

Dissociation and recombination of a diatomic gas in a background medium

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Abstract. We deal with a diatomic gas diffusing in a background medium. The gas is modelled as a mixture made up by atoms and molecules undergoing reactions of dissociation and recombination through a transition state. In the fluid–dynamic regime, two (slightly) different scalings are addressed, that lead to a formal derivation of hydrodynamic equations which are not necessarily of reaction–diffusion type though they both involve diffusive terms in the number densities.

Keywords: Kinetic theory, Chemically reacting mixtures, Dissociation/Recombination processes, Reaction–diffusion equations.

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INTRODUCTION AND KINETIC FRAMEWORK

Reactive flows are receiving increasing attention in the recent scientific literature. Such an interest finds good motivation both in the potential impact on important applications (such as reentry problems, hypersonic flows, atmospheric phenomena, pollutant formation, or chemical reactors) and in the nontrivial mathematical questions that spontaneously arise. A kinetic treatment (mesoscopic level) would be obviously desirable in several respects, but it is immediately realized that any reasonably accurate model is extremely cumbersome to deal with [1]. One of the most useful information that one might hope to extract from kinetic–like equations is a consistent derivation and justification, in some asymptotic limit, of simpler macroscopic equations for hydrodynamic variables (observable fields) to be used for practical applications. This is the problem that will be addressed here, with reference to a kind of chemical reaction that is one of the most common in nature and one of the most difficult to model at the kinetic level, namely dissociations and recombinations for diatomic gases, as they occur in the atmosphere. More specifically, we shall deal with a diatomic gas which does not constitute a closed system, but interacts with the environment in which it is embedded by binary encounters (of the same types as those experienced by gas particles between themselves). Such field particles constitute then a background host medium, to be assumed much denser than the considered gas, in the sense that its evolution is not affected by its interactions with the gas, and is assigned as one of the input data for the problem. We shall assume for simplicity the background to be in homogeneous steady state thermodynamical equilibrium with a Maxwellian distribution function at number density n_0 , mass velocity \mathbf{u}_0 , temperature T_0 . Following a classical model, based on the so–called transition–state theory [2], the diatomic gas is represented as a mixture of three different species: atoms A , stable molecules A_2 , and unstable molecules A_2^* , to be labelled by indices 1, 2, and 3, respectively, and with masses $m_3 = m_2 = 2m_1$. The unstable component disappears at its first interaction, whereas the two stable species may undergo mechanical (elastic) scattering among themselves and with field particles, described in the usual kinetic way in terms of differential cross sections. As for the internal energies of chemical link, species 1 and 2 are endowed with energies 0 and $-Q$ (with $Q > 0$) respectively, whereas for species 3 it will be an additional kinetic variable E , ranging on the positive real axis. Then, according to [3], the overall recombination/dissociation process is described in terms of the following binary irreversible events: *i*) recombination (r): two atoms coalesce to produce an unstable diatomic molecule; *ii*) inelastic scattering (i): an unstable molecule de–excites to its ground–state (stable molecule) by collision against any of the species with indices 0, 1, or 2; *iii*) dissociation (d): stable as well unstable diatomic molecules break down into two atoms, again by collision with any of the species with indices 0, 1, or 2. These interactions are described here in terms of a probabilistic formulation of the relevant collision integrals, by means of the appropriate microscopic collision frequencies ν_{ij}^α and of the associated transition probabilities $\Pi_{ij}^{k,\alpha}$. The superscript $\alpha = r, i, d$ and the subscripts i and j mean that we are referring to an encounter of type α between a particle i and a particle j ; more precisely, $\Pi_{ij}^{k,\alpha}$ represents the probability density that a particle k attains given values of its kinetic variables as a result of a collision of type α between particles i and j with assigned kinetic variables.

Even though giving explicit expressions to such collision kernels is quite a delicate question, it is remarkable that their general structure and conservation properties suffice for achieving most of the results which are aim of the present paper. As for collision frequencies, we shall assume them for simplicity to be constant (a kind of isotropic Maxwellian model for chemical reactions). A Maxwell molecule assumption will be made also for elastic scattering, so that both the total (angle-integrated) collision frequencies ν_{ij}^s and the total collision frequencies for momentum transfer $\bar{\nu}_{ij}^s$ turn out to be constant.

