



Hydrodynamic limits of kinetic equations for polyatomic and reactive gases

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Abstract

Starting from a kinetic BGK-model for a rarefied polyatomic gas, based on a molecular structure of discrete internal energy levels, an asymptotic Chapman–Enskog procedure is developed in the asymptotic continuum limit in order to derive consistent fluid–dynamic equations for macroscopic fields at Navier–Stokes level. In this way, the model allows to treat the gas as a mixture of mono–atomic species. Explicit expressions are given not only for dynamical pressure, but also for shear stress, diffusion velocities, and heat flux. The analysis is shown to deal properly also with a mixture of reactive gases, endowed for simplicity with translational degrees of freedom only, in which frame analogous results can be achieved.

Keywords: Kinetic models, Hydrodynamic limit, Polyatomic gases, Chemical reaction, Transport coefficients

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1. Introduction

Investigation of non–equilibrium effects in gas mixtures constitutes a crucial challenge in gas dynamics, especially when the complicated structure of polyatomic molecules or the occurrence of chemical reactions has to be considered, since such processes are of great interest in fields like plasma physics, aerospace engineering, energy production, etc [1,2]. They require the development of sophisticated models and solution techniques to accurately describe and simulate the diversity and complexity of non–equilibrium problems, and to effectively capture the wide range of the underlying physical–chemical phenomena. These problems can be handled in the frame of the continuum theory of fluids [3], but a rigorous derivation of the relevant fluid–dynamic equations from the deeper knowledge allowed by a kinetic approach is highly desirable, also as consistent justification or correction of the most common macroscopic descriptions [4]. Most of the kinetic literature, however, is still restricted to the simplified case of

mono-atomic particles, which, in spite of its limitation, reproduces interesting results with good agreement with reality and expectation [5–7]. On the other hand it is clear that gases involved in practical applications are typically made up by polyatomic molecules, not sufficiently described by the motion of their center of mass, and that the situation becomes even more complicated when chemical interactions with additional exchange of mass among species may take place [8–11]. Usually, in kinetic approaches, the non-translational degrees of freedom are accounted for by a suitable internal energy variable in a sort of semi-classical scheme [12], and such a variable may be either continuously ranging on the real line, or discrete, in correspondence to an internal structure of energy levels [13]. What one is most interested in is the derivation of fluid-dynamic equations governing the evolution of the main macroscopic fields, which are velocity power moments of the distribution functions, and correspond to physical observables. Exact balance equations are deduced from the kinetic level by taking moments, but their closure requires constitutive equations for the additional moments and collision contributions showing up in the procedure, which need to be expressed in terms of the main fields by means of suitable transport coefficients. This goal can be achieved in the hydrodynamic limit of dominant collisions (small Knudsen number) by resorting to an asymptotic expansion with respect to such small parameter and performing the relevant asymptotic Chapman-Enskog analysis [14].

The analytical investigation at the level of the Boltzmann equations is definitely awkward to manage, and leaves several results only in implicit form, so that simpler approximate (but still kinetic) models would be useful for practical applications. Relaxation time approximations of BGK type [15,16] seem to be the first natural candidates in that direction, also in non-classical frame [17], and this is what this paper is about. Such BGK models have to be carefully devised in order to avoid well known drawbacks arising in multi-species gases and to account properly for the presence of reactive binary encounters, and several attempts in this respect may be found in the literature. We may quote for instance [18–23], without pretending to be exhaustive. In this paper, use will be made of a BGK strategy already proposed and tested in the literature [24,25], for two separate though related problems. The first one refers to a single polyatomic gas described in terms of a discrete structure of internal energy levels, so that in some sense we are led to a sort of mixture of mono-atomic gases. The second problem deals with a reactive quaternary mixture of gases undergoing a bimolecular chemical reaction, ignoring for simplicity non-translational degrees of freedom. In both cases the model features a number of disposable parameters, and all transport coefficients are expressed in closed analytical

form, so that those free parameters can be used in order to best fit the constitutive equations closing the fluid–dynamic macroscopic description. The present results represent thus the completion of previous investigations on kinetic relaxation models for polyatomic or reactive gases and on their hydrodynamic limits, in which these achievements were left as open problems.

The paper is organized as follows. In the next Section we present the strategy of the proposed BGK kinetic approach for the test case of a single polyatomic gas, and recall, for the readers' convenience, its main features. Section 3 is devoted, in the same physical scenario, to the asymptotic Chapman–Enskog procedure for the hydrodynamic regime and to the determination, to first order accuracy, of transport coefficients like bulk viscosity, shear viscosity, and thermal conductivity. In the last Section the same strategy and procedure are used for the reactive case, with technicalities and conclusions which are similar but different in this new scenario, and lead again to a full analytical representation of constitutive equations, including Newton's law for shear stress, Fick's law for diffusion velocities, and Fourier law for heat flux, with Soret and Dufour effects.

2. Kinetic BGK equations for a polyatomic gas

It is well known that several difficulties are encountered when extending kinetic relaxation approaches to gas mixtures, but they can be overcome by suitable strategies, we can quote for instance [19]. The further extension to internal energy transitions like the ones considered here for polyatomic gases and for reactive mixtures, also requires some care, and depends on the ratio between the scales of mechanical (or elastic) and internal (or inelastic) interactions [24,26]. We shall follow here the line of the models [24,25,27], and write balance equations in phase space as

$$(1) \quad \frac{\partial f^s}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f^s = \nu^s (\mathcal{M}^s - f^s) \quad s = 1, \dots, N$$

where Maxwellian attractors \mathcal{M}^s take the form

$$(2) \quad \mathcal{M}^s(\mathbf{v}) = \tilde{n}^s \left(\frac{m}{2\pi K\tilde{T}} \right)^{3/2} \exp \left[-\frac{m}{2K\tilde{T}} |\mathbf{v} - \tilde{\mathbf{u}}|^2 \right]$$

with densities \tilde{n}^s bound together as

$$(3) \quad \tilde{n}^s = \tilde{n} \exp \left(-\frac{E^s - E^1}{K\tilde{T}} \right) / Z(\tilde{T}),$$

