Kinetic theory of a diatomic gas with reactions of dissociation and recombination through a transition state

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Abstract. Extended kinetic equations, according to the scattering kernel formulation of the Boltzmann equation, are derived for a chemical reaction of dissociation and recombination in the frame of the transition-state theory. Conservation laws and moment equations are discussed, and, in the spontaneous asymptotic limit induced by the transition species, collision equilibria are determined to leading order. In the spirit of the stationary-state approximation, a closed set of fluid-dynamic equations of the Euler type are then obtained for the main macroscopic fields. Preliminary numerical results are finally presented and briefly commented on.

1. Introduction

The kinetic theory of chemically reacting gases started in the 1940s [1], and there exists a large literature about chemically reacting rarefied flows. We may quote for instance [2,3], just to mention some of the most significant contributions from pioneering times. However, such a literature is mainly concerned with numerical results and applications. Only very recently Rossani and Spiga [4] gave a more explicit derivation of kinetic equations with chemical reactions, and, from a mathematical point of view, were able to characterize completely equilibrium distributions and to prove an H-theorem for them.

On the other hand, [4] deals with bimolecular reversible reactions only, a quite special case in the world of applications. It is very well known, for example, that the main chemical reactions occurring in the air include recombination/dissociation events as an essential ingredient [5]. It is just this kind of reaction that we shall focus on here. A formal description, at a mesoscopic level, of a diatomic gas with reactions of recombination and dissociation is available in [6]. In such a model, recombination occurs through a three-body collision. However, many authors [5,7] point out that recombination occurs through a preliminary two-body collision, according to the transition-state theory [8]. To the best of our knowledge, the only kinetic-like approach along this line available in the literature is [9], where Yoshizawa constructs a BGK model for a diatomic gas with recombination reactions through a transition state. Unfortunately, dissociation reactions are neglected in that paper.

In this paper we propose a kinetic model, at the Boltzmann level, for the mesoscopic description of a diatomic gas with both reactions of dissociation and of recombination through a transition state. We consider the diatomic gas as a mixture of three interacting populations: atoms A (mass m), stable molecules A_2 and unstable molecules A_2^*, to be labelled in the following by the indices 1, 2 and 3, respectively. A detailed discussion on the formation of

an unstable molecule can be found in [7]. It turns out that such an event is possible when the kinetic energy of relative motion falls between a lower bound E_{lb} and an upper bound E_{ub}. These values originate from the study of the atom–atom potentials for both the unbound and the bound state. However, in view of a construction of a mesoscopic model, all this microscopic information is accounted for by means of the relevant cross sections. Moreover, for the purpose of a correct energy balance, it suffices to assume that stable and unstable molecules are endowed with their own internal energies, which are denoted, respectively, by $-Q$ and E, where Q is a fixed positive quantity, while E is a continuous variable ranging on the real axis. The present model neglects rotational internal energy, so that $-Q$ is intended to be due to chemical links only, while E is the sum of chemical link plus vibrational energy. One of the key points of the model is that the unstable molecule plays the role of a transition state [8, 9]. It is created by atom–atom recombination reactions only, and does not survive any interaction. More precisely, one assumes that the mean lifetime (the average time between creation and the first, and last, interaction) of an unstable molecule is very short in comparison to the other reaction times [5]. This implies that 3–3 interactions can be neglected, and that, from a mathematical point of view, we have to deal necessarily with a singular perturbation problem.

This paper is organized as follows. After analysing the recombination/dissociation reaction and discussing the properties of the interaction probabilities, we introduce a system of Boltzmann equations for the particle distribution functions, in order to describe the evolution of the three interacting populations at a kinetic level by means of the various collision frequencies and collision kernels. In particular, conservation laws for mass, momentum and total (kinetic plus internal) energy are recognized, and the relevant macroscopic conservation equations are obtained. Then, the separate balance equations for each kind of particle, as well as for kinetic energy, are derived. Based on the stationary-state approximation [8], a closure for the moment equations above is proposed, which allows a fluid-dynamic description of the considered gas mixture in terms of six macroscopic fields. The approximate set of partial differential equations is obtained by an asymptotic limit when the appropriate collision times tend to zero, and describes the chemical kinetics of the reaction at the Euler level. The procedure goes through the determination of asymptotic collision equilibria, which satisfy a sort of mass action law. Finally, some simple numerical results are presented in order to illustrate the relaxation to equilibrium starting from any given initial condition and the role played by the small parameter.

2. Recombination/dissociation reactions and kinetic equations

Recombination in our model occurs in two steps:

$$(R1) \; A + A \rightarrow A_2^*$$
$$(R2) \; A_2^* + P \rightarrow A_2 + P$$
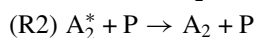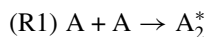
where, in what follows, P = A, A_2. The kinetic energy of the relative motion $\epsilon_{11} = (1/4)mV_{11}^2$ (V is the relative speed) gives the internal energy E of 3. According to the adopted model, reaction (R1) occurs if E belongs to the allowed energy range $E_{lb} < E < E_{ub}$, which determines upper and lower thresholds for the relative speed in order to achieve the transition state. If such conditions are not fulfilled, only the elastic scattering event

$$(E1) \; A + A \rightarrow A + A$$

occurs. Otherwise both events (R1) and (E1) are possible. The second step (R2) is an inelastic scattering, which completes the recombination process by de-excitation of A_2^* (exothermic process).

Dissociation occurs via two possible reactions:

(D1) $A_2 + P \rightarrow 2A + P$

(D2) $A_2^* + P \rightarrow 2A + P$.
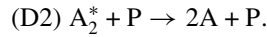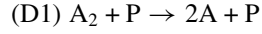
Total energy conservation imposes that the event (D1) occurs if the kinetic energy of the relative motion $\epsilon_{2p} = (1/2)\mu_{2p}V_{2p}^2$ (where $p = 1, 2$ for P = A, A_2, and $\mu_{2p} = 2pm/(2 + p)$) of the pair $(2, p)$ is such that $\epsilon_{2p} > Q$, which determines a threshold to be overcome by the relative speed (endothermic process). If conditions for occurrence of (D1) are not fulfilled, only the elastic scattering

(E2) $A_2 + P \rightarrow A_2 + P$
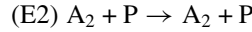
takes place. Otherwise both events (D1) and (E2) are possible. The reaction (D2) is an exothermic process, and it occurs, with different probabilities, together with the inelastic scattering (R2).