Expressions and properties of the several collision operators have been given elsewhere [3, 4] and will not be shown here for brevity; however, the ones needed in the procedure are recalled whenever convenient for a proper understanding. In particular, the fundamental macroscopic exact transport equations (weak forms of the kinetic equations relevant to the appropriate test functions) read as

$$\frac{\partial \rho}{\partial t} + \nabla_{\mathbf{x}} \cdot (\rho \mathbf{u}) = 0, \quad (1)$$

$$\begin{aligned} \frac{\partial}{\partial t}(\rho \mathbf{u}) + \nabla_{\mathbf{x}} \cdot (\rho \mathbf{u} \otimes \mathbf{u} + \mathbf{P}) = & -\frac{m_1 m_0}{m_1 + m_0} \bar{\nu}_{10}^s n_0 n_1 (\mathbf{u}_1 - \mathbf{u}_0) - \frac{2 m_1 m_0}{2 m_1 + m_0} \bar{\nu}_{20}^s n_0 n_2 (\mathbf{u}_2 - \mathbf{u}_0) \\ & + 2 m_1 \nu_{30}^d \iiint \left[\int \mathbf{v} \Pi_{30}^{1,d}(\mathbf{v}', E; \mathbf{w}' \rightarrow \mathbf{v}) d\mathbf{v} - \mathbf{v}' \right] \varphi_3(\mathbf{v}', E) f_0(\mathbf{w}') dE d\mathbf{v}' d\mathbf{w}' \\ & + 2 m_1 \nu_{20}^d \iiint \left[\int \mathbf{v} \Pi_{20}^{1,d}(\mathbf{v}; \mathbf{w}' \rightarrow \mathbf{v}) d\mathbf{v} - \mathbf{v}' \right] f_2(\mathbf{v}') f_0(\mathbf{w}') d\mathbf{v}' d\mathbf{w}' \end{aligned} \quad (2)$$

$$\begin{aligned} & + 2 m_1 \nu_{30}^i \iiint \left[\int \mathbf{v} \Pi_{30}^{2,i}(\mathbf{v}', E; \mathbf{w}' \rightarrow \mathbf{v}) d\mathbf{v} - \mathbf{v}' \right] \varphi_3(\mathbf{v}', E) f_0(\mathbf{w}') dE d\mathbf{v}' d\mathbf{w}', \\ \frac{\partial \mathcal{E}}{\partial t} + \nabla_{\mathbf{x}} \cdot [\mathcal{E} \mathbf{u} + \mathbf{P} \cdot \mathbf{u} + \mathbf{q}] = & -\frac{m_1 m_0}{(m_1 + m_0)^2} \bar{\nu}_{10}^s n_0 n_1 [3(T_1 - T_0) + (m_1 \mathbf{u}_1 + m_0 \mathbf{u}_0) \cdot (\mathbf{u}_1 - \mathbf{u}_0)] \\ & - \frac{2 m_1 m_0}{(2 m_1 + m_0)^2} \bar{\nu}_{20}^s n_0 n_2 [3(T_2 - T_0) + (2 m_1 \mathbf{u}_2 + m_0 \mathbf{u}_0) \cdot (\mathbf{u}_2 - \mathbf{u}_0)] \\ & + \nu_{30}^d \iiint \left[\int m_1 v^2 \Pi_{30}^{1,d}(\mathbf{v}', E; \mathbf{w}' \rightarrow \mathbf{v}) d\mathbf{v} - (m_1 (v')^2 + E) \right] \varphi_3(\mathbf{v}', E) f_0(\mathbf{w}') dE d\mathbf{v}' d\mathbf{w}' \\ & + \nu_{20}^d \iiint \left[\int m_1 v^2 \Pi_{20}^{1,d}(\mathbf{v}; \mathbf{w}' \rightarrow \mathbf{v}) d\mathbf{v} - (m_1 (v')^2 - Q) \right] f_2(\mathbf{v}') f_0(\mathbf{w}') d\mathbf{v}' d\mathbf{w}' \\ & + \nu_{30}^i \iiint \left[\int (m_1 v^2 - Q) \Pi_{30}^{2,i}(\mathbf{v}', E; \mathbf{w}' \rightarrow \mathbf{v}) d\mathbf{v} - (m_1 (v')^2 + E) \right] \varphi_3(\mathbf{v}', E) f_0(\mathbf{w}') dE d\mathbf{v}' d\mathbf{w}', \end{aligned} \quad (3)$$

where ρ is the mass density and \mathbf{u} the mass velocity of the whole diatomic gas. The symbol \mathbf{P} denotes the pressure tensor, and temperature T follows from the its trace like in a perfect gas. Total internal energy \mathcal{E} and heat flux vector \mathbf{q} collect thermal and chemical contributions as $\mathcal{E} = \frac{1}{2} \rho u^2 + \mathcal{E}_{\text{th}} + \mathcal{E}_{\text{ch}}$ and $\mathbf{q} = \mathbf{q}_{\text{th}} + \mathbf{q}_{\text{ch}}$, where \mathcal{E}_{th} and \mathbf{q}_{th} are the standard values for an inert mixture, and

$$\mathcal{E}_{\text{ch}} = \int \left[\int E \varphi_3(\mathbf{v}, E) dE - Q f_2(\mathbf{v}) \right] d\mathbf{v} \quad \mathbf{q}_{\text{ch}} = \int (\mathbf{v} - \mathbf{u}) \left[\int E \varphi_3(\mathbf{v}, E) dE - Q f_2(\mathbf{v}) \right] d\mathbf{v}.$$