$Z(T) = \sum_{s=1}^N \exp \left(-\frac{E^s - E^1}{KT} \right)$ representing the partition function. This is motivated by the fact that kinetic analysis at Boltzmann level [13] provides

as collision equilibria a family of Maxwellian distributions, depending on 5 free parameters (n, \mathbf{u}, T)

$$(4) \quad f_M^s(\mathbf{v}) = n^s \left(\frac{m}{2\pi KT} \right)^{3/2} \exp \left[-\frac{m}{2KT} |\mathbf{v} - \mathbf{u}|^2 \right] \quad s = 1, \dots, N,$$

with equilibrium number densities related by the constraints

$$(5) \quad n^s = \frac{n}{Z(T)} \exp \left(-\frac{E^s - E^1}{KT} \right).$$

At equilibrium, for pressure tensor, internal energy and heat flux, we have

$$\mathbf{P} = nKT\mathbf{I}, \quad U = \frac{3}{2}nKT, \quad \mathbf{q}_{th} = \mathbf{0},$$

and

$$U^* = n\bar{E}(T), \quad \bar{E}(T) = \frac{1}{Z(T)} \sum_{s=1}^N E^s \exp \left(-\frac{E^s - E^1}{KT} \right), \quad \mathbf{q}^* = \mathbf{0},$$

where a star labels excitation contributions, and $\bar{E}(T)$ represents the weighted average of the energy levels. The (scaled) specific heat at constant volume is given by [11]

$$(6) \quad \hat{c}_v = \frac{3}{2} + \hat{\sigma}(T),$$

$$\hat{\sigma}(T) = \frac{1}{Z(T)} \sum_{s=1}^N \left[\frac{E^s - \bar{E}(T)}{KT} \right]^2 \exp \left(-\frac{E^s - E^1}{KT} \right),$$

where the correction to the mono-atomic value 3/2 is thus the mean square deviation of the distribution of energy levels. Here macroscopic (observable) quantities (number densities, mass densities, mean velocities, pressure tensors, internal energies, and heat fluxes) are defined for each species in the usual way as moments of the relevant distribution functions, while global quantities for the gas as a whole are given by

$$n = \sum_{s=1}^N n^s, \quad \rho = mn, \quad \mathbf{u} = \frac{1}{n} \sum_{s=1}^N n^s \mathbf{u}^s,$$

$$\mathbf{P} = m \sum_{s=1}^N \int (\mathbf{v} - \mathbf{u}) \otimes (\mathbf{v} - \mathbf{u}) f^s(\mathbf{v}) d\mathbf{v},$$

$$U = \frac{1}{2} \text{tr}(\mathbf{P}), \quad U^* = \sum_{s=1}^N E^s n^s,$$

$$\mathbf{q}_{th} = \frac{1}{2} m \sum_{s=1}^N \int (\mathbf{v} - \mathbf{u}) |\mathbf{v} - \mathbf{u}|^2 f^s(\mathbf{v}) d\mathbf{v}, \quad \mathbf{q}^* = \sum_{s=1}^N E^s n^s (\mathbf{u}^s - \mathbf{u}).$$

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Notice that the attractor (2) is a collision equilibrium, but not at the actual macroscopic parameters of the gas, and that equation (3) provides $N - 1$ independent equilibrium conditions which reduce the number of free parameters in the Maxwellian attractors from $N + 4$ to 5, irrespective of N , and in agreement with the fact that we are dealing with a single gas. The model exhibits thus 5 free parameters, \tilde{n} , $\tilde{\mathbf{u}}$, \tilde{T} , as many as the actual conservation laws [13], so that it is spontaneous to impose that it preserves the correct collision invariants

$$(7) \quad \sum_{s=1}^N \nu^s \int (\mathcal{M}^s - f^s) d\mathbf{v} = 0, \quad \sum_{s=1}^N \nu^s \int m \mathbf{v} (\mathcal{M}^s - f^s) d\mathbf{v} = \mathbf{0},$$

$$\sum_{s=1}^N \nu^s \int \left(\frac{1}{2} m |\mathbf{v}|^2 + E^s \right) (\mathcal{M}^s - f^s) d\mathbf{v} = 0.$$

The second of equations (7) directly provides the auxiliary velocity as

$$(8) \quad \tilde{\mathbf{u}} = \left(\sum_{s=1}^N \nu^s n^s \mathbf{u}^s \right) / \left(\sum_{s=1}^N \nu^s n^s \right).$$

The first of equations (7) allows to cast the auxiliary density in terms of the auxiliary temperature, and finally the last equation in (7) yields a transcendental equation for \tilde{T} , which can be shown to admit a unique physical solution, so that all free auxiliary parameters, subject to vary during the evolution, are well defined in terms of the moments of the actual distribution functions. The model features then the correct kinetic properties, including an H -theorem with respect to the Boltzmann entropy functional. See [25] for technical details.

3. Hydrodynamic regime and transport coefficients

As usual, after re-scaling time and space variables in terms of macroscopic units, the inverse of the Knudsen number ε , ratio between the microscopic and the macroscopic time scales, automatically appears in front of the BGK relaxation operator

$$(9) \quad \frac{\partial f^s}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f^s = \frac{1}{\varepsilon} \nu^s (\mathcal{M}^s - f^s) \quad s = 1, \dots, N,$$

and we shall investigate the asymptotic limit $\varepsilon \rightarrow 0^+$ by a Chapman–Enskog procedure up to first corrections [28], in order to get consistent fluid-dynamic equations at Navier–Stokes level. We expand distribution functions in powers of the small parameter ε as $f^s = f^{s(0)} + \varepsilon f^{s(1)}$, and consequently

even actual $(n^s, \mathbf{u}^s, \mathbf{P}^s, \mathbf{q}^s)$ and auxiliary $(\tilde{n}, \tilde{\mathbf{u}}, \tilde{T})$ macroscopic fields turn out to be correspondingly expanded, with the constraint that hydrodynamic variables $n, \mathbf{u}, U + U^*$ (relevant to collision invariants) remain unexpanded, and fully represented by the leading terms only. Therefore, corresponding first order corrections have to fulfil the restrictions

$$(10) \quad \sum_{s=1}^N n^{s(1)} = 0, \quad \sum_{s=1}^N \left[n^{s(0)} \mathbf{u}^{s(1)} + n^{s(1)} \mathbf{u}^{s(0)} \right] = \mathbf{0},$$

$$\frac{3}{2} n K T^{(1)} + \sum_{s=1}^N E^s n^{s(1)} = 0.$$

Notice that kinetic temperature T (or thermal energy U) must be expanded as well, since mechanical energy is not conserved in a polyatomic gas.

