A kinetic model for a multicomponent gas

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A kinetic model for a dilute multicomponent gas system is proposed. It is constructed by replacing the Boltzmann collision operator with a relaxation-time term, in the same manner as in the Bhatnagar–Gross–Krook (BGK) model for a single gas. The model contains several parameters that are determined by keeping some of the main properties of the Boltzmann description. In contrast to previous works, the BGK equation is recovered when mechanically identical particles are considered. Thus the model can be expected to apply to systems in which masses are comparable. The transport properties to the Navier–Stokes level are studied and Onsager's reciprocal relations are found to hold.

I. INTRODUCTION

The mathematical complexity of the nonlinear Boltzmann equation has led to the proposal of several model kinetic equations. The general idea is to approximate the collision term by a simpler expression keeping the main physical properties. For a single gas, the so-called Bhatnagar–Gross–Krook (BGK) model[1] has been shown to be very fruitful. The effect of the molecular collisions in this model is represented by an exponential relaxation toward local equilibrium. For multicomponent systems, several models within the same spirit have been proposed.[2-5] Quite surprisingly, none of the models we are aware of reduce to the BGK equation when particularizing to mechanically identical components (e.g., self-diffusion). This is because of the highly nonlinear character of the modeled collision terms, in contrast to the bilinearity of the Boltzmann equation. It must be pointed out that these models are generally applied to the case of a disparate-mass binary mixture, and in this limit the above criticism is meaningless.

The aim of this paper is to present a kinetic model for a multicomponent gas that is compatible with the usual BGK equation for a single gas. Along with previous models, it conserves mass, momentum, and energy. Although the model is not formally restricted to any range of mass ratios, we expect it to be more appropriate to systems in which masses are of the same order. In this sense, it can be considered as a complement to previous works.[3-5] In our model, the separation between self- and cross-collisions is not neat but rather effective: all the collision terms take into account the local state of the system as a whole. We think that this is close to the spirit of the BGK approximation. For the sake of simplicity, we shall restrict ourselves to Maxwell molecules, for which the collision frequency is temperature independent. The generalization to other interaction potentials is straightforward.

The plan of the paper is as follows. In Sec. II the notation is established and some properties of the Boltzmann description are discussed for further reference. The model is introduced in Sec. III through the definition of a reference distribution function. It contains parameters that are determined by requiring the conservation laws to be satisfied and also the collisional transfers of momentum and energy to agree with those of the Boltzmann description for Maxwell molecules. In Sec. IV the expressions for the fluxes of mass, momentum, and energy to Navier–Stokes order are derived, and Onsager's reciprocal relations are checked. Finally, some concluding remarks are made in Sec. V.

II. BOLTZMANN DESCRIPTION

We consider an N-component mixture. In the low-density limit, the time evolution of the system is described by the set of Boltzmann equations[6]

$$\frac{\partial}{\partial t} f_i + \mathbf{v} \cdot \nabla f_i = K_{ii} + \sum_{j \neq i}^{N} K_{ij}, \tag{1}$$

where $f_i(\mathbf{r},\mathbf{v};t)$ is the one-particle distribution function of species i and $K_{ij} \equiv K_{ij}[f_i,f_j]$ is the nonlinear Boltzmann collision operator. The first and second terms on the right-hand side of Eq. (1) describe self- and cross-collisions, respectively. They obey the following collisional invariant conditions:

$$\int d\mathbf{v}(1, m_i \mathbf{v}, m_i v^2) K_{ii} = 0,$$

$$\int d\mathbf{v}\, K_{ij} = 0,$$

$$\int d\mathbf{v}\, m_i \mathbf{v} K_{ij} + \int d\mathbf{v}\, m_j \mathbf{v} K_{ji} = 0, \tag{2}$$