Distribution functions versus the velocity vector \mathbf{v} are denoted by f_i for $i = 1, 2$, whereas φ_3 is used for unstable species to emphasize the presence of an additional kinetic variable.

Having in mind a collision dominated asymptotic limit, we shall proceed to a suitable adimensionalization of independent and dependent variables, measuring lengths in units of a typical macroscopic size L of the problem and assuming microscopic and macroscopic speeds of the same order of magnitude. The scaling will be determined by the dimensionless mean free paths (Knudsen numbers) relevant to the various collision mechanisms considered. Specifically, we analyze the kinetic Boltzmann equations for the distribution functions $f_1(\mathbf{v})$, $f_2(\mathbf{v})$, $\varphi_3(\mathbf{v}, E)$ in dimensionless form. Let us introduce typical values for gas density \bar{n} , for background density \bar{n}_0 , for scattering cross section between species $\bar{\sigma}^s$, for scattering cross section with the background $\bar{\sigma}_0^s$, for chemical cross section

of the unstable species A_2^* , both with other participating species ($\bar{\sigma}^*$) and with field particles ($\bar{\sigma}_0^*$), and finally for chemical cross sections of the stable species, i.e. dissociation cross section, both between species themselves ($\bar{\sigma}^d$) and with the background ($\bar{\sigma}_0^d$), and recombination cross section $\bar{\sigma}^r$. This singles out spontaneously, after some algebra, seven corresponding dimensionless mean free paths appearing downstairs in front of the several collision integrals, that may be listed as $\lambda^s, \lambda_0^s, \lambda^*, \lambda_0^*, \lambda^d, \lambda_0^d, \lambda^r$. It is the order of magnitude of these parameters, and their interplay, which characterizes the scaling appropriate to each physical situation, and which determines accordingly via asymptotic procedure the closed fluid–dynamic equations for the corresponding hydrodynamic variables. We shall assume throughout that $\bar{n}_0 \gg \bar{n}$, consistently with the definition itself of background medium, and indeed such an assumption turns out to be crucial in order to obtain reaction-diffusion–type equations, as shown by recent investigations on asymptotic limits for the simpler scenario of bimolecular chemical reactions [4]. In fact, it makes typically elastic scattering with the background a dominant process, which induces, as well known in linear kinetic theory, a diffusive term in the fluid–dynamic limit. Also, we shall always stick to the option that the mean free path for elastic scattering of stable species among themselves λ^s is of the same order as the macroscopic scale L , so that nonlinear scattering operators always share the same level of importance with the streaming term. As concerns chemical processes, in next sections we shall deal with two slightly different situations, that however lead to very different asymptotic limits: the case of slowly reacting background, which gives rise to the three hydrodynamic variables n_1, n_2 , and the distribution φ_3 , and then the case of fast reacting background, for which a closed set of transport equations involving only n_1, n_2 is achieved. Other options are being considered separately or are scheduled as future work. The analysis is necessarily restricted for now to the formal level, also because of the hardly manageable heavy manipulations which are required. Rigorous mathematical results, as well as other important questions that are still open for the kinetic equations, will also be matter of future investigation.

ASYMPTOTIC LIMIT FOR SLOWLY REACTING BACKGROUND

The first scaling we are going to examine is relevant to a physical situation in which $\bar{\sigma}^d, \bar{\sigma}^r, \bar{\sigma}_0^*$ are comparable in magnitude, with a significantly smaller value for $\bar{\sigma}_0^d$, and simultaneously with significantly larger values for $\bar{\sigma}^*, \bar{\sigma}^s, \bar{\sigma}_0^s$, supposed again of the same order of magnitude. In this way it is easily seen that there is a single smallest Knudsen number, λ_0^s , that will be used as small parameter ε , and will mark the linear scattering operators of atoms and stable molecules with the background as the dominant ones leading the process. At the same time the dimensionless mean free paths $\lambda^s, \lambda^*, \lambda_0^*$ turn out to be $O(1)$, whereas $\lambda^d, \lambda_0^d, \lambda^r$ are $O(1/\varepsilon)$, so that the relevant events are rare on the scale of macroscopic spatial variations. The scaled kinetic equations read then as

