Mixtures of relativistic gases in gravitational fields: combined Chapman-Enskog and Grad method and the Onsager relations

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In this work we study a $r$-species mixture of gases within the relativistic kinetic theory point of view. We use the relativistic covariant full Boltzmann equation and we incorporate the Schwarzschild metric. The method of solution of the Boltzmann equation is a combination of the Chapman-Enskog and Grad representations. The thermodynamic fluxes are expressed as functions of the thermodynamic forces so that the generalized expressions for the Navier-Stokes, Fick and Fourier laws are obtained. The constitutive equations for the diffusion and heat fluxes of the mixture are functions of thermal and diffusion forces which depend on the acceleration and the gravitational potential gradient. While this dependence is of relativistic nature for the thermal force, this is not the case for the diffusion forces. We show also that the matrix of the diffusion coefficients is symmetric and the thermal-diffusion coefficient is equal to the diffusion-thermal one, proving the Onsager reciprocity relations. The entropy flux of the mixture is also expressed in terms of the thermal and diffusion forces, so that its dependence on the acceleration and gravitational potential gradient is also determined.

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I. INTRODUCTION

The relativistic kinetic theory of gases is a subject that began in 1911 when Jüttner \cite{1} proposed a relativistic version of the velocity distribution function which corresponds to the Maxwellian distribution function in the non-relativistic limiting case. Later, several studies have been made, but for brevity’s sake we mention the books \cite{2,3} where several applications of the relativistic kinetic theory of gases are discussed.

This work represents a continuation of the study of the properties of relativistic gases using the Boltzmann equation in gravitational fields, this sub-area has not yet been studied in depth. Here we quote some works \cite{4-8} on this topic which have been recently published.

The method used in this paper to solve the covariant full Boltzmann equation is a combination of the Chapman-Enskog and Grad methods \cite{9,10}. It consists essentially in doing an expansion of the distribution function for each species that is solution of the Boltzmann equation up to first correction, like in the Chapman-Enskog method. Then we impose that such an expansion must be compatible with the solution of the Boltzmann equation given by the method of Grad \cite{11}. In order to keep the linear regime we truncate the Grad distribution for each species in the terms of the non-equilibrium pressure, pressure deviator tensor, diffusion and heat fluxes. Therefore, we obtain a linearized Boltzmann equation that is written in terms of the local thermodynamic variables and the fluxes: diffusion, heat, non-equilibrium pressure and pressure deviator tensor. The next step is to generate from that linearized Boltzmann equation a set of linear algebraic system for the fluxes. We generate equations, one for each thermodynamic flux, through the multiplication of a dynamical function of the particles by the linearized Boltzmann equation and integrating over the momentum space. The solution of such system yields to the constitutive equations for the fluxes in terms of gradients of local thermodynamic variables and in this case also of a gravitational potential that arises from the Schwarzschild metric. The laws of Navier-Stokes for the non-equilibrium pressure and pressure deviator tensor are obtained as well as the generalized Fourier and Fick laws for the heat and diffusion fluxes. It will be shown that naturally appears a generalized diffusion force that has, like the temperature gradient, a contribution of the acceleration and of the gravitational potential gradient. The two contributions for the temperature gradient were analyzed separately by Eckart \cite{12} – where in a relativistic gas at equilibrium the temperature gradient is counterbalanced by an acceleration – and by Tolman \cite{13,14} – where in a relativistic gas at equilibrium the temperature gradient is counterbalanced by a gravitational potential gradient. After that we manipulate the constitutive equations for the heat and diffusion fluxes to show that the Onsager reciprocity relations hold. The demonstration made here is general in the sense that the interaction of the particles are supposed to maintain the microscopic reversibility principle.

The structure of this paper is as follows. We define the problem in section II and establish the Boltzmann equation and the definitions for both, the thermodynamical variables and fluxes. In section III we use a method of solution of the Boltzmann equation that is a combination of the Grad and Chapman-Enskog ones, the solution is truncated up to first order so we obtain linear expressions. Such a process will lead us to an algebraic system of equations for the thermodynamical fluxes that when solved expresses the thermodynamical coefficients.
for an arbitrary inter-molecular interaction. The generalized laws of Fourier and Fick are determined in section IV. Furthermore, we show that the Onsager reciprocity relations hold for arbitrary inter-molecular interactions and the laws of Fourier and Fick are expressed in terms of thermal and diffusion forces, which are generalizations of the corresponding forces of non-relativistic kinetic theory to relativistic gases in gravitational fields. The entropy flux of the mixture as a function of the thermal and diffusion forces is the subject of section V in and section VI the constitutive equation of a relativistic Newtonian fluid, i.e., the Navier-Stokes law, is determined. Ultimately, in section VII, we discuss the obtained results.

II. BACKGROUND

In this section we will define the problem of a $r$-species non-reacting mixture in a Riemannian space with metric tensor $g^\mu\nu$. The particles are supposed not have internal degrees of freedom. Each of these particles of the constituent $a = 1, \ldots, r$ have mass $m_a$ and are characterized by the space-time coordinates $x^\mu = (ct, \mathbf{x})$ and the momentum $p_a^\mu = (p_{a0}^\mu, p_a^i)$. The mass-shell condition, i.e. $g_{\mu\nu}p_a^\mu p_a^\nu = m_a^2c^2$ implies the following relationships for the contravariant and covariant temporal components,

\[
\begin{align*}
p_a^0 &= (p_{a0} - g_{a0}p_a^0)/g_{00}, \\
p_{a0} &= \sqrt{g_{00}m_a^2c^2 + (g_{00}g_{ij} - g_{00}g_{ij})p_a^ip_a^j},
\end{align*}
\]

(1)

respectively. The analysis is developed within the tenets of the general relativity, we adopt the Schwarzschild metric in which the line element reads [13]:

\[
ds^2 = \left(1 - \frac{2GM}{c^2r}\right)(dx^0)^2 - \frac{1}{\left(1 - \frac{2GM}{c^2r}\right)}d\theta^2 - R^2 (d\theta^2 + \sin^2 \theta d\psi^2),
\]

(2)

in terms of the spherical coordinates $\{R, \theta, \psi, ct = x^0\}$. Above, $M$ is the total mass of the spherical source and $G$ is the gravitational constant. Here we shall adopt the isotropic Schwarzschild metric, which reads

\[
ds^2 = g_0(r) (dx^0)^2 - g_1(r)\delta_{ij}dx^i dx^j,
\]

(3)

\[
g_0(r) = \left(1 - \frac{GM}{c^2r}\right)^2, \quad g_1(r) = \left(1 + \frac{GM}{c^2r}\right)^4.
\]

(4)

Along the calculation we use a relativistic parameter $\zeta_a = m_a^2c^2$, where $c$ is the speed of light, $k$ the Boltzmann constant and $T$ the local temperature, assumed as an invariant. This parameter is convenient because it tell us how relativistic is the system, for example, $\zeta_a \gg 1$ corresponds to a non-relativistic limit. On the other hand, $\zeta_a \ll 1$ belongs to an ultra-relativistic limit.

The most fundamental equation in the kinetic theory is the Boltzmann equation; such an equation can be obtained with two hypothesis as a basis. The first one is that particles collide elastically and only collisions of pairs are taken into account. The second one implies a description of the system with one-particle distribution function, that is equivalent to think that collisions represent a process that do not depend of what occurred in the past with the particles. This last hypothesis is also known in the literature as molecular chaos hypothesis. In our case, the Boltzmann equation reads [3]:

\[
p_a^\mu \frac{\partial f_a}{\partial x^\mu} - \Gamma^i_{\mu\nu}p_a^\mu \frac{\partial f_a}{\partial p_a^i} = \sum_{b=1}^r \int (f_a' J_b' - f_a J_b) F_{ab} \sigma_{ab} d\Omega \sqrt{-g} \frac{d^3p_b}{p_{00}},
\]

(5)

for the $a$-species. Here the Latin subindex denotes the species, note that we have one equation with the same structure of (4) for each component of the mixture $a = 1, \ldots, r$. The distribution function $f_a(x^\mu, p_a^\nu)$ has a statistical meaning, indeed the quantity $f_a(x^\mu, p_a^\nu) d^3x d^3p_a$ at time $t$, is the number of particles of the constituent $a$ in the volume element between $x, x + d^3x$ and $p_a, p_a + d^3p_a$. In equation (5) also appear the Christoffel symbols $\Gamma^i_{\mu\nu}$ and the invariant flux $F_{ab} = \sqrt{(p_a^\mu p_b^\mu - m_a^2m_b^2c^4)}$, which plays the role of the relative velocity of the non-relativistic Boltzmann equation. We have also the invariant differential elastic cross-section $\sigma_{ab}d\Omega$ for collisions of species $a$ and $b$, where $d\Omega$ is the corresponding solid angle element. Integrals are made with the invariant differential element $\sqrt{-g} d^3p_a$, being $\sqrt{-g} = \det |g^{\mu\nu}|$. In equation (5), quantities denoted with a prime are evaluated with the momentum of the particles after a binary collision occurs, i.e., $f_a' \equiv f(x, p_a, t)$ and so on. The binary collision is characterized by the energy-momentum conservation law $p_a^0 + p_b^0 = p_a'^0 + p_b'^0$.

