by Landsberg [19], their definition is preceded by Tolman [16]. On the other hand, in the Chapman-Enskog theory [6] the kinetic temperature is defined such that the equation of state in thermodynamics and in kinetic theory coincide with each other. Therefore, there appear to be two different modes of definition for temperature, but, in fact, they are identical at least in the case of ideal gases. We show it below. Since there holds the relation

\[ p_i^\mu p_i^\nu U_{e\mu} U_{e\nu} - m_i^2 c^4 = p_i^\mu p_i^\nu U_{e\mu} U_{e\nu} - p_i^\mu p_i^\nu U_{e\mu} U_{e\nu} = c^2 p_i^\mu p_i^\nu \Delta_{e\mu}, \]  \hspace{1cm} (4.15)

substitution of (4.15) into (4.13) yields

\[ \frac{3}{2} \rho k_B T_e = \frac{1}{2} \Delta_{e\mu} T_e^{\mu\nu} = \frac{3}{2} p. \]

which implies the equation of state.
5. Modified moment method.

With the equilibrium distribution function uniquely determined by the H theorem and the parameters therein identified with the thermodynamic temperature and chemical potential, it is now possible to develop a method to determine the nonequilibrium distribution function such that it is consistent with the H theorem. In the nonrelativistic theory such determination of a nonequilibrium distribution function is made possible by the modified moment method [13]. We apply the same method to the covariant Boltzmann equation. To begin with, the following consideration is helpful for adopting a general strategy.

Since the nonequilibrium distribution function must reduce to the equilibrium distribution function as the system tends toward equilibrium, it is natural to construct the former on the latter. Therefore, we look for the nonequilibrium distribution function in the form

\[ f_i = f^0_i (\beta_e, \rho_{ie}, U^\mu_e) \Delta f_i, \]

where \( f^0_i (\beta_e, \rho_{ie}, U^\mu_e) \) is the equilibrium distribution function already determined and \( \Delta f_i \) is the nonequilibrium correction. This correction term may be expressed in a variety of ways. Since the system is in nonequilibrium, it is preferable to relax the equilibrium parameters \( \beta_e, \rho_{ie}, U^\mu_e \) appearing in \( f^0_i \) and make them space-time dependent, namely,

\[ \beta_e \Rightarrow \beta; \quad \rho_{ie} \Rightarrow \rho_i; \quad U^\mu_e \Rightarrow U^\mu \]

(M.C.)

The equilibrium distribution function so relaxed and made space-time dependent becomes the local equilibrium distribution function. The latter is the building block of the solution methods in the kinetic theory of gases. These correspondences mentioned above can be made mathematically precise by the matching conditions used in kinetic theory. Since the main aim of this paper is in deriving the entropy differential and developing the basic equations for transport processes, it is not necessary to delve into the question of matching conditions for temperature, density, velocity mentioned earlier. Such question, however, will have to be dealt with when the theory of irreversible thermodynamics is further developed in depth.

Being space-time dependent, \( \beta, \rho_i, \) and \( U^\mu \) are not equilibrium quantities. They are, in fact, statistically defined in terms of nonequilibrium distribution function \( f_i \). In particular, for \( \beta = 1/k_B T \)

\[ 3 \rho k_B T = \sum_{i=1}^n c^{-2} \left( \langle p_i^\mu p_i^\nu U^\mu u_x U^\nu - m_i^2 c^4 \rangle f_i(x, \rho_i) \right). \]

(4.13')

This definition is the nonequilibrium analog of (4.13) holding for systems of particles of finite mass.

Now, the nonequilibrium distribution function is taken with the following ansatz which contains \( f_{\alpha, i} \) as a part of it and is written in an exponential form

\[ f_i = \exp \left[ -\beta (p_i^\mu U^\mu_i + H_i^{(1)} - \mu_i) \right] \]  

(5.1)

where

\[ H_i^{(1)} = \sum_{\alpha = 1} X_i^{(\alpha)} \cdot h_i^{(\alpha \cdots \nu \mu)} \]

\[ = \sum_{\alpha = 1} X_i^{(\alpha)} \otimes h_i^{(\alpha)} \]  

(5.2)
and $\mu_i$ is the normalization factor given by the formula

$$
\exp(-\beta \mu_i) = \rho_i^{-1} \left( e^{-2\beta p_i^\mu U_{\lambda}} \exp \left[ -\beta \left( p_i^\mu U_{\mu} + \sum_{n \neq 1} X_{i,\mu \nu \ldots \ell}^{(a)} h_{i}^{(a)} \cdot \nu^\mu \right) \right] \right). \quad (5.3)
$$

The parameter $\beta = 1/k_B T$ has the meaning as fixed by (4.13') and elaborated earlier. The tensors $X_{i,\mu \nu \ldots \ell}^{(a)}$ are as yet undetermined functions of macroscopic variables, but will be determined such that any approximation to them does not violate the H theorem and consequently the resulting formalism for irreversible processes remains consistent with the second law of thermodynamics.