All elastic scattering collisions (E1) and (E2) may be described by the usual methods of kinetic theory [10], and we shall not enter into the details of the relevant collision terms. A similar treatment would be in order, in the frame of extended kinetic theory [11], for the inelastic scattering process (R2). However, we will describe such collision in terms of the equivalent scattering kernel formulation of the Boltzmann equation [12]. If (v', w') and (v, w) denote the ordered velocity pairs before and after collision, momentum and energy conservation read

$$
\begin{aligned}
2v' + pw' &= 2v + pw \\
mv'^2 + E + (1/2)pmw'^2 &= mv^2 - Q + (1/2)pmw^2.
\end{aligned}
\tag{1}
$$

All requirements are modelled by the microscopic collision frequencies $g_{3p}^i = g_{p3}^i$ (relative speed multiplied by cross sections) and by the scattering probability distributions $\Pi_{3p}^{2,i}$ and $\Pi_{p3}^{p,i}$, where the superscript i stands for inelastic. For readers who are not familiar with such a formalism, we recall that, for instance, $\Pi_{3p}^{2,i}(v', E; w' \rightarrow v)$ represents the probability density that the outcoming particle 2 attains velocity v as a result of a de-excitation collision of a particle 3, with velocity v' and internal energy E, against a particle P, with velocity w'. The explicit expressions of the scattering kernels, involving necessarily also delta functions, may be deduced from [13], and satisfy all obvious indistinguishability constraints, in particular $\Pi_{32}^{2,i}(v', E; w' \rightarrow v) = \Pi_{23}^{2,i}(w'; v', E \rightarrow v)$. It suffices to report on their conservation properties:

$$
\int \Pi_{3p}^{2,i}(v', E; w' \rightarrow v)\, dv = 1 \qquad \int \Pi_{p3}^{p,i}(v'; w', E \rightarrow v)\, dv = 1
$$

$$
\int [2v\Pi_{3p}^{2,i}(v', E; w' \rightarrow v) + pv\Pi_{p3}^{p,i}(w'; v', E \rightarrow v)]\, dv = 2v' + pw'
$$

$$
\int \left[(mv^2 - Q)\Pi_{3p}^{2,i}(v', E; w' \rightarrow v) \right.
$$
$$
\left. + \frac{pm}{2}v^2\Pi_{p3}^{3,i}(w'; v', E \rightarrow v) \right] dv = mv'^2 + E + \frac{pm}{2}w'^2
$$

$$
\tag{2}
$$

where here and below it is implicitly understood that velocity vectors range all over $\mathbb{R}^3$, internal energy E between E_{lb} and E_{ub}, and the same occurs for the relevant integrations. Of course, domains of integration might be further restricted by other thresholds contributed by cross sections present in the integrand.

The same probabilistic formalism will then be adopted for all other considered interactions. In the recombination process (R1) the collision frequency g_{11}^r is affected by the constraints

explained above and depends only on the relative speed $V = |v' - w'|$, while the collision kernel is explicitly given by

$$\Pi_{11}^{3,r}(v'; w' \to v, E) = \delta(\tfrac{1}{2}(v' + w') - v)\delta(\tfrac{1}{4}m(v' - w')^2 - E) \qquad (3)$$

where δ is Dirac's delta distribution. Conservation properties then follow:

$$\int dE \int \Pi_{11}^{3,r}(v'; w' \to v, E)\, dv = 1$$
$$\int dE \int 2v\Pi_{11}^{3,r}(v'; w' \to v, E)\, dv = v' + w' \qquad (4)$$
$$\int dE \int (mv^2 + E)\Pi_{11}^{3,r}(v', w' \to v, E)\, dv = (1/2)mv'^2 + (1/2)mw'^2.$$

As regards the dissociation reaction (D1), we shift all microscopic details to appendix A, to which we refer also for the proofs of the statements below. We shall resort to collision frequencies $g_{2p}^d = g_{p2}^d$ and to the integrated probability distributions $\Pi_{2p}^{1,d}$ and $\Pi_{p2}^{p,d}$, with $\Pi_{21}^{1,d}(v', w' \to v) = \Pi_{12}^{1,d}(w', v' \to v)$, and conservation properties

$$\int \Pi_{2p}^{1,d}(v', w' \to v)\, dv = \int \Pi_{p2}^{p,d}(v', w' \to v)\, dv = 1$$
$$\int [2v\Pi_{2p}^{1,d}(v', w' \to v) + pv\Pi_{p2}^{p,d}(w', v' \to v)]\, dv = 2v' + pw' \qquad (5)$$
$$\int \left[mv^2\Pi_{2p}^{1,d}(v', w' \to v) + \frac{pm}{2}v^2\Pi_{p2}^{p,d}(w', v' \to v)\right] dv = mv'^2 - Q + \frac{pm}{2}w'^2.$$

The same as above applies, *mutatis mutandis*, to the dissociation reaction (D2). The collision frequencies $g_{3p}^d = g_{p3}^d$ may depend on the internal energy of species 3 in addition to the relative speed $V = |v' - w'|$. One can define again integrated probability distributions (see appendix A) $\Pi_{3p}^{1,d}$ and $\Pi_{p3}^{p,d}$, with $\Pi_{31}^{1,d}(v', E; w' \to v) = \Pi_{13}^{1,d}(w'; v', E \to v)$, and conservation properties

$$\int \Pi_{3p}^{1,d}(v', E; w' \to v)\, dv = \int \Pi_{p3}^{p,d}(v'; w', E \to v)\, dv = 1$$
$$\int [2v\Pi_{3p}^{1,d}(v', E; w' \to v) + pv\Pi_{p3}^{p,d}(w'; v', E \to v)]\, dv = 2v' + pw' \qquad (6)$$
$$\int \left[mv^2\Pi_{3p}^{1,d}(v', E; w' \to v) + \frac{pm}{2}v^2\Pi_{p3}^{p,d}(w'; v', E \to v)\right] dv = mv'^2 + E + \frac{pm}{2}w'^2.$$