Without solving Boltzmann’s equation we can obtain two important results. The first one, that we will not describe here, is the obtention of a local equilibrium distribution function which reads

\[
f_a^{(0)} = \frac{n_a}{4\pi kT m_a^2 c K_2(\zeta_a)} \exp \left(-\frac{U_{\zeta_a} p_a^0}{kT}\right),
\]

(6)

where $n_a$ is the local number of particles of species $a$, the modified Bessel function of second kind is represented by

\[
K_n(\zeta) = \left(\frac{\zeta}{2}\right)^{n/2} \Gamma(1/2) \Gamma(n + 1/2) \int_1^{\infty} e^{-\zeta y} (y^2 - 1)^{n-1/2} dy,\]

(7)

and $U_{\zeta} - \mu_0$ with $U_{\zeta} = c^2 - \zeta$ is the hydrodynamical four-velocity. The set of local hydrodynamical variables that describes the local equilibrium is $\{n_1, \ldots, n_r, U_{\zeta}, \mu_0\}$. For the calculations that will be performed, it is convenient to evaluate Eq. (6) in a co-moving frame, that is $U_{\zeta} = (c/\sqrt{g_{00}}, 0)$ yielding

\[
f_a^{(0)} = \frac{n_a}{4\pi kT m_a^2 c K_2(\zeta_a)} \exp \left(-U_{\zeta_a} |P_a|^2/2kT\right),
\]

(8)
The second important result that arises from the Boltzmann equation is the obtention of the balance equations, for this purpose we proceed as follows. We multiply the Boltzmann equation \( \mathbf{10} \) by the collisional invariants, that is, microscopic dynamical quantities that are conserved between collisions, i.e., \( \Psi_a + \Psi_b = \Psi'_a + \Psi'_b \) and integrate the resulting equation over \( -g^{3/2} p_a p_b \). The collisional invariants \( \Psi_a \) can take the value of the mass \( m_a \) and the energy-momentum \( p_a^\mu \). To obtain the particle four-flow balance equation of the \( a \)-species we take \( \Psi_a = c \) and integrate, this process leads to the conservation law

\[
N_{\mu}^{a;\nu} = 0, \quad (9)
\]

the semicolon denoting the covariant derivative and we have defined

\[
N_{\mu}^{a} = c \int p^\mu f_a \sqrt{-g} \frac{d^3p_a}{p_{a0}}, \quad (10)
\]

as the particle four-flow of species \( a \). We introduce a general decomposition of \( N_{\mu}^{a} \), in terms of the hydrodynamic four-velocity as

\[
N_{\mu}^{a} = n_a U^\mu + J_{\mu}^a, \quad \text{where} \quad n_a = \frac{N_{\mu}^{a} U_{\mu}}{c^2}, \quad (11)
\]

denotes the partial particle number density. The quantity \( J_{\mu}^a \) is a space-like vector defined as

\[
J_{\mu}^a = \Delta_{\mu}^a c \int p^\nu f_a \frac{d^3p_a}{p_{a0}}, \quad (12)
\]

and holds the property \( J_{\mu}^a U_{\mu} = 0 \). Above, we introduce the projector

\[
\Delta_{\mu}^a = g_{\mu\nu} - \frac{1}{c^2} U^\mu U^\nu, \quad (13)
\]

that has the property \( \Delta_{\mu}^a U_{\mu} = 0 \). Equation \( \mathbf{12} \) is the corresponding diffusion flux of species \( a \) of the mixture and by taking the sum of \( \mathbf{11} \) over all the components we easily note that

\[
N^\mu = \sum_{a=1}^{r} N^\mu_{a} = n U^\mu, \quad n = \sum_{a=1}^{r} n_a, \quad \sum_{a=1}^{r} J_{\mu}^a = 0, \quad (14)
\]

where the last equation implies that there exist only \( (r - 1) \) partial diffusion fluxes that are linearly independent for a mixture of \( r \) constituents.

On the other hand, to obtain the balance equation for the energy-momentum of the \( a \)-species defined by

\[
T_{\mu\nu}^{a} = c \int p^\mu p^\nu f_a \sqrt{-g} \frac{d^3p_a}{p_{a0}}, \quad (15)
\]

we multiply the Boltzmann equation \( \mathbf{13} \) by the collisional invariant \( \Psi_a = c p_a^\mu \) and integrate the resulting equation over \( -g^{3/2} p_a p_b \), then we get that

\[
T_{\mu\nu}^{a} = P_{\mu}^{a}; \quad (16)
\]

where the production term \( P_{\mu}^{a} \) is given by

\[
P_{\mu}^{a} = \sum_{b=1}^{r} c \int (p_{\mu}^{b} - p_{\mu}^{a}) f_a f_b F_{ba} \sigma_{ab} d\Omega \sqrt{-g} \frac{d^3p_b}{p_{b0}} \sqrt{-g} \frac{d^3p_a}{p_{a0}}. \quad (17)
\]

Note that this equation does not represent a conservation law, but if we sum Eq. \( \mathbf{16} \) over all species we obtain

\[
T_{\mu\nu} = \sum_{a=1}^{r} P_{\mu}^{a} = 0, \quad (18)
\]

that represents a conservation equation for the energy-momentum tensor of the mixture \( T_{\mu\nu} = \sum_{a=1}^{r} T_{\mu\nu}^{a} \). By following the decomposition of Eckart (see e.g. \([21][22]\)), the energy-momentum tensor of the \( a \)-species can be written as

\[
T_{\mu\nu}^{a} = \frac{n_a e_a}{c^2} U^\mu U^\nu + \frac{1}{c^2} U^\mu (q_a^\nu + h_a J_a^\nu) \quad + \frac{1}{c^2} U^\nu (q_a^\mu + h_a J_a^\mu) - (p_a + \omega_a) \Delta^{\mu\nu} + p_{a}^{(\mu\nu)}, \quad (19)
\]

where several definitions are to be made. First we can list the local equilibrium quantities: energy per particle \( e_a \), hydrostatic pressure \( p_a \) and the enthalpy per particle \( h_a = e_a + p_a/n_a \). Next, the non-equilibrium quantities are: dynamical pressure \( \omega_a \), heat flux \( q_a^\mu \) and pressure deviator tensor \( p_{a}^{(\mu\nu)} \). They are given in terms of the following projections of the energy-momentum tensor of the \( a \)-species:

\[
q_a^\mu + h_a J_a^\mu = \Delta_a^\mu \Delta_a^\nu U_a^\nu, \quad e_a = \frac{1}{n_a c^2} U_a^{\mu} T_a^{\mu\nu} U_a^\nu, \quad (20)
\]

\[
p_a^{(\mu\nu)} = \left( \Delta_a^\mu \Delta_a^\nu - \frac{1}{3} \Delta_a^{\tau\nu} \Delta_a^{\mu\tau} \right) T_a^{\tau\nu}, \quad (21)
\]

\[
p_a + \omega_a = \frac{1}{3} \Delta^{\mu\nu} T_a^{\mu\nu}. \quad (22)
\]

The corresponding quantities for the mixture are:

\[
e = \sum_{a=1}^{r} \frac{n_a}{n} e_a, \quad p = \sum_{a=1}^{r} p_a, \quad \omega = \sum_{a=1}^{r} \omega_a, \quad (23)
\]

\[
h = \sum_{a=1}^{r} \frac{n_a}{n} h_a, \quad p^{(\mu\nu)} = \sum_{a=1}^{r} p_{a}^{(\mu\nu)}, \quad (24)
\]

\[
q = \sum_{a=1}^{r} (q_a^\mu + h_a J_a^\mu), \quad (25)
\]

so that the energy-momentum tensor of the mixture is written as

\[
T^{\mu\nu} = \frac{ne}{c^2} U^\mu U^\nu + \frac{1}{c^2} (U^\mu q^\nu + U^\nu q^\mu) \quad - (p + \omega) \Delta^{\mu\nu} + p^{(\mu\nu)}. \quad (26)
\]

Note that the heat flux \( q^\mu \) of the mixture has two contributions, this is in accordance with the linear irreversible thermodynamics \([10]\), one term is related with the partial heat flux and another with the energy transported with the matter (diffusion).
Another quantity which is important in the analysis of mixtures of relativistic gases is the entropy four-flow of the mixture $S^\mu$, defined by

$$S^\mu = -k c \sum_{a=1}^r \int p^\mu_a f_a \ln(b_a f_a) \sqrt{-g} d^3p_a p_a \theta,$$  

(27)

where $b_a$ is a constant which has inverse units of $f_a$. Its balance equation is obtained through the multiplication of the Boltzmann equation (4) by $-k c \ln(b_a f_a)$, the subsequent integration over $\sqrt{-g} d^3p_a$ and the sum over all species, yielding

$$\sigma = \frac{c k}{4} \sum_{a=1}^r \sum_{b=1}^r \int f_a f_b \ln \left( \frac{f_a f_b}{f_a f_b} \right) \frac{\partial f_a}{\partial \ln b_a} \frac{\partial f_b}{\partial \ln b_b} - 1 \right) \times F_{ab} \sigma_{ab} d\Omega \sqrt{-g} d^3p_a p_a \theta,$$  

(28)

The quantity $\sigma$ is the entropy four-flow production of the mixture, which is always positive semi-definite, thanks to the relationship $(x-1) \ln x \geq 0$ valid for $x > 0$. The entropy four-flow of the mixture is decomposed according to:

$$S^\mu = ns U^\mu + \Phi^\mu, \hspace{1cm} s = \frac{1}{c^2 n} S^\mu U_\mu, \hspace{1cm} \Phi^\mu = \Delta^\mu S^\nu,$$  

(30)

where the quantity $s$ is identified as the entropy per particle of the mixture and $\Phi^\mu$ its entropy flux. The entropy per particle of species $a$ is given by

$$s_a = -\frac{k U_\mu}{c n_a} \int p^\mu_a f_a \ln(b_a f_a) \sqrt{-g} d^3p_a,$$  

(31)

so that we have $ns = \sum_{a=1}^r n_a s_a$.