The leading order equation is simply $f^{s(0)} = \mathcal{M}^{s(0)}$ from which in cascade $n^{s(0)} = \tilde{n}^{s(0)}$, $n^{(0)} = n = \tilde{n}^{(0)}$, $\mathbf{u}^{s(0)} = \mathbf{u} = \tilde{\mathbf{u}}^{(0)}$, $T^{s(0)} = \tilde{T}^{(0)} = T^{(0)}$, so that

$$(11) \quad f^{s(0)} = \mathcal{M}^{s(0)} = n^{s(0)} \left(\frac{m}{2\pi K T^{(0)}} \right)^{3/2} \exp \left[- \frac{m}{2K T^{(0)}} |\mathbf{v} - \mathbf{u}|^2 \right]$$

with

$$(12) \quad n^{s(0)} = \frac{n}{Z(T^{(0)})} \exp \left(- \frac{E^s - E^1}{K T^{(0)}} \right)$$

and then $\mathbf{P}^{(0)} = n K T^{(0)} \mathbf{I}$, $U^{(0)} = \frac{3}{2} n K T^{(0)}$, $U^{*(0)} = n \bar{E}(T^{(0)})$, $\mathbf{q}_{th}^{(0)} = \mathbf{0}$, $\mathbf{q}^{*(0)} = \mathbf{0}$. Conservation equations for the unknowns $n, \mathbf{u}, T^{(0)}$ read as

$$(13) \quad \frac{\partial n}{\partial t} + \nabla_{\mathbf{x}} \cdot (n \mathbf{u}) = 0,$$

$$\frac{\partial}{\partial t} (\rho \mathbf{u}) + \nabla_{\mathbf{x}} \cdot (\rho \mathbf{u} \otimes \mathbf{u}) + \nabla_{\mathbf{x}} (n K T^{(0)}) + \varepsilon \nabla_{\mathbf{x}} \cdot \mathbf{P}^{(1)} = \mathbf{0},$$

$$\frac{\partial}{\partial t} \left(\frac{1}{2} \rho |\mathbf{u}|^2 + \frac{3}{2} n K T^{(0)} + n \bar{E}(T^{(0)}) \right)$$

$$+ \nabla_{\mathbf{x}} \cdot \left[\left(\frac{1}{2} \rho |\mathbf{u}|^2 + \frac{5}{2} n K T^{(0)} + n \bar{E}(T^{(0)}) \right) \mathbf{u} \right] + \varepsilon \nabla_{\mathbf{x}} \cdot (\mathbf{P}^{(1)} \cdot \mathbf{u})$$

$$+ \varepsilon \nabla_{\mathbf{x}} \cdot \mathbf{q}_{th}^{(1)} + \varepsilon \nabla_{\mathbf{x}} \cdot \left(\sum_{s=1}^N E^s n^{s(0)} \mathbf{u}^{s(1)} \right) = 0,$$

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and, for their closure, constitutive equations are needed for

$$\begin{aligned}
 \mathbf{u}^{s(1)} &= \frac{1}{n^{s(0)}} \int (\mathbf{v} - \mathbf{u}) f^{s(1)}(\mathbf{v}) d\mathbf{v}, \\
 \mathbf{P}^{(1)} &= m \sum_{s=1}^N \int (\mathbf{v} - \mathbf{u}) \otimes (\mathbf{v} - \mathbf{u}) f^{s(1)}(\mathbf{v}) d\mathbf{v} = \Pi \mathbf{I} + \mathbf{p}^{(1)}, \\
 \mathbf{q}_{th}^{(1)} &= \frac{1}{2} m \sum_{s=1}^N \int (\mathbf{v} - \mathbf{u}) |\mathbf{v} - \mathbf{u}|^2 f^{s(1)}(\mathbf{v}) d\mathbf{v},
 \end{aligned}
 \tag{14}$$

where the so-called dynamical pressure Π , typical of polyatomic gases [29], provided by

$$\Pi = \frac{1}{3} \text{tr}(\mathbf{P}^{(1)}) = \frac{2}{3} U^{(1)} = nKT^{(1)} = \frac{1}{3} m \sum_{s=1}^N \int |\mathbf{v} - \mathbf{u}|^2 f^{s(1)}(\mathbf{v}) d\mathbf{v},$$

has been singled out, together with the traceless shear stress $\mathbf{p}^{(1)}$.

The first order correction to the distribution function is immediately given by the next order step in the procedure, as

$$f^{s(1)} = \mathcal{M}^{s(1)} - \frac{1}{\nu^{s(0)}} \left(\frac{\partial_0 f^{s(0)}}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f^{s(0)} \right)$$

where use has been made of the zero-th order time derivative, which has to be eliminated by the leading order Euler equations [14]. Lengthy but standard calculations usual in kinetic theory lead to the expressions

$$\begin{aligned}
 \mathcal{M}^{s(1)} &= f^{s(0)} \left\{ \frac{\tilde{n}^{(1)}}{n} + \frac{m}{KT^{(0)}} \tilde{\mathbf{u}}^{(1)} \cdot (\mathbf{v} - \mathbf{u}) \right. \\
 &\quad \left. + \frac{\tilde{T}^{(1)}}{T^{(0)}} \left[\frac{1}{KT^{(0)}} \left(\frac{1}{2} m |\mathbf{v} - \mathbf{u}|^2 + E^s - \bar{E}(T^{(0)}) \right) - \frac{3}{2} \right] \right\},
 \end{aligned}$$

and

$$\begin{aligned}
 \frac{\partial_0 f^{s(0)}}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f^{s(0)} &= f^{s(0)} \left\{ \frac{m}{KT^{(0)}} \nabla_{\mathbf{x}} \mathbf{u} : (\mathbf{v} - \mathbf{u}) \otimes (\mathbf{v} - \mathbf{u}) \right. \\
 &\quad - \frac{1}{\hat{c}_v(T^{(0)})} \left[\frac{m}{2KT^{(0)}} |\mathbf{v} - \mathbf{u}|^2 + \frac{E^s - \bar{E}(T^{(0)})}{KT^{(0)}} + \hat{\sigma}(T^{(0)}) \right] \nabla_{\mathbf{x}} \cdot \mathbf{u} \\
 &\quad \left. + \frac{1}{T^{(0)}} \nabla_{\mathbf{x}} T^{(0)} \cdot (\mathbf{v} - \mathbf{u}) \left[\frac{m}{2KT^{(0)}} |\mathbf{v} - \mathbf{u}|^2 + \frac{E^s - \bar{E}(T^{(0)})}{KT^{(0)}} - \frac{5}{2} \right] \right\}.
 \end{aligned}$$

