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Elemental transport coefficients in viscous plasma flows near local thermodynamic equilibrium

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We propose a convenient formulation of elemental transport coefficients in chemically reacting and plasma flows locally approaching thermodynamic equilibrium. A set of transport coefficients for elemental diffusion velocities, heat flux, and electric current is introduced. These coefficients relate the transport fluxes with the electric field and with the spatial gradients of elemental fractions, pressure, and temperature. The proposed formalism based on chemical elements and fully symmetric with the classical transport theory based on chemical species, is particularly suitable to model mixing and demixing phenomena due to diffusion of chemical elements. The aim of this work is threefold: to define a simple and rigorous framework suitable for numerical implementation, to allow order of magnitude estimations and qualitative predictions of elemental transport phenomena, and to gain a deeper insight into the physics of chemically reacting flows near local equilibrium.

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I. INTRODUCTION

Extensive interest in the mathematical modeling of chemically reacting mixtures has grown significantly over the past decades. The subject is indeed related to a vast amount of applications such as hypersonic flows, combustion problems, plasma torches, and electric plasma thrusters.

High-temperature gases are made of several chemical species, each of them behaving with good approximation as a thermally perfect gas. Under strong nonequilibrium conditions (SNE), such mixtures can be described as a continuum governed by an extended Navier-Stokes system [1] including global continuity, momentum and total-energy equations, a continuity equation for each chemical species accounting for finite-rate chemistry, and an energy equation for each internal energy mode.

This formalism has two drawbacks. The computational complexity is considerable due to the large number of equations and to the presence stiff source terms in the species and energy equations; reaction rates and energy relaxation rates are affected by considerable uncertainties.

In many practical circumstances, the gas mixture locally approaches thermodynamic equilibrium (intended as the combination of thermal equilibrium and chemical equilibrium). While an inviscid gas can attain local thermodynamic equilibrium, a viscous flow always remains in nonequilibrium due to the dissipative effects. Therefore, in near-equilibrium viscous flows we deal with weak deviations from equilibrium or weak nonequilibrium (WNE). The flow classification as WNE and SNE is widely used in the modern kinetic theory [2–4] (the notations SNE and WNE were introduced by Brun [2]). This subdivision is based on the relations between the characteristic times of collisional processes and the macroscopic flow time.

In WNE conditions, species and internal energy modes equations can be discarded; only the global energy equation should be retained together with global continuity and momentum. In the Euler approximation of an inviscid nonconducting flow, the chemical composition is calculated from an algebraic system [4,5] which requires the knowledge of the local pressure, temperature, and elemental fractions. In this case, the elemental fractions remain constant along a trajectory. In the viscous gas approximation, we should account for mixing and demixing phenomena and therefore solve, for each element, a continuity equation containing the corresponding diffusion velocity [4,6,7]. In practical implementations, mixing and demixing are often neglected and hence the elemental fractions are assumed to be constant even in viscous flow regimes. A constant elemental fraction is a reasonable approximation for high-speed flows with uniform upstream composition. In low speed or mixing regions, when transport phenomena such as mass diffusion become important [8], mixing and demixing should be taken into account.

The extended equilibrium formalism suggested in the present paper takes into account mixing and demixing and, at the same time, overcomes the two drawbacks previously mentioned: the number of equations is reasonably low and the source terms disappear together with the related uncertainties.

The transport terms appearing in the WNE governing equations are element diffusion velocities, heat flux, electric current, and viscous stress tensor. In the recent years, several methods were proposed to calculate these quantities in a manner which is fully consistent with the WNE formalism. We provide here a brief overview of the major findings; for a detailed literature review, the reader should refer to [9,10].

In the SNE case, the transport terms, with the exception of the viscous stress tensor, are related to the gradients of pressure, temperature, and species molar fractions through transport coefficients. In the WNE case, a description of the flow is provided by another set of macroscopic parameters, namely, the number densities of elements appear in the gov-

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erning equations as independent variables rather than the number densities of chemical species. Consequently, the transport terms should be associated to the gradients of number densities of elements instead of species.

A rigorous kinetic formalism for the WNE transport properties was developed by Rydalevskaya and co-workers [4,7]. In these studies, the elemental and species diffusion velocities and the heat flux were expressed in terms of the gradients of temperature, total number density, and number densities of elements; new diffusion and thermal diffusion coefficients for elements were introduced. Later on, Ern and Giovangigli [6] using a similar approach suggested a formulation relating the transport terms with the gradients of pressure, temperature, and molar fractions of chemical elements. In their work Ern and Giovangigli introduced the coefficients for elemental diffusion velocities; an analogous formulation for the heat flux and electric current was not proposed. A few years before, a simplified and physically appealing version of elemental diffusion coefficients was given by Murphy [11–13]; however Murphy's work was limited to the special case of two homonuclear gases and a proper formulation for the heat flux was not included.

Both, Murphy before and Ern and Giovangigli later, introduced certain quantities named here as *chemical derivatives*. Chemical derivatives provide a measure of the change in mixture composition with respect to a variation in temperature, pressure, or elemental fractions [14]. In the two aforementioned works, the calculation of these quantities was not explicitly addressed. In Murphy's work, the chemical derivatives are probably calculated numerically by finite differences. This procedure is computationally expensive and prone to numerical error since it requires evaluating several times the mixture composition. Ern and Giovangigli suggested to calculate the chemical derivatives by solving a set of linear systems; however details of the procedure are not provided.

More recently, Rini [9,10] *et al.* derived a complete set of elemental transport coefficients without using chemical derivatives. Differently from the previous works, elemental mass fraction gradients were used instead of molar fraction gradients. This method was conceptually new; however the mathematical procedure adopted is lengthy and the physical interpretation of this formulation is not straightforward.