The main problem in the kinetic theory is to find a solution of the Boltzmann equation (4), because as we have seen, all the above definitions can be evaluated by integrating functions that involve $f_a(x^\mu, p^\mu_a)$. The equilibrium quantities can be evaluated with the local equilibrium distribution function (3) and read:

$$e_a = m_a c^2 \left( G_a - \frac{1}{\zeta_a} \right),$$  

(32)

$$p_a = n_a k T,$$  

(33)

$$s_a = k \left\{ \ln \left[ \frac{4 \pi m_a^2 c k T K_2(\zeta_a)}{n_b b_a} \right] + \zeta_a G_a - 1 \right\}.$$  

(34)

The chemical potential of species $a$ is introduced through the Gibbs function per particle, namely, $\mu_a = e_a - T s_a + p_a/n_a$ and by taking into account the above expressions we get

$$\mu_a = k T \ln \left( \frac{c n_a b_a}{4 \pi m_a^2 c k T K_2(\zeta_a)} \right).$$  

(35)

In next sections, we will use a method that allow to obtain expressions for the diffusion fluxes $J^\mu_a$, heat flux $q^\mu_a$, non-equilibrium pressure $\pi$, pressure deviator tensor $p^{(\mu\nu)}$ and entropy flux $\Phi^\mu$. Furthermore, we will show the dependence of $J^\mu_a$ and $q^\mu_a$ in terms of the gravitational potential and demonstrate the validity of the Onsager reciprocity relations.

### III. COMBINED CHAPMAN-ENSKOG AND GRAD METHOD

In this section we make use of a method [10, 11] that combines the features of the Chapman-Enskog [17] with the Grad’s moment [11] to extract thermodynamic information from the Boltzmann equation. In this method neither a solution of the integro-differential Boltzmann equation is needed (as in the Chapman-Enskog method) nor field equations for the moments (as in the Grad method) are used.

First we are going to describe how does the moment Grad method is constructed, the central idea is to expand the distribution function that is solution of the Boltzmann equation $f_a(x^\mu, p^\mu_a)$ around the local equilibrium $f_a^{(0)}$ in a series of an ortho-normal set. In this case, we have $13r+1$ unknown variables (fields) that are described with the quantities $\{n_a, U^\mu, J^\mu_a, T, \pi, q^\mu_a, p^{(\mu\nu)}_a\}$ (see Ref. [11]). Then, we can expand $f_a(x^\mu, p^\mu_a)$ as

$$f_a = f_a^{(0)} \left[ 1 + A_{a}^{\mu} p_{a \mu} + A_{a a}^{\mu\nu} p_{a \mu} p_{a \nu} \right],$$  

(36)

where $f_a^{(0)}$ is the local equilibrium distribution function (Jüttner distribution) described by Eq. (3). In Eq. (36) the unknown tensorial coefficients $\{A_{a}^{\mu}, A_{a a}^{\mu\nu}\}$ are calculated by constructing an algebraic system using the definitions of the particle-flow $N_a^\mu$ and of the energy-momentum tensor $T_{a}^{\mu\nu}$. The details of such calculation are long and unnecessary to do here, it can be consulted in Refs. [3, 10]. As a result of such development the distribution function $f_a$ will depend on linear terms of the thermodynamical fluxes, namely,

$$f_a = f_a^{(0)} \left\{ 1 - \frac{J_{a \mu}}{p_{a \mu}} p_a^\mu + \frac{q_{a \mu}}{T p_a c_v} \left[ \frac{\zeta_a G_a - U_a T_p^\mu}{k T} \right] + \frac{p_{a \mu}}{m_a h_a} c_v^\mu p_a^\mu \right. \right.$$  

$$+ \frac{\pi_{a \mu \nu}}{p_a c_v} \left[ \frac{U_a U_{a \mu} p_a^\mu}{k T^2} - \frac{3 (c_v^a + b_a/T) U_a T_p^\mu}{k T} - \frac{c_v^a \zeta_a^2}{k T^2} \right] \right\},$$  

(37)
where we have introduced the abbreviation 
\( G_a = K_3 (\zeta_a) / K_2 (\zeta_a) \) and the specific heats per particle of species \( a \) at constant volume 
\( c_v^a = k (\zeta_a^2 + 5 G_a \zeta_a - G_a^2 \zeta_a^2 - 1) \) and at constant pressure \( c_v^a = c_v^a + k \).

Then, following the combined Chapman-Enskog-Grad method \( [9] \), the expansion \( f^{(0)}_a \) must be compatible with the truncated Chapman-Enskog series up to first order, that is 
\( f_a = f^{(0)}_a (1 + \phi_a) \) where \( \phi_a \) is the first approximation to the distribution function.

We can proceed to linearize the Boltzmann equation as follows, we substitute the local equilibrium distribution \( f^{(0)}_a \) in the left hand side of the Boltzmann equation \( 4 \) and keep the linear terms, this process is technically the same that in the Chapman-Enskog method. We also use the so called functional hypothesis, namely, 
\( f_a = f_a (x^\mu, p^a_\mu | n_a, U^\mu, T) \), leading to

\[
p_a \frac{\partial f^{(0)}_a}{\partial x^\mu} - \Gamma^i_{\mu \nu} p^a_\mu a \frac{\partial f^{(0)}_a}{\partial \nu} = f^{(0)}_a \left\{ p^\mu_a \frac{\partial n_a}{n_a \partial x^\mu} + \frac{p^\mu_a}{T} \left[ 1 - \zeta_a G_a + \frac{p^\mu_a U^\lambda}{kT} \right] \frac{\partial U^\lambda}{\partial x^\mu} - \frac{c^2}{2kT} \frac{p^\mu_a p^\nu_a \delta_{ij} \delta_{kl}}{U^\tau p_{a\tau}} \frac{dg_1}{r} \frac{x^l}{dr} + \frac{c^2}{kT} g_1 \Gamma^i_{\mu \nu} \frac{p^\mu_a p^\nu_a \delta_{ij}}{U^\tau p_{a\tau}} \right\},
\]

(38)

On the other hand, we substitute the Grad function Eq. \( 27 \) in the collisional term (right hand side) of the Boltzmann equation \( 4 \), by keeping only the linear terms. This process yields

\[
-\mathcal{I}_{ab} \left[ \frac{p^\mu_b}{c_p} \left( \zeta_b G_b - \frac{U^\mu_b p^\nu_b}{kT} \right) \right] \frac{q_{ab}}{T p_b} - \mathcal{I}_{ab} \left[ \frac{p^\mu_a}{T p_a} \left( \zeta_a G_a - \frac{U^\mu_a p^\nu_a}{kT} \right) \right] \frac{q_{ab}}{T p_a} - \mathcal{I}_{ab} \left[ \frac{\zeta_b}{m_b h_b} \frac{p^\mu_b}{2 p_b} \right] \frac{p^\nu_a}{p_a} - \mathcal{I}_{ab} \left[ \frac{\partial \ln \zeta_a}{\partial \ln c_v} \left( \frac{U^\mu_a U^\nu_a p_{a\mu}}{kT^2} - \frac{3 \left( c^b_p + h_b / T \right) U^\mu_a p_{a\mu}}{c_v^a} \right) \right] \frac{\omega_b}{p_b} - \mathcal{I}_{ab} \left[ \frac{\partial \ln \zeta_b}{\partial \ln c_v} \left( \frac{U^\mu_a U^\nu_a p_{a\mu}}{kT^2} - \frac{3 \left( c^b_p + h_b / T \right) U^\mu_a p_{a\mu}}{c_v^a} \right) \right] \frac{\omega_a}{p_a}.
\]

(39)

Here we have introduced the collision operators
\[
\mathcal{I}_{ab} [\varphi_a] = \int f^{(0)}_a f^{(0)}_b (\varphi'_a - \varphi_a) F_{ab} \sigma_{ab} d\Omega \sqrt{-g} \frac{d^3 p_a}{p_0},
\]

(40)

for any function that depends on the momentum four-vector \( \varphi_a (p^a_\mu) \). Note that Eq. \( 40 \) imply that we can write for an arbitrary function \( \psi_b (p^b_\mu) \)

\[
\int \psi_b \mathcal{I}_{ab} [\varphi_a] \sqrt{-g} \frac{d^3 p_a}{p_0} = \int \varphi_a \mathcal{I}_{ab} [\psi_b] \sqrt{-g} \frac{d^3 p_a}{p_0},
\]