To construct such a formalism, we assume that $X_{i}^{(a)}$ are somehow known and then proceed to construct the formalism. (In this sense the attitude taken here is similar to that by the Gibbs ensemble theory where the partition function is assumed to be known and with it thermodynamic functions and their relations are sought after.) By making sure that the entropy production remains positive in the approximation to be made to the unknowns $X_{i}^{(a)}$ in the future, the consistency of the formalism with the second law of thermodynamics is assuredly preserved. For $\alpha = 1$ the unknown is a second rank tensor since $h_{i}^{(1)}$ is a second rank covariant tensor; for $\alpha = 2$ it is a scalar; while for $\alpha = 3$ and 4 the unknowns are vectors. We will dispense with the first mode of expression in (5.2) and use the symbol $\bigcirc$ whenever convenient. The sum over $\alpha$ in (5.2) in principle runs over any number of terms, but it must be such that $f_i$ is normalizable. Only this restriction is necessary in formulating the theory since the distribution function is explicitly used only to define macroscopic observables in the moment method, and once that is done, its role in the kinetic theory is basically over except for the entropy production which must be computed with $f_i$ in (5.1) such that the restriction just mentioned is met. The exponential form for $f_i$ will be called the nonequilibrium canonical form.

Substitution of the nonequilibrium canonical form for $f_i$ into (4.2) for the entropy production yields the formula

$$
\sigma_{\text{ent}} = T^{-1} \sum_{i} \sum_{n \neq 1} X_i^{(a)} h_i^{(a)} \bigcirc \Lambda_i^{(a)}
= T^{-1} \sum_{i} \sum_{n \neq 1} X_i^{(a)} \bigcirc \Lambda_i^{(a)}
$$

for which the collisional invariants of the Boltzmann collision integral are exploited. As in the case of its nonrelativistic version [13], the entropy production in this form suggests that energy dissipation arises owing to the dissipative evolution of nonconserved macroscopic variables $\phi_i^{(a) \mu \nu \ldots \ell}$. As it stands in (5.4), $\sigma_{\text{ent}}$ is easily seen to remain positive no matter what approximation is made to the unknown $X_i^{(a)}$, thanks to the H theorem and the nonequilibrium canonical form for $f_i$. Since it is not possible to determine $X_i^{(a)}$ exactly, this property of $\sigma_{\text{ent}}$ to remain positive is very useful to have in formulating a thermodynamically consistent theory of irreversible processes. This is made possible by the nonequilibrium canonical form for the distribution function.

The entropy balance equation (4.4), as it stands, does not reveal how the second law works to conform irreversible processes to it. With the nonequilibrium canonical form, the situation is greatly improved and we are now able to calculate the entropy differential accompanying irreversible processes in a way consistent with the second law.

On substitution of the nonequilibrium canonical form into the statistical mechanical formula (2.6) and the entropy flux (4.5) and use of the decomposition (2.21) for $T_i^{\mu \nu}$, we obtain the
entropy flux four-vector in the form

$$J_\mu^i = T^{-1} \sum_{r=1}^{r} (Q_i^\mu - \mu_i J_\mu^i) + T^{-1} \sum_{i=1}^{\infty} \sum_{a \neq 1} X_{i(a)}^{(a)} \quad \Omega_i^{(a) \nu \ldots \sigma \mu}$$  \hspace{1cm} (5.5)

where

$$\Omega_i^{(a) \nu \ldots \sigma \mu} = \psi_i^{(a) \nu \ldots \sigma \mu} - \phi_i^{(a) \nu \ldots \sigma} N^{\mu} = - \psi_i^{(a) \nu \ldots \sigma} \Delta_i^{\mu \nu}.$$  \hspace{1cm} (5.6)

Now, by substituting (5.4) and (5.5) into the entropy balance equation (4.4) and eliminating the dissipation term $\Delta_i^{\mu \nu}$ and the divergences of $Q_i^\mu$ and $J_\mu^i$ with the help of the evolution equation for $\phi_i^{(a)}$ and the balance equations, we obtain $D\mathcal{S}$ in the form

$$D\mathcal{S} = T^{-1} \left( D\mathcal{E} + pD\mathcal{v} - \sum_{r=1}^{r} \mu_i Dc_i + \sum_{i=1}^{r} \sum_{a \neq 1} X_{i(a)}^{(a)} \quad D\phi_i^{(a)} - c^{-2} \dot{Q}_i^{\mu} DU_{\mu} \right) + \mathcal{R} \hspace{1cm} (5.7)$$

where

$$\mathcal{R} = \mathcal{R}_d - \mathcal{R}_c,$$  \hspace{1cm} (5.8)

$$\mathcal{R}_d = (\rho T)^{-1} \sum_{i=1}^{r} \left( - \Pi_i^\mu \nu \nabla_\nu U_\mu - \Delta_i \Delta_i^{\mu \nu} \nabla_\nu U_\mu + Q_i^\mu \partial_\mu \ln T + J_\mu^i T \partial_\mu \mu_i \right) \hspace{1cm} (5.9a)$$

$$\mathcal{R}_c = \rho^{-1} \sum_{i=1}^{r} \sum_{a \neq 1} \left[ \partial_\mu (\tilde{X}_i^{(a)} \quad \Omega_i^{(a) \mu} + \tilde{X}_i^{(a)} \quad Z_i^{(a)}) \right],$$  \hspace{1cm} (5.9b)

$$\tilde{X}_i^{(a)} = X_i^{(a)} / T; \quad \tilde{\mu}_i = \mu_i / T; \quad v = \rho^{-1}; \quad \dot{Q}_i^{\mu} = Q_i^{\mu} / \rho.$$  \hspace{1cm} (5.10)