In a recent publication [14], a new technique to calculate the chemical derivatives using a fully analytical method was introduced. This technique strongly reduces the computational effort and improves the calculation accuracy. Starting from these findings, the present research is aimed to simplify and rearrange in a complete form the general framework of transport properties in WNE reacting flows. The underlying physics we propose is identical to the formulation of Ern and Giovangigli which is extended to include also the heat flux vector and electric current. Moreover, we introduce a formalism for elemental transport coefficients which is fully symmetric with the one used by the transport theory in the SNE case [3] or in the case of frozen chemical reactions [15], when molar (or mass) fractions of chemical species are considered as macroscopic variables.

The reduction to elemental diffusion coefficients is applied to the symmetric formulation of species diffusion coefficients (Waldmann [16], Waldmann and Trübenbacher [17], Van de Ree [18], Curtiss [19], and Ferziger and Kaper [15]). An equivalent approach applies to the asymmetric formulation (Hirschfelder *et al.* [20] and Chapman and Cowling [21]).

II. GAS MIXTURE PROPERTIES

This section is dedicated to summarize some properties which characterize a perfect gas made of several chemical species. To make the exposition easier, we can use as an example a simple mixture of carbon and oxygen with a set of chemical species given by $\{C,O,CO_2,CO,O_2\}$. The total number of species is n_s. All the quantities related to a given species are labeled using roman subscripts i,j,k. Each species is obtained by combining n_e chemical elements which, for this particular example, are {C, O}. Elemental properties are identified by the Greek indices α,β,γ. We also define a chemical matrix whose elements $\phi_{\alpha i}$ indicate the number of particles of element α contained in species i, for example, $\phi_{OO_2}=2$, $\phi_{OC}=0$, and $\phi_{CC}=1$.

A. Molar and mass fractions

The chemical composition of a mixture of perfect gases is usually defined by giving species molar fractions x_i or mass fractions y_i. Species molar fractions represent the ratio between the number density of a given species n_i and the total number density of the mixture $n=\Sigma_i n_i$. Analogously, species mass fractions are defined as the ratio between the partial density of a given species ρ_i and the total density of the mixture $\rho=\Sigma_i\rho_i$. By definition, both quantities satisfy the constraints $\Sigma_i x_i=1$ and $\Sigma_i y_i=1$.

Molar and mass fractions of elements are defined in analogy with chemical species. Element molar fractions represent the ratio between the number density of a given element $n_\alpha=\Sigma_i\phi_{\alpha i}n_i$ and the total number density of elements in the mixture $\Sigma_\alpha n_\alpha$. The same definition applies to element mass fractions when the appropriate partial densities $\rho_\alpha=\Sigma_i\phi_{\alpha i}(M_\alpha/M_i)\rho_i$ are considered. Here M_i and M_α are the molar masses of chemical species and chemical elements, respectively. From the definition, element and species fractions are related as

$$x_\alpha=\frac{\sum_i \phi_{\alpha i}x_i}{\sum_{\beta,i}\phi_{\beta i}x_i},\qquad y_\alpha=\sum_i \phi_{\alpha i}\frac{M_\alpha}{M_i}y_i. \tag{1}$$

Both these quantities are subjected to the usual constraints $\Sigma_\alpha x_\alpha=1$ and $\Sigma_\alpha y_\alpha=1$. Relations similar to those relative to chemical species link element molar and mass fractions

$$x_\alpha=\frac{y_\alpha/M_\alpha}{\sum_\beta y_\beta/M_\beta},\qquad y_\alpha=\frac{x_\alpha M_\alpha}{\sum_\beta x_\beta M_\beta}. \tag{2}$$

B. Chemical derivatives

When a reacting gas mixture is in local thermodynamic equilibrium, its complete thermodynamic state is known if pressure, temperature, and element molar fractions (or mass fractions) are assigned at each point in space. All the remaining mixture properties, including the chemical composition, are functions of these quantities [5]. In this case, the gradients of species molar and mass fractions can be expressed in terms of the gradients of element fractions, pressure, and temperature,

$$\vec{\nabla} x_i = \sum_{\alpha} \frac{\partial x_i}{\partial x_\alpha} \vec{\nabla} x_\alpha + P \frac{\partial x_i}{\partial P} \vec{\nabla} \ln P + T \frac{\partial x_i}{\partial T} \vec{\nabla} \ln T, \tag{3}$$

$$\vec{\nabla} y_i = \sum_{\alpha} \frac{\partial y_i}{\partial y_\alpha} \vec{\nabla} y_\alpha + P \frac{\partial y_i}{\partial P} \vec{\nabla} \ln P + T \frac{\partial y_i}{\partial T} \vec{\nabla} \ln T. \tag{4}$$

The quantities appearing in Eqs. (3) and (4) are named *chemical derivatives* for molar and mass fractions, respectively. In a recent work [14], it was shown how they can be calculated using simple analytical expressions; the order of magnitude of these quantities is $\partial x_i / \partial x_\alpha$, $P \partial x_i / \partial P$, and $T \partial x_i / \partial T = \mathcal{O}(1)$ and $\partial y_i / \partial y_\alpha$, $P \partial y_i / \partial P$, and $T \partial y_i / \partial T = \mathcal{O}(1)$.