For a description at a mesoscopic level of the present model, we resort to the usual distribution functions $f_1(v)$ and $f_2(v)$ for atoms 1 and molecules 2, respectively, and to a distribution function $\varphi_3(v, E)$ for excited molecules 3, which exhibit the additional kinetic variable E. Explicit dependence on (x, t) will not be shown here, in order to simplify notation. We might define the following (integer) energy moments of such distribution function:

$$\mathcal{M}_{3\ell}(v) = \int \varphi_3(v, E)E^\ell\, dE. \qquad (7)$$

In particular, $\mathcal{M}_{30}(v) = f_3(v)$ is the usual velocity distribution function for particles 3. Under the usual hypotheses of validity of the Boltzmann equation [10], by resorting to its scattering kernel formulation [12], we can write down the following system of coupled kinetic equations governing the evolution of f_1, f_2 and φ_3

$$\frac{\partial f_1}{\partial t} + v \cdot \frac{\partial f_1}{\partial x} = \mathcal{Q}_{11}(f_1, f_2) + \mathcal{Q}_{12}(f_1, f_2) + \mathcal{J}_1(f_1, f_2, \varphi_3)$$
$$\frac{\partial f_2}{\partial t} + v \cdot \frac{\partial f_2}{\partial x} = \mathcal{Q}_{21}(f_2, f_1) + \mathcal{Q}_{22}(f_2, f_2) + \mathcal{J}_2(f_1, f_2, \varphi_3) \qquad (8)$$
$$\frac{\partial \varphi_3}{\partial t} + v \cdot \frac{\partial \varphi_3}{\partial x} = \mathcal{J}_3(f_1, f_2, \varphi_3)$$

where $\mathcal{Q}_{k\ell}$ is the usual [10] elastic collision integral and $\mathcal{J}_k$ is the chemical collision term for particles k, including the proper recombination, inelastic scattering and dissociation contributions, whose explicit expression is given in appendix B. Indistinguishability of particles has been taken into account by the relevant symmetry properties of the scattering kernels.

3. Conservation and moment equations

The conservation properties established in (2) and (4)–(6) lead, after some algebra, to the conservation laws, of clear physical meaning:

$$\int \mathcal{J}_1(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} + 2\int \mathcal{J}_2(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} + 2\iint \mathcal{J}_3(\boldsymbol{v}, E)\,\mathrm{d}\boldsymbol{v}\,\mathrm{d}E = 0$$

$$\int \boldsymbol{v}\mathcal{J}_1(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} + 2\int \boldsymbol{v}\mathcal{J}_2(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} + 2\iint \boldsymbol{v}\mathcal{J}_3(\boldsymbol{v}, E)\,\mathrm{d}\boldsymbol{v}\,\mathrm{d}E = \boldsymbol{0} \tag{9}$$

$$\int \tfrac{1}{2}mv^2 \mathcal{J}_1(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} + \int (mv^2 - Q)\mathcal{J}_2(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} + \iint (mv^2 + E)\mathcal{J}_3(\boldsymbol{v}, E)\,\mathrm{d}\boldsymbol{v}\,\mathrm{d}E = 0.$$

Elastic collision terms satisfy in turn, as well known,

$$\int \mathcal{Q}_{k\ell}(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} = 0\ \forall k, \ell \qquad \int \boldsymbol{v}\mathcal{Q}_{kk}(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} = \boldsymbol{0}\ \forall k \qquad \int v^2 \mathcal{Q}_{kk}(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} = 0\ \forall k$$

$$\int \boldsymbol{v}(\mathcal{Q}_{12} + 2\mathcal{Q}_{21})\,\mathrm{d}\boldsymbol{v} = \boldsymbol{0} \qquad \int v^2(\mathcal{Q}_{12} + 2\mathcal{Q}_{21})\,\mathrm{d}\boldsymbol{v} = 0. \tag{10}$$

The five scalar strings $(1, 2, 2)$, $(\boldsymbol{v}, 2\boldsymbol{v}, 2\boldsymbol{v})$, $(mv^2/2, mv^2 - Q, mv^2 + E)$, representing the total number of atoms, total momentum (per unit mass) and total energy (kinetic plus internal), respectively, are then collision invariants for the considered mixture. We can draw from this immediate consequences at the macroscopic level.

Integration and summation of the kinetic equations (8) after multiplication by the string $(m, 2m, 2m)$ yields in fact the mass conservation equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \boldsymbol{u}) = 0 \tag{11}$$

where mass density ρ and drift velocity $\boldsymbol{u}$ are defined in appendix C, together with all moments of the distribution functions introduced below.

The string $(m\boldsymbol{v}, 2m\boldsymbol{v}, 2m\boldsymbol{v})$ yields the momentum conservation equation

$$\frac{\partial}{\partial t}(\rho \boldsymbol{u}) + \nabla \cdot (\rho \boldsymbol{u} \otimes \boldsymbol{u} + \boldsymbol{P}) = \boldsymbol{0} \tag{12}$$

where $\boldsymbol{P}$ is the pressure tensor.

The string $(mv^2/2, mv^2 - Q, mv^2 + E)$ yields finally the total energy conservation equation

$$\frac{\partial \mathcal{E}}{\partial t} + \nabla \cdot [(\mathcal{E}\boldsymbol{I} + \boldsymbol{P}) \cdot \boldsymbol{u} + \boldsymbol{q}] = 0 \tag{13}$$

where $\boldsymbol{I}$ is the unit tensor, and energy density $\mathcal{E}$ and heat flux $\boldsymbol{q}$ are given by

$$\mathcal{E} = (1/2)\rho u^2 + \mathcal{E}_{\text{th}} + \mathcal{E}_{\text{int}} \tag{14}$$

and

$$\boldsymbol{q} = \boldsymbol{q}_{\text{th}} + \boldsymbol{q}_{\text{int}} \tag{15}$$

with thermal and internal contributions defined again in appendix C.

These five scalar partial differential equations are of course exact but not closed, since they involve a much larger number of moments of the distribution functions. Some more detailed

information may be achieved by partial integrations, as shown below, at the price that collision contributions do not necessarily cancel out.

In fact, simple integration of the three kinetic equations give balance equations for the number of particles in each species. They read as

$$\frac{\partial n_\ell}{\partial t} + \nabla \cdot (n_\ell \boldsymbol{u}_\ell) = \mathcal{S}_\ell \qquad \ell = 1, 2, 3 \tag{16}$$

with appearance of collision terms $\mathcal{S}_\ell$ listed in appendix D.

The string $(mv^2/2, mv^2, mv^2)$ yields the kinetic energy balance equation

$$\frac{\partial}{\partial t}(\mathcal{E}_{\text{th}} + (1/2)\rho u^2) + \nabla \cdot \{[(\mathcal{E}_{\text{th}} + (1/2)\rho u^2)\boldsymbol{I} + \boldsymbol{P}] \cdot \boldsymbol{u} + \boldsymbol{q}_{\text{th}}\} = \mathcal{S}_{\text{th}} \tag{17}$$

where $\mathcal{S}_{\text{th}}$ is also given in appendix D.

The moment equations (12), (16), (17) are again exact but not closed, and the source terms $\mathcal{S}_\ell$ and $\mathcal{S}_{\text{th}}$ are complicated integrals of the unknown distribution functions.