Note that $- \Delta_i^{\mu \nu} \nabla_\nu U_\mu = \nabla_\mu U_\mu$. As in the nonrelativistic theory [13], we define the compensation differential

$$D\Psi = T^{-1} \left( D\mathcal{E} + pD\mathcal{v} - \sum_{i=1}^{r} \mu_i Dc_i + \sum_{i=1}^{r} \sum_{a \neq 1} X_{i(a)}^{(a)} \quad D\phi_i^{(a)} - c^{-2} \dot{Q}_i^{\mu} DU_{\mu} \right)$$  \hspace{1cm} (5.11)

which differs from the classical formula only by the appearance of the velocity derivative term that is $O(c^{-2})$ and thus vanishes in the nonrelativistic limit. It is interesting to see that in relativistic theory the fluid velocity appears explicitly as a Gibbs variable in contrast to the nonrelativistic theory.

Since the term $\mathcal{R}$ does not vanish if the system is away from equilibrium owing to the fact that the fluxes do not vanish in a nonequilibrium condition, the entropy differential $D\mathcal{S}$ is not equal to the compensation differential $D\Psi$ and hence does not become a Pfaffian form. Equation (5.7) presages the invalidity of the extended Gibbs relation for $D\mathcal{S}$ unless $\mathcal{R} = 0$ identically. To answer this question more definitely, we examine $\mathcal{R}$ in detail.

The nonequilibrium contribution $\mathcal{R}$ may be cast into a more transparent and useful form. To this end, the following relations are useful. The nonequilibrium canonical form for $f_i$ may be recast into the form

$$\sum_{a \neq 1} \tilde{X}_i^{(a)} \quad h_i^{(a)} = \Delta \tilde{\mu}_i - k_B \ln (f_i f_i^0),$$  \hspace{1cm} (5.12)

where

$$\Delta \tilde{\mu}_i = \tilde{\mu}_i - \tilde{\mu}_i^c, \quad \tilde{\mu}_i^c = \mu_i^c / T.$$
By using the kinetic equation and formula (3.9), it is possible to show
\[
\sum_{i=1}^{r} \sum_{\alpha=1}^{\rho} \tilde{X}_{i}^{(\alpha)} \otimes Z_{i}^{(\alpha)} = \sum_{i=1}^{r} \sum_{\alpha=1}^{\rho} \left[ \left\langle f_{i}, p_{i}^{\mu} \partial_{\mu} (\tilde{X}_{i}^{(\alpha)} \otimes h_{i}^{(\alpha)}) \right\rangle + \partial_{\mu} (\Delta_{i}^{\mu} \tilde{X}_{i}^{(\alpha)} \otimes \psi_{i}^{(\alpha)}) \right] \\
- \sum_{i=1}^{r} \sum_{\alpha=1}^{\rho} \left[ \left\langle f_{i}, p_{i}^{\mu} (\partial_{\mu} \tilde{X}_{i}^{(\alpha)}) \otimes h_{i}^{(\alpha)} \right\rangle + (\partial_{\mu} \tilde{X}_{i}^{(\alpha)}) \otimes \Delta_{i}^{\mu} \psi_{i}^{(\alpha)} \right] .
\]  
(5.13)

Since from the kinetic equation
\[
\sum_{i=1}^{r} \left\langle f_{i}, p_{i}^{\mu} \partial_{\mu} \ln \left( \frac{f_{i}}{f_{i}^{0}} \right) \right\rangle = 0
\]  
(5.14)

and in view of (2.27) and the decomposition $\partial_{\mu} = c^{-2} U_{\mu} \nabla + \nabla_{\mu}$
\[
\left\langle f_{i}, p_{i}^{\mu} (\partial_{\mu} \tilde{X}_{i}^{(\alpha)}) \otimes h_{i}^{(\alpha)} \right\rangle + (\partial_{\mu} \tilde{X}_{i}^{(\alpha)}) \otimes \Delta_{i}^{\mu} \psi_{i}^{(\alpha)}
\]  
(5.15)

there follows the relation
\[
\mathcal{R}_{c} = \rho^{-1} \sum_{i=1}^{r} \left[ N_{i}^{\mu} \partial_{\mu} \Delta \mu_{i} - \Phi_{i}^{(\alpha)} \otimes D \tilde{X}_{i}^{(\alpha)} \right]
\]  
(5.16)

The Gibbs-Duhem relation follows from the statistical mechanical definition of $\mu^{\xi}$ if the local equilibrium Jüttner function $f_{i}^{0} = \exp \left( -\beta p_{i}^{\mu} U_{\mu} + \beta \mu_{i}^{\xi} \right)$ is used. It may be written in the form
\[
\sum_{i=1}^{r} c_{i} D \tilde{\mu}_{i}^{\xi} = \mathcal{E} D \left( 1/T \right) + v D \left( p/T \right).
\]  
(5.17)

