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Relaxation of Rotational-Vibrational Energy and Volume Viscosity in H–H_2 Mixtures

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Abstract

We investigate a kinetic model for $\mathrm{H}-\mathrm{H}_2$ mixtures in a regime where translational/rotational and vibrational-resonant energy exchanges are fast whereas vibrational energy variations are slow. In a relaxation regime, the effective volume viscosity is found to involve contributions from the rotational volume viscosity, the vibrational volume viscosity, the relaxation pressure and the perturbed source term. In the thermodynamic equilibrium limit, the sum of these four terms converges toward the one-temperature two-mode volume viscosity. The theoretical results are applied to the calculation of the volume viscosities of molecular hydrogen on the basis of a complete set of state-selected cross sections for the $\mathrm{H}+\mathrm{H}_2(v,j)$ system.

1 Introduction

Modeling thermodynamic nonequilibrium and coupled rotational-vibrational energy relaxation is an important issue in reentry problems, laboratory and atmospheric plasmas, as well as discharges [1, 2, 3, 4, 5, 6, 7, 8]. The most general thermodynamic nonequilibrium model is the state to state model where each internal state of a molecule is independent and considered as a separate species [4, 5, 6, 7]. When there are partial equilibria between some of these states, species internal energy temperatures can be defined and the complexity of the model is correspondingly reduced [1, 2, 3, 4, 5, 6, 7, 8]. The next reduction step then consists in equating some of the species internal temperatures [7] and it yields the two temperature models investigated in this paper. Relaxation of internal temperatures then leads to volume viscosity coefficients [8, 9, 10, 11, 12, 13, 14, 15, 16] and theoretical models as well as experimental measurements have confirmed that this coefficient is of the order of the shear viscosity for polyatomic gases [21, 22, 18, 19, 17, 20]. The impact of volume viscosity in fluid mechanics—especially for fast flows—has also been established [28, 29, 30, 31, 32].

We investigate in this paper a kinetic model for $\mathrm{H}-\mathrm{H}_2$ nonequilibrium mixtures where translational/rotational and vibrational-resonant collisions are fast whereas collisions with vibrational energy variations are slow, reactive aspects between H and H_2 lying beyond the scope of the present study. The relaxation of the translational-rotational temperature $\overline{T}$ and of the vibrational temperature T^{v} as well as the concept of volume viscosity are investigated in a kinetic theory framework where the rotational and vibrational energies are assumed to be coupled. We also use Galerkin variational approximation spaces introduced in References [33, 34] emphasizing exchanges of energy and both the zeroth order as well as the first order asymptotic models are considered.

We establish that, in a relaxation regime, there are four contributions to the volume viscosity, namely the rotational volume viscosity, the vibrational mode volume viscosity, the relaxation pressure and the perturbed source term. In the thermodynamic equilibrium limit, the sum of these four terms converges toward the one-temperature two-mode volume viscosity. These results extend previous work concerning single gas and independent energy modes [8].

Theoretical results are then applied to the calculation of volume viscosities and relaxation times in molecular hydrogen. The required collision integrals are evaluated from a complete set of state-to-state cross sections for the $\mathrm{H}+\mathrm{H}_2(v,j)$ collisional system. The latter have been obtained using an implementation of the quasiclassical method [35, 36, 37, 38, 39], on the accurate BKMP2 potential energy surface (PES) [40].

Comparisons between one-temperature and two-temperature model predictions are performed and conclusions are drawn on the domain of validity of each regime.

2 A Nonequilibrium Kinetic Model for Gas Mixtures

We investigate in this section a kinetic model for a gas mixture with two internal energy modes.