$$\begin{aligned} \frac{\partial f_1}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_1 &= \frac{1}{\varepsilon} Q_{10} + Q_{11} + Q_{12} + J_1^*(f_1, f_2, \varphi_3) + \varepsilon J_1^d(f_1, f_2) + \varepsilon J_1^r(f_1) + I_1^*(\varphi_3, f_0) + \varepsilon I_1^d(f_2, f_0) \\ \frac{\partial f_2}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_2 &= \frac{1}{\varepsilon} Q_{20} + Q_{21} + Q_{22} + J_2^*(f_1, f_2, \varphi_3) + \varepsilon J_2^d(f_1, f_2) + I_2^*(\varphi_3, f_0) + \varepsilon I_2^d(f_2, f_0), \\ \frac{\partial \varphi_3}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} \varphi_3 &= J_3^*(f_1, f_2, \varphi_3) + \varepsilon J_3^r(f_1) + I_3^*(\varphi_3, f_0), \end{aligned} \quad (4)$$

where $Q_{ij} \equiv Q_{ij}(f_i, f_j)$ denotes the scattering collision operator between species i and j , whereas the symbols J_i^α and I_i^α are used to collect all binary chemical contributions of type α which result in gain and/or loss for species i . Specifically, J_i refers to encounters between participating species, and I_i to encounters involving a field particle. Moreover, the symbol $*$ is intended to mean that the relevant operator collects contributions of any type in which the excited species A_2^* is one of the colliding partners. For explicit expressions and properties of all the above collision integrals and for more details, the reader is referred to [3].

In the present scaling the dominant role is played by the operators Q_{10} and Q_{20} alone, which preserve only the total mass of species 1 and of species 2. Consequently, bearing in mind the philosophy of the Chapman–Enskog expansion, one should in a sense expect that hydrodynamic variables will be the two number densities n_1 and n_2 , plus the distribution function φ_3 itself for the third species. This leads to the quite unusual and degenerate scenario in which the Navier–Stokes–type hydrodynamic equations are constituted by coupled macroscopic and kinetic equations, which is worth to be made formally explicit. Expanding f_i as $f_i^{(0)} + \varepsilon f_i^{(1)}$, $i = 1, 2$, the $O(\varepsilon^{-1})$ terms in the kinetic equations (4) yield immediately $f_i \propto M_i(\mathbf{v})$, where M_i is the normalized Maxwellian

$$M_i = \left(\frac{m_i}{2\pi T_0} \right)^{\frac{3}{2}} \exp \left[-\frac{m_i}{2T_0} (\mathbf{v} - \mathbf{u}_0)^2 \right]. \quad (5)$$

We have then

$$f_i = n_i M_i + \varepsilon f_i^{(1)} \quad \text{with} \quad \int f_i^{(1)}(\mathbf{v}) d\mathbf{v} = 0, \quad i = 1, 2, \quad (6)$$

due to the fact that n_1, n_2 , as well as φ_3 , are kept unexpanded. The weak form of (4) relevant to the collision invariants $(1, 0, 0)$ and $(0, 1, 0)$ reads as

$$\begin{aligned} \frac{\partial n_1}{\partial t} + \nabla_{\mathbf{x}} \cdot \left(n_1 \mathbf{u}_0 + \varepsilon \int \mathbf{v} f_1^{(1)} d\mathbf{v} \right) &= \int J_1^*(n_1 M_1, n_2 M_2, \varphi_3) d\mathbf{v} \\ + \varepsilon \int J_1^d(n_1 M_1, n_2 M_2) d\mathbf{v} + \varepsilon \int J_1^i(n_1 M_1) d\mathbf{v} + \varepsilon \int I_1^*(\varphi_3, n_0 M_0) d\mathbf{v} + \varepsilon \int I_1^d(n_2 M_2, n_0 M_0) d\mathbf{v}, \\ \frac{\partial n_2}{\partial t} + \nabla_{\mathbf{x}} \cdot \left(n_2 \mathbf{u}_0 + \varepsilon \int \mathbf{v} f_2^{(1)} d\mathbf{v} \right) &= \int J_2^*(n_1 M_1, n_2 M_2, \varphi_3) d\mathbf{v} \\ + \varepsilon \int J_2^d(n_1 M_1, n_2 M_2) d\mathbf{v} + \varepsilon \int I_2^*(\varphi_3, n_0 M_0) d\mathbf{v} + \varepsilon \int I_2^d(n_2 M_2, n_0 M_0) d\mathbf{v}, \end{aligned} \quad (7)$$