$$\int d\mathbf{v}\, m_i v^2 K_{ij} + \int d\mathbf{v}\, m_j v^2 K_{ji} = 0,$$

with m_i being the mass of a particle of species i. As a consequence, the number of particles of each species, the total momentum, and the total energy are conserved. In terms of the distribution functions, the densities of these quantities are given by

$$n_i = \int d\mathbf{v}\, f_i, \tag{3}$$

$$\rho \mathbf{u} = \sum_i \int d\mathbf{v}\, m_i \mathbf{v} f_i = \sum_i \rho_i \mathbf{u}_i, \tag{4}$$

$$\frac{3}{2} n k_B T + \frac{1}{2} \rho u^2 = \sum_i \int d\mathbf{v}\, \frac{m_i}{2} v^2 f_i, \tag{5}$$

where $\rho_i = m_i n_i$ is the mass density of species i, $\rho = \sum_i \rho_i$ is

the total mass density, and $n = \Sigma_i \, n_i$ is the total number density. Equation (4) defines the local velocity of the mixture, $\mathbf{u}$. Equation (5) defines the local temperature of the mixture, T. It is convenient to define also a local "temperature" T_i for each species as

$$\frac{3}{2} \, n_i \, k_B T_i = \int d\mathbf{v} \, \frac{1}{2} \, m_i (\mathbf{v} - \mathbf{u}_i)^2 f_i. \tag{6}$$

From Eqs. (5) and (6) it is easy to obtain

$$\frac{3}{2} \, n k_B T = \sum_i \left(\frac{3}{2} \, n_i \, k_B T_i + \frac{1}{2} \, m_i n_i (\mathbf{u}_i - \mathbf{u})^2 \right). \tag{7}$$

It is worth remarking that in the special case of all the species being mechanically identical, the total distribution function

$$f = \sum_i f_i \tag{8}$$

itself obeys the Boltzmann equation

$$\frac{\partial}{\partial t} f + \mathbf{v} \cdot \nabla f = K[f, f]. \tag{9}$$

This follows from the fact that all the cross sections are equal and from the bilinear character of the collision operator K. Of course, the above result is not accidental, but a direct consequence of mechanics laws.

Before closing this section, we quote a result that will be used later. For Maxwell molecules, one obtains[7]

$$\int d\mathbf{v} \, m_i \mathbf{v} K_{ij} = - \, v_{ij} \, \frac{m_i m_j}{m_i + m_j} \, n_i (\mathbf{u}_i - \mathbf{u}_j), \tag{10}$$

$$\int d\mathbf{v} \, \frac{1}{2} \, m_i (\mathbf{v} - \mathbf{u}_i)^2 K_{ij}$$

$$= - \, v_{ij} \, \frac{m_i m_j}{(m_i + m_j)^2} \, n_i \, [\, 3k_B (T_i - T_j)$$

$$- m_j (\mathbf{u}_i - \mathbf{u}_j)^2 \,], \tag{11}$$

where

$$v_{ij} = A n_j (\chi_{ij} (m_i + m_j)/m_i m_j)^{1/2} \tag{12}$$

is a collision frequency. Here, A is a pure number and χ_{ij} is the proportionality constant in the force law. Equations (10) and (11) characterize the collisional transfer of momentum and energy between particles of different species.

III. DEFINITION OF THE MODEL

As mentioned in the Introduction, several kinetic models for the Boltzmann equations (1) have been proposed.[3–5] The general idea is to approximate the Boltzmann collision operator K_{ij} by a relaxation-time term of the form

$$\widehat{K}_{ij} = - \, \zeta_{ij} (f_i - f_{ij}^R). \tag{13}$$

Here, ζ_{ij} is an effective collision frequency of a particle of species i with particles of species j. It has the general property $n_i \zeta_{ij} = n_j \zeta_{ji}$. Also, f_{ij}^R is a reference distribution function whose functional dependence on the velocity is assumed. It contains position- and time-dependent fields that are determined by requiring $\widehat{K}_{ij}$ to keep some of the main properties of the Boltzmann operator.