III. GOVERNING EQUATIONS

As anticipated in Sec. I, the basic equations of WNE reacting mixtures express the conservation laws of mass, momentum, and energy [22]. If ionization occurs, in addition to the gravitational field $\vec{g}$, the electric field $\vec{E}$ and magnetic field $\vec{B}$ must be accounted among the external forces. These fields' behavior is governed by the Maxwell equations [23]. In the most general case of a WNE flow, the extended Navier-Stokes system reads as

(i) global continuity equation

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{u}) = 0, \tag{5}$$

(ii) momentum equation

$$\frac{\partial \rho \vec{u}}{\partial t} + \vec{\nabla} \cdot (\rho \vec{u} \vec{u}) = - \vec{\nabla} P + \vec{\nabla} \cdot \bar{\bar{\tau}} + \rho \vec{g} + \mathcal{Q} \vec{E} + \vec{J} \wedge \vec{B}, \tag{6}$$

(iii) global energy equation

$$\frac{\partial \rho e_0}{\partial t} + \vec{\nabla} \cdot (\rho e_0 \vec{u}) = - \vec{\nabla} \cdot (P \vec{u}) + \vec{\nabla} \cdot (\bar{\bar{\tau}} \cdot \vec{u}) - \vec{\nabla} \cdot \vec{q} + \rho \vec{u} \cdot \vec{g} + \vec{J} \cdot \vec{E}, \tag{7}$$

(iv) element continuity equations

$$\frac{\partial \rho_\alpha}{\partial t} + \vec{\nabla} \cdot (\rho_\alpha \vec{u}) = - \vec{\nabla} \cdot (\rho_\alpha \vec{v}_\alpha). \tag{8}$$

Some new variables are introduced: $\vec{u}$ and $\vec{v}_\alpha$ are the mean fluid velocity and the elemental diffusion velocities; $\bar{\bar{\tau}}$ is the viscous stress tensor; $\vec{J}$ is the electric current; e_0 is the mixture total energy per unit mass, i.e., the sum of internal and kinetic energy; and $\vec{q}$ is the heat flux. The mixture charge per unit volume is $\mathcal{Q} = ne\Sigma_i x_i q_i$ where e is the elementary charge and q_i is the number of elementary charges contained in a particle of species i. In many practical circumstances, even if ionized, the mixture is quasineutral, therefore $\mathcal{Q}$ is neglected. More details on the derivation of this set of equations and on their field of application are provided in Ref. [24].

IV. TRANSPORT TERMS

This section is dedicated to express the elemental diffusion velocities, heat flux, and electric current as linear functions of the spatial gradients of elemental fractions, pressure, and temperature in addition to the electric field. Chemical derivatives, as derived in Ref. [14], are used. Such a model is valid for the general case of a reacting flow near local equilibrium. The exposition starts summarizing some properties regarding the species diffusion velocities and the related set of diffusion coefficients. Afterward, elemental diffusion coefficients are introduced. Finally, heat flux and electric current are included in the overall framework.

A. Species diffusion velocities

According to the classical transport theory for a nonreacting mixture [15] or for the SNE flow with finite-rate chemistry [3,25], species diffusion velocities are linearly related to the driving forces through the multicomponent diffusion coefficients,

$$\vec{v}_i = - \sum_j D_{ij} \vec{d}_j. \tag{9}$$

The D_{ij} matrix, consistently with the Onsager reciprocal relations, is symmetric and the diagonal terms are positive. The driving forces consist of species molar fractions gradients, pressure gradient, temperature gradient, and electric field,

$$\vec{d}_i = \vec{\nabla} x_i + k_i^P \vec{\nabla} \ln P + k_i^T \vec{\nabla} \ln T + k_i^E \vec{\mathcal{E}}. \tag{10}$$

The quantities $k_i^P = x_i - y_i$ and k_i^T are the pressure and thermal diffusion ratios, respectively; we define as electric diffusion ratios $k_i^E = \Sigma_j (y_i x_j q_j - y_j x_i q_i)$ which are zero in case of nonionized mixture. The electric field is scaled as $\vec{\mathcal{E}} = e\vec{E} / k_B T$ where k_B is the Boltzmann constant. In a thermal equilibrium partially ionized and unmagnetized plasma, the magnetic field does not play any role in species diffusion as well as the gravitational field [24]. Equation (9) may be rearranged as

$$\vec{v}_i = - \sum_j D_{ij} \vec{\nabla} x_j - D_i^P \vec{\nabla} \ln P - D_i^T \vec{\nabla} \ln T - D_i^E \vec{\mathcal{E}}, \tag{11}$$

where the pressure, thermal, and electric diffusion coefficients are

$$D_i^{P/T/E} = \sum_j D_{ij} k_j^{P/T/E}. \tag{12}$$

Sometimes the species diffusion velocities are evaluated from a different approach which makes use of the Stefan-Maxwell equations [8] (δ_{ij} is the Kronecker tensor),

$$\vec{d}_i = \sum_j A_{ij} \vec{v}_j, \tag{13}$$

$$A_{ij} = \frac{x_i x_j}{\mathcal{D}_{ij}\chi_{ij}(\ell)} - \delta_{ij}\sum_k \frac{x_i x_k}{\mathcal{D}_{ik}\chi_{ik}(\ell)}. \tag{14}$$

The Stefan-Maxwell coefficients A_{ij} are symmetric as well as the binary diffusion coefficients $\mathcal{D}_{ij}$ and the factors $\chi_{ij}(\ell)$ taking into account the contribution of Laguerre-Sonine [24] polynomials of order ℓ with $\chi_{ij}(1)=1$.

All these quantities satisfy a set of constraints derived from the mass conservation,

$$\sum_i y_i \vec{v}_i = 0, \tag{15}$$

$$\sum_i \vec{d}_i = 0, \tag{16}$$

$$\sum_i y_i D_{ij} = 0, \tag{17}$$

$$\sum_i y_i D_i^{P/T/E} = 0, \tag{18}$$

$$\sum_i A_{ij} = 0, \tag{19}$$

$$\sum_i k_i^{P/T/E} = 0. \tag{20}$$

Due to Eq. (16), if we replace the multicomponent diffusion coefficients in Eq. (9) with $\hat{D}_{ij}=D_{ij}+\tau_i$ where τ_i are arbitrary quantities, the latter equations remain unchanged. Analogously, because of Eq. (15), if we exchange the Stefan-Maxwell coefficients with $\hat{A}_{ij}=A_{ij}+y_j\tau_i$, Eq. (13) retains its validity.

