

TRANSPORT PROCESSES AND CROSS-COUPLING EFFECTS IN NON-EQUILIBRIUM CHEMICALLY REACTING MIXTURES

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ABSTRACT

Studying of transport processes in non-equilibrium chemically reacting mixtures is of vital importance for aerospace applications, chemical reactor technology and plasma-chemical technologies. Irreversible thermodynamics establishes phenomenological relations for fluxes in terms of generalized thermodynamic forces [1; 2; 3] but cannot give expressions for the coefficients in these relations. On the other hand, kinetic theory of strongly non-equilibrium gases is an efficient tool which allows closing fluid dynamic equations of reacting flows and provides algorithms for the calculation of kinetic coefficients such as viscosity, heat conductivity, multi-component and thermal diffusion, chemical pressure and reaction rate coefficients as functions of collision integrals [4; 5; 6].

For non-equilibrium flows, the generalized Chapman–Enskog formalism is commonly used to develop a closed self-consistent description of fluid dynamics and transport processes [4; 5; 6]. In the case of strong deviation from equilibrium, the main idea is to separate collisional processes to "rapid" and "slow" accordingly to the relation between characteristic times of various internal energy transitions and chemical reactions. The number of slow processes in a system specifies the degree of non-equilibrium and the number of fluid-dynamic variables (and corresponding fluid-dynamic equations) required for the closed flow description. In modern non-equilibrium fluid dynamics, different levels of flow description are used [6]: the conventional one-temperature approach implying weak deviations from thermal equilibrium and highly non-equilibrium chemical reactions; the state-to-state approach considering the internal (vibrational or ro-vibrational) energy exchanges as slow processes and thus suitable for extremely non-equilibrium situations (the price for this is the great number of fluid-dynamic equations which have to be solved for the populations of all internal energy states); and intermediate multi-temperature models suitable for thermal non-equilibrium and not as much detailed as the state-to-state one. In the present work transport properties of thermochemically non-equilibrium reacting mixtures with internal degrees of freedom are discussed in different approaches; the main focus is on generalized fluxes corresponding to scalar thermodynamic forces.

One-temperature approach. Consider the case of strong chemical non-equilibrium and weak thermal non-equilibrium:

$$\tau_{tr} \sim \tau_{int} \ll \tau_{react} \sim \theta, \quad (1)$$

τ_{tr} , τ_{int} are the characteristic times for the relaxation of translational and internal energy, τ_{react} is the characteristic time of chemical reactions, θ is the gas-dynamic time scale. Accurate theoretical models for the transport properties under this relation are developed on the basis of the kinetic theory methods (see [5; 6] and other studies). The fluxes attributed to the tensor and vector thermodynamic forces (shear stress, mass diffusion, heat flux) are widely studied in the literature. On the other hand, the fluxes associated to the scalar forces which in the present case are the chemical reaction affinities and velocity divergence have not received as much attention. The cross coupling between chemical-reaction rates and mean normal stress was brought forth by linear irreversible thermodynamics [1; 2; 7]. In general, linear irreversible thermodynamics deals only with the case of small affinities and cannot give the expressions of the kinetic coefficients in the phenomenological relations; however some results can be obtained in the frame of extended thermodynamics. Thus in [8], the existence of non-equilibrium (dynamic) pressure is indicated. More appropriate methods to develop self-consistent models for scalar fluxes are based on the kinetic theory; they usually apply the generalized Chapman–Enskog formalism [9; 10; 11; 5; 12]; recently the non-equilibrium pressure was found also using the regularized moment method [13].

The detailed one-temperature model of scalar fluxes under condition (1) is developed in [12]. The distribution function is expanded into the series in the small parameter $\varepsilon = \tau_{tr}/\theta$. In the zero-order approximation of the Chapman–Enskog method corresponding to the inviscid (Euler) flow equations, the distribution function is the Maxwell–Boltzmann one, and the stress tensor \mathbf{P} becomes diagonal

$$\mathbf{P}^{(0)} = -p\mathbf{I}. \quad (2)$$

Here \mathbf{I} is the unit tensor and p is the thermodynamic (hydrostatic) pressure. The rate of reaction r , $\dot{\xi}_r$, in the zero-order approximation is given by

$$\dot{\xi}_r^{(0)} = \omega_r k_{f,r}^{(0)} \prod_{c=1}^L \left(\frac{\rho_c}{M_c} \right)^{\nu_{rc}^{(r)}}, \quad (3)$$