In the next section we propose a closure approach for these moment equations, in order to achieve an approximate fluid-dynamic description of the gas mixture we deal with. Such a procedure, at a mesoscopic level, basically follows the philosophy of the stationary-state approximation, which is a popular approach to the chemical kinetics of complex reactions [5,8].

4. Fluid-dynamic equations

Suppose that, consistently with our model, all frequencies $g_{\ell 3}^\alpha$ and all elastic frequencies $g_{k\ell}^e$ are affected, upon adimensionalization, by a factor $1/\epsilon$, where ϵ is a smallness parameter. This indeed occurs when collision times relevant to the excited species, together with elastic collision times, are much shorter than all other typical relaxation times. The kinetic equations now read

$$\frac{\partial f_1}{\partial t} + \boldsymbol{v} \cdot \frac{\partial f_1}{\partial \boldsymbol{x}} = \frac{1}{\epsilon}(\mathcal{Q}_{11} + \mathcal{Q}_{12}) + \mathcal{J}_1^\times + \frac{1}{\epsilon}\mathcal{J}_1^*$$

$$\frac{\partial f_2}{\partial t} + \boldsymbol{v} \cdot \frac{\partial f_2}{\partial \boldsymbol{x}} = \frac{1}{\epsilon}(\mathcal{Q}_{21} + \mathcal{Q}_{22}) + \mathcal{J}_2^\times + \frac{1}{\epsilon}\mathcal{J}_2^* \tag{18}$$

$$\frac{\partial \varphi_3}{\partial t} + \boldsymbol{v} \cdot \frac{\partial \varphi_3}{\partial \boldsymbol{x}} = \mathcal{J}_3^\times + \frac{1}{\epsilon}\mathcal{J}_3^*$$

where $\mathcal{J}_k^*$ is the part of $\mathcal{J}_k$ which involves φ_3, while $\mathcal{J}_k^\times$ is the part of $\mathcal{J}_k$ which does not. As typical in kinetic theory, in order to look for the asymptotic (hydrodynamic) limit, all distribution functions, and consequently all collision integrals, are expanded in non-negative powers of ϵ. If one looks for collision equilibria, the last equation gives at once $\mathcal{J}_{3(0)}^* = 0 \implies \varphi_3^{(0)} = 0$ and $\mathcal{J}_{3(0)}^\times + \mathcal{J}_{3(1)}^* = 0$. Since $\varphi_3^{(0)} = 0 \implies \mathcal{J}_{\ell(0)}^* = 0$ ($\ell = 1, 2$), the first two equations give, respectively,

$$\mathcal{Q}_{11}^{(0)} + \mathcal{Q}_{12}^{(0)} = 0 \qquad \mathcal{Q}_{12}^{(0)} + \mathcal{Q}_{22}^{(0)} = 0 \tag{19}$$

whose exact solution $f^{(0)}$ is explicitly known in terms of Maxwellian distributions [10]. So, if n_ℓ, $\boldsymbol{u}_{12}$ and T_{12} denote arbitrary parameters (functions of $\boldsymbol{x}$ and t), the zero-order collision equilibrium for atoms and molecules is given by $f_\ell = n_\ell M_\ell(|\boldsymbol{v} - \boldsymbol{u}_{12}|, T_{12})$, where M_ℓ is the normalized Maxwellian

$$M_\ell(v, \theta) = \left(\frac{m_\ell}{2\pi K\theta}\right)^{3/2} \exp\left(-\frac{m_\ell}{2K\theta}v^2\right). \tag{20}$$

Now, again to leading order, and in dimensional form, from $\mathcal{J}_{3(0)}^\times + \mathcal{J}_{3(1)}^* = 0$, we obtain the collision equilibrium for the excited species

$$\varphi_3(\boldsymbol{v}, E) = \psi_3(|\boldsymbol{v} - \boldsymbol{u}_{12}|, E)\chi(E) \tag{21}$$

with

$$\psi_3(v, E) = \frac{n_1^2 M_3(v, T_{12})}{\int [n_1 M_1(w, T_{12}) g_{13}^t(|v - w|, E) + n_2 M_2(w, T_{12}) g_{23}^t(|v - w|, E)] \, dw}$$

$$\chi(E) = \left(\frac{E}{\pi(kT_{12})^3}\right)^{1/2} 2g_{11}^r\left(2\sqrt{E/m}\right) \exp\left(-\frac{E}{kT_{12}}\right) \tag{22}$$

where ψ_3 depends on E only through the collision frequencies $g_{\ell 3}^t = g_{\ell 3}^i + g_{\ell 3}^d$. If we introduce the effective (averaged) collision frequencies

$$\nu_{k\ell}^\alpha(T_{12}) = \iint g_{k\ell}^\alpha(|v - w|) M_k(v, T_{12}) M_\ell(w, T_{12}) \, dv \, dw \qquad k, \ell \neq 3 \tag{23}$$

it is not difficult to prove that the shape function χ satisfies the normalization condition

$$\int \chi(E) \, dE = \nu_{11}^r(T_{12}). \tag{24}$$

The equilibrium φ_3 does not introduce new parameters with respect to f_1 and f_2. It is remarkable that it depends on v only through $|v - u_{12}|$, so we have

$$u_3 = u_{12} \implies u = u_{12} \qquad P_3 = 2m \iint v \otimes v \psi_3(v, E) \chi(E) \, dv \, dE = P_3 I \tag{25}$$

where

$$P_3 = P_3(n_1, n_2, T_{12}) = \frac{2m}{3} \iint v^2 \psi_3(v, E) \chi(E) \, dv \, dE = n_3 K T_3 \tag{26}$$

and

$$n_3 = n_3(n_1, n_2, T_{12}) = \iint \psi_3(v, E) \chi(E) \, dv \, dE. \tag{27}$$