Here, the equilibrium energy $\mathcal{E}_{e}$ is matched with the nonequilibrium energy $\mathcal{E}$ and the equilibrium density $n_{e}$ matched with the density $n$ to obtain (5.17). Since $J_{i}^{\mu} U_{\mu} = 0$ and thus
\[
\sum_{i=1}^{r} J_{i}^{\nu} \nabla_{\nu} \tilde{\mu}_{i} = \sum_{i=1}^{r} J_{i}^{\nu} \nabla_{\nu} \mu_{i} ,
\]  
with (5.16) for $\mathcal{R}_{c}$ and (5.17), $\mathcal{R}$ can be recast into a more transparent form
\[
\mathcal{R} = \sum_{i=1}^{r} \left[ \sum_{\alpha=1}^{\rho} \Phi_{i}^{(\alpha)} \otimes D \tilde{X}_{i}^{(\alpha)} - c_{i} D \tilde{\mu}_{i} \right] + \mathcal{E} D \left( 1/T \right) + v D \left( p/T \right) - \hat{\sigma}_{L}
\]  
(5.18)

where
\[
\hat{\sigma}_{L} = - (\rho T)^{-1} \sum_{i=1}^{r} \left( - J_{i}^{\mu} \nabla_{\nu} U_{\mu} + \Delta_{i} \nabla_{\mu} U_{\mu} + Q_{i}^{\mu} \nabla_{\mu} \ln T + J_{i}^{\mu} T \nabla_{\mu} \tilde{\mu}_{i}^{\xi} \right).
\]  
(5.19)
Note that this quantity is a measure of energy dissipation due to irreversible processes in the system. By defining the Boltzmann function $\mathcal{B}$

$$\mathcal{B} = \mathcal{S} - T^{-1} \left( \mathcal{S} + pv - \sum_{i=1}^{r} c_{i} \mu_{i} - \sum_{i=1}^{r} \sum_{\alpha = 1}^{l} \phi_{i}^{(\alpha)} \otimes X_{i}^{(\alpha)} \right)$$  \hspace{1cm} (5.20)

and combining (5.7) with (5.18), we finally obtain a differential equation for $\mathcal{B}$ which is equivalent to the entropy balance equation (4.4):

$$D\mathcal{B} = - \sigma_{L} - c^{-2} T^{-1} \tilde{\Omega} p D\mu_{\mu}.$$  \hspace{1cm} (5.21)

This equation differs from the classical analog [13] by the last term which vanishes in the nonrelativistic limit. Since by the momentum balance equation

$$c^{-2} \tilde{\Omega} p D\mu_{\mu} = h^{-1} \tilde{\Omega} p [\nabla_{\mu} p + \Delta_{r} \partial_{r} \tilde{\rho}^{\sigma} v^{\sigma} + c^{-2} (\Delta_{\mu} DQ^{\nu} - Q^{\mu} \nabla_{\nu} U^{\nu} - Q^{\nu} \nabla_{\nu} U^{\mu})]$$  \hspace{1cm} (5.22)

we may write (5.21) in the form

$$D\mathcal{B} = - \Xi_{d}$$  \hspace{1cm} (5.23)

where

$$\Xi_{d} = -(\rho T)^{-1} \sum_{i=1}^{r} \left[ \Pi^{i r} \nabla_{r} U_{\mu} - \Delta_{i} \Delta^{i r} \nabla_{i} U_{\mu} + Q_{i}^{\mu} (\nabla_{\mu} \ln T + h^{-1} \nabla_{\mu} p) + J_{i}^{\mu} T \nabla_{\mu} \tilde{\rho}^{r} \right]$$

$$- T^{-1} \tilde{\Omega} p [\Delta_{\mu} \partial_{\nu} \tilde{\rho}^{\sigma v} + c^{-2} (\Delta_{\mu} DQ^{\nu} - Q^{\mu} \nabla_{\nu} U^{\nu} - Q^{\nu} \nabla_{\nu} U_{\mu})].$$  \hspace{1cm} (5.24)

The dissipation term $\Xi_{d}$ contains terms quadratic in fluxes such as $Q^{\mu}$ and $\tilde{\rho}^{\sigma v}$ which are one order higher than the terms in $\sigma_{L}$. They are relativistic effects.

The dissipation term $\Xi_{d}$ does not vanish if there is an irreversible process present in the system, and consequently $D\mathcal{B} \neq 0$ except at equilibrium. This means that $D\mathcal{S}$ is not even a Pfaffian differential and therefore not an exact differential in the space of variables $\mathcal{S}$, $v_{r}$, $c_{i}$, $\phi_{i}^{(\alpha)}$, ($1 \leq i \leq r$, $\alpha \geq 1$). It is not equal to the compensation differential $D\Psi$ away from equilibrium. That is, the extended Gibbs relation for $D\mathcal{S}$ does not exist if the system is away from equilibrium, in contradiction with the premise made in the relativistic version of extended irreversible thermodynamics. In a recent work [13, 20] it is shown that the extended Gibbs relation for $D\mathcal{S}$ does not exist in the nonrelativistic theory either. This is a rigorous result based on the covariant Boltzmann equation and does not require an explicit solution for the unknowns $X_{i}^{(\alpha)}$ for its validity as long as the latter exist. There, however, exists a differential form for the compensation function $\Psi$ that looks like an extended Gibbs relation. It may be used to construct a thermodynamic theory of irreversible processes in a way parallel to equilibrium thermodynamics. The theory will provide various relations between nonequilibrium thermodynamic quantities that can be related to experimental observables. In any case, the present result on $D\mathcal{S}$ calls for revision of the existing notions of nonequilibrium entropy and entropy fluxes and of the applications thereof in extended irreversible thermodynamics [21], including its relativistic version.