Relations between multicomponent diffusion coefficients and Stefan-Maxwell coefficients can be retrieved following the approach first proposed by Condiff [26] and detailed later on by Giovangigli [27]:

$$\vec{d}_i = \sum_j A_{ij}\vec{v}_j = -\sum_{k,j} A_{ij}D_{jk}\vec{d}_k = -\sum_{k,j} \hat{A}_{ij}D_{jk}\vec{d}_k = \sum_k (\delta_{ik} - y_i)\vec{d}_k, \tag{21}$$

$$\vec{v}_i = -\sum_j D_{ij}\vec{d}_j = -\sum_{k,j} D_{ij}A_{jk}\vec{v}_k = -\sum_{k,j} \hat{D}_{ij}A_{jk}\vec{v}_k = \sum_k (\delta_{ik} - y_k)\vec{v}_k. \tag{22}$$

The equations we are looking for are

$$\sum_j \hat{A}_{ij}D_{jk} = y_i - \delta_{ik}, \tag{23}$$

$$\sum_j \hat{D}_{ij}A_{jk} = y_k - \delta_{ik}. \tag{24}$$

The linear systems (23) and (24) may be solved by choosing the arbitrary constants τ_i to have $\hat{A}_{ij}=A_{ij}+y_i y_j \Sigma_{h,k}|A_{hk}|$ and $\hat{D}_{ij}=D_{ij}+\Sigma_{h,k}|D_{hk}|/n_s^2$. This choice (as many others) guarantees that the matrices $\hat{A}_{ij}$ and $\hat{D}_{ij}$ are nonsingular and therefore invertible.

Diffusion ratios can be derived from diffusion coefficients using Eqs. (12) and (23),

$$k_i^{P/T/E} = -\sum_j A_{ij}D_j^{P/T/E}. \tag{25}$$

B. Elemental diffusion velocities

Elemental diffusion velocities are traditionally calculated as linear combinations of species diffusion velocities,

$$\vec{v}_\alpha = \sum_i c_{\alpha i}\vec{v}_i, \quad c_{\alpha i} = \phi_{\alpha i}\frac{M_\alpha/y_\alpha}{M_i/y_i}. \tag{26}$$

We propose here an alternative method for evaluating these quantities which is fully symmetric with the formalism adopted for species diffusion velocities and relies on the use of chemical derivatives. Combining Eqs. (9) and (10) with Eqs. (3) and (26) yields,

$$\begin{aligned}\vec{v}_\alpha &= \sum_i c_{\alpha i}\vec{v}_i = -\sum_{i,j} c_{\alpha i}D_{ij}(\vec{\nabla}x_j + k_j^P\vec{\nabla}\ln P + k_j^T\vec{\nabla}\ln T + k_j^E\vec{\mathcal{E}})\\ &= -\sum_{\beta,i,j} c_{\alpha i}D_{ij}\frac{\partial x_j}{\partial x_\beta}\vec{\nabla}x_\beta - \sum_{i,j} c_{\alpha i}D_{ij}\\ &\quad\times\left(P\frac{\partial x_j}{\partial P} + k_j^P\right)\vec{\nabla}\ln P - \sum_{i,j} c_{\alpha i}D_{ij}\\ &\quad\times\left(T\frac{\partial x_j}{\partial T} + k_j^T\right)\vec{\nabla}\ln T - \sum_{i,j} c_{\alpha i}D_{ij}k_j^E\vec{\mathcal{E}}.\end{aligned} \tag{27}$$

Defining the elemental diffusion coefficients as

$$D_{\alpha\beta} = \sum_{i,j} c_{\alpha i}D_{ij}\frac{\partial x_j}{\partial x_\beta}, \tag{28}$$

$$D_\alpha^P = \sum_{i,j} c_{\alpha i}D_{ij}\left(P\frac{\partial x_j}{\partial P} + k_j^P\right), \tag{29}$$

$$D_\alpha^T = \sum_{i,j} c_{\alpha i}D_{ij}\left(T\frac{\partial x_j}{\partial T} + k_j^T\right), \tag{30}$$

$$D_\alpha^E = \sum_{i,j} c_{\alpha i}D_{ij}k_j^E, \tag{31}$$

we reduce Eq. (27) to the well-known form of Eq. (11),

$$\vec{v}_\alpha = -\sum_\beta D_{\alpha\beta}\vec{\nabla}x_\beta - D_\alpha^P\vec{\nabla}\ln P - D_\alpha^T\vec{\nabla}\ln T - D_\alpha^E\vec{\mathcal{E}}. \tag{32}$$

Introducing the elemental Stefan-Maxwell coefficients $A_{\alpha\beta}$, we obtain relations similar to Eqs. (23) and (24),

$$\sum_\beta \hat{A}_{\alpha\beta}D_{\beta\gamma} = y_\alpha - \delta_{\alpha\gamma}, \tag{33}$$

$$\sum_{\beta} \hat{D}_{\alpha\beta} A_{\beta\gamma} = y_\gamma - \delta_{\alpha\gamma}. \tag{34}$$

Equations (33) and (34) are two systems of n_e equations which can be solved choosing $\hat{A}_{\alpha\beta}=A_{\alpha\beta}+y_\beta\tau_\alpha=A_{\alpha\beta}+y_\alpha y_\beta\Sigma_{\gamma,\delta}|A_{\gamma\delta}|$ and $\hat{D}_{\alpha\beta}=D_{\alpha\beta}+\tau_\alpha=D_{\alpha\beta}+\Sigma_{\gamma,\delta}|D_{\gamma\delta}|/n_e^2$ among the many possible choices of the arbitrary quantities τ_α. In opposition to what happens for chemical species, the matrices $D_{\alpha\beta}$ and $A_{\alpha\beta}$ are in general not symmetric except when $n_e=2$.