The six free parameters defining f_1, f_2 and φ_3 can be identified with the densities n_1 and n_2, the components of the drift velocity u of the whole mixture, and the temperature T_{12} common to particles 1 and 2. The sought approximate (asymptotic with respect to the small parameter) closure of the moment equations is now achieved by using the previous collision equilibria in order to express all integrals of the distribution functions. Retaining only leading-order terms, since also $q_{th} = 0$, one is left, after some algebra, with

$$\frac{\partial n_1}{\partial t} + \nabla \cdot (n_1 u) = -2\hat{\mathcal{S}}_2$$

$$\frac{\partial n_2}{\partial t} + \nabla \cdot (n_2 u) = \hat{\mathcal{S}}_2$$

$$\frac{\partial}{\partial t}(\hat{\rho} u) + \nabla \cdot (\hat{\rho} u \otimes u + (n_1 + n_2) K T_{12} I) = 0 \tag{28}$$

$$\frac{\partial}{\partial t}[(3/2)(n_1 + n_2) K T_{12} + (1/2)\hat{\rho} u^2] + \nabla \cdot [((5/2)(n_1 + n_2) K T_{12} + (1/2)\hat{\rho} u^2) u] = Q\hat{\mathcal{S}}_2$$

where $\hat{\rho} = m(n_1 + 2n_2)$ and

$$\hat{\mathcal{S}}_2 = \nu_{13}^i(n_1, n_2, T_{12}) n_1 n_3 + \nu_{23}^i(n_1, n_2, T_{12}) n_2 n_3 - [\nu_{12}^d(T_{12}) n_1 n_2 + \nu_{22}^d(T_{12}) n_2^2] \tag{29}$$

with

$$\nu_{\ell 3}^\alpha(n_1, n_2, T_{12}) = \frac{1}{n_3} \iiint g_{\ell 3}^\alpha(|v - w|, E) M_\ell(v, T_{12}) \psi_3(w, E) \chi(E) \, dv \, dw \, dE. \tag{30}$$

The macroscopic system (28) is self-consistent, even though partial density n_3 and effective collision frequencies ν may be complicated functions of its unknown fields. It describes evolution of the chemical reaction at an hydrodynamic level, after the short initial transient

dominated by fast processes, and represents fluid-dynamic equations of Euler type. It also shares with the mesoscopic system (8) the existence of five conservation equations (three from momentum equations, and the other two by elimination of $\hat{S}_2$, yielding mass and energy conservation) and occurrence of collision terms, represented here by the single quantity $\hat{S}_2$, which accounts for all non-conservative (inelastic, dissociation and recombination) interactions.

The further assumption that the collision frequencies $g_{\ell 3}^t$ are constants (to be labelled by $v_{\ell 3}^t$) would lead to a much simpler model. In fact, we have in this case

$$\varphi_3(\boldsymbol{v}, E) = n_3 M_3(|\boldsymbol{v} - \boldsymbol{u}|, T_{12})\chi(E)/v_{11}^r(T_{12}) \tag{31}$$

which implies

$$T_3 = T_{12} \Longrightarrow T = T_{12} \tag{32}$$

and n_3 can be cast in the explicit form

$$n_3 = \frac{v_{11}^r(T)n_1^2}{v_{13}^t n_1 + v_{23}^t n_2}. \tag{33}$$

Then $P_3 = n_3 K T$, $\boldsymbol{P} = nKT\boldsymbol{I}$ and the functions $v_{\ell 3}^i$ may depend at most only on T (they do not, when $g_{\ell 3}^i$ are constant). 'Collision' equilibria for the fluid-dynamic equations (28) are given by the requirement $\hat{S}_2 = 0$, that now reads simply as

$$v_{22}^d(T)v_{23}^t n_2^3 + [v_{12}^d(T)v_{23}^t + v_{22}^d(T)v_{13}^t]n_1 n_2^2$$
$$+ [v_{12}^d(T)v_{13}^t - v_{11}^r(T)v_{23}^i(T)]n_1^2 n_2 - v_{11}^r(T)v_{13}^i(T)n_1^3 = 0. \tag{34}$$

The existence and uniqueness of a real positive root for the ratio n_2/n_1 is easily proven on the basis of the sign of coefficients in this cubic equation. Equations (33) and (34) play thus the role of the mass action law of chemical equilibrium, since their unique physical solution determines the ratios n_2/n_1 and n_3/n_1 in terms of temperature T.

5. Numerical experiments

For a numerical illustration of the proposed model, we report here preliminarily on the closed macroscopic set of equations for the densities n_k, $k = 1, 2, 3$, which is in order in space homogeneous conditions when, in addition to all previous assumptions, effective collision frequencies are constant (isothermic reaction in a thermal bath). Actual computations at a kinetic level, either by discretization [14] or by multigroup methods [15], are planned as future work. In this situation we may take $\boldsymbol{u} = \boldsymbol{0}$ without loss of generality, and, from (16), the three-dimensional dynamical system

$$\begin{aligned}
\dot{n}_1 &= -2v_{11}^r n_1^2 + 2v_{12}^d n_1 n_2 + 2v_{22}^d n_2^2 + 2v_{13}^d n_1 n_3 + 2v_{23}^d n_2 n_3 \\
\dot{n}_2 &= -v_{12}^d n_1 n_2 - v_{22}^d n_2^2 + v_{13}^i n_1 n_3 + v_{23}^i n_2 n_3 \\
\dot{n}_3 &= -v_{13}^t n_1 n_3 - v_{23}^t n_2 n_3 + v_{11}^r n_1^2
\end{aligned} \tag{35}$$

is left, with first integral $n_1 + 2n_2 + 2n_3 = N$, where the constant N is determined by initial conditions. Notice that (35) is itself a singular perturbation problem, since all $v_{k\ell}$ with $\ell < 3$ have to be taken much smaller than v_{k3}. Fixed points of the dynamical system are the zeros of the vector field on the right-hand sides, and the relevant equations coincide exactly with the mass action law (33) and (34) discussed at the end of the previous section, with fixed T. For $n_1 \neq 0$ the ratios $a = n_2/n_1$ and $b = n_3/n_1$ are then uniquely determined. For $n_1 = 0$ we

have the additional equilibrium $n_2 = 0$ with n_3 arbitrary. Given the initial data, elimination of n_3 yields

$$\dot{n}_1 = v_{13}^d N n_1 + v_{23}^d N n_2 - (v_{13}^d + 2v_{11}^r)n_1^2 + (2v_{12}^d - 2v_{13}^d - v_{23}^d)n_1 n_2 + (2v_{22}^d - 2v_{23}^d)n_2^2$$

$$\dot{n}_2 = v_{13}^i \frac{N}{2} n_1 + v_{23}^i \frac{N}{2} n_2 - \frac{1}{2}v_{13}^i n_1^2 - \left(v_{12}^d + v_{13}^i + \frac{1}{2}v_{23}^i\right)n_1 n_2 - (v_{22}^d + v_{23}^i)n_2^2$$

(36)

whose admissible phase space is the triangle $0 \leqslant n_1 \leqslant N$, $0 \leqslant n_2 \leqslant N$, $0 \leqslant n_1 + 2n_2 \leqslant N$ in the (n_1, n_2) plane. It is easy to check that there is a unique internal fixed point compatible with the assigned data, namely

$$n_1 = \frac{N}{1 + 2a + 2b} \qquad n_2 = \frac{aN}{1 + 2a + 2b}$$

(37)

with $n_3 = bN/(1 + 2a + 2b)$, plus the boundary equilibrium point $(0, 0)$, with $n_3 = N$. For the latter, standard techniques show that it is unstable, whereas, in all the numerical experiments that have been performed, the former has turned out to be an asymptotically stable equilibrium (with real negative eigenvalues), and a global attractor for any initial point, except the origin, in the phase space.