where ρ_c is the density of species c , L is the number of chemical species in a mixture, M_c is the molecular weight, $\nu_{rc}^{(r)}$ are stoichiometric coefficients of reagents, $k_{f,r}^{(0)}$ is the zero-order forward reaction rate coefficient. The chemical-reaction characteristic

$$\omega_r = 1 - \exp\left(-\frac{\mathcal{A}_r}{R_G T}\right) \quad (4)$$

is associated to the chemical affinity \mathcal{A}_r defined as linear combination of the chemical potentials μ_c . In the last expression, R_G is the universal gas constant, T is the temperature. For instance, the affinity of an exchange reaction is introduced as

$$\mathcal{A}_{r,ex} = \frac{3}{2}kT \ln \frac{m_c m_d}{m_{c'} m_{d'}} + kT \ln \frac{Z_c^{int} Z_d^{int}}{Z_{c'}^{int} Z_{d'}^{int}} - kT \ln \frac{n_c n_d}{n_{c'} n_{d'}} + (\varepsilon_{c'} + \varepsilon_{d'} - \varepsilon_c - \varepsilon_d), \quad (5)$$

k is the Boltzmann constant, m_c is the mass of species c , Z_c^{int} , n_c are the internal partition function and number density of species c , ε_c is its formation energy. Subscripts c , d are related to the reagents whereas c' , d' to the reaction products.

Equation (3) is equivalent to the law of mass action (LMA). Therefore, in the one-temperature approach, LMA is valid in the zero-order approximation of the modified Chapman–Enskog method.

Linear irreversible thermodynamics deals with chemical reactions whose departure from equilibrium is small

$$\left| \frac{\mathcal{A}_r}{RGT} \right| \ll 1, \quad \text{and therefore} \quad \omega_r \approx -\frac{\mathcal{A}_r}{RGT}. \quad (6)$$

According to (3), $\dot{\xi}_r^{(0)}$ represents a linear function of ω_r . In the limit case of near equilibrium we can write

$$\dot{\xi}_r^{(0)} = -l_{rr}^{(0)} \mathcal{A}_r, \quad l_{rr}^{(0)} = l_r^{(0)} = \frac{k_{f,r}^{(0)}}{RGT} \prod_{c=1}^L \left(\frac{\rho_c}{M_c} \right)^{\nu_c^{(r)}}. \quad (7)$$

It is important to emphasize that, in the zero-order approximation, the rate of chemical reaction r depends only on the affinity of the corresponding reaction \mathcal{A}_r and does not depend on the affinities of other reactions. Thus the cross effects between chemical reactions do not manifest in inviscid gas flows. Moreover, it is evident that no connection between stress tensor and reaction rates arises in the zero-order approximation.

In the first-order approximation corresponding to the viscous (Navier–Stokes) fluid dynamic equations, the stress tensor is obtained as [12]

$$\mathbf{P} = -p\mathbf{I} - \mathbf{P}^{(1)}. \quad (8)$$

Denoting with π the sum of the diagonal terms of the stress tensor and after some manipulations, we obtain

$$\mathbf{P} = \pi\mathbf{I} + 2\mu(\nabla\mathbf{v})_s^*. \quad (9)$$

The traceless symmetric part of the stress tensor includes the shear viscosity coefficient μ , whereas the expressions for the normal mean stress

$$\pi = -p - RGT \sum_r l_{vr} \omega_r + l_{vv} \nabla \cdot \mathbf{v}, \quad (10)$$

contains kinetic coefficients l_{vr} , l_{vv} . The coefficient l_{vv} is the bulk viscosity; the coefficients l_{vr} bring into account the cross effects associated to the chemical reactions that contribute to build up the mean normal stress. Thus the existence of cross-coupling between chemical reactions and mean normal stress predicted by linear irreversible thermodynamics [1; 7] is proven also by kinetic theory.

The expressions of the first-order reaction rates are derived in the form

$$\dot{\xi}_r = \dot{\xi}_r^{(0)} + \dot{\xi}_r^{(1)} \quad (11)$$

where $\dot{\xi}_r^{(0)}$ is the LMA given by (3), and

$$\dot{\xi}_r^{(1)} = RGT \sum_s l_{rs} \omega_s - l_{rv} \nabla \cdot \mathbf{v} \quad (12)$$

with the corresponding kinetic coefficients l_{rv} , l_{rs} . Thus, in viscous gas flows, the reaction rates depend on the velocity divergence $\nabla \cdot \mathbf{v}$ and, therefore, the chemical reactions are influenced by the flow compressibility. Moreover, the existence of cross effects among the chemical reactions themselves becomes evident because the rate of the r th reaction is affected by all the reaction characteristics ω_s . It is also clear that LMA does not hold in the first-order approximation, in the sense that it turns out to be just a partial contribution to the global expression of the reaction rate.