(41)
	hanks{thanks to the symmetry properties of the collision operator.}

Now the linearized Boltzmann equation in the combined Chapman-Enskog-Grad method becomes

\[
f_a^{(0)} \left\{ p^\mu_a \frac{\partial n_a}{n_a \partial x^\mu} + \frac{p^\mu_a}{T} \left[ 1 - \zeta_a G_a + \frac{p^\mu_a U^\lambda}{kT} \right] \frac{\partial U^\lambda}{\partial x^\mu} - \frac{c^2}{2kT} \frac{p^\mu_a p^\nu_a \delta_{ij} \delta_{kl}}{U^\tau p_{a\tau}} \frac{dg_1}{r} \frac{x^l}{dr} + \frac{c^2}{kT} g_1 \Gamma^i_{\mu \nu} \frac{p^\mu_a p^\nu_a \delta_{ij}}{U^\tau p_{a\tau}} \right\} = - \sum_{b=1} \mathcal{I}_{ab} \left[ \frac{q_{ab}}{T p_b} \right] \frac{J_{\mu b}}{p_b} + \mathcal{I}_{ab} \left[ \frac{q_{ab}}{T p_a} \right] \frac{J_{\mu a}}{p_a} - \mathcal{I}_{ab} \left[ \frac{\zeta_a}{m_a h_a} \frac{p^\mu_a}{2 p_a} \right] \frac{p_a}{p_a} - \mathcal{I}_{ab} \left[ \frac{\partial \ln \zeta_a}{\partial \ln c_v} \left( \frac{U^\mu_a U^\nu_a p_{a\mu}}{kT^2} - \frac{3 \left( c^b_p + h_b / T \right) U^\mu_a p_{a\mu}}{c_v^a} \right) \right] \frac{\omega_a}{p_a}.
\]
by taking into account \( \{a,b\} \) and \( \{a,c\} \).

In the next sections we shall use \( \{a\} \) in order to determine the constitutive equations for the diffusion fluxes \( J_a^\mu \), heat flux \( q_a \), non-equilibrium pressure \( \tilde{\varpi} \) and pressure deviator tensor \( p^{(\mu\nu)} \).

IV. FICK AND FOURIER LAWS

Now we will obtain a system of linear equations for the determination of the the diffusion fluxes \( J_a^\mu \) and the heat flux of the mixture \( q_a \). The solution of such a system will represent the form of the linear fluxes in terms of the thermodynamic forces. The integral functions for the transport coefficients and therefore the Onsager reciprocity relations will be analyzed in the next subsection.

To obtain the first one of the looked set of equations, we multiply Eq. (42) by \( c \Delta^\mu \mu_p^\alpha n_a \) and integrate over \( \sqrt{-g} d^3 p_a / p_a \), where the integrals for this process can be consulted in the Appendix. The resulting equation is

\[
-\frac{1}{n_a} \nabla^\mu p_a + \frac{h_a}{c^2} \Delta^\mu_i \left[ U^\nu_i \frac{\partial U_i}{\partial x^\nu} - \frac{1}{\Phi^2/4c^4} \frac{\partial \Phi}{\partial x^i} \right]
= \sum_{b=1}^r \left( A_{ab} \mu^\mu - F_{ab} q_b^b \right) - \frac{c^r}{3n_a n_b kT} \int p_a I_{ab} \left[ \frac{\partial U_i}{\partial x^\nu} - \frac{1}{\Phi^2/4c^4} \frac{\partial \Phi}{\partial x^i} \right] \nabla^\nu T \frac{\partial \Phi}{\partial x^i} \nabla^\nu T - T \Delta^\mu_i \left[ U^\nu_i \frac{\partial U_i}{\partial x^\nu} - \frac{1}{\Phi^2/4c^4} \frac{\partial \Phi}{\partial x^i} \right]
\]

where \( \nabla^\mu = \Delta^\mu \nu \partial_\nu \) is the gradient operator and \( \Phi = -\frac{\mu}{kT} \) is the gravitational potential. In Eq. (43) we have introduced the matrices \( A_{ab} \) and \( F_{ab} \). We can split \( A_{ab} \) for different indices \( \{a,b\} \)

\[
A_{ab} = -\frac{c^r}{3n_a n_b kT} \int p_a I_{ab} \left[ \frac{\partial U_i}{\partial x^\nu} - \frac{1}{\Phi^2/4c^4} \frac{\partial \Phi}{\partial x^i} \right] \nabla^\nu T \frac{\partial \Phi}{\partial x^i} \nabla^\nu T - T \Delta^\mu_i \left[ U^\nu_i \frac{\partial U_i}{\partial x^\nu} - \frac{1}{\Phi^2/4c^4} \frac{\partial \Phi}{\partial x^i} \right]
\]

and for equal indices \( \{a,b\} \),

\[
A_{aa} = -\frac{c^r}{3n_a kT} \int p_a I_{aa} \left[ \frac{\partial U_i}{\partial x^\nu} - \frac{1}{\Phi^2/4c^4} \frac{\partial \Phi}{\partial x^i} \right] \nabla^\nu T \frac{\partial \Phi}{\partial x^i} \nabla^\nu T - T \Delta^\mu_i \left[ U^\nu_i \frac{\partial U_i}{\partial x^\nu} - \frac{1}{\Phi^2/4c^4} \frac{\partial \Phi}{\partial x^i} \right]
\]

The matrix \( F_{ab} \) introduced in Eq. (43) is written by doing the same splitting, for unlike indices \( \{a,b\} \) we have

\[
F_{ab} = -\frac{c^r}{3n_a n_b kT} \int p_a I_{ab} \left[ \frac{\partial U_i}{\partial x^\nu} - \frac{1}{\Phi^2/4c^4} \frac{\partial \Phi}{\partial x^i} \right] \nabla^\nu T \frac{\partial \Phi}{\partial x^i} \nabla^\nu T - T \Delta^\mu_i \left[ U^\nu_i \frac{\partial U_i}{\partial x^\nu} - \frac{1}{\Phi^2/4c^4} \frac{\partial \Phi}{\partial x^i} \right]
\]

and for like indices \( \{a,b\} \),

\[
F_{aa} = -\frac{c^r}{3n_a kT} \int p_a I_{aa} \left[ \frac{\partial U_i}{\partial x^\nu} - \frac{1}{\Phi^2/4c^4} \frac{\partial \Phi}{\partial x^i} \right] \nabla^\nu T \frac{\partial \Phi}{\partial x^i} \nabla^\nu T - T \Delta^\mu_i \left[ U^\nu_i \frac{\partial U_i}{\partial x^\nu} - \frac{1}{\Phi^2/4c^4} \frac{\partial \Phi}{\partial x^i} \right]
\]

Next we look for a second equation that is independent from Eq. (43), to do so, we multiply the linearized Boltzmann equation (42) by \( \Delta^\mu \mu_p^\alpha \) and integrate over \( \sqrt{-g} d^3 p_a / p_a \) for this long process we use also the integrals that appear in the Appendix. The result becomes

\[
\frac{1}{T} \int \left( \nabla^\mu T - T \Delta^\mu_i \left[ U^\nu_i \frac{\partial U_i}{\partial x^\nu} - \frac{1}{\Phi^2/4c^4} \frac{\partial \Phi}{\partial x^i} \right] \right)
= \sum_{b=1}^r \left( F_{ab} J_b^\mu - H_{ab} q_b^b \right),
\]

where another matrix \( H_{ab} \) is defined. As with the others operators, we split \( H_{ab} \) in the part for unlike indices \( \{a,b\} \)

\[
H_{ab} = -\frac{c^r}{3n_a n_b kT} \int \left[ c_p \left( G_a - \frac{U_{\nu p}^\alpha}{m_a c^2} \right) p_{av} \right]
\]

and the corresponding for same indices

\[
H_{aa} = -\frac{c^r}{3n_a kT} \int \left[ c_p \left( G_a - \frac{U_{\nu p}^\alpha}{m_a c^2} \right) p_{av} \right]
\]

Hence, we have obtained the desired system of algebraic equations, namely (43) and (44) which are an independent set of linear equations for the determination of the diffusion \( J_a^\mu \) and heat \( q_a^\mu \) fluxes.

A. Onsager reciprocity relations

In this section we show that the Onsager reciprocity relations hold for the system under consideration. The idea is to verify that the matrix associated with the diffusion coefficients is symmetric and that the so-called cross effects are equal as it is described from the hypothesis of the Linear Irreversible Thermodynamics \( \{16\} \). One cross effect for our system is the contribution to diffusion due to a temperature gradient, this is often called “Soret” effect. The other cross effect is the contribution to the heat flux due to a chemical potential gradient or a concentration gradient, when it is due to the last, it is called “Dufour” effect. This demonstration is general in the sense
that no interaction between the particles is established, but of course, the microscopic reversibility principle is called for the collisional term of the Boltzmann equation.

Let us now write the thermodynamic forces in order to identify clearly the Soret and Dufour effects in terms of the temperature and chemical potential gradients.