Multiplying Eq. (32) by $A_{\beta\alpha}$ and summing over the diffusion velocities, we retrieve the Stefan-Maxwell equations for elemental diffusion,

$$\vec{d}_\alpha = \sum_{\beta} A_{\alpha\beta} \vec{v}_\beta. \tag{35}$$

Elemental driving forces should be defined as

$$\vec{d}_\alpha = \vec{\nabla} x_\alpha + k_\alpha^P \vec{\nabla} \ln P + k_\alpha^T \vec{\nabla} \ln T + k_\alpha^E \vec{\mathcal{E}}, \tag{36}$$

where the diffusion ratios are related to the diffusion coefficients in the customary way,

$$k_\alpha^{P/T/E} = -\sum_{\beta} A_{\alpha\beta} D_\beta^{P/T/E}. \tag{37}$$

The inverse relations are

$$D_\alpha^{P/T/E} = \sum_{\beta} D_{\alpha\beta} k_\beta^{P/T/E}. \tag{38}$$

Multiplying Eq. (35) by $D_{\beta\alpha}$, we obtain the classical relation between diffusion velocities and driving forces,

$$\vec{v}_\alpha = -\sum_{\beta} D_{\alpha\beta} \vec{d}_\beta. \tag{39}$$

The usual constraints deriving from mass conservation apply,

$$\sum_{\alpha} y_\alpha \vec{v}_\alpha = 0, \tag{40}$$

$$\sum_{\alpha} \vec{d}_\alpha = 0, \tag{41}$$

$$\sum_{\alpha} y_\alpha D_{\alpha\beta} = 0, \tag{42}$$

$$\sum_{\alpha} y_\alpha D_\alpha^{P/T/E} = 0, \tag{43}$$

$$\sum_{\alpha} A_{\alpha\beta} = 0, \tag{44}$$

$$\sum_{\alpha} k_\alpha^{P/T/E} = 0. \tag{45}$$

The mass conservation constraints are usually enforced while solving for species or elemental diffusion velocities. Indeed, in complex chemistry solvers, it is sometimes the case that all the species mass fractions are considered as independent unknowns. In this situation, the mass conservation constraint must result from the governing equations, the initial conditions, and the boundary conditions. This aspect was investigated by Giovangigli [27] within the chemical species formalism and it is known to provide a stabilizing effect which is beneficial for the solution of the discrete governing equations. An analogous approach can easily be adapted to the elemental coefficients and could be useful for flows at chemical equilibrium when the elemental mass fractions are all considered as independent unknowns.

From an operative point of view, within the chemical species framework, one can choose to calculate independently either the diffusion coefficients D_{ij} or the Stefan-Maxwell coefficients A_{ij}. On the other hand, the elemental diffusion coefficients $D_{\alpha\beta}$ should be first deduced from D_{ij} and then the elemental Stefan-Maxwell coefficients $A_{\alpha\beta}$ can be evaluated (if needed) from $D_{\alpha\beta}$.

As a last remark, we remind that in this section, the elemental diffusion coefficients have been defined starting from the symmetric formulation of the species diffusion coefficients. The extension to the asymmetric coefficients can be performed in an analogous manner and it is left to the reader.

C. Heat flux

The heat flux vector is calculated according to the classical kinetic theory as [15]

$$\vec{q} = \sum_{i} h_i \rho_i \vec{v}_i - \lambda' \vec{\nabla} T - P \sum_{i} D_i^T (\vec{d}_i - k_i^T \vec{\nabla} \ln T). \tag{46}$$

Here h_i are the species enthalpies per unit mass and λ' is the mixture partial thermal conductivity. Replacing the diffusion velocities and driving forces in the above equation, the heat flux becomes a function of the spatial gradients of the elemental fractions, pressure, temperature, and of the electric field,

$$\vec{q} = -\sum_{\alpha} \lambda_\alpha \vec{\nabla} x_\alpha - \lambda^P \vec{\nabla} \ln P - (\lambda^T + \lambda T) \vec{\nabla} \ln T - \lambda^E \vec{\mathcal{E}}. \tag{47}$$

Generalized heat conduction coefficients are defined as

$$\lambda_\alpha = \sum_{i,j} (h_i \rho_i + P k_i^T) D_{ij} \frac{\partial x_j}{\partial x_\alpha}, \tag{48}$$

$$\lambda^P = \sum_{i,j} (h_i \rho_i + P k_i^T) D_{ij} \left(P \frac{\partial x_j}{\partial P} + k_j^P \right), \tag{49}$$

$$\lambda^T = \sum_{i,j} (h_i \rho_i + P k_i^T) D_{ij} \left(T \frac{\partial x_j}{\partial T} + k_j^T \right), \tag{50}$$

$$\lambda^E = \sum_{i,j} (h_i \rho_i + P k_i^T) D_{ij} k_j^E. \tag{51}$$

Equation (47) can be considered as an extension of the well-known formulation proposed by Brokaw and Butler [28,29]. The mixture thermal conductivity is $\lambda=\lambda' - n k_B \Sigma_i D_i^T k_i^T$.