The expression for $f^{s(1)}$ is not yet explicit because of the presence of some of its moments on the right hand side. We can however obtain $n^{s(1)}$ by simple integration, and use the constraint $\sum_{s=1}^N n^{s(1)} = 0$ to yield

$$(16) \quad \tilde{n}^{(1)} = - \frac{1}{\hat{c}_v(T^{(0)})} \sum_{s=1}^N \frac{E^s - \bar{E}(T^{(0)})}{KT^{(0)}} \frac{n^{s(0)}}{\nu^{s(0)}} \nabla_{\mathbf{x}} \cdot \mathbf{u}.$$

Now, by an argument already used in [27], the relation between \tilde{n} and \tilde{T} , not given here for brevity, may be also expanded in powers of ε , in order to achieve the relationship between $\tilde{n}^{(1)}$ and $\tilde{T}^{(1)}$, that can be worked out, and, after some algebra, yields

$$(17) \quad \begin{aligned} \tilde{T}^{(1)} = & \frac{T^{(0)}}{n [\hat{c}_v(T^{(0)})]^2} \left[\hat{\sigma}(T^{(0)}) \sum_{s=1}^N \frac{n^{s(0)}}{\nu^{s(0)}} \right. \\ & \left. - \sum_{s=1}^N \left(\frac{E^s - \bar{E}(T^{(0)})}{KT^{(0)}} \right)^2 \frac{n^{s(0)}}{\nu^{s(0)}} \right] \nabla_{\mathbf{x}} \cdot \mathbf{u}. \end{aligned}$$

At this point, in order to make equation (15) fully explicit, we need only $\tilde{\mathbf{u}}^{(1)}$, which follows from (8), again by expansion in powers of ε , in terms of the $\mathbf{u}^{s(1)}$. Therefore, one would have to re-compute these moments, which still appear in the definition of $f^{s(1)}$, by suitable integrations of (15) itself, in order to get a linear algebraic system for those diffusion velocities. They will have to fulfil the constraint

$$(18) \quad \sum_{s=1}^N n^{s(0)} \mathbf{u}^{s(1)} = \mathbf{0}.$$

However we shall show here that such a machinery can be avoided if one is interested in closing the fluid-dynamic equations and in making explicit the constitutive relations. First of all, the unknown diffusion velocities do not appear in the computation of the pressure tensor $\mathbf{P}^{(1)}$. In fact, upon setting $\mathbf{c} = \mathbf{v} - \mathbf{u}$ for the peculiar molecular velocities, and resorting to (14) and (15), it is not difficult to show that

$$(19) \quad m \sum_{s=1}^N \int c_i c_j \mathcal{M}^{s(1)} d\mathbf{v} = \delta_{ij} \left(\tilde{n}^{(1)} KT^{(0)} + n K \tilde{T}^{(1)} \right),$$

where δ is the Kronecker symbol. The computation of the remaining contribution from (15) is again matter of standard, though cumbersome, calculations, involving also the fourth order tensor

$$\int x_i x_j x_h x_k \exp(-x^2) d\mathbf{x} = \frac{1}{4} \pi^{3/2} (\delta_{ih} \delta_{jk} + \delta_{ik} \delta_{jh} + \delta_{ij} \delta_{hk}).$$

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The final result reads as

$$(20) \quad P_{ij}^{(1)} = -KT^{(0)} \left(\frac{\partial u_j}{\partial x_i} + \frac{\partial u_i}{\partial x_j} \right) \sum_{s=1}^N \frac{n^{s(0)}}{\nu^{s(0)}} + \delta_{ij} \left[\tilde{n}^{(1)} KT^{(0)} + nK\tilde{T}^{(1)} + \frac{KT^{(0)}}{\hat{c}_v(T^{(0)})} \sum_{s=1}^N \left(1 + \frac{E^s - \bar{E}(T^{(0)})}{KT^{(0)}} \right) \frac{n^{s(0)}}{\nu^{s(0)}} \nabla_{\mathbf{x}} \cdot \mathbf{u} \right].$$

This allows a direct evaluation of the dynamical pressure as $\Pi = \frac{1}{3} \text{tr}(\mathbf{P}^{(1)})$, which, after a little algebra, takes the form, common in the literature [30] for many important physical regimes,

$$(21) \quad \Pi = nKT^{(1)} = -\nu \nabla_{\mathbf{x}} \cdot \mathbf{u},$$

where $\nu > 0$ represents the bulk viscosity, and is given by

$$(22) \quad \nu = \frac{KT^{(0)}}{[\hat{c}_v(T^{(0)})]^2} \left\{ \frac{2}{3} [\hat{\sigma}(T^{(0)})]^2 \sum_{s=1}^N \frac{n^{s(0)}}{\nu^{s(0)}} + \sum_{s=1}^N \left(\frac{E^s - \bar{E}(T^{(0)})}{KT^{(0)}} \right)^2 \frac{n^{s(0)}}{\nu^{s(0)}} \right\}.$$

The present result coincides with an equivalent expression obtained in [27], by a different technique, in a preliminary asymptotic investigation of the model, and, above all, it relates such a transport coefficient to the free parameters of the kinetic model, so that a quantitative knowledge of the bulk viscosity and of the specific heat allows to tune the relaxation coefficients $\nu^{s(0)}$ in order to fit correctly this constitutive equation. We remark also that in the bulk viscosity (22) we may factor out the standard scalar pressure $nKT^{(0)}$. Finally, we notice that in the mono-atomic gas limit ($N = 1$, $\bar{E} = E^1$, and $\hat{\sigma} = 0$), the bulk viscosity vanishes, and the dynamical pressure disappears, an expected result correctly reproduced.