First we introduce the thermal force defined by

$$\nabla \mu T = \nabla \mu T - \frac{T}{c^2} \Delta \mu \left[ U^{\alpha} \frac{\partial U^{\beta}}{\partial x^\beta} - \frac{1}{\Phi^2/4a^4} \frac{\partial \Phi}{\partial x^\alpha} \right],$$

(51)

where the first term contains a temperature gradient while the second one – of a strict relativistic nature due to the factor $T/c^2$ – is proportional to the four-acceleration and the gravitational potential gradient. The term due to the four-acceleration was proposed by Eckart [12] while the one due to the gravitational potential gradient by Tolman [13, 14]. Separately, these two terms can be interpreted as follows: (i) in the absence of a gravitational potential gradient, the temperature gradient of a relativistic gas at equilibrium must be counterbalanced by a gravitational potential gradient. The term due to the temperature and chemical potential gradients.

Above we have considered the constraint $\sum_{a=1}^r J_a^\mu = 0$ which implies that there exist only $r-1$ linearly independent diffusion fluxes.

We recall that the chemical potential of species $a$ is introduced through the Gibbs function per particle ($\mu_a = e_a - T s_a + p_a/n_a$), so that the following important relationship for its gradient holds

$$\nabla \mu \left( \frac{\mu_a}{T} \right) = \frac{1}{n_a T} \nabla \mu p_a - \frac{\mu_a}{T^2} \nabla \mu T.$$  

(53)

From the substitution of Eq. (53) into (40), we get

$$- T \nabla \mu \left( \frac{\mu_a}{T} \right) - \frac{\mu_a}{T} \nabla \mu T = \sum_{b=1}^r ( \mathcal{A}_{ab} J_b^\mu - F_{ab} Q_b^\mu ).$$  

(54)

Again by considering that there exist $r-1$ independent diffusion fluxes, we can take the $r$th component of Eq. (54) and subtract it from itself, yielding

$$- T \nabla \mu \left( \frac{\mu_a - \mu_r}{T} \right) - \frac{\mu_a - \mu_r}{T} \nabla \mu T =$$

$$= \sum_{b=1}^{r-1} ( \mathcal{A}_{ab} - \mathcal{A}_{rb} - \mathcal{A}_{ar} + \mathcal{A}_{rr} ) J_b^\mu - \sum_{b=1}^r ( F_{ab} - F_{rb} ) Q_b^\mu.$$  

(55)

Now we can proceed to solve the system of linear equations formed by Eqs. (52) and (55). First we solve Eq. (52) for $Q_b^\mu$, yielding

$$Q_b^\mu = \sum_{d=1}^r \left( \mathcal{H}^{-1} \right)_{cd} \left( - \frac{1}{T} \nabla \mu T \right)$$

$$+ \sum_{d=1}^r \sum_{b=1}^{r-1} \left( \mathcal{H}^{-1} \right)_{cd} ( F_{bd} - F_{rd} ) J_d^\mu,$$

(56)

where $( \mathcal{H}^{-1} )_{cd}$ is the inverse matrix of $\mathcal{H}_{cd}$ so that $( \mathcal{H}^{-1} )_{a \delta} = \delta_{ca}$ is the identity matrix. Then we insert Eq. (56) into Eq. (55) and solve for $J_a^\mu$,

$$J_a^\mu = - T \sum_{b=1}^{r-1} D_{ab} \nabla \mu \left( \frac{\mu_b - \mu_r}{T} \right) - \frac{D_a}{T} \nabla \mu T.$$  

(57)

We identify the above equation as the generalized Fick law, where the coefficients $D_{ab}$ and $D_a$ are related with the diffusion and thermal-diffusion (Soret) effects, respectively. The inverse of the diffusion matrix reads

$$\left( D^{-1} \right)_{ab} = \mathcal{A}_{ab} - \mathcal{A}_{rb} - \mathcal{A}_{ar} + \mathcal{A}_{rr} - \sum_{c=1}^r \sum_{d=1}^r ( F_{ac} - F_{rc} ) ( \mathcal{H}^{-1} )_{cd} ( F_{bd} - F_{rd} ),$$

(58)

while the thermal-diffusion coefficients are given by

$$D_a = \sum_{b=1}^r D_{ab} \left\{ h_b - h_r + \sum_{c=1}^r ( F_{bc} - F_{rc} ) ( \mathcal{H}^{-1} )_{cd} \right\}.$$  

(59)

Now we have to obtain the total heat flux as a function of the temperature and chemical potential gradients. For this end we insert into the expression for the total flux [26], written as

$$q^\mu = \sum_{a=1}^r q_a^\mu + \sum_{a=1}^{r-1} ( h_a - h_r ) J_a^\mu,$$

(60)

the expressions found for the fluxes $q_a^\mu$ and $J_a^\mu$, namely (55) and (57). Hence it follows Fourier’s law

$$q^\mu = \frac{\lambda'}{T} \nabla \mu T - T \sum_{a=1}^r D_a \nabla \mu \left( \frac{\mu_a - \mu_r}{T} \right),$$

(61)

where we have introduced the thermal conductivity coefficient

$$\lambda' = \sum_{a=1}^r \sum_{b=1}^{r-1} ( \mathcal{H}^{-1} )_{ab} + \sum_{b=1}^{r-1} D_b \left[ h_b - h_r + \sum_{c=1}^r \sum_{d=1}^r ( \mathcal{H}^{-1} )_{cd} ( F_{bd} - F_{rd} ) \right]$$

(62)

and the diffusion-thermal coefficient, which is related with the Dufour effect

$$\mathcal{D}_a = \sum_{b=1}^r D_{ba} \left[ h_b - h_r + \sum_{c=1}^r \sum_{d=1}^r ( \mathcal{H}^{-1} )_{cd} ( F_{bd} - F_{rd} ) \right].$$

(63)
Ultimately, we make a close inspection of the matrices \( \mathcal{A}_{ab} \), \( \mathcal{F}_{ab} \) and \( \mathcal{H}_{ab} \) which are given as functions of the collision operators \( \mathcal{I}_{ab} \). From \([13, 16, 19]\), we infer that only \( \mathcal{A}_{ab} \) and \( \mathcal{H}_{ab} \) are symmetric matrices, while \( \mathcal{F}_{ab} \) is non-symmetric. Hence we may conclude from \([18]\) that the matrix related with the diffusion coefficients are symmetric, i.e., \( \mathcal{D}'_{ab} = \mathcal{D}'_{ba} \). Moreover, for the coefficients of cross effects – namely the Soret \( \mathcal{D}_a \) and Dufour \( \mathcal{D}'_{a} \) – we note from the symmetry of \( \mathcal{H}_{ab} \) and \( \mathcal{D}_{ab} \) that \([15, 17]\) and \([19]\) are equivalent so that \( \mathcal{D}_a = \mathcal{D}'_a \). The relationships \( \mathcal{D}_a = \mathcal{D}'_a \) and \( \mathcal{D}_a = \mathcal{D}'_a \) imply a demonstration of the validity of the Onsager reciprocity relations. Note that, as in another’s demonstrations \([20]\), it appears to be an ultimate macroscopic effect that can only be proved because of the symmetries that belong to the collisional term of the Boltzmann equation \([3]\) given from the H-theorem i.e. microscopic reversibility principle.

**B. Thermal and diffusion forces**

It is usual in the theory of fluid mixtures to express the diffusion fluxes and the heat flux of the mixture in terms of thermal and generalized diffusion forces. The thermal force for a relativistic fluid was introduced in the last section (see \([51]\)). We follow \([7]\) and define the generalized diffusion force of species \( a \) as

\[
d_{a}^\mu = \nabla^\mu x_a + (x_a - 1) \frac{\partial \ln p}{\partial x^\mu} - \frac{n_{a} h_a - n h_{a}}{\rho c^2} \Delta^\mu \nu \frac{U^\nu \partial U^\mu}{\partial x^\nu} - \frac{1}{1 - \Phi^2/4c^2} \frac{\partial \Phi^\mu}{\partial x^\nu} \frac{\partial \Phi^\nu}{\partial x^\mu},
\]

where \( x_a = p_a/\rho = n_a/n \) is the concentration of species \( a \). We can identify four contributions to the generalized diffusion force: a concentration gradient, a pressure gradient, a term proportional to the four-acceleration and the gradient of the gravitational potential. Here is important to call attention that contrary to the thermal force this last term is not of relativistic nature, since \( (n_{a} h_a - n h_{a})/\rho c^2 p = (n_{a} n_{a} G_a - \sum_{b=1}^{r} n_{a} n_{b} G_{b})/\rho p \) and \( G_{b} \to 1 \) for \( c_{b} \gg 1 \). This equation has a very important feature because it represents the generalization of the diffusion force originally written for the non-relativistic case \([17, 18]\). More discussions about this point can be found in \([7]\). Due to the relationship \( \sum_{a=1}^{r} d_{a}^\mu = 0 \) there exist only \( r - 1 \) linearly independent generalized diffusion forces.