D. Electric current

The electric current vector is given by

$$\vec{J} = ne\sum_{i} x_i q_i(\vec{u} + \vec{v}_i) = \mathcal{Q}\vec{u} - ne\sum_{i,j} x_i q_i D_{ij}\vec{d}_j. \quad (52)$$

Expanding the driving forces in terms of gradients and electric field, we obtain

$$\vec{J} = \mathcal{Q}\vec{u} - \sum_{\alpha} \sigma_\alpha \vec{\nabla} x_\alpha - \sigma^P \vec{\nabla} \ln P - \sigma^T \vec{\nabla} \ln T - \sigma^E \vec{\mathcal{E}}. \quad (53)$$

Generalized electric conduction coefficients are defined as

$$\sigma_\alpha = ne\sum_{i,j} x_i q_i D_{ij} \frac{\partial x_j}{\partial x_\alpha}, \quad (54)$$

$$\sigma^P = ne\sum_{i,j} x_i q_i D_{ij}\left(P\frac{\partial x_j}{\partial P} + k_j^P\right), \quad (55)$$

$$\sigma^T = ne\sum_{i,j} x_i q_i D_{ij}\left(T\frac{\partial x_j}{\partial T} + k_j^T\right), \quad (56)$$

$$\sigma^E = ne\sum_{i,j} x_i q_i D_{ij} k_j^E. \quad (57)$$

In case of quasineutral mixture and in the absence of external fields, it is a common assumption to consider the plasma as current free [10]; in such conditions, an ambipolar electric field is generated by the plasma itself to maintain the quasineutrality,

$$\sigma^E \vec{\mathcal{E}}^{\mathrm{amb}} = -\sum_{\alpha} \sigma_\alpha \vec{\nabla} x_\alpha - \sigma^P \vec{\nabla} \ln P - \sigma^T \vec{\nabla} \ln T. \quad (58)$$

If we substitute $\vec{\mathcal{E}}^{\mathrm{amb}}$ in the driving forces, these become functions only of elemental fractions, pressure, and temperature gradients. As suggested by Murphy, new transport coefficients can be defined for all the transport terms previously considered; however their derivation is trivial and it is a particular case of the present formulation.

E. Mass fractions formulation

In many circumstances, such as the numerical solution of the flow governing equations, it is practical to express the transport fluxes in terms of elemental mass fraction gradients instead of using molar fractions [9,30]. This is particularly true for the numerical solution of the elemental continuity (8) where the unknown variables are the elemental partial densities. From the first part of Eq. (2), we obtain

$$\vec{\nabla} x_\alpha = \sum_{\beta} \frac{\partial x_\alpha}{\partial y_\beta} \vec{\nabla} y_\beta, \quad (59)$$

$$\frac{\partial x_\alpha}{\partial y_\beta} = \frac{\delta_{\alpha\beta}/M_\alpha - x_\alpha/M_\beta}{\sum_{\gamma} y_\gamma/M_\gamma}. \quad (60)$$

The expressions of the transport terms (elemental diffusion velocities, heat flux, and electric current) are

$$\vec{v}_\alpha = -\sum_{\beta} \tilde{D}_{\alpha\beta} \vec{\nabla} y_\beta - D_\alpha^P \vec{\nabla} \ln P - D_\alpha^T \vec{\nabla} \ln T - D_\alpha^E \vec{\mathcal{E}}, \quad (61)$$

$$\vec{q} = -\sum_{\beta} \tilde{\lambda}_\beta \vec{\nabla} y_\beta - \lambda^P \vec{\nabla} \ln P - (\lambda^T + \lambda T)\vec{\nabla} \ln T - \lambda^E \vec{\mathcal{E}}, \quad (62)$$

$$\vec{J} = \mathcal{Q}\vec{u} - \sum_{\beta} \tilde{\sigma}_\beta \vec{\nabla} y_\beta - \sigma^P \vec{\nabla} \ln P - \sigma^T \vec{\nabla} \ln T - \sigma^E \vec{\mathcal{E}}. \quad (63)$$

In the above equations, new transport coefficients are used

$$\tilde{D}_{\alpha\beta} = \sum_{\gamma} D_{\alpha\gamma} \frac{\partial x_\gamma}{\partial y_\beta}, \quad (64)$$

$$\tilde{\lambda}_\beta = \sum_{\gamma} \lambda_\gamma \frac{\partial x_\gamma}{\partial y_\beta}, \quad (65)$$

$$\tilde{\sigma}_\beta = \sum_{\gamma} \sigma_\gamma \frac{\partial x_\gamma}{\partial y_\beta}. \quad (66)$$

Analogous expressions hold for elemental Stefan-Maxwell coefficients and diffusion ratios.

F. General considerations

In the present work we consider flows in WNE conditions, i.e., flows approaching local thermodynamic equilibrium. Accordingly, both chemical composition and chemical derivatives used in the relations for the transport coefficients are calculated within the framework of the law of mass action (LMA), which makes it possible to write relations (3) and (4). However, several studies [3,4,31,32] demonstrated that the LMA is not valid when deviations from equilibrium occur. Therefore, even for the WNE case, Eqs. (3) and (4) are valid only in the inviscid flow approximation; whereas in viscous flows, these expressions may include the higher-order gradients of the macroscopic variables.

Nevertheless, the approach suggested in the present study is not in contradiction with the rigorous kinetic theory formulation. Transport terms and transport coefficients, consistently with the philosophy underlying the Chapman-Enskog theory, represent first-order deviations from the flow equations given by a local equilibrium Boltzmann distribution (Euler equations). Indeed, the first-order correction to the distribution function is calculated using the zero-order (equilibrium) distribution and the corresponding Euler equations. Starting from this point, it is easy to show that the chemical derivatives arising in the transport terms should be calculated within the zero-order solution, i.e., on the basis of the LMA.