6. Cumulant expansion for the dissipation terms $\Lambda_{i}^{(\alpha)}$

The dissipation terms $\Lambda_{i}^{(\alpha)}$ defined in (3.6) must be calculated in terms of macroscopic variables before the evolution equations for $\phi_{i}^{(\alpha)}$ are solved for specific flow problems. Since
$A_i^{(\sigma)}$ are intimately related to the entropy production and the latter must remain positive regardless of the approximation made to $A_i^{(\sigma)}$, it is best to calculate the dissipation terms through the entropy production that is manifestly positive. As in the nonrelativistic kinetic theory, the aim is nicely achieved if a cumulant expansion is employed.

To this end, we first write the distribution function in the form

$$f_i = f_i^0 \exp(-\omega_i) \quad (6.1)$$

where $f_i^0$ is the local Jüttner (equilibrium distribution) function

$$f_i^0 = \exp[-\beta (p_i^\mu U_\mu - \mu_i^\sigma)], \quad (6.2a)$$

$$\exp(-\beta \mu_i^\sigma) = \rho_i^{-1} \langle c^{-2} p_i^\mu U_\nu \exp(-\beta p_i^\mu U_\mu) \rangle, \quad (6.2b)$$

$$\omega_i = \beta (H_i^{(1)} - \Delta \mu_i). \quad (6.3)$$

We also define the abbreviations

$$x_{ij} = \omega_i + \omega_j, \quad y_{ij} = \omega_i^* + \omega_j^* \quad (6.4)$$

and the following reduced variables

$$\pi_i^\mu = \rho_i \beta, \quad \bar{U}_\mu = U^\mu/c. \quad (6.5)$$

We also scale the distribution function with the factor $\rho/(mk_B T)^{3/2}$ where $m$ is the mean rest mass of the mixture; that is,

$$f_i^0 = [\rho/(mk_B T)^{3/2}] \tilde{f}_i^0. \quad (6.6)$$

Therefore, $\tilde{f}_i^0$ is dimensionless. The transition rate $W_{ij}$ is scaled by $\lambda^2/mk_B T$ where $\lambda$ is a parameter of dimension length; we may take it with the mean free path or with the interaction range or the size parameter. Thus, we write

$$W_{ij} = \tilde{W}_{ij} (\lambda^2/mk_B T) \quad (6.7)$$

so that $\tilde{W}_{ij}$ is dimensionless. It is then convenient to define the parameter

$$g = (mc^2/k_B T)^{1/3}/c \lambda^2 \rho^2 \quad (6.8)$$

which has a dimension of volume $\times$ time. If this parameter is multiplied to the collision integral for the entropy production, it is nondimensionalized as follows:

$$\sigma_{\text{ent}}(x) = k_B \tilde{\sigma}_{\text{ent}}/g \quad (6.9)$$

where the nondimensional reduced entropy production $\tilde{\sigma}_{\text{ent}}$ is given by the integral

$$\tilde{\sigma}_{\text{ent}} = \frac{1}{4} \sum_{i=1}^4 \sum_{j=1}^4 \left\langle (x_{ij} - y_{ij})[\exp(-y_{ij}) - \exp(-x_{ij})] \right\rangle, \quad (6.10)$$

where

$$\left\langle \cdots \right\rangle = G_{ij} \int d^3 \pi_i d^3 \pi_j d^3 \pi_i^* d^3 \pi_j^* f_i^0 \tilde{f}_j^0 \tilde{W}_{ij}. \quad (6.11)$$
with \(d^3\pi_i = d^3\pi_i/\pi_i^0\). Then, with the definitions

\[
R^{(+)}(\epsilon) = \sum_{i=1}^r \sum_{j=1}^r \langle (x_{ij} - y_{ij}) \exp(\epsilon y_{ij} - 1) \rangle ,
\]

\[
R^{(-)}(\epsilon) = \sum_{i=1}^r \sum_{j=1}^r \langle (x_{ij} - y_{ij}) \exp(\epsilon x_{ij} - 1) \rangle ,
\]

the reduced entropy production may be written as

\[
\dot{\sigma}_{\text{ent}} = \frac{1}{4} [R^{(+)}(\epsilon) - R^{(-)}(\epsilon)] ,
\]