and are non closed merely because of the presence of the integrals involving $\mathbf{v} f_i^{(1)}$. Resorting to the $O(\varepsilon^0)$ terms of the first two of equations (4) we get linear integral equations for $f_i^{(1)}$, which, after applying the usual compatibility conditions of the Chapman–Enskog procedure (that ensure existence and uniqueness of solutions), read as

$$\begin{aligned} Q_{10}(f_1^{(1)}, n_0 M_0) &= (\mathbf{v} - \mathbf{u}_0) M_1 \cdot \nabla_{\mathbf{x}} n_1 + 2(\mathbf{v}_{30}^d n_0 + \mathbf{v}_{31}^d n_1 + \mathbf{v}_{32}^d n_2) n_3 M_1 - J_1^*(n_1 M_1, n_2 M_2, \varphi_3) - I_1^*(\varphi_3, n_0 M_0), \\ Q_{20}(f_2^{(1)}, n_0 M_0) &= (\mathbf{v} - \mathbf{u}_0) M_2 \cdot \nabla_{\mathbf{x}} n_2 + (\mathbf{v}_{30}^i n_0 + \mathbf{v}_{31}^i n_1 + \mathbf{v}_{32}^i n_2) n_3 M_2 - J_2^*(n_1 M_1, n_2 M_2, \varphi_3) - I_2^*(\varphi_3, n_0 M_0). \end{aligned} \quad (8)$$

In the case of Maxwellian molecules analytical manipulations may be pushed up to the very end thanks to the fact that

$$\int \mathbf{v} f_i^{(1)} d\mathbf{v} = -\frac{m_i + m_0}{2m_0} \frac{1}{n_0 \bar{v}_{i0}^s} \int \mathbf{v} Q_{i0}(f_i^{(1)}, f_0) d\mathbf{v}, \quad i = 1, 2, \quad (9)$$

which allow to obtain the sought quantities just by integration of (8) over the velocity variable \mathbf{v} after multiplication by \mathbf{v} itself. On using such results we end up with the partial differential equations for n_1 and n_2 in the \mathbf{x} and t variables, with $O(\varepsilon)$ correction terms

$$\begin{aligned} \frac{\partial n_1}{\partial t} + \mathbf{u}_0 \cdot \nabla_{\mathbf{x}} n_1 - \varepsilon \frac{m_1 + m_0}{2m_0} \frac{1}{n_0 \bar{v}_{10}^s} \frac{T_0}{m_1} \Delta_{\mathbf{x}} n_1 + \varepsilon \frac{m_1 + m_0}{2m_0} \frac{1}{n_0 \bar{v}_{10}^s} \nabla_{\mathbf{x}} \cdot \\ \cdot \left\{ 3 \mathbf{v}_{31}^d n_1 \left[\iiint \mathbf{v} \Pi_{13}^{1,d}(\mathbf{v}'; \mathbf{w}', E \rightarrow \mathbf{v}) M_1(\mathbf{v}') \varphi_3(\mathbf{w}', E) dE d\mathbf{v} d\mathbf{v}' d\mathbf{w}' - n_3 \mathbf{u}_0 \right] \right. \\ + 2 \mathbf{v}_{32}^d n_2 \left[\iiint \mathbf{v} \Pi_{32}^{1,d}(\mathbf{v}', E; \mathbf{w}' \rightarrow \mathbf{v}) \varphi_3(\mathbf{v}', E) M_2(\mathbf{w}') dE d\mathbf{v} d\mathbf{v}' d\mathbf{w}' - n_3 \mathbf{u}_0 \right] \\ + 2 \mathbf{v}_{30}^d n_0 \left[\iiint \mathbf{v} \Pi_{30}^{1,d}(\mathbf{v}', E; \mathbf{w}' \rightarrow \mathbf{v}) \varphi_3(\mathbf{v}', E) M_0(\mathbf{w}') dE d\mathbf{v} d\mathbf{v}' d\mathbf{w}' - n_3 \mathbf{u}_0 \right] \\ \left. + \mathbf{v}_{31}^i n_1 \left[\iiint \mathbf{v} \Pi_{13}^{1,i}(\mathbf{v}'; \mathbf{w}', E \rightarrow \mathbf{v}) M_1(\mathbf{v}') \varphi_3(\mathbf{w}', E) dE d\mathbf{v} d\mathbf{v}' d\mathbf{w}' - n_3 \mathbf{u}_0 \right] \right\} \\ = 2n_3 (\mathbf{v}_{30}^d n_0 + \mathbf{v}_{31}^d n_1 + \mathbf{v}_{32}^d n_2) + 2\varepsilon \left[n_2 (\mathbf{v}_{20}^d n_0 + \mathbf{v}_{21}^d n_1 + \mathbf{v}_{22}^d n_2) - \mathbf{v}_{11}^i (n_1)^2 \right], \end{aligned} \quad (10)$$