The original form proposed by Gross and Krook[2] for f_{ij}^R is

$$f_{ij}^R = n_i (m_i/2\pi k_B T_{ij})^{3/2}$$

$$\times \exp[- (m_i/2k_B T_{ij})(\mathbf{v} - \mathbf{u}_{ij})^2], \tag{14}$$

where $\mathbf{u}_{ij}$ and T_{ij} are the above-mentioned fields. For the case of a disparate-mass binary mixture, some authors[3–5] have used linearizations of (14) about the local equilibrium distribution function of species i.

The collision term (13) with f_{ij}^R given by Eq. (14) can be made to satisfy the conservation laws, but it has the following shortcoming. When a system of mechanically identical particles is considered, the total distribution function f, as defined by Eq. (8), does not obey a closed equation. This is due to the highly nonlinear character of f_{ij}^R in Eq. (14). Although the same limitation is present in the forms proposed in Refs. 3–5, it is not relevant as long as some limit of disparate masses is considered.

In order to avoid the above difficulty, we propose for f_{ij}^R the form

$$f_{ij}^R = n_i (m_i/2\pi k_B T)^{3/2}$$

$$\times \exp(- m_i V^2/2k_B T)(1 + A_{ij} + \mathbf{B}_{ij} \cdot \mathbf{V} + C_{ij} V^2), \tag{15}$$

where $\mathbf{V} \equiv \mathbf{v} - \mathbf{u}$, and A_{ij}, $\mathbf{B}_{ij}$, and C_{ij} are parameters to be determined later. This expression has the same structure of some kind of linearization about a local equilibrium characterized by the temperature and the flow velocity of the whole system. In this sense, $\widehat{K}_{ij}$ now depends on the state of the system and not only on the species i and j. The physical picture is that the main global effect of the collisions on particles of species i is to produce a tendency toward the local equilibrium state defined by the parameters of the mixture. The peculiarities of collisions between two given species are taken into account as a correction through the parameters A_{ij}, $\mathbf{B}_{ij}$, and C_{ij} in Eq. (15). Because of this description of collisions, we do not expect our model to apply to a system composed of very dissimilar particles. In this latter case the effects of different collisions could not be treated in a global way.

In order to specify the model, the $5N^2$ parameters A_{ij}, $\mathbf{B}_{ij}$, and C_{ij} must be fixed. First, as usual,[3–5] we require $\widehat{K}_{ij}$ to satisfy the conservation laws, Eqs. (2). This gives the following $3N^2 + 2N$ relations:

$$A_{ij} = - \, 3(k_B T/m_i) C_{ij}, \tag{16}$$

$$\mathbf{B}_{ij} + \mathbf{B}_{ji} = (1/k_B T) [\, m_i (\mathbf{u}_i - \mathbf{u}) + m_j (\mathbf{u}_j - \mathbf{u}) \,], \tag{17}$$

$$\frac{C_{ij}}{m_i} + \frac{C_{ji}}{m_j} = \frac{1}{2k_B T} \left(\frac{T_i - T}{T} + \frac{m_i}{3k_B T} (\mathbf{u}_i - \mathbf{u})^2 \right.$$

$$\left. + \frac{T_j - T}{T} + \frac{m_j}{3k_B T} (\mathbf{u}_j - \mathbf{u})^2 \right). \tag{18}$$

Thus it is seen that the self-collision terms are already univocally identified, but $2N(N - 1)$ additional conditions are needed in order to complete the specification of the cross-collision terms. Before choosing them, we will show that Eqs. (16)–(18) are sufficient to guarantee that our model

reduces to a proper closed kinetic equation when mechanically equivalent particles are considered. In this case, the exact velocity-dependent collision frequencies derived from the Boltzmann equation have the property

$$\sum_j \zeta_{ij} = \zeta \tag{19}$$

for any species i. This equation defines the collision frequency of the system ζ, and holds for any interaction potential. We want the effective collision frequencies of our model to keep the above property. This implies that either ζ_{ij} is temperature independent or that it depends only on the mixture temperature T. The former case corresponds to Maxwell molecules, while the latter is in the spirit of our approximation as discussed immediately after Eq. (15).