Now, the factors \(R^{(\pm)}(\epsilon)\) are in exactly the same form as for the factors appearing in the nonrelativistic version \([13]\) of the entropy production. We therefore may apply the same cumulant expansion method as for the nonrelativistic version to obtain the cumulant expansion for \(\dot{\sigma}_{\text{ent}}\). Since the method is now well documented \([22]\), we will simply list the result. Let

\[
\kappa = \left\langle \frac{1}{4} \sum_{i,j} (x_{ij} - y_{ij})^2 \right\rangle^{1/2} ,
\]

\[
\kappa_2 = \left\langle \frac{1}{4} \sum_{i,j} (x_{ij} - y_{ij})^2 (x_{ij} + y_{ij}) \right\rangle ,
\]

\[
\kappa_3 = \left\langle \frac{1}{4} \sum_{i,j} (x_{ij} - y_{ij})^2 (x_{ij}^2 + x_{ij} y_{ij} + y_{ij}^2) \right\rangle ,
\]

Then, we find to the first order cumulant approximation the reduced entropy production in the form

\[
\dot{\sigma}_{\text{ent}} = \kappa \sinh \kappa \geq 0 .
\]

It is easy to see that \(\dot{\sigma}_{\text{ent}}\) is always positive and therefore the second law of thermodynamics is satisfied completely. The higher order cumulant approximations can be obtained in exactly the same forms as for the nonrelativistic versions.

Having obtained a positive entropy production, it is possible to obtain the corresponding dissipation terms. First, let us observe that \(\kappa\) may be expressed in the quadratic form

\[
\kappa = \left[ \sum_{i,j} \sum_{\alpha} \sum_{\gamma} X_i^{(\alpha)} \otimes R^{(\alpha \gamma)} \otimes X_j^{(\gamma)} \right]^{1/2}
\]

where \(R^{(\alpha \gamma)}\) are the collision bracket integrals appearing in the Chapman-Enskog method. To write them more explicitly, we define the brackets as follows:

\[
[A \otimes B]_{ij} = G_{ij} \int d\tilde{\pi}_i \ d\tilde{\pi}_j \ d\tilde{\pi}_i^* \ d\tilde{\pi}_j^* \ \tilde{f}_i \ \tilde{f}_j \ \tilde{W}_{ij} \ A \otimes B.
\]

Then, the collision bracket integrals are:

\[
R^{(\alpha \gamma)} = \frac{1}{4} \beta^2 \left[ (h_i^{(\alpha)} + h_i^{(\alpha)} - h_i^{(\alpha)} - h_i^{(\alpha)}) (h_i^{(\gamma)} + h_i^{(\gamma)} - h_i^{(\gamma)} - h_i^{(\gamma)}) \right]_{ij},
\]

\[
+ \frac{1}{2} \beta^2 \sum_{j, \delta, \gamma} [(h_i^{(\alpha)} - h_i^{(\alpha)}) (h_i^{(\gamma)} - h_i^{(\gamma)})]_{ij},
\]

(6.17a)
These integrals satisfy the Onsager reciprocal relations. These collision bracket integrals may be decomposed into irreducible tensor products of $\Delta^{a\beta}$ and $U^{\gamma}$. Since the procedure is well documented in the literature [6], we will not dwell on it. We remark that $\kappa^2$ is intimately related to the Rayleigh-Onsager dissipation function which is quadratic in fluxes.

By using (6.16) in (6.15) and comparing the latter with (5.4), we find the dissipation terms to the first order cumulant approximation:

$$
\Lambda_i^{(\alpha)} = (\beta g)^{-1} \sum_{j=1}^{r} \sum_{\gamma=1}^{\infty} \mathbb{R}_{ij}^{(\alpha\gamma)} \circ X_j^{(\gamma)} (\sinh \kappa / \kappa).
$$

This form of dissipation terms is completely consistent with the second law of thermodynamics inasmuch as the entropy production as in (6.15) is positive. Higher order forms $\Lambda_i^{(\alpha)}$ can be similarly found from the higher order cumulant approximation for $\dot{\sigma}_{\text{ent}}$.

7. Determination of the unknowns $X_i^{(\alpha)}$

With various thermodynamically consistent macroscopic evolution equations and the entropy differential in place in the theory, there now remains the task of determining the unknowns $X_i^{(\alpha)}$ appearing in the nonequilibrium canonical form. They can be determined in a manner completely parallel to the case of the nonrelativistic theory [23]. Therefore, the discussion will be brief.

Since the distribution function can be expanded into moments as in the conventional moment method, we may write

$$
f_i = f_i^0 \left( 1 + \sum_{\alpha=1}^{r} A_i^{(\alpha)} \circ h_i^{(\alpha)} \right),
$$

where the coefficients $A_i^{(\alpha)}$ are functions of macroscopic variables such as temperature, fluxes, etc. as will be shown presently. If one attempts to construct a theory of irreversible processes with the form (7.1), the attempt will be frustrated because the form is not appropriate for calculating the entropy, entropy flux and entropy production which should be manifestly positive. Nevertheless, it is a mathematically acceptable way of expressing the nonequilibrium distribution function. The nonequilibrium canonical form used in the modified moment method allows to avoid the aforementioned difficulty associated with the entropy and related quantities. The nonequilibrium canonical form and the moment expansion (7.1) share the same set of moments. This means that the unknowns $X_i^{(\alpha)}$ in the nonequilibrium canonical form can be determined from (7.1) by equating them and solving the equation for the unknowns. We thereby obtain the equation

$$
\kappa_{\beta}^{-1} \left( \Delta \vec{\mu}_i - \sum_{\alpha=1}^{r} X_i^{(\alpha)} \circ h_i^{(\alpha)} \right) = \ln \left( 1 + \sum_{\gamma=1}^{\infty} A_i^{(\gamma)} \circ h_i^{(\gamma)} \right).
$$