$$\begin{aligned} \frac{\partial n_2}{\partial t} + \mathbf{u}_0 \cdot \nabla_{\mathbf{x}} n_2 - \varepsilon \frac{2m_1 + m_0}{2m_0} \frac{1}{n_0 \bar{v}_{20}^s} \frac{T_0}{2m_1} \Delta_{\mathbf{x}} n_2 + \varepsilon \frac{2m_1 + m_0}{2m_0} \frac{1}{n_0 \bar{v}_{20}^s} \nabla_{\mathbf{x}} \cdot \\ \cdot \left\{ \mathbf{v}_{32}^d n_2 \left[\iiint \mathbf{v} \Pi_{23}^{2,d}(\mathbf{v}'; \mathbf{w}', E \rightarrow \mathbf{v}) M_2(\mathbf{v}') \varphi_3(\mathbf{w}', E) dE d\mathbf{v} d\mathbf{v}' d\mathbf{w}' - n_3 \mathbf{u}_0 \right] \right. \\ \left. + \mathbf{v}_{30}^i n_0 \left[\iiint \mathbf{v} \Pi_{30}^{2,i}(\mathbf{v}', E; \mathbf{w}' \rightarrow \mathbf{v}) \varphi_3(\mathbf{v}', E) M_0(\mathbf{w}') dE d\mathbf{v} d\mathbf{v}' d\mathbf{w}' - n_3 \mathbf{u}_0 \right] \right\} \end{aligned} \quad (11)$$

$$\begin{aligned}
& + v_{31}^i n_1 \left[\iiint \mathbf{v} \Pi_{31}^{2,i}(\mathbf{v}'; E; \mathbf{w}' \rightarrow \mathbf{v}) \varphi_3(\mathbf{v}', E) M_1(\mathbf{w}') dE d\mathbf{v} d\mathbf{v}' d\mathbf{w}' - n_3 \mathbf{u}_0 \right] \\
& + 2 v_{32}^i n_2 \left[\iiint \mathbf{v} \Pi_{23}^{2,i}(\mathbf{v}'; \mathbf{w}', E \rightarrow \mathbf{v}) M_2(\mathbf{v}') \varphi_3(\mathbf{w}', E) dE d\mathbf{v} d\mathbf{v}' d\mathbf{w}' - n_3 \mathbf{u}_0 \right] \Big\} \\
& = n_3 (v_{30}^i n_0 + v_{31}^i n_1 + v_{32}^i n_2) - \varepsilon n_2 (v_{20}^d n_0 + v_{21}^d n_1 + v_{22}^d n_2).
\end{aligned}$$

They contain the additional unknown φ_3 , but the system can be closed by using the previous results for f_i in the third of (4), which yields

$$\frac{\partial \varphi_3}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} \varphi_3 = - (v_{30}^t n_0 + v_{31}^t n_1 + v_{32}^t n_2) \varphi_3(\mathbf{v}, E) + \varepsilon v_{11}^t (n_1)^2 M_3(\mathbf{v}) \chi(E), \quad (12)$$

with $v_{3k}^t = v_{3k}^d + v_{3k}^i$, and normalized energy spectrum

$$\chi(E) = 2 \left(\frac{E}{\pi(T_0)^3} \right)^{\frac{1}{2}} \exp \left(-\frac{E}{T_0} \right). \quad (13)$$

The appearance of the system (10), (11), (12) is quite horrible because of the presence of several complicated vector functions such as

$$\int \mathbf{v} \Pi_{23}^{2,d}(\mathbf{v}'; \mathbf{w}', E \rightarrow \mathbf{v}) d\mathbf{v} \quad (14)$$

which are known in principle, but not easy to estimate in practice (they would reduce to \mathbf{u}_0 for the synthetic approximation $\Pi_{ij}^{k,\alpha} = M_k(\mathbf{v})$, $k = 1, 2$, so that all curly brackets would vanish in this case). However the system presents nice features like the presence of expected $O(\varepsilon)$ diffusive terms of the type $\Delta_{\mathbf{x}} n_i$, with well defined diffusion coefficients, and the fulfilment of overall mass conservation by chemically reactive terms on the right hand sides, in the sense that, if \mathcal{R}_i denotes such term in the i -th equation of the system, it is easily checked that

$$\mathcal{R}_1 + 2\mathcal{R}_2 + 2 \iint \mathcal{R}_3 d\mathbf{v} dE = 0. \quad (15)$$