In order to write the diffusion fluxes \( [57] \) and the heat flux of the mixture \( [61] \) in terms of thermal force \( [51] \) and generalized diffusion force \( [64] \) we use the momentum density balance equation for the mixture (see \([7]\))

\[
\frac{\partial p}{\partial x^3} - \frac{\rho h_{a}}{c^2} \left[ U_{a} \frac{\partial U_{a}}{\partial x^\mu} - \frac{1}{1 - \Phi^2/4c^2} \frac{\partial \Phi^\mu}{\partial x^3} \right] = 0, \quad (65)
\]

the constraint \( \sum_{a=1}^{r} d_{a}^\mu = 0 \) and write the gradient of chemical potential as

\[
-T \nabla^\mu \left( \frac{\mu_a - \mu_r}{T} \right) = -\frac{D}{n_a} (\nabla^\mu x_a + x_a \nabla^\mu \ln p)
\]

After some rearrangements we write \([57]\) and \([61]\) as

\[
J_{a}^\mu = -\sum_{b=1}^{r-1} \mathcal{D}_{ab} d_{b}^\mu - \mathcal{D}_{a} \frac{\partial}{\partial x^\mu} \mathcal{T}, \quad (67)
\]

\[
q_{a}^\mu = -\frac{\lambda}{T} \nabla^\mu \mathcal{T} - \sum_{b=1}^{r-1} \mathcal{D}_{a} d_{b}^\mu. \quad (68)
\]

Now the new coefficients read:

\[
\mathcal{D}_{ab} = \sum_{c=1}^{r-1} \mathcal{D}_{ac} \frac{p_{b}}{n_{b}} \left( \delta_{bc} + \frac{n_{b}}{n_{r}} \right), \quad (69)
\]

\[
\mathcal{D}_{a} = \sum_{b=1}^{r-1} \sum_{c=1}^{r} \mathcal{D}_{ab} \left( \mathcal{F}_{bc} - \mathcal{F}_{rb} \right) (\mathcal{H}^{-1})_{cd}, \quad (70)
\]

\[
\mathcal{D}_{a} = \sum_{c=1}^{r-1} \sum_{b=1}^{r} \left[ (\mathcal{H}^{-1})_{ab} + \sum_{c=1}^{r} \mathcal{D}_{c} (\mathcal{H}^{-1})_{cb} (\mathcal{F}_{rb} - \mathcal{F}_{rb}) \right], \quad (71)
\]

\[
\mathcal{D}_{a} = \sum_{b=1}^{r-1} \sum_{c=1}^{r} \left[ (\mathcal{H}^{-1})_{ab} + \sum_{c=1}^{r} \mathcal{D}_{c} (\mathcal{H}^{-1})_{cb} (\mathcal{F}_{rb} - \mathcal{F}_{rb}) \right], \quad (72)
\]

In the absence of a temperature gradient the constitutive equation for the diffusion fluxes are proportional only to the generalized diffusion forces and \( \mathcal{D}_{ab} \) is identified as the matrix of the diffusion coefficients. Furthermore, due to the expression of the generalized diffusion force \( [64] \) the diffusion flux is a consequence of (i) a flux of a concentration gradient that tends to reduce the non-homogeneity of the mixture; (ii) a flux of a pressure gradient, where heavy particles tend to diffuse to places with high pressures, e.g. in centrifuges; (iii) a flux due to the acceleration which acts on different masses; and (iv) a flux of a gravitational potential gradient. Here it is interesting to call attention to the fact that a mixture subjected to a uniform pressure and in the absence of an acceleration, the diffusion fluxes vanish if the concentration gradients are counterbalanced by the gravitational potential gradient.

The thermal conductivity coefficient \( \lambda \) in a mixture is defined as the ratio of the heat flux to the temperature gradient, when there is no diffusion, i.e., when \( J_{a}^\mu = 0 \). From \([50]\) and \([61]\) we have

\[
\lambda = \sum_{a=1}^{r} \sum_{b=1}^{r} (\mathcal{H}^{-1})_{ab}. \quad (73)
\]
V. ENTROPY FLUX OF THE MIXTURE

According to (27) and (30) the entropy flux of the mixture is given by

\[
\Phi^\mu = -k_c \Delta^\mu \sum_{a=1}^r p_a^\mu f_a \ln(b_a f_a) \sqrt{-g} \frac{\partial f_a}{\partial p_{c a}}. \tag{74}
\]

If we insert Grad’s distribution function (37) into the above expression, linearize the resulting equation in the fluxes \(J^\mu, \Phi, \varpi, \nu(p^{\mu\nu})\) and integrate, it follows

\[
\Phi^\mu = \frac{1}{T} \sum_{a=1}^r q_a^\mu + \sum_{a=1}^r \delta_a J_a^\mu - \sum_{a=1}^r \mu_a \frac{\Delta J_a^\mu}{T} = \frac{q^\mu}{T} - \sum_{a=1}^{r-1} \frac{\mu_a - \mu_r}{T} J_a^\mu. \tag{75}
\]

The first equality above shows that the entropy flux of the mixture is a sum of two terms: one refers to the sum of all partial heat fluxes divided by the temperature and the other is a sum of the transport due to diffusion of the partial entropies per particle. The second equality is well-known from non-relativistic Linear Irreversible Thermodynamics where the entropy flow of the mixture is equal to the mixture heat flux divided by the temperature minus the sum of the transport due to diffusion of the partial chemical potentials divided by the temperature.

We can also express the entropy flux of the mixture in terms of the thermal and diffusion generalized forces by substituting the representations (62) into (63), yielding

\[
\Phi^\mu = -\mathcal{L} \nabla^\mu T - \frac{1}{T} \sum_{a=1}^r \mathcal{L}_a \frac{\Delta \tilde{\mu}}{}.
\]

Here the scalar coefficients \(\mathcal{L}\) and \(\mathcal{L}_a\) read

\[
\mathcal{L} = \tilde{\lambda} - \sum_{a=1}^{r-1} (\mu_a - \mu_r) \tilde{D}_a, \tag{77}
\]

\[
\mathcal{L}_a = \tilde{D}_a' - \sum_{b=1}^{r-1} (\mu_b - \mu_r) \tilde{D}_{ba}. \tag{78}
\]

It is clear from the definitions of the thermal (51) and diffusive (52) forces that the entropy flux of the mixture (70) depends on the temperature, concentration and pressure gradients as well as on the acceleration and gravitational potential gradient.

VI. NAVIER-STOKES LAW

The constitutive equations for the partial non-equilibrium pressures \(\varpi_a\) are obtained as follows. We multiply (32) by \(\Delta_{\sigma}^\tau p_a^\tau p_a^\sigma\), integrate the resulting equation over \(\sqrt{-g} \partial^\mu p_{c a}\), use the table of integrals of the Appendix and eliminate the derivative projections \(U^\tau \partial^\mu\) through the balance equations of partial particle number density and partial energy per particle of an Eulerian gas mixture, where non-equilibrium quantities \(J^\mu, q^\mu, \varpi, \nu(p^{\mu\nu})\) vanish. These balance equations read

\[
U^\tau \partial^\mu n_a + n_a \nabla^\mu U_\mu = 0, \tag{79}
\]

\[
n_a c^a_u U^\tau \partial^\mu T + \nu_a \nabla^\mu U_\mu = 0. \tag{80}
\]

The resulting system of equations for \(\varpi_b\) becomes

\[
- \left[ p_b k T \frac{\partial \ln \varpi_a}{\partial \ln c_b^a} \right] \nabla^\mu U_\mu = \sum_{b=1}^r \mathcal{R}_{ab} \varpi_b. \tag{81}
\]

In the above equation it was introduced the matrix \(\mathcal{R}_{ab}\). For different indices \(a,b\) the elements of this matrix are given in terms of the following integral of the collision operator \(I_{ab}\):

\[
\mathcal{R}_{ab} = \sum_{b=1}^r \mathcal{R}_{ab} \varpi_b \nabla^\mu U_\mu = \sum_{b=1}^r \mathcal{R}_{ab} \varpi_b. \tag{82}
\]

For equal indices \(a,b\) the elements of the matrix read

\[
\mathcal{R}_{aa} = \sum_{b=1}^r \mathcal{R}_{ab} \varpi_b \nabla^\mu U_\mu = \sum_{b=1}^r \mathcal{R}_{ab} \varpi_b. \tag{83}
\]

The solution of the linear system of equations (81) for the partial non-equilibrium pressures \(\varpi_a\) is given by

\[
\varpi_a = - \sum_{b=1}^r (\mathcal{R}^{-1})_{ab} \frac{p_b k T \partial \ln \varpi_a}{c_b^a \partial \ln c_b^a} \nabla^\mu U_\mu, \tag{84}
\]

where \((\mathcal{R}^{-1})_{ab}\) denotes the inverse of the matrix \(\mathcal{R}_{ab}\). The constitutive equation for the non-equilibrium pressure of the mixture is obtained from the sum of (84) over all constituents, since according to (24) we have that \(\varpi = \sum_{a=1}^r \varpi_a\). Hence it follows

\[
\varpi = -\eta \nabla^\mu U_\mu, \tag{85}
\]

where the bulk viscosity coefficient of the mixture reads

\[
\eta = \sum_{a,b=1}^r (\mathcal{R}^{-1})_{ab} \frac{p_b k T \partial \ln \varpi_a}{c_b^a \partial \ln c_b^a}. \tag{86}
\]

Following the same methodology, the multiplication of (42) by \(\Delta_{\sigma}^\tau \Delta_{\sigma}^\tau / 3 p_a^\sigma p_a^\sigma\) and integration over
\(\sqrt{-g} \frac{\partial^2 R}{\partial x^a \partial x^b}\) leads to the following linear system of equations for the partial pressure deviator tensors \(p_b^{(\mu \nu)}\):

\[
2\nabla^{(\mu U^\nu)} = \sum_{b=1}^{r} K_{ab} p_b^{(\mu \nu)},
\]