Examples of the general trend, describing relaxation to the internal equilibrium, are shown in figures 1–4. Quantities are measured in arbitrary units, and numerical values have been selected in order to fulfill the physical requirements of the previous sections. In all figures shown below the collision frequencies $v_{k\ell}^i$ and $v_{k\ell}^d$ with $\ell = 3$ have been taken equal to unity, and N has been set equal to 10. In figure 1 all other collision frequencies are equal to 0.05. It illustrates a typical phase diagram, with all phase trajectories converging to the unique internal fixed point (37), given now by $(5.6540, 2.0695)$. Though ϵ turns out to be not particularly small in this case, the asymptotic predictions of the previous section clearly show up. In fact, the solution undergoes a fast initial transient, approaching the manifold corresponding to (33), namely the curve of the phase space

$$(v_{13}^t + 2v_{11}^r)n_1^2 + 2v_{23}^t n_2^2 + (2v_{13}^t + v_{23}^t)n_1 n_2 - v_{13}^t N n_1 - v_{23}^t N n_2 = 0 \qquad (38)$$

which is marked by a dashed line in the figure. It is a conic (in this case, a hyperbola), which the fixed point belongs to, and whose branch of interest in the phase space runs close to the straight borderline $n_1 + 2n_2 = N$, characterized by $n_3 = 0$. Then, the evolution occurs on a slower time scale, follows essentially the manifold (38) and is just governed by the specialization of the macroscopic equations (28) to the present simpler context, leading eventually to the equilibrium (37). Indeed, the conic can hardly be seen on the figure, being almost entirely hidden by the asymptotic part of all phase trajectories. The distance between the hyperbola and the dotted line $n_3 = 0$, though small, is instead visible, but just because of the relatively high value of ϵ. Pushing further the asymptotic limit would make the two curves indistinguishable, and n_3 vanishingly small during the whole fluid-dynamic evolution.

The initial layer is apparent in figure 2, where, for the same values of parameters as in figure 1, n_1 and n_2 are plotted versus time, with n_3 given by the dashed–dotted curve. It represents the particular solution starting from the initial point $(0, 1)$, with the dashed curves to indicate the continuation backwards, into the initial layer, of the asymptotic regime valid in the bulk region. Of course, an analytical treatment of the initial layer, in order to determine the effective initial conditions for the bulk solution, could be performed in the frame of singular perturbations [16], but the problem will not be considered here. The initial layer effect is much less apparent in figure 3, for the simple reason that, with all other parameters kept equal to the previous ones, the initial point $(10, 0)$ has been chosen very close to the asymptotic manifold (38). In general, notice that the densities versus time are not always monotonic. However, oscillating trends generated by nonreal eigenvalues of the Jacobian
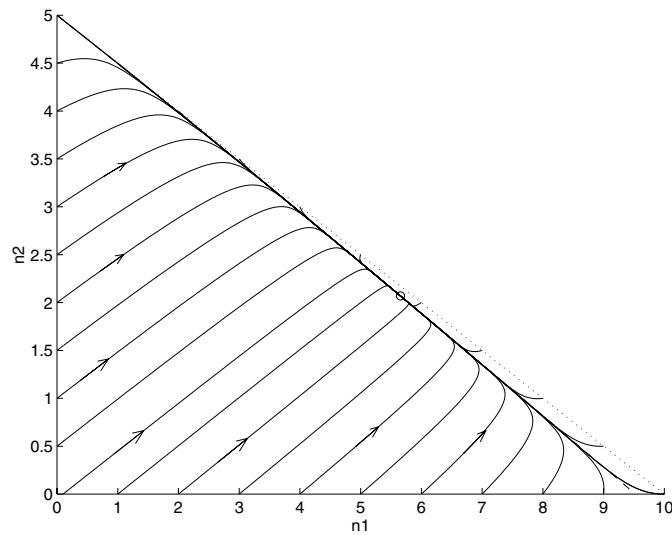
Figure 1. Phase portrait in the n_1–n_2 plane for the parameter values given in the text.
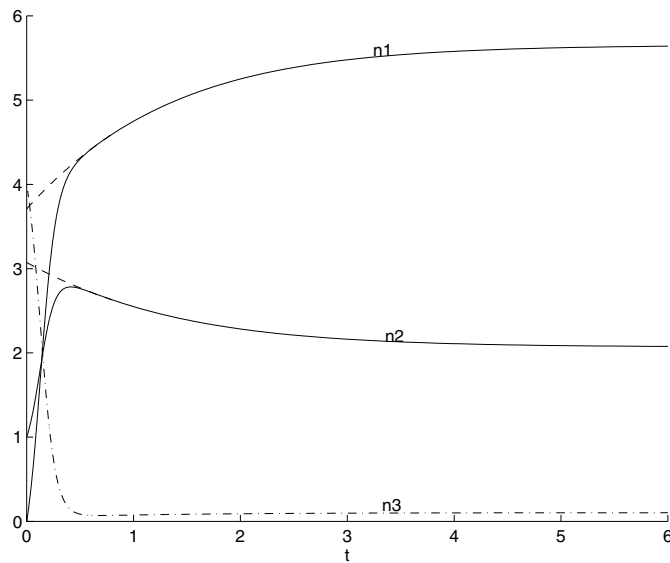

Figure 2. Densities versus time when initial conditions correspond to the point $(0, 1)$.

