On the effect of a chemical reaction on heat conduction and dynamic pressure

G. M. Kremer, Curitiba, Brazil, and I. Müller, Berlin, Germany

Dedicated to Prof. Franz Ziegler on the occasion of his 60th birthday

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Summary. When a chemical reaction occurs in a mixture of gases it facilitates heat conduction and creates a non-equilibrium pressure. Both phenomena are explicitly related to the heat of reaction in this paper.

1 Introduction

Recently the authors [1] have formulated a relativistic theory of a non-diffusive, but chemically reacting binary mixture of ideal gases. In the non-relativistic limit we found that

- The thermal conductivity contains a term proportional to the heat of reaction. This term increases the thermal conductivity by as much as 100% in the temperature range where the reaction occurs; it vanishes at low temperatures where the reaction has not yet started and at high temperatures where the reaction is finished.
- There is a non-zero bulk viscosity due to the heat of reaction. Normally in ideal gases the bulk viscosity is considered to vanish or, if there is one, it is due to internal degrees of freedom, like rotation or vibration. The present observation, that there is a bulk viscosity when a reaction occurs seems to be new.

The referees have pointed out that the paper [1] is hard to read, because of the relativistic setting. And yet the results quoted above are valid for the non-relativistic case and they may be worth knowing for people interested in flames, detonations, explosions, etc. Most such people, however, will miss the results in the format of [1].

Therefore in this paper we confirm and rederive the results in the simplest possible manner: by combining well-known principles of the kinetic theory of gases, of extended thermodynamics and of continuum mechanics.

While the above mentioned result on the bulk viscosity is new, the effect of a chemical reaction on thermal conduction was already known to Nernst [2]. In the early 1950's there were several attempts to explain phenomenon, employing the tools of thermodynamics of irreversible processes, see [3]–[5]. In the argument of these authors diffusion and thermal diffusion play an important role. Contrary to that we show that the effect is present even when diffusion is absent.
2 Balance equations

2.1 Boltzmann equations and generic equations of transfer

The kinetic theory of a binary mixture of gases $\alpha = 1, 2$ describes the state of the mixture by the phase densities $f_\alpha$, such that

$$f_\alpha(x, c_\alpha, t) \, dc_\alpha$$

is the number density of molecules $\alpha$ at $x$ and $t$ with velocities between $c_\alpha$ and $c_\alpha + dc_\alpha$.

The phase densities obey the Boltzmann equations

$$\frac{\partial f_\alpha}{\partial t} + c_\alpha \frac{\partial f_\alpha}{\partial x_i} = S_\alpha,$$

(2.1)

where $S_\alpha$ is due to collisions and reactions. Multiplication by a generic function $\psi_\alpha(x, c_\alpha, t)$ and integration over $c_\alpha$ provides the equations of transfer

$$\frac{\partial}{\partial t} \int \psi_\alpha f_\alpha \, dc_\alpha + \frac{\partial}{\partial x_i} \int \psi_\alpha c_\alpha f_\alpha \, dc_\alpha - \int \left[ \frac{\partial \psi_\alpha}{\partial t} + c_\alpha \frac{\partial \psi_\alpha}{\partial x_i} \right] f_\alpha \, dc_\alpha = \int \psi_\alpha S_\alpha \, dc_\alpha.$$

(2.2)

We allow for a chemical reaction with the stoichiometric coefficients $\gamma_\alpha$ so that the reaction may be written in the schematic form

$$\sum_{\alpha=1}^{2} \gamma_\alpha m_\alpha = 0.$$ (2.3)

Since $m_\alpha$ is the molecular mass, this relation represents not only the reaction formula but also the mass conservation during the reaction.

2.2 Transfer equations for moments

We choose $\psi_\alpha = 1$ and $\psi_\alpha = c_\alpha$ and define the number densities $n_\alpha$ and the (common) velocity $v_i$ of all constituents by

$$n_\alpha = \int f_\alpha \, dc_\alpha \quad \text{and} \quad n_\alpha v_i = \int c_\alpha f_\alpha \, dc_\alpha.$$ (2.4)

Thus insertion of $\psi_\alpha = 1$ into (2.2) provides the balance of particle numbers, viz. - with

$$\dot{\eta}_\alpha + n_\alpha \frac{\partial v_i}{\partial x_i} = \gamma_\alpha l.$$ (2.5)

$l$ is the reaction rate density and $\gamma_\alpha m_\alpha l$ is the mass production of constituent $\alpha$.

It is useful to introduce the relative molecular velocity $C_i^\alpha = c_i^\alpha - v_i$ in order to introduce the non-convective moments with

$$\psi_\alpha = m_\alpha C_i^\alpha C_j^\alpha : \quad \text{pressure tensors } p_{ij}^\alpha = \frac{3}{2} (n_\alpha kT + \pi_\alpha) \delta_{ij} + \rho_{ij}^\alpha$$

$$\psi_\alpha = \frac{m_\alpha}{2} C_\alpha^2 + m_\alpha \varepsilon_\alpha : \quad \text{internal energy densities } \varepsilon_\alpha = \frac{3}{2} (n_\alpha kT + \pi_\alpha) + n_\alpha m_\alpha \varepsilon_\alpha$$

$$= \int m_\alpha C_\alpha^2 + \frac{1}{2} C_\alpha^2 + \varepsilon_\alpha f_\alpha \, dc_\alpha.$$