(87)

where we have introduced the following abbreviation for the symmetric and traceless four-velocity gradient

\[
\nabla^{(\mu U^\nu)} = \left( \frac{\Delta^\nu \Delta^\mu + \Delta^\mu \Delta^\nu}{2} - \frac{\Delta^{\mu \nu} \Delta^{\sigma \tau}}{3} \right) \partial \sigma \partial \tau .
\]

(88)

In (87) the elements of the matrix \(K_{ab}\) are also functions of the integral of the collision operator \(T_{ab}\) and read

\[
K_{ab} = \frac{c^2 \Delta_{(a} \Delta_{\nu)} \mu}{10 p_a h_a p_b} \int p^\sigma_a p^\tau_a T_{ab} \left[ \frac{\zeta_b}{m_b h_b} p^\mu_b p^\nu_b \right] \times \sqrt{-g} \frac{\partial^3 p_a}{p_a} , \quad a \neq b
\]

(89)

\[
K_{aa} = \frac{c^2 \Delta_{(a} \Delta_{\nu)} \mu}{10 p_a h_a p_a} \left\{ \sum_{b=1}^{r} p^\sigma_a p^\tau_a T_{ab} \left[ \frac{\zeta_a}{m_a h_a} p^\mu_a p^\nu_a \right] \right. \\
\left. + \int p^\sigma_a p^\tau_a T_{aa} \left[ \frac{\zeta_a}{m_a h_a} p^\mu_a p^\nu_a \right] \right\} \sqrt{-g} \frac{\partial^3 p_a}{p_a} .
\]

(90)

From the solution of the linear system of equations (87) for \(p_b^{(\mu \nu)}\) and from the relationship \(p_b^{(\mu \nu)} = \sum_{b=1}^{r} p_b^{(\mu \nu)}\) it follows the constitutive equation for the pressure deviator tensor of the mixture:

\[
p^{(\mu \nu)} = 2 \mu \nabla^{(\mu U^\nu)},
\]

(91)

where the shear viscosity coefficient of the mixture is given by

\[
\mu = \sum_{a,b=1}^{r} (K^{-1})_{ab}.
\]

(92)

Equations (90) and (91) are the constitutive equations of a relativistic Newtonian fluid, also known as the Navier-Stokes constitutive equations.

VII. CONCLUSIONS

In this work we have studied a \(r\)-mixture of relativistic gases in the presence of gravitational fields by incorporating a term with the Christoffel symbols into the Boltzmann equation and using the Schwarzschild metric. A linearized Boltzmann equation was obtained by following the methodology which combines the features of the methods of Chapman-Enskog and Grad.

By applying the Chapman-Enskog-Grad combined method to the Boltzmann equation we obtained an equation which was used for the determination of the thermodynamic fluxes as functions of the thermodynamic forces. The Navier-Stokes law was derived as well as the generalized laws of Fourier and Fick. The proof of the validity of the Onsager reciprocity relations was possible lastly because the symmetries of the collisional term of the Boltzmann equation. These symmetries are those associated with the H-theorem and the microscopic reversibility principle. This reinforces the idea that the Onsager reciprocity relations are the macroscopic manifestation of the microscopic symmetries of the trajectories of the particles that conform the gas.

We have introduced the thermal force

\[
\nabla^{(\mu T)} = \nabla^{(\mu T)} - \frac{T}{c^2} \Delta^{(\mu} \frac{\partial U_i}{\partial x^\nu} - \frac{1}{1 - \Phi^2 / 4 c^4} \frac{\partial \Phi}{\partial x^\nu}.
\]

(93)

which is a very eloquent result. Indeed, Eq. (93) turns to be just the gradient of the temperature in the non-relativistic limit i.e. \(\nabla^{(\mu T)}\) because of the factor \(T/c^2\) of the second term is of relativistic order. The inclusion of the acceleration term into the thermal force was proposed by Eckart [12] while the one relating the gravitational potential gradient by Tolman [13, 14]. Here these terms appear as a natural consequence of the solution of the relativistic Boltzmann equation in gravitational fields.

On the other hand we have identified the generalized diffusion force with

\[
d_\nu^\mu = \nabla^\mu x_\nu + (x_\nu - 1) \nabla^\mu \ln p
\]

\[
- \frac{n_a h_a - n h}{pc^2} \Delta^{(\mu} \frac{\partial U_i}{\partial x^\nu} - \frac{1}{1 - \Phi^2 / 4 c^4} \frac{\partial \Phi}{\partial x^\nu}.
\]

(94)

this is a new and interesting result because the third term – which is related with the four-acceleration and the gradient of the gravitational potential – does not go to zero in the non-relativistic limiting case as the thermal force. As it was pointed out in the work [7], the diffusion force that came out from a non-relativistic kinetic theory [17, 18] has a similar expression to (94). It depends on the concentration and pressure gradients, but it has a term depending on the forces which act on the particle of different species, such a term vanishes when only gravitational forces are acting on the particles.

Another result obtained is the entropy flux of the relativistic mixture through the use of Grad’s distribution function, which has a similar expression as the one of non-relativistic Linear Irreversible Thermodynamics [12]. Its constitutive equation was written in terms of the thermal and diffusion forces, so that it depends also on the acceleration and on the gravitational potential gradient.

As a final comment we call attention to the fact that for the determination of all the transport coefficients, we have to specify the interaction potential of the relativistic particles and evaluate the matrices \(\{R_{ab}, K_{ab}, A_{ab}, F_{ab}, H_{ab}\}\). This work is in progress and will be published in the future.

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\[ X_{ab}^{\mu \nu} = \int p_a^0 I_{ab} [p_b^0] \sqrt{-g} \frac{d^3p_a}{p_a} = \frac{1}{3c^3} (4I_{ab}^1 - I_{ab}^2) U^\mu U^\nu + \frac{1}{3} (I_{ab}^2 - I_{ab}^3) g^{\mu \nu}, \]  

\[ X_{ab}^{\mu \nu \sigma \tau} = \int p_a^0 p_b^0 I_{ab} [p_b^0] \sqrt{-g} \frac{d^3p_a}{p_a} = \frac{2}{15c^4} (24I_{ab}^3 - 12I_{ab}^4 + I_{ab}^5) U^\mu U^\nu U^\sigma U^\tau + \frac{1}{15c^6}(I_{ab}^4 - 2I_{ab}^6) \]

\[ -6I_{ab}^3 \left( g^{\mu \nu} U^\tau + g^{\tau \sigma} U^\mu U^\nu \right) + \frac{1}{30c^2} \left( 16I_{ab}^6 - 3I_{ab}^7 - 24I_{ab}^5 \right) \left( g^{\sigma \tau} U^\mu U^\tau + g^{\tau \mu} U^\sigma U^\tau + g^{\sigma \tau} U^\mu U^\nu + g^{\sigma \tau} U^\mu U^\nu \right) + \frac{1}{15} (I_{ab}^5 - I_{ab}^7 + 2I_{ab}^6) g^{\mu \nu} g^{\sigma \tau}, \]

where \( I_{ab}^1 \ldots I_{ab}^7 \) are given by

\[ I_{ab}^1 = \frac{1}{c^2} U_{ab} X_{ab}^{\mu \nu}, \quad I_{ab}^2 = g_{\mu \nu} X_{ab}^{\mu \nu}, \quad I_{ab}^3 = \frac{U_{ab} X_{ab}^{\mu \nu \sigma \tau}}{c^4}, \quad I_{ab}^4 = \frac{g_{\mu \nu} X_{ab}^{\mu \nu \sigma \tau}}{c^4}, \quad I_{ab}^5 = \frac{g_{\mu \nu} U_{ab} X_{ab}^{\mu \nu \sigma \tau}}{c^4}, \quad I_{ab}^6 = \frac{g_{\mu \nu} g_{\sigma \tau} X_{ab}^{\mu \nu \sigma \tau}}{c^4}, \quad I_{ab}^7 = \frac{g_{\mu \nu} g_{\sigma \tau} X_{ab}^{\mu \nu \sigma \tau}}{c^4}. \]  