We can complete now, by the present approach, the closure procedure at first order accuracy by making explicit the additional fields $\mathbf{u}^{s(1)}$, $\mathbf{p}^{(1)}$, and $\mathbf{q}_{th}^{(1)}$. To begin with, the deviatoric part of the pressure tensor, the shear stress $\mathbf{p}^{(1)}$, is simply recovered by difference between (20) and its isotropic component $\Pi \mathbf{I}$, provided by (21) and (22). It is readily obtained

$$(23) \quad p_{ij}^{(1)} = -2\mu \left(\frac{1}{2} \frac{\partial u_j}{\partial x_i} + \frac{1}{2} \frac{\partial u_i}{\partial x_j} - \frac{1}{3} \delta_{ij} \nabla_{\mathbf{x}} \cdot \mathbf{u} \right), \quad \mu = KT^{(0)} \sum_{s=1}^N \frac{n^{s(0)}}{\nu^{s(0)}},$$

namely the well known Newtonian constitutive equation, with a shear viscosity μ expressed again in terms of kinetic model parameters, to be used

for a best fit of its actual physical value. The standard BGK expression of this transport coefficient is recovered in the mono-atomic case $N = 1$.

In order to compute now $\mathbf{u}^{s(1)}$, we multiply (15) by $\mathbf{c}/n^{s(0)}$ and integrate with respect to \mathbf{v} . We split the result as the sum of the contributions of the two addends in (15) itself. The first is easily seen to be $\tilde{\mathbf{u}}^{(1)}$, independent of s . A standard calculation shows that the second contribution leaves only a term proportional to $\nabla_{\mathbf{x}}T^{(0)}$. The final result is

$$(24) \quad \mathbf{u}^{s(1)} = \tilde{\mathbf{u}}^{(1)} - \frac{1}{\nu^{s(0)}} \frac{K}{m} \frac{E^s - \bar{E}(T^{(0)})}{KT^{(0)}} \nabla_{\mathbf{x}}T^{(0)},$$

and this, bearing in mind (8), constitutes a formally complicated linear algebraic system for determining diffusion velocities. However, the constraint (18) allows to get rid of the left hand side and to single out $\tilde{\mathbf{u}}^{(1)}$ as

$$(25) \quad \tilde{\mathbf{u}}^{(1)} = \frac{K}{m} \frac{1}{Z(T^{(0)})} \sum_{s=1}^N \frac{1}{\nu^{s(0)}} \frac{E^s - \bar{E}(T^{(0)})}{KT^{(0)}} \exp\left(-\frac{E^s - E^1}{KT^{(0)}}\right) \nabla_{\mathbf{x}}T^{(0)}.$$

In particular, $\tilde{\mathbf{u}}^{(1)}$ would vanish for all equal $\nu^{s(0)}$. In conclusion, diffusion velocities are explicitly given by

$$(26) \quad \mathbf{u}^{s(1)} = -\frac{K}{m} \left[\frac{E^s - \bar{E}(T^{(0)})}{\nu^{s(0)}KT^{(0)}} - \frac{1}{Z(T^{(0)})} \sum_{r=1}^N \frac{E^r - \bar{E}(T^{(0)})}{\nu^{r(0)}KT^{(0)}} \exp\left(-\frac{E^r - E^1}{KT^{(0)}}\right) \right] \nabla_{\mathbf{x}}T^{(0)},$$

and are all proportional to the temperature gradient. Indeed, no Fick matrix appears, nor density gradients, in agreement with the fact that the gas is single and species densities are not hydrodynamic variables, so that diffusion is driven solely by space inhomogeneity of the temperature field.

Finally, we have to determine the total heat flux as the the sum of its thermal and excitation components

$$(27) \quad \mathbf{q}^{(1)} = \mathbf{q}_{th}^{(1)} + \mathbf{q}^{*(1)} = \mathbf{q}_{th}^{(1)} + \sum_{s=1}^N E^s n^{s(0)} \mathbf{u}^{s(1)}.$$

For the evaluation of $\mathbf{q}_{th}^{(1)}$ we resort to the last of (14) and split again the integration as the sum of the contributions from the two addends in (15). The first one is easily seen to be $(5/2)nKT^{(0)}\tilde{\mathbf{u}}^{(1)}$. It is not too difficult

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to check that the second one is once more proportional to the gradient of temperature, precisely

$$(28) \quad -\frac{5}{2} \frac{K}{m} K T^{(0)} \sum_{s=1}^N \left(1 + \frac{E^s - \bar{E}(T^{(0)})}{K T^{(0)}} \right) \frac{n^{s(0)}}{\nu^{s(0)}} \nabla_{\mathbf{x}} T^{(0)}.$$

Upon putting all together and using (25) yields finally for the thermal heat flux the simple result

$$(29) \quad \mathbf{q}_{th}^{(1)} = -\frac{5}{2} \frac{K}{m} K T^{(0)} \sum_{s=1}^N \frac{n^{s(0)}}{\nu^{s(0)}} \nabla_{\mathbf{x}} T^{(0)},$$

namely a familiar expression proportional to $-\nabla_{\mathbf{x}} T^{(0)}$, without any density gradient for the same reasons as for the diffusion velocities. The factor in front of the gradient reduces to the well known mono-atomic value for $N = 1$. Equations (13) contain of course also the contribution of the excitation heat flux to the energy balance, and that is the only place where diffusion velocities appear, in a suitable linear combination. By means of (26) this term also can be explicitly evaluated, depends only on temperature gradient, and reads as

$$(30) \quad \sum_{s=1}^N E^s n^{s(0)} \mathbf{u}^{s(1)} = -\frac{K}{m} K T^{(0)} \sum_{s=1}^N \left(\frac{E^s - \bar{E}(T^{(0)})}{K T^{(0)}} \right)^2 \frac{n^{s(0)}}{\nu^{s(0)}} \nabla_{\mathbf{x}} T^{(0)}.$$

Therefore the overall heat flux may be cast, to the present level of asymptotic accuracy, as

$$(31) \quad \mathbf{q}^{(1)} = -\frac{K}{m} K T^{(0)} \left[\frac{5}{2} \sum_{s=1}^N \frac{n^{s(0)}}{\nu^{s(0)}} + \sum_{s=1}^N \left(\frac{E^s - \bar{E}(T^{(0)})}{K T^{(0)}} \right)^2 \frac{n^{s(0)}}{\nu^{s(0)}} \right] \nabla_{\mathbf{x}} T^{(0)},$$

the well known Fourier conduction law for a single gas, with a conductivity $\lambda > 0$ given by