By adding the kinetic equations for all species, and using the relations (16)–(18) and the property (19), one easily obtains

$$\frac{\partial}{\partial t} f + \mathbf{v}\cdot\nabla f = -\zeta(f - f^{\text{LE}}), \tag{20}$$

where f is the distribution function defined by Eq. (8) and f^{LE} is the local equilibrium distribution function:

$$f^{\text{LE}} = n(m/2\pi k_B T)^{3/2} \exp(-mV^2/2k_B T). \tag{21}$$

Equation (20) is the usual BGK kinetic equation.[1] Therefore our model can be considered as a consistent extension to a multicomponent system of the BGK equation.

As mentioned above, we still have $2N(N-1)$ free parameters. Following other authors,[3–5] we require the collisional transfer of momentum and energy to be the same as that of the Boltzmann equation for Maxwell molecules. Therefore, according to Eqs. (10) and (11), we impose the conditions

$$\int d\mathbf{v}\, m_i \mathbf{v}\, \hat{K}_{ij} = -\zeta_{ij} \frac{m_i m_j}{m_i + m_j} n_i (\mathbf{u}_i - \mathbf{u}_j), \tag{22}$$

$$\int d\mathbf{v}\, \frac{1}{2} m_i (\mathbf{v} - \mathbf{u}_i)^2 \hat{K}_{ij}$$

$$= -\zeta_{ij} \frac{m_i m_j}{(m_i + m_j)^2} n_i$$

$$\times [3k_B(T_i - T_j) - m_j(\mathbf{u}_i - \mathbf{u}_j)^2], \tag{23}$$

where the Boltzmann collision frequency ν_{ij} has been replaced by the effective collision frequency ζ_{ij}. Equations (22) and (23) give

$$\mathbf{B}_{ij} = (m_i/k_B T)(\mathbf{u}_{ij} - \mathbf{u}), \tag{24}$$

$$C_{ij} = \frac{m_i}{2k_B T}\left(\frac{T_{ij} - T}{T} + \frac{m_i}{3k_B T}(\mathbf{u}_{ij} - \mathbf{u})^2\right). \tag{25}$$

In these expressions,

$$\mathbf{u}_{ij} = (m_i \mathbf{u}_i + m_j \mathbf{u}_j)/(m_i + m_j), \tag{26}$$

$$T_{ij} = T_i + 2[m_i m_j/(m_i + m_j)^2][(T_j - T_i)$$

$$+ (m_j/6k_B)(\mathbf{u}_i - \mathbf{u}_j)^2]. \tag{27}$$

It is worth noting that these are the same as those used by other authors in models based on Eq. (14).[3–5] In summary, our model is defined by the set of coupled equations

$$\frac{\partial}{\partial t} f_i + \mathbf{v}\cdot\nabla f_i = -\sum_{j=1}^{N} \zeta_{ij}(f_i - f_{ij}^R), \tag{28}$$

with f_{ij}^R given by Eqs. (15), (16), (24), and (25).

IV. TRANSPORT PROPERTIES

As an application of the model proposed in the previous section, we are going to study the transport properties in the first Chapman–Enskog approximation. Following the general method,[6] we expand around the local equilibrium of the mixture:

$$f_i = \sum_{l=0}^{\infty} f_i^{(l)}, \tag{29}$$

where

$$f_i^{(0)} = n_i(m_i/2\pi k_B T)^{3/2} \exp(-m_i V^2/2k_B T). \tag{30}$$

A standard calculation yields, for the first-order correction,

$$-\sum_{j=1}^{N} \zeta_{ij} \left\{ f_i^{(1)} - f_i^{(0)} \left[\frac{m_i}{k_B T} \mathbf{V}\cdot(\mathbf{u}_{ij} - \mathbf{u}) \right.\right.$$