Since the moments $h_i^{(\alpha)}$ are chosen such that they are orthogonal in the following sense

$$
\left\langle f_i^0 \left( p_i \right| U_\lambda \right)^{-1} \tilde{h}_i^{(\alpha)} \bar{h}_i^{(\gamma)} \right\rangle = \delta_{\alpha\gamma} \left\langle f_i^0 \left( p_i \right| U_\lambda \right)^{-1} \bar{h}_i^{(\alpha)} \bar{h}_i^{(\gamma)} \right\rangle.
$$

where $\tilde{h}_i^{(\alpha)}$ are defined by

$$
\tilde{h}_i^{(\alpha)} = c^{-2} \left( p_i \right| U_\lambda \right)^{\alpha} h_i^{(\alpha)},
$$
$A_i^{(a)}$ are given in terms of fluxes as follows:

$$\Phi_i^{(a)\mu\nu} \cdot \ell = \left\langle \int_i^0 \tilde{h}_i^{(a)\mu\nu} \cdot \ell \left( 1 + \sum_{\gamma=1} A_i^{(\gamma)} \circ h_i^{(\gamma)} \right) \right\rangle = A_i^{(a)} \circ \left\langle \int_i^0 \tilde{h}_i^{(a)\mu\nu} \cdot \ell h_i^{(\gamma)} \right\rangle.$$  \hspace{1cm} (7.5)

Note that the fluxes on the left-hand side are determined from the flux evolution equations. The quantity in the angular brackets in (7.5) is a function of temperature only. Therefore, the coefficient $A_i^{(a)}$ is directly proportional to $\Phi_i^{(a)\mu\nu} \cdot \ell$. In fact, it is possible to write

$$A_i^{(1)\mu\nu} = \frac{1}{3} \Phi_i^{(1)\mu\nu} \left\langle \int_i^0 \tilde{h}_i^{(1)} \cdot h_i^{(1)} \right\rangle,$$  \hspace{1cm} (7.6a)

$$A_i^{(2)} = \Phi_i^{(2)} \left\langle \int_i^0 \tilde{h}_i^{(2)} h_i^{(2)} \right\rangle,$$  \hspace{1cm} (7.6b)

$$A_i^{(3)\mu} = \frac{1}{3} \Phi_i^{(3)\mu} \left\langle \int_i^0 \tilde{h}_i^{(3)} h_i^{(3)} \right\rangle,$$  \hspace{2cm} (7.6c)

$$A_i^{(4)\mu} = \frac{1}{3} \Phi_i^{(4)\mu} \left\langle \int_i^0 \tilde{h}_i^{(4)} h_i^{(4)} \right\rangle,$$  \hspace{1cm} (7.6d)

By applying the same procedure as for (7.5), we obtain from (7.2) the equation for $X_i^{(a)}$ in terms of $A_i^{(\gamma)}$:

$$- \beta X_i^{(a)} \circ \left\langle \int_i^0 \tilde{h}_i^{(a)} \circ h_i^{(a)} \right\rangle = \left\langle \int_i^0 \tilde{h}_i^{(a)} \ln \left( 1 + \sum_{\gamma=1} A_i^{(\gamma)} \circ h_i^{(\gamma)} \right) \right\rangle.$$  \hspace{1cm} (7.7)

The orthogonality relation (7.3) has been used for (7.7). The right-hand side of (7.7) may be calculated by a variety of methods [23]. If the logarithmic function is expanded and only the first term is retained, we obtain the lowest order result for the unknowns as follows:

$$- \beta X_i^{(a)} \circ \left\langle \int_i^0 \tilde{h}_i^{(a)} \circ h_i^{(a)} \right\rangle = A_i^{(a)} \left\langle \int_i^0 \tilde{h}_i^{(a)} \circ h_i^{(a)} \right\rangle,$$

which implies that

$$X_i^{(a)} = - \beta^{-1} A_i^{(a)}.$$  \hspace{1cm} (7.8)

where $A_i^{(a)}$ are given by (7.5) in general and by (7.6a)-(7.6d) in particular. It is convenient to write the results in the form

$$X_i^{(a)} = - \Phi_i^{(a)} g_i^{(a)}$$  \hspace{1cm} (7.9)

where $g_i^{(a)}$ can be easily identified from (7.6); their nonrelativistic limits are

$$g_i^{(1)} = 2 \rho_i; \quad g_i^{(2)} = 2 \rho_i / 3; \quad g_i^{(3)} = T \dot{C}_p \rho_i; \quad g_i^{(4)} = m, n_i.$$  \hspace{1cm} (7.10)

Here $\dot{C}_p$ is the specific heat of species $i$ at constant pressure. The approximate result (7.9) can be used for various calculations regarding nonlinear transport processes as has been shown in the nonrelativistic theory in the past.