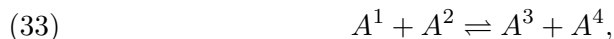
$$(32) \quad \lambda = \frac{K}{m} n K T^{(0)} \frac{1}{Z(T^{(0)})} \sum_{s=1}^N \frac{1}{\nu^{s(0)}} \left[\frac{5}{2} + \left(\frac{E^s - \bar{E}(T^{(0)})}{K T^{(0)}} \right)^2 \right] \times \exp \left(-\frac{E^s - E^1}{K T^{(0)}} \right).$$

Once more, this observable transport coefficient is expressed in terms of kinetic relaxation parameters, as well as of the internal structure of energy

levels. This completes the sought closure of the macroscopic conservation equations at Navier–Stokes level as deduced consistently from a kinetic relaxation model. Transport coefficients are explicitly given by (22) for the bulk viscosity, (23) for the shear viscosity, and (32) for the heat conductivity, in terms of velocity and temperature gradients, and of all hydrodynamic variables, including density. We remark that, since in general the collision frequencies $\nu^{s(0)}$ are different for different s , the ratio λ/μ , making up essentially the Prandtl number, is not bound to any specific heat, so that one of the main drawbacks typical of BGK approaches can be overcome.

4. BGK hydrodynamics for a reactive gas mixture

As stated in the Introduction, the previous kinetic approach and relevant asymptotic limit for dominant collisions may be extended to a mixture of reacting gases, and this will be matter of future investigation. In this Section we shall consider preliminarily the easiest test case in which all non-translational degrees of freedom of participating molecules are ignored, which, though oversimplified, has been shown to capture most of the essentials of the reactive encounters. Specifically, we will be dealing with the bimolecular reversible chemical reaction



where each species A^s is endowed with a mass m^s and an energy of chemical bond E^s , and it is conventionally assumed that $\Delta E = -\sum_{s=1}^4 \lambda^s E^s > 0$, where the λ^s constitute the string of stoichiometric coefficients (1, 1, -1, -1). Kinetic relaxation approaches to this problem have been proposed in the literature (see for instance [26,31]), but the research line which more closely resembles the strategy behind the analysis developed in the previous Sections for polyatomic molecules is the one worked out in [24,32]. In particular, we shall push up to end the hydrodynamic limit of [24] by making explicit all constitutive equations and transport coefficients.

We recall that, for the present problem, the space of collision invariants is seven dimensional, and conserved quantities are mass in three independent pairs of species (which, for instance, may be chosen as (1, 3), (1, 4), (2, 4)), momentum and total (kinetic plus chemical) energy. Again thermal energy (namely, temperature) is not a conserved macroscopic quantity. Collision equilibria are determined as the seven parameter family of local Maxwellians

$$(34) \quad f_M^s(\mathbf{v}) = n^s \left(\frac{m^s}{2\pi KT} \right)^{3/2} \exp \left[-\frac{m^s}{2KT} |\mathbf{v} - \mathbf{u}|^2 \right] \quad s = 1, \dots, 4$$

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where number densities n^s must be related by the mass action law

$$(35) \quad \frac{n^1 n^2}{n^3 n^4} = \left(\frac{\mu^{12}}{\mu^{34}} \right)^{3/2} \exp\left(\frac{\Delta E}{KT} \right),$$

in which use has been made of the reduced masses $\mu^{sr} = m^s m^r / (m^s + m^r)$. Consistently, model kinetic BGK equations (in dimensionless form) read as

$$(36) \quad \frac{\partial f^s}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f^s = \frac{1}{\varepsilon} \nu^s (\mathcal{M}^s - f^s) \quad s = 1, \dots, 4,$$

where \mathcal{M}^s are the family of local Maxwellians

$$(37) \quad \mathcal{M}^s(\mathbf{v}) = \tilde{n}^s \left(\frac{m^s}{2\pi K\tilde{T}} \right)^{3/2} \exp\left[-\frac{m^s}{2K\tilde{T}} |\mathbf{v} - \tilde{\mathbf{u}}|^2 \right] \quad s = 1, \dots, 4$$

with seven disposable scalar parameters, provided by $\tilde{n}^s, \tilde{\mathbf{u}}, \tilde{T}$, bound together by the mass action law

$$(38) \quad \frac{\tilde{n}^1 \tilde{n}^2}{\tilde{n}^3 \tilde{n}^4} = \left(\frac{\mu^{12}}{\mu^{34}} \right)^{3/2} \exp\left(\frac{\Delta E}{K\tilde{T}} \right).$$

We recall from [24] that all auxiliary parameters are determined in terms of actual fields going through (as before) a uniquely solvable transcendental equation, and that the ‘‘exact’’ set of 7 scalar non-closed macroscopic conservation equations to be closed by the asymptotic procedure (not written here for brevity) involve now the partial densities $n^s + n^r$, with $(s, r) = (1, 3), (1, 4), (2, 4)$, the total momentum density $\rho \mathbf{u}$, and the total (mechanical and chemical) energy density $\frac{1}{2} \rho u^2 + \frac{3}{2} nKT + \sum_{s=1}^4 E^s n^s$. Expanding again distribution functions as $f^s = f^{s(0)} + \varepsilon f^{s(1)}$, hydrodynamic quantities remaining unexpanded are

$$(39) \quad \begin{aligned} n^s + n^r &= n^{s(0)} + n^{r(0)} \quad (s, r) = (1, 3), (1, 4), (2, 4), \\ \mathbf{u} &= \frac{1}{\rho} \sum_{s=1}^4 m^s n^{s(0)} \mathbf{u}^{s(0)}, \\ \frac{3}{2} nKT + \sum_{s=1}^4 E^s n^s &= \frac{3}{2} nKT^{(0)} + \sum_{s=1}^4 E^s n^{s(0)}, \end{aligned}$$

with $n = \sum_{s=1}^4 n^{s(0)}$ and $\rho = \sum_{s=1}^4 m^s n^{s(0)}$, yielding the constraints

$$(40) \quad \begin{aligned} n^{1(1)} &= n^{2(1)} = -n^{3(1)} = -n^{4(1)} = \frac{3nK}{2\Delta E} T^{(1)} \\ \sum_{s=1}^4 m^s n^{s(0)} \mathbf{u}^{s(1)} + \sum_{s=1}^4 m^s n^{s(1)} \mathbf{u}^{s(0)} &= \mathbf{0}. \end{aligned}$$