matrix are excluded in the bulk evolution, which is, in practice, one dimensional. For the sake of completeness, we report finally in figure 4 on the phase diagram when the parameters of figure 1 are changed only in that v_{11}^r takes the value 0.5. Here, the dashed–dotted line separates the two regions with positive (bottom) and negative (top) divergence. Relaxation to the unique internal equilibrium still occurs (indeed, the fixed point belongs to a compact positively invariant region with negative divergence), but now the asymptotic approach of section 4 becomes questionable, as clearly indicated by the sensible deviation of the phase trajectories with respect to the curve (38) (an ellipse now, marked by a dashed curve), and by the analogous deviation of the latter with respect to the manifold $n_3 = 0$.
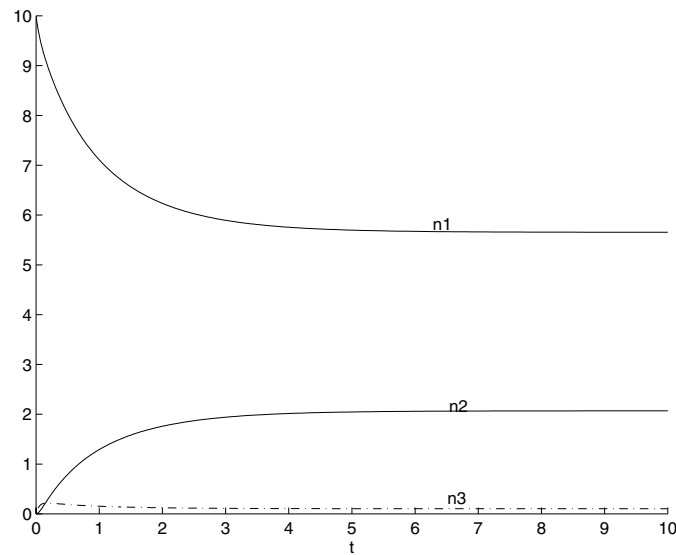
Figure 3. Densities versus time when initial conditions correspond to the point $(10, 0)$.
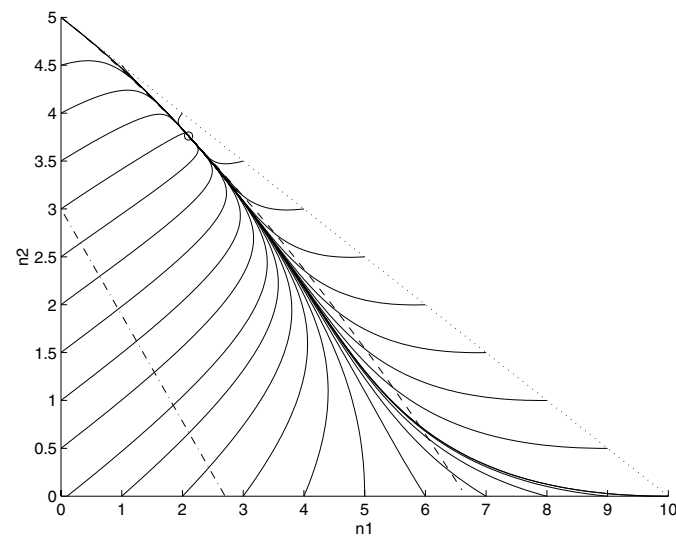
Figure 4. Phase portrait when v_{11}^r is increased from 0.05 to 0.5.

6. Conclusions

We have proposed a kinetic model for a diatomic gas with reactions of dissociation and recombination through a transition state. Boltzmann-type equations have been derived in the frame of a probabilistic formulation. Though they are quite awkward at first glance, some exact significant results on collision invariants and macroscopic conservation equations can be achieved even without an explicit knowledge of the collision kernels, only by virtue of their axiomatic properties. In addition, the definition of transition state itself suggests a

spontaneous asymptotic limit (the stationary-state approximation) in which it is possible to evaluate approximate collision equilibria, that turn out to be Maxwellian distributions for both atoms and molecules. The relevant Euler-type equations provide a closed approximate set of partial differential equations for six unknown macroscopic fields (atomic density, molecular density, drift velocity and temperature) governing the fluid-dynamic evolution of the system. We have also presented some preliminary numerical results for the simple space homogeneous problem in a thermal bath. They show the typical trends which are expected from a physical point of view, and whose theoretical investigation is in progress: relaxation to equilibrium from any given initial condition, and reduction to the fluid-dynamic regime when the smallness parameter (mean lifetime of the transition state) tends to zero.

Acknowledgments

Appendix A

In (D1), let (v', w') and $(v_\circ, v_\bullet, w)$ denote the velocity strings before and after collision. They are bound by momentum and energy conservation

$$
\begin{aligned}
2v' + pw' &= v_\circ + v_\bullet + pw \\
2v'^2 - 2Q/m + pw'^2 &= v_\circ^2 + v_\bullet^2 + pw^2.
\end{aligned}
\tag{A1}
$$

We shall resort to the 'scattering' kernels $\Pi_{2p}^{11p}(v', w' \to v_\circ, v_\bullet, w)$, symmetric with respect to the pair $(v_\circ, v_\bullet)$, with the obvious indistinguishability requirements and $\Pi_{p2}^{p11}(v', w' \to v, w_\circ, w_\bullet) = \Pi_{2p}^{11p}(w', v' \to w_\circ, w_\bullet, v)$. It is worth introducing the integrated probability distributions

$$
\begin{aligned}
\Pi_{2p}^{1,d}(v', w' \to v) &= \iint \Pi_{2p}^{11p}(v', w' \to v, v_\circ, w) \, dv_\circ \, dw \\
\Pi_{p2}^{p,d}(v', w' \to v) &= \iint \Pi_{p2}^{p11}(v', w' \to v, w_\circ, w_\bullet) \, dw_\circ \, dw_\bullet
\end{aligned}
\tag{A2}
$$

which satisfy by definition the first of (5) and $\Pi_{21}^{1,d}(v', w' \to v) = \Pi_{12}^{1,d}(w', v' \to v)$. The other conservation properties in (5) follow from integration of equation (A1) after multiplication by Π_{2p}^{11p}.

Analogously, one can define for (D2)

$$
\begin{aligned}
\Pi_{3p}^{1,d}(v', E; w' \to v) &= \iint \Pi_{3p}^{11p}(v', E; w' \to v, v_\circ, w) \, dv_\circ \, dw \\
\Pi_{p3}^{p,d}(v'; w', E \to v) &= \iint \Pi_{p3}^{p11}(v'; w', E \to v, w_\circ, w_\bullet) \, dw_\circ \, dw_\bullet
\end{aligned}
\tag{A3}
$$

and equation (6) follows in the same manner.