8. Discussion and conclusion.

In this paper we have applied the modified moment method to solve the covariant Boltzmann equation for a relativistic monatomic gas mixture. The method affords us a rigorous conclusion concerning the entropy differential when the system is away from equilibrium; it is not an
exact differential since $\mathcal{F}$, or equivalently $\mathcal{E}_d$, is not equal to zero if there exists a nonequilibrium process in the system. This means that the extended Gibbs relation forming the basis of extended irreversible thermodynamics (EIT) does not hold valid at least from the viewpoint of the covariant Boltzmann equation. However, there is the compensation differential that looks like the extended Gibbs relation used in EIT, but this means a revision of the existing EIT formalism and its logical structure. The entropy balance equation is put into another equivalent form in terms of the Boltzmann function $\mathcal{B}$ introduced as a Legendre transformation of the entropy density. However, the differential of $\mathcal{B}$ is not exact, since $\mathcal{E}_d$ is not even a differential form in the nonequilibrium Gibbs space. Because this Boltzmann function is not equal to zero if the system is away from equilibrium, the Boltzmann function $\mathcal{B}$ is dependent on the initial condition and the history of the process involved, namely, $\mathcal{B}$ is path-dependent. This means that $d\mathcal{F}$ is not integrable, that is, not an exact differential, and the extended Gibbs relation simply does not exist. As mentioned earlier, the non-vanishing $\mathcal{B}$ for irreversible processes has some significant consequences for irreversible thermodynamics and, in particular, for the EIT formalism. The most immediate and obvious consequence is the fact that the extended Gibbs relation for $d\mathcal{F}$ cannot be taken for granted and the notion and role of entropy density for nonequilibrium systems should be basically revised. In fact, for nonequilibrium systems the entropy density itself is a quantity depending on the path taken in the nonequilibrium thermodynamic phase space (nonequilibrium Gibbs space) by the system when it makes transition from a state to another in the space. Therefore, the notion of equilibrium entropy, which is a state function, does not apply to the nonequilibrium entropy if it is defined by the statistical formula (2.6) or its scalar version.

In the case of the extended Gibbs relation for $d\mathcal{F}$, if the processes are steady so that $D\mathcal{E}, Dv, D\hat{\Phi}_{i}^{(\alpha)},$ and $DU_{\mu}$ are equal to zero, then the entropy does not change despite the fact that the system is in nonequilibrium. Contrary to this situation, since as long as there are spatial gradients of velocity, temperature, concentrations, etc. so that $\mathcal{E}_d \neq 0$, the Boltzmann function changes even if the processes are steady. $d\mathcal{F}$ does not vanish according to the result obtained in this paper. Therefore, the entropy density evolves on a constant hypersurface $\Psi(\mathcal{E}, v, c, \hat{\Phi}_{i}^{(\alpha)}, U_{\mu}) = \text{constant}$ (a surface in the nonequilibrium Gibbs space); figuratively speaking, it winds the aforementioned surface, which may be imagined to be a hypercylinder in the Gibbs space, owing to the steady production of entropy since the entropy is produced even at a steady state. This difference in the behaviour of entropy in EIT, where the extended Gibbs relation is assumed, and the present theory is significant and important.

A recent study in the nonrelativistic theory [24] indicates that the compensation differential may be used to investigate the thermodynamics of nonequilibrium systems in a way rather parallel to equilibrium thermodynamics. Nevertheless, such a formalism still requires integration of generalized hydrodynamic equations as an integral part of the theory. Since the latter are not trivial to solve, there remains a great deal of work to be done on the subject matter in the future.

The present formalism in essence puts the statistical mechanics of nonequilibrium thermodynamics on a par with the Gibbs ensemble theory of equilibrium statistical thermodynamics in the sense that all thermodynamic functions and evolution equations are expressed in terms of $\mathcal{X}_i^{(\alpha)}$, which must be ultimately obtained by solving the generalized hydrodynamics, just as all equilibrium thermodynamic functions and relations are expressed in the Gibbs ensemble theory in terms of a partition function which must be computed for each and every system in the end.

All the macroscopic evolution equations are presented in such forms that they consist of terms which are easily identifiable with the corresponding terms in their nonrelativistic versions and purely relativistic terms which vanish in the nonrelativistic limit. Thus, the
relativistic corrections to the classical generalized hydrodynamic equations are clearly exposed and made easy to obtain. Since the full relativistic generalized hydrodynamic equations are much more complicated to solve than already difficult nonrelativistic generalized hydrodynamic equations, the first-order relativistic corrections to the latter are all one can hope for in practice at present, and the relativistic generalized hydrodynamic equations presented here should be useful for such studies.

Finally, we reiterate as a part of the conclusion that with the dissipation terms as given in (6.18) the generalized hydrodynamic equations presented in this work are consistent with the second law of thermodynamics for all approximate forms for the unknowns \( X_i^{(a)} \). We hope to investigate the question of hyperbolicity of the generalized hydrodynamic equations in the future when hydrodynamics is studied with the generalized hydrodynamic equations presented.

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References