APPENDICES

Table of integrals

For the purposes of this work, it is convenient to do the following unique decomposition of the integral operators:

\[ \int e^{-\frac{1}{kT} U_{\lambda} \lambda} \frac{d^3p}{p_0} = 4 \pi m k T K_1(\zeta), \quad \int p^\mu e^{-\frac{1}{kT} U_{\lambda} \lambda} \frac{d^3p}{p_0} = 4 \pi m^2 k T K_2(\zeta) U^\mu, \]  

\[ \int p^\mu p^\nu e^{-\frac{1}{kT} U_{\lambda} \lambda} \frac{d^3p}{p_0} = -4 \pi (m k T)^2 \left[ K_2(\zeta) g^{\mu \nu} - K_3(\zeta) \frac{U^\mu U^\nu}{c^2} \right], \]  

\[ \int p^\mu p^\nu p^\rho e^{-\frac{1}{kT} U_{\lambda} \lambda} \frac{d^3p}{p_0} = -4 \pi m^3 k T \left[ K_3(\zeta) g^{(\mu \nu \rho \sigma)} - K_4(\zeta) \frac{U^\mu U^\nu U^\rho U^\sigma}{c^2} \right], \]  

\[ \int p^\mu p^\nu p^\rho p^\sigma e^{-\frac{1}{kT} U_{\lambda} \lambda} \frac{d^3p}{p_0} = 4 \pi m (k T)^3 \left[ K_4(\zeta) \frac{g^{(\rho \sigma \tau \mu)}}{6 c^2} + K_5(\zeta) \frac{U^\mu U^\nu U^\rho U^\sigma}{10 c^2} \right], \]  

\[ + \frac{1}{c^2} \int \left[ K_6(\zeta) \frac{U^\mu U^\nu U^\rho U^\sigma}{c^4} \right]. \]  

\[ \int \frac{e^{-\frac{1}{U^\tau} U_{\lambda} \lambda} d^3p}{U^\tau p_0} = 4 \pi m \left[ K_1(\zeta) - K_1(\zeta) \right], \quad \int p^\mu e^{-\frac{1}{U^\tau} U_{\lambda} \lambda} \frac{d^3p}{p_0} = 4 \pi m^2 K_1(\zeta) U^\mu, \]  

\[ \int p^\mu p^\nu e^{-\frac{1}{U^\tau} U_{\lambda} \lambda} \frac{d^3p}{p_0} = -4 \pi m^2 k T \left( \frac{1}{3} \left[ K_2(\zeta) - K_2(\zeta) \right] U^\mu \right), \]  

\[ \int p^\mu p^\nu p^\rho e^{-\frac{1}{U^\tau} U_{\lambda} \lambda} \frac{d^3p}{p_0} = -4 \pi m^3 k T \left( \frac{1}{3} \left[ K_2(\zeta) - K_2(\zeta) \right] U^\mu \right), \]  

\[ - \frac{1}{c^2} \left[ 4 K_2(\zeta) - K_3(\zeta) \right] U^\mu U^\nu \right]. \]  

\[ \int p^\mu p^\nu p^\rho p^\sigma e^{-\frac{1}{U^\tau} U_{\lambda} \lambda} \frac{d^3p}{p_0} = -4 \pi m^2 k T \left( \frac{1}{3} \left[ K_2(\zeta) - K_2(\zeta) \right] U^\mu U^\nu \right). \]
\[
\int p^{\mu}p^{\nu}p^{\tau} \frac{e^{-\frac{1}{2}U^\tau p_\tau}}{U^\rho p_\rho} \, d^3p \bigg|_{p_0} = \frac{4\pi n_0 k^2 T^2}{15} \left\{ \frac{3K_3(\zeta) - \zeta K_2(\zeta) + \zeta^2 [K_1(\zeta) - K_1(\zeta)]}{3} \right\} g^{(\mu \nu) \sigma \tau} \\
- \frac{1}{6c^2} \left[ 18K_3(\zeta) - \zeta K_2(\zeta) + \zeta^2 (K_1(\zeta) - K_1(\zeta)) \right] g^{(\mu \nu) U^\rho U^\sigma} \\
+ \frac{3}{c^4} \left\{ 48K_3(\zeta) + 4\zeta K_2(\zeta) + \zeta^2 (K_1(\zeta) - K_1(\zeta)) \right\} U^{(\mu \nu) U^\rho U^\sigma} \right\}, \\
(108)
\]

\[
\int p^{\mu}p^{\nu}p^{\tau} \frac{e^{-\frac{1}{2}U^\tau p_\tau}}{U^\rho p_\rho} \, d^3p \bigg|_{p_0} = \frac{4\pi n_0 k^2 c^4}{15} \left\{ \frac{K_3(\zeta)}{15} U^{(\mu \rho \nu \sigma \tau \epsilon) \rho} - \frac{1}{10c^2} [8K_3(\zeta) + \zeta K_2(\zeta)] g^{(\mu \nu) U^\rho U^\sigma U^\tau} \\
+ \frac{1}{c^4} (\zeta^2 K_3(\zeta) + 12\zeta K_2(\zeta) + 80K_3(\zeta)] U^{(\mu \nu) U^\rho U^\sigma U^\tau} \right\}. \\
(109)
\]

Above the parenthesis around \( N \) indexes indicate a sum over all permutations of these indexes divided by \( N! \). Furthermore, \( K_{i_0}(\zeta) \) denotes the integral

\[
K_{i_0}(\zeta) = \int_0^\infty \frac{e^{-\zeta \cosh t}}{\cosh^n t} \, dt. \\
(110)
\]

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**Cristoffel symbols for the Schwarzschild isotropic metric**

\[
\Gamma^0_{00} = 0, \quad \Gamma^0_{0j} = 0, \quad \Gamma^j_{ij} = 0 \quad (i \neq j \neq k), \quad \Gamma^i_{0j} = 0, \quad \Gamma^i_{ij} = \frac{1}{2g_1(r)} \frac{dg_1(r)}{dr} \delta_{jk} \frac{x^k}{r}, \\
(111)
\]

\[
\Gamma^0_{0j} = \frac{1}{2g_0(r)} \frac{dg_0(r)}{dr} \delta_{ij} \frac{x^j}{r}, \quad \Gamma^i_{0j} = \frac{1}{2g_0(r)} \frac{dg_0(r)}{dr} x^j \frac{x^i}{r}, \quad \Gamma^j_{ij} = -\frac{1}{2g_1(r)} \frac{dg_1(r)}{dr} \frac{x^j}{r} \quad (i \neq j). \\
(112)
\]

The underlined indices above are not summed and

\[
\frac{dg_0(r)}{dr} = \frac{2GM}{{c^2 r^2} \left( 1 + \frac{2GM}{c^2 r} \right)} , \quad \frac{dg_1(r)}{dr} = -\frac{2GM}{{c^2 r^2} \left( 1 + \frac{GM}{2c^2 r} \right)^3} . \\
(113)
\]

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[1] F. Jüttner, Das Maxwellsche Gesetz der Geschwindigkeitsverteilung in der Relativtheorie, Ann. Physik und Chemie 34 (1911) 856.
[2] S. R. de Groot, W. A. van Leeuwen, Ch. G. van Weert, Relativistic Kinetic Theory, North-Holland, Amsterdam, 1980.
[3] C. Cercignani, G.M. Kremer, The Relativistic Boltzmann Equation: Theory and Applications, Birkhäuser, Basel, 2002.
[4] A. Sandoval-Villalbazo, A. L. García-Perciante, D. Brun-Battistini, Tolman’s Law in Linear Irreversible Thermodynamics: a Kinetic Theory Approach, Phys. Rev. D 86 (2012) 084015.
[5] M. Smerlak, Diffusion in Curved Spacetimes, New Journal of Physics 14 (2012) 023019.
[6] G. M. Kremer, Relativistic Gas in a Schwarzschild Metric, J. Stat. Mech. (2013) P04016, E05001, E10001.
[7] G. M. Kremer, Diffusion of Relativistic Gas Mixtures in Gravitational Fields, Physica A 393 (2014) 76.
[8] W. Zimdahl and G. M. Kremer, Temperature Oscillations of a Gas in Circular Geodesic Motion in the Schwarzschild Field, Phys. Rev. D 91 (2015) 024003.
[9] A. G. Bezerra Jr., S. Reinecke, G. M. Kremer, A Combined Chapman-Enskog and Grad Method. I. Monoatomic Gases and Mixtures, Continuum Mech. Thermodyn. 6 (1994) 149.
[10] G. M. Kremer, On the Kinetic Theory of Relativistic Gases, Continuum Mech. Thermodyn. 9, (1997), 13.
[11] H. Grad, On the Kinetic Theory of Rarefied Gases, Commun. Pure Appl. Math. 2 (1949) 331.
[12] C. Eckart, The Thermodynamics of Irreversible Processes, III. Relativistic Theory of a Simple Fluid, Phys. Rev. 58 (1940) 919.
[13] R. C. Tolman, On the Weight of Heat and Thermal Equilibrium in General Relativity, Phys. Rev. 35 (1930) 904.
[14] R. C. Tolman, Temperature Equilibrium in a Static Gravitational Field, Phys. Rev. 36 (1930) 1791.
[15] C. W. Misner, K. S. Thorne, J. A. Wheeler, *Gravitation*, W. H. Freeman and Company, San Francisco, 1973.

[16] S. R. de Groot, P. Mazur, *Non-equilibrium Thermodynamics*, Dover Publications, New York, 1984.

[17] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 3rd. edition, Cambridge University Press, Cambridge, 1970.

[18] J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, *Molecular Theory of Gases and Liquids*, John Wiley, New York, 1964.

[19] G. M. Kremer, W. Marques Jr., *Grad’s Moment Method for Relativistic Gas Mixtures of Maxwellian Particles*, Phys.Fluids 25 (2013) 017102.

[20] V. Moratto, A. L. García-Perciante, L. S. García-Colín, *Validity of the Onsager Relations in Relativistic Binary Mixtures*, Phys. Rev. E 84 (2011) 021132.

[21] E. C. G. Stueckelberg, G. Wanders, *Thermodynamique en Relativité Générale*, Helv. Phys. Acta 26 (1953) 417.

[22] H. Hebenstreit, *Balance Equations for a Relativistic Plasma, I. Differential Term*, Physica A 117 (1983) 631.

[23] G. M. Kremer, C. H. Patsko, *Relativistic Ionized Gases: Ohm and Fourier Laws from Anderson and Witting Model Equation*, Physica A 322 (2003) 329.