$$\left.\left. + \left(\frac{m_i V^2}{2k_B T} - \frac{3}{2}\right)\frac{T_{ij} - T}{T} \right] \right\}$$

$$= f_i^{(0)} \left[\left(\frac{m_i V^2}{2k_B T} - \frac{5}{2}\right)\mathbf{V}\cdot\frac{\nabla T}{T} + \frac{m_i}{k_B T}\left(\mathbf{V}\mathbf{V} - \frac{V^2}{3}\mathbf{I}\right)\right.$$

$$\left. :\nabla\mathbf{u} + \frac{n}{n_i}\mathbf{V}\cdot\mathbf{d}_i \right], \tag{31}$$

where $\mathbf{I}$ is the unit tensor and

$$\mathbf{d}_i = \frac{n_i}{n}\nabla\ln(n_i k_B T) - \frac{\rho_i}{\rho}\nabla\ln(nk_B T)$$

$$= \frac{\rho_i}{nk_B T}\sum_{j=1}^{N}\left(\delta_{ij} - \frac{\rho_j}{\rho}\right)(\nabla\mu_j)_T. \tag{32}$$

Here, we have introduced the chemical potential (per unit mass) μ_i defined by[8]

$$\mu_i = \frac{k_B T}{m_i}\left(\ln n_i - \frac{3}{2}\ln\frac{2k_B T}{m_i}\right). \tag{33}$$

Upon writing Eq. (31), we have neglected a term proportional to $(\mathbf{u}_{ij} - \mathbf{u})^2$, since $f_i^{(0)}$ gives $\mathbf{u}_i = \mathbf{u}$ and therefore $(\mathbf{u}_i - \mathbf{u})$ is at least of first order. In fact, it is easy to show that $T_{ij} - T$ can also be neglected to first order. Multiplication of Eq. (31) by V^2 and integration give

$$\sum_{j=1}^{N} \zeta_{ij} \frac{m_j}{(m_i + m_j)^2}(T_j - T_i) = 0, \tag{34}$$

whose solution is $T_i = T_j$ for all i, j. Therefore Eq. (7) implies that, to first order, $T_i = T$ for all i.

Now, we are going to use Eqs. (30) and (31) to compute the fluxes in the system. As usual, we define the mass flux of species i, the pressure tensor, and the heat flux by

$$\mathbf{J}_i = \int d\mathbf{v}\, m_i \mathbf{V} f_i$$

$$= \rho_i(\mathbf{u}_i - \mathbf{u}), \tag{35}$$

$$\mathbf{P} = \sum_i \int d\mathbf{v}\, m_i \mathbf{V}\mathbf{V} f_i, \tag{36}$$

$$\mathbf{J}_q = \sum_i \int d\mathbf{v} \frac{1}{2} m_i \, V^2 \mathbf{V} f_i, \tag{37}$$

respectively. From Eqs. (30) and (31) we easily obtain

$$\sum_{j=1}^{N} \zeta_{ij} \frac{m_i}{m_i + m_j} \left(\mathbf{J}_i - \frac{\rho_i}{\rho_j} \mathbf{J}_j \right)$$

$$= -\rho_i \sum_{j=1}^{N} \left(\delta_{ij} - \frac{\rho_j}{\rho} \right) (\nabla \mu_j)_T, \tag{38}$$

$$\mathsf{P} = nk_B T \mathsf{I} - \eta [\nabla \mathbf{u} + (\nabla \mathbf{u})^+ - \tfrac{2}{3} (\nabla \cdot \mathbf{u}) \mathsf{I}], \tag{39}$$

$$\mathbf{J}_q = \frac{5}{2} k_B T \sum_{i=1}^{N} \frac{\mathbf{J}_i}{m_i} - \lambda \nabla T. \tag{40}$$