The only limitation of the above derivation is that while passing from the SNE to WNE descriptions, we neglect the cross sections of chemically reactive collisions in the linearized integral operator. Indeed, the first-order distribution functions in the SNE and WNE cases are found from different integral equations [2,3]. The differential operator in these equations is calculated using the zero-order solution; in this operator the transition from the SNE to WNE case can be

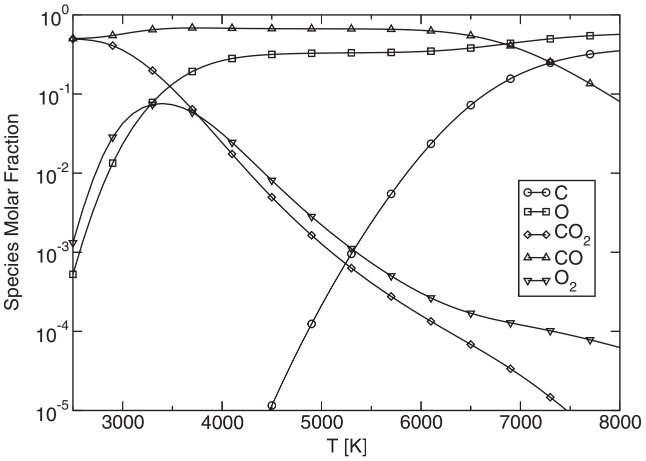

FIG. 1. Equilibrium species molar fractions.

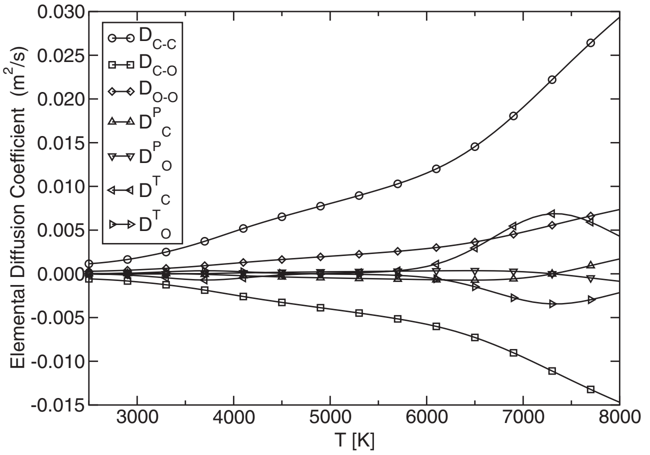

FIG. 2. Elemental diffusion coefficients ($D_{\mathrm{OC}}=D_{\mathrm{CO}}$).

accurately performed by substituting the equilibrium chemical composition and Eq. (3). The integral part of equations includes the linearized integral operator for rapid processes specified by the cross sections of the most frequent collisions. In the SNE case, the most frequent collisions do not include those resulting in chemical reactions (since chemical reactions occur on the gas-dynamic time scale). In the WNE case, all collisional processes are assumed to be rapid. Therefore, the transition between the SNE and WNE cases can be carried out only if we neglect the cross sections of chemically reactive collisions in the integral operator. The intuitive approach suggested above is implicitly based on this assumption. This, however, essentially does not reduce the accuracy of the proposed relations since the transport coefficients are specified mainly by the cross sections of elastic collisions, whereas the contribution of those of inelastic collisions (excepting for some particular polar gases) is found to be weak (see, for instance, discussion in Refs. [3,15]). Moreover, all reliable data on the collision integrals used in practical calculations are obtained neglecting inelastic collisions.

Finally, although the method suggested in the present study is not completely rigorous, it provides an excellent tool to calculate the transport coefficients in the WNE conditions within the accuracy of assumptions commonly used in the kinetic theory.

V. DIMENSIONAL ANALYSIS

Elemental diffusion velocities depend on four different contributions: elemental fractions gradients, pressure gradient, temperature gradient, and normalized electric field. For a given flow, not all these contributions have the same importance. It could happen that one or more of them are negligible with respect to the others. Having a methodology to discern in advance which terms could be neglected represents a useful mean to identify the main contributions to the diffusion velocities and to simplify eventual numerical calculations. This is achieved if we demonstrate that all the elemental diffusion coefficients $D_{\alpha\beta}$, D^P_α, D^T_α, and D^E_α are of the same order of magnitude. In such a case, the terms $\vec{\nabla} x_\alpha$, $\vec{\nabla} \ln P$, $\vec{\nabla} \ln T$, and $\vec{\mathcal{E}}$ could be directly compared to assess if some of them are dominant with respect to the others.

Elemental diffusion coefficients (28)–(31) are different only for the terms containing chemical derivatives and species diffusion ratios: $\partial x_i/\partial x_\alpha$, $P\,\partial x_i/\partial P + k^P_i$, $T\,\partial x_i/\partial T + k^T_i$, and k^E_i. All the chemical derivatives terms have been demonstrated to have the same order of magnitude in Ref. [14], in particular they are on the order of 1. By definition, also the pressure and electric diffusion ratios are on the order of 1. Concerning the thermal diffusion ratios, Furth [33] developed an approximate expression from which it can be deduced that also these quantities are on the order of 1. From these considerations, we conclude that all the elemental diffusion coefficients have the same order of magnitude

Identical considerations apply to the generalized heat conduction coefficients λ_α, λ^P, λ^T, and λ^E in Eq. (47) and to the electric conduction coefficients σ_α, σ^P, σ^T, and σ^E in Eq. (53). Also the term λT can be demonstrated to have the same order of magnitude as the other generalized heat conduction coefficients (note that Lewis number $\lambda/\rho\bar{D}c_p$, where

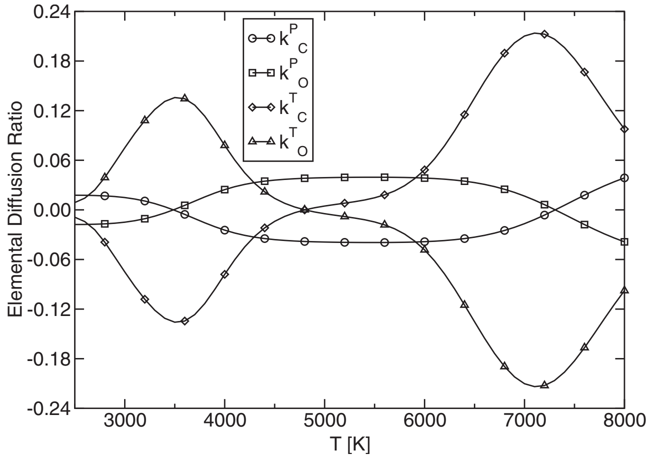

FIG. 3. Elemental diffusion ratios.