HYDRODYNAMIC EQUATIONS FOR FAST REACTING BACKGROUND

The second physical situation we deal with is aimed at showing how a slight variant of the preceding scaling leads to completely different asymptotic limits and fluid-dynamic “Navier–Stokes” equations, restoring a more classical and less degenerate scenario. Here chemical reactions involving the host medium are assumed faster, i.e. we change physical parameters only in that $\bar{\sigma}_0^*$ joins $\bar{\sigma}^*$, $\bar{\sigma}^s$ and $\bar{\sigma}_0^s$ in the class of large cross sections, and $\bar{\sigma}_0^d$ joins $\bar{\sigma}^d$ and $\bar{\sigma}^r$ to make up a class of small cross sections. In this way, with the same choice for the small parameter ε , λ_0^* also becomes $O(\varepsilon)$, whereas λ^s , λ^* , λ_0^d result to be $O(1)$, and only λ^d and λ^r are left as $O(1/\varepsilon)$. The scaled system of kinetic Boltzmann-like equations takes the form

$$\begin{aligned}
\frac{\partial f_1}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_1 &= \frac{1}{\varepsilon} Q_{10} + Q_{11} + Q_{12} + J_1^*(f_1, f_2, \varphi_3) + \varepsilon J_1^d(f_1, f_2) + \varepsilon J_1^r(f_1) + \frac{1}{\varepsilon} I_1^*(\varphi_3, f_0) + I_1^d(f_2, f_0), \\
\frac{\partial f_2}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_2 &= \frac{1}{\varepsilon} Q_{20} + Q_{21} + Q_{22} + J_2^*(f_1, f_2, \varphi_3) + \varepsilon J_2^d(f_1, f_2) + \frac{1}{\varepsilon} I_2^*(\varphi_3, f_0) + I_2^d(f_2, f_0), \\
\frac{\partial \varphi_3}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} \varphi_3 &= J_3^*(f_1, f_2, \varphi_3) + \varepsilon J_3^r(f_1) + \frac{1}{\varepsilon} I_3^*(\varphi_3, f_0),
\end{aligned} \quad (16)$$

and the asymptotic procedure may be repeated, expanding now also φ_3 as much as necessary. Now chemical collision terms involving both the unstable species and the background are as important as linear elastic scattering and it is worth analyzing their effects on the evolution at the hydrodynamic level. It is easily realized that $O(\varepsilon^{-1})$ terms yield $\varphi_3^{(0)} = 0$ and reproduce (6) for f_1, f_2 . The third equation in (16) to $O(\varepsilon^0)$ terms yields again $\varphi_3^{(1)} = 0$, so that it is necessary one step further, which is now non-trivial and solvable as

$$\varphi_3^{(2)} = \frac{v_{11}^r (n_1)^2}{v_{30}^t n_0} M_3(\mathbf{v}) \chi(E) \quad \text{hence} \quad n_3 = \varepsilon^2 n_3^{(2)} = \varepsilon^2 \frac{v_{11}^r (n_1)^2}{v_{30}^t n_0}. \quad (17)$$

Equations for $f_i^{(1)}$ are obtained as before, and after application of compatibility conditions read as

$$\begin{aligned} Q_{10}(f_1^{(1)}, n_0 M_0) &= (\mathbf{v} - \mathbf{u}_0) M_1 \cdot \nabla_{\mathbf{x}} n_1 + 2 v_{20}^d n_0 n_2 M_1 - 2 v_{20}^d n_0 n_2 \iint \Pi_{20}^{1,d}(\mathbf{v}'; \mathbf{w}' \rightarrow \mathbf{v}) M_2(\mathbf{v}') M_0(\mathbf{w}') d\mathbf{v}' d\mathbf{w}', \\ Q_{20}(f_2^{(1)}, n_0 M_0) &= (\mathbf{v} - \mathbf{u}_0) M_2 \cdot \nabla_{\mathbf{x}} n_2, \end{aligned} \quad (18)$$

from which

$$\begin{aligned} \int \mathbf{v} Q_{10}(f_1^{(1)}, n_0 M_0) d\mathbf{v} &= \frac{T_0}{m_1} \nabla_{\mathbf{x}} n_1 - 2 v_{20}^d n_0 n_2 \left[\iiint \mathbf{v} \Pi_{20}^{1,d}(\mathbf{v}'; \mathbf{w}' \rightarrow \mathbf{v}) M_2(\mathbf{v}') M_0(\mathbf{w}') d\mathbf{v} d\mathbf{v}' d\mathbf{w}' - \mathbf{u}_0 \right], \\ \int \mathbf{v} Q_{20}(f_2^{(1)}, n_0 M_0) d\mathbf{v} &= \frac{T_0}{2 m_1} \nabla_{\mathbf{x}} n_2. \end{aligned} \quad (19)$$