From the kinetic-theory results provided in [12], the Onsager–Casimir reciprocal relations, $l_{rv} = l_{vr}$, $l_{rs} = l_{sr}$ turn out to be in force. These reciprocal relations are valid even for phenomenological relations that are non-linear with respect to the chemical affinities.

In the case of small chemical affinities (6), the expressions of mean normal stress and reaction rates become linear functions of the affinities

$$\pi = -p + \sum_r l_{vr} \mathcal{A}_r + l_{vv} \nabla \cdot \mathbf{v}, \quad (13)$$

$$\dot{\xi}_r = - \sum_s (l_{rr}^{(0)} \delta_{rs} + l_{rs}) \mathcal{A}_s - l_{rv} \nabla \cdot \mathbf{v} \quad (14)$$

in full compliance with linear irreversible thermodynamics.

Algorithms for the calculation of kinetic coefficients l_{vv} , l_{rv} , l_{rs} are developed in [6; 12]. They include reducing integral equations for the distribution function to the sets of algebraic equations and their numerical solution. Coefficients of algebraic equations are the bracket integrals which can be calculated if the cross sections of corresponding collisional processes are known.

To assess the role of the cross-coupling effects, the normal mean stress and the reaction rates have been evaluated in compressive and expanding N_2/N flows. As a compressive flow example, the flow behind a strong shock wave is considered. The initial conditions are: Mach number $M_0 = 15$, $T_0 = 293$ K, $p_0 = 100$ Pa. In Fig. 1a, the hydrostatic pressure p and the normal mean stress π calculated taking into account cross-coupling terms are given as functions of the distance x from the shock front. One can see that the contribution of cross-coupling terms to the normal mean stress is rather weak: taking them into account leads to a slight increase of π compared to the pressure p . The reaction rate $\dot{\xi}^{(0)}$ calculated using the mass action law (in the inviscid flow approximation) and $\dot{\xi}$ taking into account the cross-coupling terms (in viscous flow approximation) are given in Fig. 1b. The difference between $\dot{\xi}$ and $\dot{\xi}^{(0)}$ achieves 80%; the main contribution to this discrepancy is due to dissociation reactions.

A similar study has been performed for an expanding N_2/N flow in a conic nozzle with an angle 21° . The throat conditions are $T_* = 7000$ K, $p_* = 1$ atm. The results are given in Fig. 2. Once again, the effect of cross-coupling terms on the normal mean stress is negligible whereas they influence significantly the reaction rate; in this case the difference is attributed to the recombination reaction. One can see that close to the throat, the cross-coupling terms even modify the qualitative behaviour of the reaction rate altering its sign.

It is worth mentioning that the same cross-coupling terms give different contributions to various fluxes. Strictly speaking, it is necessary to include all the first-order correction terms for a physically consistent and correct simulation of viscous compressible flows. However, as it is shown above, quantitatively physical effects involving symmetric coefficients may not have the same impact, and only numerical simulations based on reliable data would safely establish which terms are important quantitatively and when they can be neglected.

