C19032 - INFLUENCE OF GAS-MIXTURE COMPRESSIBILITY ON THE REACTION RATES IN CHEMICALLY REACTIVE FLOWS

SUMMARY

This activity is devoted to theoretical modelling of chemical-reaction rates and transport processes in non-equilibrium reacting gas flows and understanding the influence of gas mixture compressibility on the normal mean stress and reaction rates.

We study the chemical-reaction rates and the normal mean stress in one-temperature chemically non-equilibrium viscous flows. The main idea is to prove that, in a viscous compressible flow, the use of the law of mass action (LMA) as well as the Arrhenius law is not correct in the case when chemical reactions proceed on the gas dynamic time scale. Moreover, under the non-equilibrium conditions, the normal mean stress may involve the first-order corrections associated to the velocity divergence and non-equilibrium chemical reactions. These facts were mentioned by several authors in the kinetic theory studies; the cross effects were discovered also in the framework of the linear irreversible thermodynamics. However, no complete theoretical model accounting for the influence of compressibility and the mutual effects of the chemical-reaction rates and normal mean stress was developed until the present time. On the other hand, in the computational fluid dynamics (CFD), the common practice is to use the LMA and the Stokes relation for the simulation of non-equilibrium viscous compressible flows, which is not justified theoretically and can lead to inaccuracy in the predicted values of the flow parameters.

The objectives of the present study were:

- to develop, in the framework of the kinetic theory, a self-consistent theoretical model describing correctly the chemical-reaction rates and the normal mean stress in a non-equilibrium viscous flow;
- to show the correlation between these terms and evaluate the role of compressibility;
- to consider the law of mass action (LMA) in the zero and first-order approximations;
- to obtain the cross-coupling effects between the chemical-reaction rates and the normal mean stress in the symmetric form, and to verify the Onsager-Casimir relations;
- to check the consistency of the results derived using the kinetic theory methods with those obtained in the framework of the linear irreversible thermodynamics;
- to develop the algorithm for the calculation of the first-order corrections to the chemical-reaction rates and the normal mean stress;
- to study the entropy production in a viscous chemically non-equilibrium flow.

Several theoretical models based on the kinetic theory and taking into account the effect of dissipative processes on the reaction rates have already been developed earlier in the literature for both particular reactions [1,2] and general cases [3-7]. As a rule, general models propose specific algorithms for the calculation of the first-order corrections to the reaction-rate coefficients but fail to establish properly the reciprocity relations between normal mean stress and chemical-reaction rates. In the present study we overcame this problem. The details of the suggested formalism are published as ESA Technical report STR-255 [8].

We considered the tempered reaction regime in the frame of the one-temperature approximation. Gas mixtures with bimolecular reactions, dissociation and recombination were studied. A closed set of non-equilibrium gas dynamic equations coupled to the equations of chemical kinetics in a flow was derived, and distribution functions in the zero and first-order approximations and corresponding

expressions for the transport and source terms were obtained. The algorithms for the calculation of the transport and reaction-rate coefficients were elaborated, allowing to reduce integral equations to the linear algebraic equations. An alternative formulation relating the reaction rates and reaction contribution to the normal mean stress to the chemical reaction affinities was proposed, and cross effects between the reaction rates and diagonal elements of the viscous stress tensor were found.

The main results of the present study are the following [8]:

- A kinetic model relating the reaction rates and the normal mean stress to the velocity divergence and chemical reaction affinities is proposed.
- A consistency of the linearized kinetic theory results with those given by linear irreversible thermodynamics is demonstrated.
- It is shown that in the zero-order (inviscid) approximation, the cross effects between the reaction rates and diagonal elements of the viscous stress tensor do not appear.
- In the first-order (viscous) approximation, the rate of each reaction is affected by other reactions and flow compressibility; the law of mass action does not hold for viscous flows.
- The symmetric expressions for the normal mean stress and the reaction rates are derived; these terms are not independent and are specified by the same macroscopic variables. It is found that the normal mean stress is also influenced by both flow compressibility and chemical reactions.
- The reciprocity relations between the kinetic coefficients are verified and it is shown that the generalized Onsager-Casimir relations are valid for the proposed model.
- The entropy production in a viscous flow is evaluated. The non-negativeness of the entropy production associated to the scalar functions is proved for the linear case. For the general case, the scalar entropy production has no sign.

We hope that the results of the present study will encourage the CFD community to use rigorous theoretical models instead of applying simple but doubtful relations for the simulations of non-equilibrium viscous reacting gas flows.

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