To leading order we get easily

$$(41) \quad f^{s(0)} = \mathcal{M}^{s(0)} = n^{s(0)} \left(\frac{m^s}{2\pi KT^{(0)}} \right)^{3/2} \exp \left[-\frac{m^s}{2KT^{(0)}} |\mathbf{v} - \mathbf{u}|^2 \right],$$

for $s = 1, \dots, 4$, with seven free parameters, since the $n^{s(0)}$ and $T^{(0)}$ must be bound together by the zero-th order mass action law

$$(42) \quad \frac{n^{1(0)}n^{2(0)}}{n^{3(0)}n^{4(0)}} = \left(\frac{\mu^{12}}{\mu^{34}} \right)^{\frac{3}{2}} \exp \left(\frac{\Delta E}{KT^{(0)}} \right).$$

Conservation equations may be rewritten as

$$(43) \quad \begin{aligned} & \frac{\partial}{\partial t} (n^{s(0)} + n^{r(0)}) + \nabla_{\mathbf{x}} \cdot \left[(n^{s(0)} + n^{r(0)}) \mathbf{u} \right] \\ & + \varepsilon \nabla_{\mathbf{x}} \cdot \left(n^{s(0)} \mathbf{u}^{s(1)} + n^{r(0)} \mathbf{u}^{r(1)} \right) = 0 \quad (s, r) = (1, 3), (1, 4), (2, 4), \\ & \frac{\partial}{\partial t} (\rho \mathbf{u}) + \nabla_{\mathbf{x}} \cdot (\rho \mathbf{u} \otimes \mathbf{u}) + \nabla_{\mathbf{x}} (nKT^{(0)}) \\ & + \varepsilon \nabla_{\mathbf{x}} (nKT^{(1)}) + \varepsilon \nabla_{\mathbf{x}} \cdot \mathbf{p}^{(1)} = \mathbf{0}, \\ & \frac{\partial}{\partial t} \left(\frac{1}{2} \rho u^2 + \frac{3}{2} nKT^{(0)} + \sum_{s=1}^4 E^s n^{s(0)} \right) \\ & + \nabla_{\mathbf{x}} \cdot \left[\left(\frac{1}{2} \rho u^2 + \frac{5}{2} nKT^{(0)} + \sum_{s=1}^4 E^s n^{s(0)} \right) \mathbf{u} \right] + \varepsilon \nabla_{\mathbf{x}} \cdot (nKT^{(1)} \mathbf{u}) \\ & + \varepsilon \nabla_{\mathbf{x}} \cdot (\mathbf{p}^{(1)} \cdot \mathbf{u}) + \varepsilon \nabla_{\mathbf{x}} \cdot \mathbf{q}_{th}^{(1)} + \varepsilon \nabla_{\mathbf{x}} \cdot \left(\sum_{s=1}^4 E^s n^{s(0)} \mathbf{u}^{s(1)} \right) = 0, \end{aligned}$$

and their closure is achieved if we are able to determine, resorting to (15), constitutive equations for the quantities $\mathbf{u}^{s(1)}$, $T^{(1)}$, $\mathbf{p}^{(1)}$, and $\mathbf{q}_{th}^{(1)}$. We remark that the corresponding inert mixture, with chemical reaction switched off, is reproduced by the option $E^s = 0$ for any s (in the non-reacting case the scenario would be of course different, since single number densities and kinetic temperature would be hydrodynamic variables). In particular, in (43) the last quantity in the third equation under the divergence operator represents the reactive heat flux $\mathbf{q}_{ch}^{(1)}$. The diffusion velocities $\mathbf{u}^{s(1)}$ are subject to the constraint

$$(44) \quad \sum_{s=1}^4 \rho^{s(0)} \mathbf{u}^{s(1)} = \mathbf{0}.$$

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Manipulations for those first order corrections become quite tedious and cumbersome. Some of them were performed in [24], and we address interested readers to that paper for details and technicalities. After some algebra, it was found there

$$(45) \quad T^{(1)} = -\frac{2}{3}T^{(0)} \frac{\frac{1}{n} \sum_{s=1}^4 \frac{n^{s(0)}}{\nu^{s(0)}} + \frac{3}{2}n \left(\frac{KT^{(0)}}{\Delta E} \right)^2 \sum_{s=1}^4 \frac{1}{\nu^{s(0)} n^{s(0)}}}{\left[1 + \frac{3}{2}n \left(\frac{KT^{(0)}}{\Delta E} \right)^2 \sum_{s=1}^4 \frac{1}{n^{s(0)}} \right]^2} \nabla_{\mathbf{x}} \cdot \mathbf{u},$$

a temperature correction, inducing a corresponding pressure correction, which is specific of reactive mixtures (it is not present in any inert mixture of mono-atomic gases), and that plays a role analogous to the dynamical pressure of a polyatomic gas, with corresponding dependence on the divergence of the velocity field, without any other spatial gradient. Notice that in the present frame the $n^{s(0)}$ are actual unknowns in (43), whereas in the preceding Sections they were byproducts of other hydrodynamic variables, n and $T^{(0)}$, via (12). Notice also that we would have consistently $T^{(1)} = 0$ for the non-reactive mixture ($\Delta E \rightarrow 0$).

Another result already derived in [24] concerns the deviatoric part of the pressure tensor

$$(46) \quad p_{ij}^{(1)} = -KT^{(0)} \sum_{s=1}^4 \frac{n^{s(0)}}{\nu^{s(0)}} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \nabla_{\mathbf{x}} \cdot \mathbf{u} \delta_{ij} \right),$$

a Newtonian constitutive equation corresponding to a viscosity coefficient

$$(47) \quad \mu = KT^{(0)} \sum_{s=1}^4 \frac{n^{s(0)}}{\nu^{s(0)}},$$

which, *mutatis mutandis*, corresponds to the polyatomic result (23).