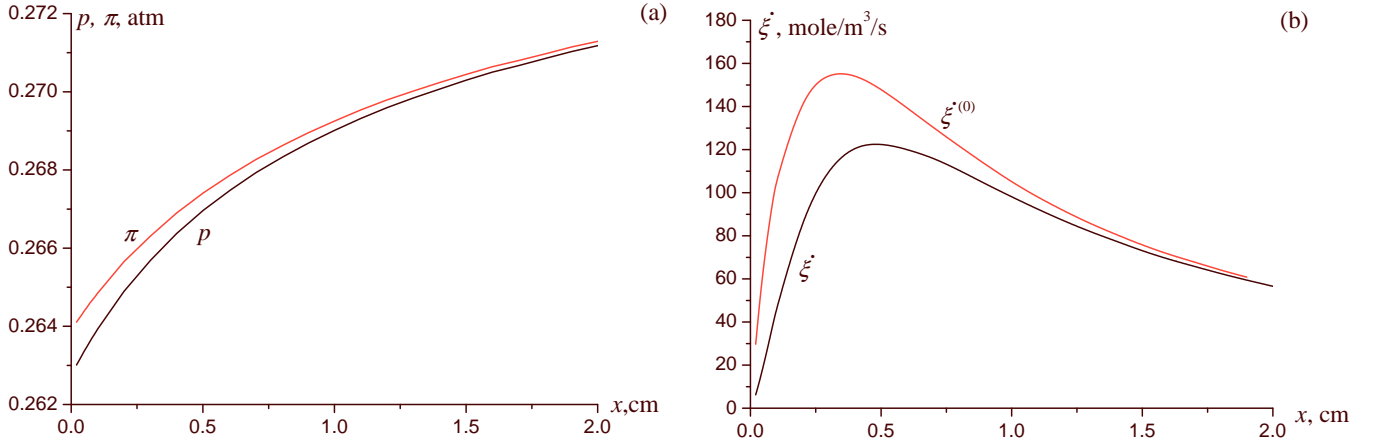


Figure 1: (a): Pressure, p , and normal mean stress, π ; (b): Reaction rates in inviscid, $\xi^{(0)}$, and viscous, ξ , approximations as functions of the distance x from the shock front.

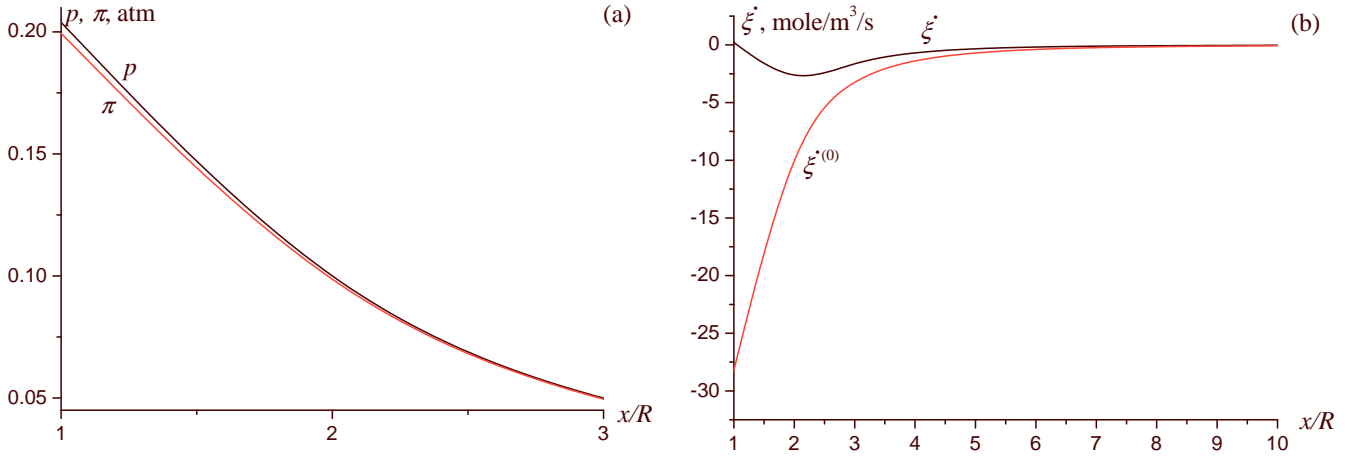


Figure 2: (a): Pressure, p , and normal mean stress, π ; (b): Reaction rates in inviscid, $\xi^{(0)}$, and viscous, ξ , approximations as functions of the distance x/R from the nozzle throat.

Internal energy relaxation. Relaxation of internal energy essentially complicates flow physics and its theoretical description. More sophisticated theoretical models are required for accurate predictions of fluid-dynamic variables and transport properties. The state-to-state model is valid under the following relation between the characteristic times

$$\tau_{tr} \ll \tau_{int} \sim \tau_{react} \sim \theta. \quad (15)$$

It is clear that the number of non-equilibrium processes greatly increases and includes now all internal energy exchanges (or, as is assumed in the majority of state-to-state models, vibrational energy transitions). In the state-to-state transport model, diffusion of all excited states has to be taken into account along with usual mass diffusion and thermal diffusion. The heat flux in this case depends on the temperature gradient as well as on the gradients of all internal state populations [6], and under specific flow conditions, diffusion of internal states contributes significantly to the mass and heat transfer.