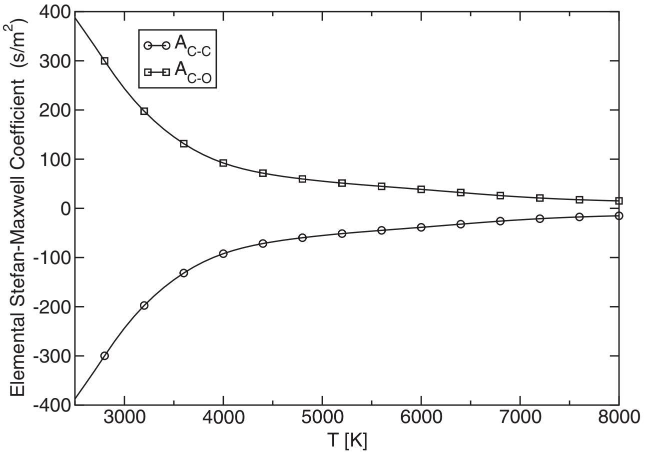

FIG. 4. Elemental Stefan-Maxwell coefficients ($A_{OO}=A_{CC}$ and $A_{OC}=A_{CO}$).

$\bar{D}$ is an average diffusion coefficient and c_p is the mixture specific heat at constant pressure, is always of order unity).

VI. ILLUSTRATIVE EXAMPLE

As a numerical example, the elemental transport coefficients for the mixture considered in Sec. II are calculated. We choose a reference pressure of 1 atm and a temperature range of 2500–8000 K. The temperature is high enough so that chemical reactions significatively affect the composition but ionization remains negligible. The molar fractions of the chemical elements {C, O} are {0.4, 0.6}. In these calculations, the database provided by Burcat and Ruscic [34] is used for the thermodynamic properties of the chemical species. The collision integrals required for the computation of the transport coefficients D_{ij}, D_i^T, and λ' are calculated using the approximate formulae proposed by Bzowski *et al.* [35]. In the recent review by Wright *et al.* [36], this data set is recognized as one of the most reliable for the mixture considered in the present paper.

In Fig. 1 the equilibrium composition in terms of species molar fractions is given. For low temperatures, only carbon monoxide and dioxide are present in a relevant quantity while at the top of the temperature range the atomic species prevail. The presence of molecular oxygen is always scarce. Figures 2–5 show the elemental diffusion coefficients, diffusion ratios, Stephan-Maxwell coefficients, and heat conduction coefficients, respectively. The generalized electric conduction coefficients, as well as the transport coefficients related to the electric field, are zero since the mixture is nonionized. The dimensional analysis proposed in the previous section is supported by the numerical results since, for a given temperature, all the transport coefficient in each figure have the same order of magnitude.

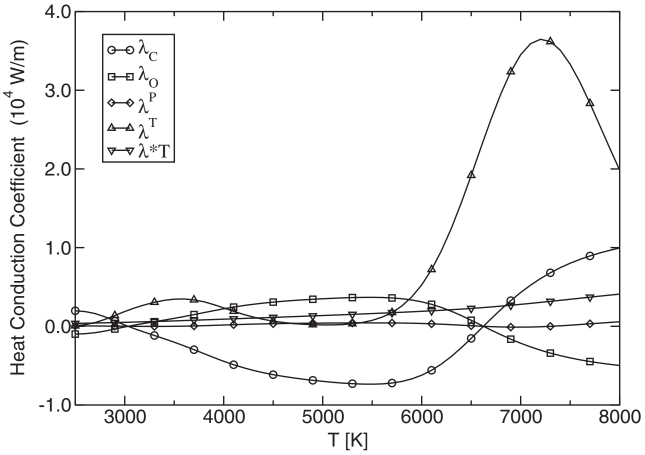

FIG. 5. Generalized heat conduction coefficients.

A curious feature can be observed in Fig. 3. The pressure diffusion ratios k_α^P are zero around 3500 and 7300 K; approximately at the same temperatures, the thermal diffusion ratios k_α^T show a relative maximum or minimum. This behavior is related to the fact that around 3500 K the atomic oxygen outnumbers the carbon dioxide, while around 7300 K the atomic carbon number density becomes greater than the carbon monoxide's. Regarding the generalized heat conduction coefficients in Fig. 5, we note a remarkable increase of λ^T above 6500 K; the contribution related to the pressure gradient remains always small.

VII. CONCLUSIONS

Elemental transport coefficients are extensively used for modeling chemically reacting and plasma flows in which the proximity to the local equilibrium is utilized to combine the ordinary transport coefficients into just a few elemental coefficients.

In a recent work, we introduced a technique to calculate chemical derivatives using a fully analytical method which strongly reduces computational effort and numerical errors. Starting from these findings, the general formalism of elemental transport coefficients for elemental diffusion velocities, heat flux, and electric current is exposed in detail. The resulting theoretical framework is particularly suitable for numerical implementation.

An order-of-magnitude analysis gives the possibility to estimate in advance which are the main drivers of the transport fluxes: gradients in elemental fractions, pressure or temperature gradients, and electric field. A deeper insight into the physics of chemically reacting flows near local equilibrium can be gained by looking only at a reduced number of relevant parameters in the expression of the flow transport properties.

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