Appendix B

Chemical collision integrals in the kinetic equations (8) read as

$$
\mathcal{J}_1 = 3 \iint g_{12}^d(|v' - w'|) \Pi_{12}^{1,d}(v', w' \to v) f_1(v') f_2(w') \, dv' \, dw'
$$

$$+3 \iiint g_{13}^d(|v'-w'|, E)\Pi_{13}^{1;d}(v'; w', E \to v) f_1(v')\varphi_3(w', E) \,\mathrm{d}E \,\mathrm{d}v' \,\mathrm{d}w'$$

$$+2 \iiint g_{32}^d(|v'-w'|, E)\Pi_{32}^{1;d}(v', E; w' \to v)\varphi_3(v', E) f_2(w') \,\mathrm{d}E \,\mathrm{d}v' \,\mathrm{d}w'$$

$$+2 \iint g_{22}^d(|v'-w'|)\Pi_{22}^{1;d}(v', w' \to v) f_2(v') f_2(w') \,\mathrm{d}v' \,\mathrm{d}w'$$

$$+ \iiint g_{13}^i(|v'-w'|, E)\Pi_{13}^{1;i}(v'; w', E \to v) f_1(v')\varphi_3(w', E) \,\mathrm{d}E \,\mathrm{d}v' \,\mathrm{d}w'$$

$$-2 f_1(v) \int g_{11}^r(|v-w|) f_1(w) \,\mathrm{d}w$$

$$- f_1(v) \iint g_{13}^d(|v-w|, E)\varphi_3(w, E) \,\mathrm{d}E \,\mathrm{d}w$$

$$- f_1(v) \int g_{12}^d(|v-w|) f_2(w) \,\mathrm{d}w$$

$$- f_1(v) \iint g_{13}^i(|v-w|, E)\varphi_3(w, E) \,\mathrm{d}E \,\mathrm{d}w$$

$$\text{(B1)}$$

$$\mathcal{J}_2 = \iiint g_{23}^d(|v'-w'|, E)\Pi_{23}^{2,d}(v'; w', E \to v) f_2(v')\varphi_3(w', E) \,\mathrm{d}E \,\mathrm{d}v' \,\mathrm{d}w'$$

$$+ \iint g_{22}^d(|v'-w'|)\Pi_{22}^{2;d}(v', w' \to v) f_2(v') f_2(w') \,\mathrm{d}v' \,\mathrm{d}w'$$

$$+ \iiint g_{31}^i(|v'-w'|, E)\Pi_{31}^{2;i}(v', E; w' \to v)\varphi_3(v', E) f_1(w') \,\mathrm{d}E \,\mathrm{d}v' \,\mathrm{d}w'$$

$$+2 \iiint g_{23}^i(|v'-w'|, E)\Pi_{23}^{2;i}(v'; w', E \to v) f_2(v')\varphi_3(w', E) \,\mathrm{d}E \,\mathrm{d}v' \,\mathrm{d}w'$$

$$- f_2(v) \int g_{21}^d(|v-w|) f_1(w) \,\mathrm{d}w - 2 f_2(v) \int g_{22}^d(|v-w|) f_2(w) \,\mathrm{d}w$$

$$- f_2(v) \iint [g_{23}^d(|v-w|, E) + g_{23}^i(|v-w|, E)]\varphi_3(w, E) \,\mathrm{d}E \,\mathrm{d}w$$

$$= \iint g_{11}^r(|v'-w'|)\Pi_{11}^{3;r}(v', w' \to v, E) f_1(v') f_1(w') \,\mathrm{d}v' \,\mathrm{d}w'$$

$$-\varphi_3(v, E) \int f_1(w)[g_{31}^d(|v-w|, E) + g_{31}^i(|v-w|, E)] \,\mathrm{d}w$$

$$-\varphi_3(v, E) \int f_2(w)[g_{32}^d(|v-w|, E) + g_{32}^i(|v-w|, E)] \,\mathrm{d}w. \tag{B2}$$

Appendix C

Mass density and drift velocity in (11) are defined by

$$\rho = m[n_1 + 2(n_2 + n_3)]$$
$$\rho u = m[n_1 u_1 + 2(n_2 u_2 + n_3 u_3)] \tag{C1}$$

with

$$n_\ell = \int f_\ell(v) \,\mathrm{d}v \qquad u_\ell = (1/n_\ell) \int f_\ell(v) v \,\mathrm{d}v \qquad \ell = 1, 2, 3. \tag{C2}$$

The pressure tensor in (12) is

$$P = \sum_{\ell=1}^{3} m_\ell \int (v - u) \otimes (v - u) f_\ell(v) \, dv = \sum_{\ell=1}^{3} P_\ell. \tag{C3}$$

Energy densities and heat fluxes in (13) read

$$\mathcal{E}_{\text{th}} = (3/2)nKT = (1/2)I : P \qquad n = \sum_{\ell=1}^{3} n_\ell$$

$$\mathcal{E}_{\text{int}} = \int [\mathcal{M}_{31}(v) - Q f_2(v)] \, dv \tag{C4}$$

and

$$q_{\text{th}} = (1/2) \sum_{\ell=1}^{3} m_\ell \int (v - u)^2 (v - u) f_\ell(v) \, dv$$

$$q_{\text{int}} = \int (v - u)[\mathcal{M}_{31}(v) - Q f_2(v)] \, dv \tag{C5}$$

respectively, where K is the Boltzmann constant.

Appendix D

The source terms in (16) are, respectively,

$$\begin{aligned}
\mathcal{S}_1 &= 2G_{12}^d + 2G_{13}^d + 2G_{22}^d + 2G_{23}^d - 2G_{11}^r \\
\mathcal{S}_2 &= G_{13}^i + G_{23}^i - G_{12}^d - G_{22}^d \\
\mathcal{S}_3 &= G_{11}^r - G_{13}^d - G_{23}^d - G_{13}^i - G_{23}^i
\end{aligned} \tag{D1}$$

with

$$G_{k\ell}^\alpha = \iint g_{k\ell}^\alpha(|v - w|) f_k(v) f_\ell(w) \, dv \, dw \qquad \ell \neq 3 \tag{D2}$$

and

$$G_{k3}^\alpha = \iiint g_{k3}^\alpha(|v - w|, E) f_k(v) \varphi_3(w, E) \, dv \, dw \, dE. \tag{D3}$$

The source term in the energy equation (17) turns out to be

$$\mathcal{S}_{\text{th}} = Q\mathcal{S}_2 + K_{13}^t + K_{23}^t - K_{11}^r \tag{D4}$$

with

$$K_{11}^r = (m/4) \iint (v - w)^2 g_{11}^r(|v - w|) f_1(v) f_1(w) \, dv \, dw$$

$$K_{\ell 3}^t = \iiint E g_{\ell 3}^t(|v - w|, E) f_\ell(v) \varphi_3(w, E) \, dv \, dw \, dE \tag{D5}$$

$(g_{\ell 3}^t = g_{\ell 3}^d + g_{\ell 3}^i)$.

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