Multi-temperature approach is based on the assumption that some kinds of internal energy transitions proceed faster than others. For instance VV (vibration-vibration) transitions are much more probable than VT (vibration-translation) energy exchanges, which justifies such an assumption for the case of vibrational non-equilibrium. This allows introducing temperatures of different internal modes [6]; populations of internal states follow quasi-stationary distributions with corresponding temperatures T_{int} . The set of fluid-dynamic equations is noticeably reduced compared to the state-to-state model and includes relaxation equations for internal energy. On the other hand, the expression for the heat flux becomes more complicated (especially if the level populations are described by non-Boltzmann distributions) and depends on the gradients of internal temperatures of molecular species.

While diffusion and energy fluxes differ essentially in the state-to-state and multi-temperature approaches, the stress tensor and production rates associated with chemical reactions and internal energy can be calculated using the similar strategy as discussed above [14; 15; 16]. As a result, the normal mean stress and rates of reactions/relaxation can be expressed as linear combinations of velocity divergence and affinities of corresponding transitions [14]. The main difference is in the number and type of elementary transitions accounted in the production terms and in the form of affinities. Indeed, the generalized affinities in the case of coupled internal energy relaxation and chemical reactions include the internal energy variation during the collision (in the state-to-state approach) or the difference $T - T_{int}$ (in multi-temperature models). For instance, in the state-to-state approach, the generalized affinity of exchange reaction/vibrational energy transition takes the form [14]

$$\mathcal{A}_{r,ex} = \frac{3}{2}kT \ln \frac{m_c m_d}{m_{c'} m_{d'}} + kT \ln \frac{Z_{ci}^{rot} Z_{dk}^{rot}}{Z_{c'i'}^{rot} Z_{d'k'}^{rot}} - kT \ln \frac{n_{ci} n_{dk}}{n_{c'i'} n_{d'k'}} + (\epsilon_{c'} + \epsilon_{d'} - \epsilon_c - \epsilon_d) + (\epsilon_{i'}^c + \epsilon_{k'}^{d'} - \epsilon_i^c - \epsilon_k^d), \quad (16)$$

where i, k and i', k' are respectively the vibrational states of reagents and products in the reaction/energy transition, Z_{ci}^{rot} is the partition function of rotational degrees of freedom of a molecule c in the vibrational state i , n_{ci} is the population of the vibrational level i of c species, ϵ_i^c is its vibrational energy.

For the multi-temperature model of vibrational relaxation, if n_{ci} are distributed according to the Boltzmann distribution with the vibrational temperature T_v^c , the generalized affinity is given by [14]

$$\mathcal{A}_{r,ex} = \frac{3}{2}kT \ln \frac{m_c m_d}{m_{c'} m_{d'}} + kT \ln \frac{Z_c^{rot} Z_d^{rot}}{Z_{c'}^{rot} Z_{d'}^{rot}} \frac{Z_c^{vibr}(T_{v,c}) Z_d^{vibr}(T_{v,d})}{Z_{c'}^{vibr}(T_{v,c'}) Z_{d'}^{vibr}(T_{v,d'})} - kT \ln \frac{n_c n_d}{n_{c'} n_{d'}} + (\epsilon_{c'} + \epsilon_{d'} - \epsilon_c - \epsilon_d) + (\epsilon_i^{c'} + \epsilon_k^{d'} - \epsilon_i^c - \epsilon_k^d) - kT \left(\frac{\epsilon_i^{c'}}{kT_{v,c'}} + \frac{\epsilon_k^{d'}}{kT_{v,d'}} - \frac{\epsilon_i^c}{kT_{v,c}} - \frac{\epsilon_k^d}{kT_{v,d}} \right), \quad (17)$$

$Z_c^{vibr}(T_{v,c})$ is the non-equilibrium vibrational partition function.

Using the above definitions, in the zero-order approximation one can obtain the rates of chemical reactions and energy transitions in the form similar to (3). It however differs from the LMA in its conventional form since it includes the dependence on the internal states populations and internal temperatures through the values ω_r . In the first-order approximation, the normal mean stress and the rates of reaction/relaxation can be obtained in the symmetric form similar to (10) and (12), and the reciprocal Onsager–Casimir relations can be proven. It is interesting to note that while multi-temperature models are developed in the frame of non-equilibrium thermodynamics, the generalized scalar thermodynamic force related to internal energy relaxation is often introduced as the inverse temperature difference $\frac{1}{T} - \frac{1}{T_{int}}$. Such a choice however does not yield symmetric cross-coupling terms in the normal mean stress and reaction rates and does not guarantee the Onsager–Casimir relations for the kinetic coefficients.

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