Kinetic theory analysis of a binary mixture reacting on a surface

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Abstract. A mixture of two rarefied gases is considered between two parallel planes. On one side of the domain evaporation/condensation conditions are imposed, while on the other side accommodation at the temperature of the wall and chemical equilibrium conditions are considered. The small Knudsen number asymptotics of this problem is performed at the formal level, and fluid-dynamic equations are derived and then solved numerically. We discuss the possible appearance of a ghost effect in this situation.

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1 Introduction

Kinetic theory of gases plays an important role in microfluidics, since the mean free path of gas molecules is comparable to the characteristic length in micro-scale systems and thus the gas is not in a local equilibrium state [1–4]. On the other hand, one expects the validity of fluid-dynamic (or macroscopic) approach when the mean free path is much shorter than the characteristic length, i.e., near continuum regime including the continuum (or fluid-dynamic) limit. In general, however, it is not clear from macroscopic or phenomenological considerations what type of fluid-dynamic equations and boundary conditions are appropriate when surface phenomena, such as phase transition and chemical reaction, take place on the boundary. Most of such problems can be solved by considering the continuum limit and its neighborhood on the basis of kinetic theory. In other words, careful asymptotic analyses for small values of the Knudsen number (the ratio of the mean free path to the characteristic length) based on the Boltzmann equation and its kinetic boundary condition [5–9] lead to fluid-dynamic-type equations and their boundary conditions appropriate to the considered physical situations (see [8]). A good example is the fluid-dynamic-type systems for the vapor flows around its condensed phases, on (see [8]). These fluid-dynamic-type systems have been extended to the case where another gas that neither evaporates nor condenses (noncondensable gas) is contained in the domain (e.g., [10–13]). For instance, the behavior of a mixture of vapors and noncondensable gases in the continuum limit has been studied systematically in a one-dimensional setting (that is, for the mixture confined between two parallel planes) in [10,12,13]. It should also be mentioned that a mathematical study of the same setting was carried out recently [14].

In the present paper, we wish to extend somewhat the study in [12,13] by considering the possibility that two gases can react at (part of) the boundary of the domain. We present here the simplest possible case when such a situation occurs. That is, we consider two species $A, B$ of gases evolving in the domain $[0, D] \times \mathbb{R}^2$, which undergo a reversible reaction $A \rightleftharpoons B$ (or $M + A \rightleftharpoons N + B$, where $M, N$ are in excess and are not considered in the modeling), supposed to occur only at the boundary $X_1 = 0$ ($X_2, X_3 \in \mathbb{R}$) and to be instantaneous. After having performed the reaction, the molecules are reflected diffusively (still at $X_1 = 0$). On the other boundary (that is, $X_1 = D$), evaporation/condensation conditions are imposed for both species $A$ and $B$.

We are looking for solutions of the steady Boltzmann equation (including hard-sphere-type collisions for couples of molecules $A - A$, $A - B$ and $B - B$) with the boundary condition described above. The set of kinetic equations (and boundary conditions) modeling the mixture is presented in Section 2 in its original form, and then in Section 3 in non dimensional form. The asymptotic analysis when the Knudsen number tends to 0 is performed in Section 4. We obtain in this way a set of ODEs which models the mixture at the fluid-dynamical level. When the molecules of species $A$ and $B$ have same radius and same mass, this set of ODEs becomes particularly simple and can be solved explicitly. This is done in Section 5. It is however not easy to extend this explicit computation in the more general case when the mass and/or the radius of the molecules of species $A$ and $B$ are different.
Once all the end up with a boundary value problem for two first-order ODEs. The computations describing how to reach this problem are described in Section 6. Section 7 is devoted to the presentation of the numerical procedure and of typical results for the system of ODEs obtained in Section 6. We use for this the database on transport coefficients in binary gas mixtures presented in [15]. We also comment there the appearance of a ghost effect [9] (that does not occur in the case of equal masses and radii). Finally, some concluding remarks are summarized in Section 8.

2 Presentation of the model

We use here the notations of [12] for our presentation of the problem at the kinetic level. We denote by $F^\alpha(X_1, \xi) \geq 0$ (with $\alpha = A$ or $B$) the number density of molecules of species $\alpha$ which at point $X_1 \in [0, D]$ ($D > 0$) have velocity $\xi$. The steady Boltzmann equation for this problem writes

$$\xi_1 \frac{\partial F^\alpha}{\partial X_1} = \sum_{\beta=A,B} J^{\beta\alpha}(F^\beta, F^\alpha), \quad (1)$$

where $J^{\beta\alpha}$ is the collision operator for hard-sphere interactions between molecules of species $\beta, \alpha$:

$$J^{\beta\alpha}(F,G)(X_1, \xi) = \frac{(d^{3\alpha})^2}{2} \times \int_{\omega \in S^2} \int_{\xi \in \mathbb{R}^3} \left( F(X_1, \xi^\beta) G(X_1, \xi^\alpha) - F(X_1, \xi^\alpha) G(X_1, \xi^\beta) \right) \left| \omega \cdot (\xi^\beta - \xi^\alpha) \right| \, d\xi^\beta d\omega, \quad (2)$$

the pre-collisional velocities $\xi_{\beta\alpha}^\alpha$ and $\xi_{\beta\alpha}^\beta$ are given by the formulas

$$\xi_{\beta\alpha}^\beta = \xi + \frac{\mu_{3\alpha}}{m_{\beta}} \left[ \omega \cdot (\xi_{\beta\alpha}^\beta - \xi) \right] \omega, \quad \xi_{\beta\alpha}^\alpha = \xi - \frac{\mu_{3\alpha}}{m_{\beta}} \left[ \omega \cdot (\xi_{\beta\alpha}^\beta - \xi) \right] \omega, \quad (3)$$

where $m_{\alpha}$ is the mass of a molecule of species $\alpha$, and $\mu_{3\alpha} = 2m_{\alpha} + m_{\beta}$ is twice the reduced mass. At last, in (2)

$$d^{3\alpha} = \frac{(d^\alpha + d^\beta)^2}{2},$$

where $d^\alpha$ is the diameter of a molecule of species $\alpha$, is the mean diameter.

Then, we impose on the wall $X_1 = D$ the following evaporation/condensation boundary condition:

$$F^\alpha(D, \xi) = \frac{n_{R}^\alpha}{\sqrt{2 \pi k T_R / m_{\alpha}}} e^{-\frac{m_{\alpha} |\xi|^2}{2k T_R}} \quad \text{when } \xi_1 \leq 0, \quad (4)$$

where $k$ is Boltzmann’s constant, $T_R$ is the temperature of the wall $X_1 = D$, and $n_{R}^\alpha = p_{R}^\alpha / (kT_R)$, where $p_{R}^\alpha$ is the pressure given by the modified Raoult’s law (cf. [12]).

The main novelty of this work is that we impose on the wall $X_1 = 0$ a specific boundary condition, which expresses the fact that through a (infinitely fast) chemical reversible reaction, species $A$ and $B$ are at chemical equilibrium on this wall. Therefore, there exists a fixed number $a \in [0, 1]$ (proportion of molecules of species $A$ at chemical equilibrium given by the mass action law) such that when $\xi_1 > 0$, defining the incoming flux of molecules

$$J = \int_{\xi \in \mathbb{R}^3, \xi_1 < 0} \langle -\xi_1 \rangle [F^A(0, \xi) + F^B(0, \xi)] \, d\xi,$$

one has

$$F^A(0, \xi) = \frac{a}{2\pi} \sqrt{\frac{m^B}{a \sqrt{m^B} + (1-a) \sqrt{m^A}}} \left( \frac{m^A}{kT_L} \right)^2 \cdot \exp \left( -\frac{m^A |\xi|^2}{2kT_L} \right), \quad (5)$$

$$F^B(0, \xi) = \frac{1-a}{2\pi} \sqrt{\frac{m^A}{a \sqrt{m^B} + (1-a) \sqrt{m^A}}} \left( \frac{m^B}{kT_L} \right)^2 \cdot \exp \left( -\frac{m^B |\xi|^2}{2kT_L} \right).$$

Those formulas are best understood in two special cases:

1. When $a = 1$ (resp. $a = 0$), the reaction will in fact become the irreversible reaction $B \rightarrow A$ (resp. $A \rightarrow B$) and only molecules of species $A$ (resp. $B$) are emitted, with the usual law of diffuse reflection.

2. When the masses $m^A$ and $m^B$ are equal, it is easy to see that the proportion of molecules of species $A$ emitted (with any velocity) by the wall is $a$ and corresponds to the proportion of molecules of species $A$ present on the wall.

In this boundary condition, the net flux of molecules across the boundary is zero ($\int_{\xi \in \mathbb{R}^3} \xi [F^A(0, \xi) + F^B(0, \xi)] \, d\xi = 0$) whereas that of the mass does not vanish (except when $m^A = m^B$). Finally, the problem that we consider at the kinetic level is (1)–(5).

3 Non dimensional form of the equations and macroscopic quantities

Introducing (in addition to the parameters already considered) various reference quantities (including the mean free path), we end up with the following non dimensional form of the equation (most of the computations leading to these equations are done in [12]).

The function $f^\alpha(x, \xi)$ is the unknown and depends upon the new variables $x \in [0, 1]$ and $\xi \in \mathbb{R}^3$. It satisfies

$$\xi_1 \frac{\partial f^\alpha}{\partial x_1} = \frac{2}{\sqrt{\pi}} K n^{-1} \sum_{\beta=A,B} K^{\beta\alpha} j^{\beta\alpha} (f^\beta, f^\alpha), \quad (6)$$