Again equations for n_1 and n_2 follow by integration of the first two of (4) over \mathbf{v} , and their closure requires once more only the calculation of the fluxes $\int \mathbf{v} f_i^{(1)} d\mathbf{v}$, for which we may rely on (9) and (19). On using all these results, we finally end up with

$$\begin{aligned} \frac{\partial n_1}{\partial t} + \mathbf{u}_0 \cdot \nabla_{\mathbf{x}} n_1 - \varepsilon \frac{m_1 + m_0}{2 m_0} \frac{1}{n_0 \bar{v}_{10}^s} \frac{T_0}{m_1} \Delta_{\mathbf{x}} n_1 \\ + \varepsilon \frac{m_1 + m_0}{2 m_0} \frac{1}{n_0 \bar{v}_{10}^s} \nabla_{\mathbf{x}} \cdot \left\{ 2 v_{20}^d n_0 n_2 \left[\iiint \mathbf{v} \Pi_{20}^{1,d}(\mathbf{v}'; \mathbf{w}' \rightarrow \mathbf{v}) M_2(\mathbf{v}') M_0(\mathbf{w}') d\mathbf{v} d\mathbf{v}' d\mathbf{w}' - \mathbf{u}_0 \right] \right\} \\ = 2 v_{20}^d n_0 n_2 + 2 \varepsilon n_2 (v_{12}^d n_1 + v_{22}^d n_2) + 2 \varepsilon v_{30}^d n_0 n_3^{(2)} - 2 \varepsilon v_{11}^r (n_1)^2, \end{aligned} \quad (20)$$

$$\frac{\partial n_2}{\partial t} + \mathbf{u}_0 \cdot \nabla_{\mathbf{x}} n_2 - \varepsilon \frac{2 m_1 + m_0}{2 m_0} \frac{1}{n_0 \bar{v}_{20}^s} \frac{T_0}{2 m_1} \Delta_{\mathbf{x}} n_2 = -v_{20}^d n_0 n_2 - \varepsilon n_2 (v_{12}^d n_1 + v_{22}^d n_2) + \varepsilon v_{30}^i n_0 n_3^{(2)}, \quad (21)$$

where $n_3^{(2)}$ is given by (17). This is a more familiar reaction–diffusion system, involving only one of the velocity vectors of type (14). Reaction terms fulfil again mass conservation, since it is easily seen that, with the same meaning of symbols as before, we have $\mathcal{R}_1 + 2\mathcal{R}_2 = 0$, representing then chemical equilibrium. Such equilibrium takes the form $n_2 = \varepsilon (v_{30}^i v_{11}^r (n_1)^2) / (v_{30}^i v_{20}^d n_0) + O(\varepsilon^2)$, and collapses to $n_2 = 0$ (all molecules are dissociated in atoms) when $\varepsilon \rightarrow 0$ (Euler limit). It is remarkable that the system (20), (21) involves only the densities of stable species as unknowns, consistently with the fact that n_3 vanishes to $O(\varepsilon)$ accuracy, when $\varepsilon \rightarrow 0$. However, the third species affects the evolution of stable species via the presence in (20), (21) of $n_3^{(2)}$, which may be viewed as $\lim_{\varepsilon \rightarrow 0} \frac{n_3}{\varepsilon^2}$, and reproduces a kind of ghost effect, as it occurs in many other asymptotic limits of kinetic theory [5].

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REFERENCES

1. C. Cercignani, *Rarefied Gas Dynamics: from Basic Concepts to Actual Calculations*, Cambridge Univ. Press, Cambridge, 2000.
2. Y. Yoshizawa, “Wave structures of a chemically reacting gas by the kinetic theory of gases”, in *Rarefied Gas Dynamics*, edited by J. L. Potter, A.I.A.A., New York, 1977, pp. 501–517.
3. M. Groppi, A. Rossani, and G. Spiga, *J. Phys. A* **33**, 8819–8833 (2000).
4. M. Bisi, and L. Desvillettes, *J. Stat. Phys.*, in press.
5. Y. Sone, *Kinetic Theory and Fluid Dynamics*, Birkhäuser, Boston, 2002.