Now we are able to proceed here to the explicit calculation of the other extra-fields and relevant transport coefficients. Diffusion velocities follow from their own definition (14) and the expression of $f^{s(1)}$, omitted here, which replaces in this frame the one given in (15). Going through several gaussian integrals, and upon resorting to the compatibility condition

$$(48) \quad \frac{\partial_0 \mathbf{u}}{\partial t} = -\mathbf{u} \cdot \nabla_{\mathbf{x}} \mathbf{u} - \frac{1}{\rho} \nabla_{\mathbf{x}} (nKT^{(0)}),$$

one ends up with

$$(49) \quad \mathbf{u}^{s(1)} = \tilde{\mathbf{u}}^{(1)} + \frac{KT^{(0)}}{\nu^{s(0)}} \left(\frac{\nabla_{\mathbf{x}} n}{\rho} - \frac{\nabla_{\mathbf{x}} n^{s(0)}}{\rho^{s(0)}} \right) + \frac{K}{\nu^{s(0)}} \left(\frac{n}{\rho} - \frac{1}{m^s} \right) \nabla_{\mathbf{x}} T^{(0)}.$$

Use of the constraint (44) allows now to single out $\tilde{\mathbf{u}}^{(1)}$ irrespective of its definition in terms of the diffusion velocities themselves, leading to the explicit expression

$$(50) \quad \begin{aligned} \tilde{\mathbf{u}}^{(1)} = & \frac{KT^{(0)}}{\rho} \sum_{r=1}^4 \frac{1}{\nu^{r(0)}} \left(\nabla_{\mathbf{x}} n^{r(0)} - \frac{\rho^{r(0)}}{\rho} \nabla_{\mathbf{x}} n \right) \\ & + \frac{nK}{\rho} \sum_{r=1}^4 \frac{1}{\nu^{r(0)}} \left(\frac{n^{r(0)}}{n} - \frac{\rho^{r(0)}}{\rho} \right) \nabla_{\mathbf{x}} T^{(0)}. \end{aligned}$$

Putting together the above results yields finally

$$(51) \quad \mathbf{u}^{s(1)} = \sum_{r=1}^4 F_{sr} \nabla_{\mathbf{x}} n^{r(0)} + \alpha_s \nabla_{\mathbf{x}} T^{(0)}.$$

The contribution from the density gradients is a Fick diffusion law with matrix

$$(52) \quad F_{sr} = KT^{(0)} \left[\frac{1}{\nu^{s(0)}} \left(\frac{1}{\rho} - \frac{\delta_{sr}}{\rho^{s(0)}} \right) + \frac{1}{\nu^{r(0)}} \frac{1}{\rho} - \frac{1}{\rho^2} \sum_{k=1}^4 \frac{\rho^{k(0)}}{\nu^{k(0)}} \right].$$

The Fick matrix is symmetric and it is easily seen that it satisfies the well known condition

$$(53) \quad \sum_{r=1}^4 \rho^{r(0)} F_{rs} = 0, \quad \forall s.$$

A little algebra shows that, as physically expected, the diagonal terms are negative

$$(54) \quad F_{ss} = -\frac{KT^{(0)}}{\rho^{s(0)}\rho^2} \left(\frac{(\rho - \rho^{s(0)})^2}{\nu^{s(0)}} + \rho^{s(0)} \sum_{k \neq s} \frac{\rho^{k(0)}}{\nu^{k(0)}} \right) < 0.$$

The coefficients of the temperature gradient in (51) (so called Soret effect) are

$$(55) \quad \begin{aligned} \alpha_s = & \frac{1}{T^{(0)}} \sum_{r=1}^4 F_{sr} n^{r(0)} \\ = & K \left[\frac{1}{\nu^{s(0)}} \left(\frac{n}{\rho} - \frac{1}{m^s} \right) + \frac{n}{\rho} \sum_{r=1}^4 \frac{1}{\nu^{r(0)}} \left(\frac{n^{r(0)}}{n} - \frac{\rho^{r(0)}}{\rho} \right) \right] \end{aligned}$$

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and also obey the condition $\sum_{s=1}^4 \alpha_s \rho^{s(0)} = 0$. Notice that diffusion velocities may be cast also as

$$\mathbf{u}^{s(1)} = \sum_{r=1}^4 A_{sr} \nabla_{\mathbf{x}} (n^{r(0)} K T^{(0)})$$

where $A_{sr} = F_{sr}/KT^{(0)}$ is a symmetric matrix, reproducing thus the Onsager relations [33]. Knowledge of velocity corrections determines also the reactive heat flux as

$$(56) \quad \mathbf{q}_{ch}^{(1)} = \sum_{s=1}^4 \nabla_{\mathbf{x}} n^{s(0)} \sum_{r=1}^4 F_{rs} E^r n^{r(0)} + \nabla_{\mathbf{x}} T^{(0)} \sum_{s=1}^4 \alpha_s E^s n^{s(0)}.$$

The thermal heat flux may be deduced, after some algebra, by integration of the first order corrections to the distribution function, and reads as

$$(57) \quad \mathbf{q}_{th}^{(1)} = -\frac{5}{2} K T^{(0)} \sum_{s=1}^4 \frac{K n^{s(0)}}{m^s \nu^{s(0)}} \nabla_{\mathbf{x}} T^{(0)} + \frac{5}{2} K T^{(0)} \sum_{s=1}^4 n^{s(0)} \mathbf{u}^{s(1)}.$$

Resorting again to (51) for the diffusion velocities, the contribution of the temperature gradient becomes

$$-\frac{5}{2} K T^{(0)} \sum_{s=1}^4 \frac{K n^{s(0)}}{m^s \nu^{s(0)}} + \frac{5}{2} K T^{(0)} \sum_{s=1}^4 \alpha_s n^{s(0)},$$

where it is not too difficult to prove that

$$(58) \quad \sum_{s=1}^4 \alpha_s n^{s(0)} = -\frac{nK}{\rho} \sum_{s=1}^4 \left(\sqrt{\frac{m^s n}{\rho}} - \sqrt{\frac{\rho}{m^s n}} \right)^2 \frac{n^{s(0)}}{\nu^{s(0)}} < 0.$$

In conclusion, the thermal heat flux takes the form

$$(59) \quad \mathbf{q}_{th}^{(1)} = -\lambda_{th} \nabla_{\mathbf{x}} T^{(0)} + \frac{5}{2} K (T^{(0)})^2 \sum_{s=1}^4 \alpha_s \nabla_{\mathbf{x}} n^{s(0)},$$

with a conduction coefficient

$$(60) \quad \lambda_{th} = \frac{5}{2} K T^{(0)} \sum_{s=1}^4 \left[\frac{K}{m^s} + \frac{nK}{\rho} \left(\sqrt{\frac{m^s n}{\rho}} - \sqrt{\frac{\rho}{m^s n}} \right)^2 \right] \frac{n^{s(0)}}{\nu^{s(0)}} > 0,$$

and a second addend contributed by density gradients (Dufour effect).

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