In the last two equations, we have introduced the shear viscosity coefficient

$$\eta = k_B T \sum_{i=1}^{N} \frac{n_i}{\zeta_i}, \tag{41}$$

and the thermal conductivity coefficient

$$\lambda = \frac{5}{2} k_B^2 T \sum_{i=1}^{N} \frac{n_i}{m_i \, \zeta_i}, \tag{42}$$

where

$$\zeta_i = \sum_{j=1}^{N} \zeta_{ij} \tag{43}$$

is the total collision frequency for particles of species i. The linear set of equations (38) must be solved subject to the constraint

$$\sum_{i=1}^{N} \mathbf{J}_i = 0, \tag{44}$$

which follows from the definition (35). By taking this into account, Eqs. (38) can be rewritten as

$$\sum_{j=1}^{N} \Lambda_{ij} \mathbf{J}_j = \sum_{j=1}^{N} \Omega_{ij} (\nabla \mu_j)_T, \tag{45}$$

where

$$\Lambda_{ij} = \begin{cases} 0, & i = j, \\ \dfrac{1}{\rho_j} \zeta_{ij} \dfrac{m_j}{m_i + m_j} + \dfrac{1}{\rho_i} \sum_{k \neq i}^{N} \zeta_{ik} \dfrac{m_k}{m_i + m_k}, & i \neq j, \end{cases} \tag{46}$$

and

$$\Omega_{ij} = \delta_{ij} - \rho_j / \rho. \tag{47}$$

Now, the set of equations (45) can be solved to give

$$\mathbf{J}_i = -\sum_{j=1}^{N} L_{ij} \left(\frac{\nabla \mu_j}{T} \right)_T, \tag{48}$$

with the matrix of transport coefficients L_{ij} being

$$L_{ij} = -T \sum_{k=1}^{N} (\Lambda^{-1})_{ik} \Omega_{kj}. \tag{49}$$

Equations (39), (40), and (48), with transport coefficients

given by Eqs. (41), (42), and (49) are the constitutive equations to Navier–Stokes order of our model. They have a similar structure to those obtained with the Boltzmann equation for Maxwell molecules.[3] For more general interaction potentials the Boltzmann equation leads to additional crossed contributions to the heat flux (the so-called Dufour effect) and to the mass fluxes (Soret effect).[6,8]

Before closing this section, let us check that our model is consistent with Onsager's reciprocal relations. The general form of the constitutive equations to Navier–Stokes order is[8]

$$\mathbf{J}_i = -L_{iq} \frac{\nabla T}{T^2} - \sum_j L_{ij} \left(\frac{\nabla \mu_j}{T} \right)_T, \tag{50}$$

$$\mathbf{J}_q' \equiv \mathbf{J}_q - \frac{5}{2} k_B T \sum_i \frac{\mathbf{J}_i}{m_i}$$

$$= -L_{qq} \frac{\nabla T}{T^2} - \sum_i L_{qi} \left(\frac{\nabla \mu_i}{T} \right)_T. \tag{51}$$

Onsager's relations state $L_{iq} = L_{qi}, L_{ij} = L_{ji}$, whereas in our case, $L_{iq} = L_{qi} = 0$. Besides, from Eqs. (46) and (47) it is easily seen that $\Omega \Lambda^+ = \Lambda \Omega^+$, and then from the definition (49) one obtains $L_{ij} = L_{ji}$.

V. CONCLUSIONS

In this paper we have proposed a kinetic model for a multicomponent gas mixture that is an extension of the BGK kinetic equation for a single gas. The model is expected to be suitable for systems of like particles, in contrast to the results of some previous works. The proposed set of equations keeps the main properties of the Boltzmann description. In particular, Onsager's reciprocal relations are verified. Also the validity of the model is not restricted to near-equilibrium states, and therefore it may be useful to study general transport properties. Work is now in progress to extend to mixtures some recent results for monocomponent systems.[9]

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