2.1 A multi-temperature kinetic framework

We consider a kinetic framework for a mixture of gases with the species Boltzmann equation written in the form

$$\partial_t f_i + \boldsymbol{c}_i \cdot \boldsymbol{\nabla} f_i = \frac{1}{\epsilon} \mathcal{J}_i^{\mathrm{rap}} + \mathcal{J}_i^{\mathrm{sl}}, \qquad i \in \mathfrak{S}, \tag{1}$$

where t denotes time, i the species index, $\mathfrak{S}$ the species indexing set, ∂_t the time derivative operator, $\boldsymbol{x}$ the spatial coordinate, ∇ the space derivative operator, $\boldsymbol{c}_i$ the velocity of the particle of the ith species, $f_i(t, \boldsymbol{x}, \boldsymbol{c}_i, \mathrm{I})$ the distribution function for the ith species, I the index of the quantum energy state for the particles of the ith species, $\mathcal{J}_i^{\mathrm{rap}}$ the rapid collision operator for the ith species, $\mathcal{J}_i^{\mathrm{sl}}$ the slow collision operator for the ith species, and ϵ the formal parameter associated with the Chapman-Enskog procedure. We will frequently assume that the mixture of gases is arbitrary with $\mathfrak{S} = \{1, \dots, \mathrm{N}^s\}$ where N^s is the number of species and then specialize to the particular case $\mathfrak{S} = \{\mathrm{H}, \mathrm{H}_2\}$ only at a later stage. We assume for the sake of simplicity that the particles are not influenced by an external force field and reactive aspects lie beyond the scope of the present study.

The complete collision operator for the ith species $\mathcal{J}_i = \mathcal{J}_i^{\mathrm{rap}} + \mathcal{J}_i^{\mathrm{sl}}$ is in the form

$$\mathcal{J}_i(f) = \sum_{j \in \mathfrak{S}} \sum_{\mathrm{J}, \mathrm{I}', \mathrm{J}'} \int \Big(f_i(\boldsymbol{c}_i', \mathrm{I}') f_j(\widetilde{\boldsymbol{c}}_j', \mathrm{J}') \frac{a_{i\mathrm{I}} a_{j\mathrm{J}}}{a_{i\mathrm{I}'} a_{j\mathrm{J}'}} - f_i(\boldsymbol{c}_i, \mathrm{I}) f_j(\widetilde{\boldsymbol{c}}_j, \mathrm{J}) \Big) g_{ij} \sigma_{ij}^{\mathrm{IJI'J'}} \mathrm{d}\widetilde{\boldsymbol{c}}_j \, \mathrm{d}\boldsymbol{e}_{ij}', \tag{2}$$

where (in a direct collision) j denotes the species index of the colliding partner, I and J denote the indices of the quantum energy states before collision, I' and J' the corresponding numbers after collision, $\widetilde{\boldsymbol{c}}_j$ the velocity of the colliding partner, $\boldsymbol{c}_i'$ and $\widetilde{\boldsymbol{c}}_j'$ the velocities after collision, $a_{i\mathrm{I}}$ the degeneracy of the Ith quantum energy state of the ith species, $\sigma_{ij}^{\mathrm{IJI'J'}}$ the collision cross section for the species pair (i, j), g_{ij} the absolute value of the relative velocity $\boldsymbol{c}_i - \widetilde{\boldsymbol{c}}_j$ of the incoming particles and $\boldsymbol{e}_{ij}'$ the unit vector in the direction of the relative velocity $\boldsymbol{c}_i' - \widetilde{\boldsymbol{c}}_j'$ after collision. Only binary collisions are considered since the system is dilute and the cross sections satisfy the reciprocity relations [10, 16]

$$a_{i\mathrm{I}} a_{j\mathrm{J}} g_{ij} \sigma_{ij}^{\mathrm{IJI'J'}} \mathrm{d}\boldsymbol{c}_i \, \mathrm{d}\widetilde{\boldsymbol{c}}_j \, \mathrm{d}\boldsymbol{e}_{ij}' = a_{i\mathrm{I}'} a_{j\mathrm{J}'} g_{ij}' \sigma_{ij}^{\mathrm{I'J'IJ}} \mathrm{d}\boldsymbol{c}_i' \mathrm{d}\widetilde{\boldsymbol{c}}_j' \mathrm{d}\boldsymbol{e}_{ij}. \tag{3}$$

Denoting by $W_{ij}^{\mathrm{IJI'J'}}$ the transition probability for collisions, we also have the identity $g_{ij} \sigma_{ij}^{\mathrm{IJI'J'}} \mathrm{d}\boldsymbol{e}_{ij}' = W_{ij}^{\mathrm{IJI'J'}} \mathrm{d}\boldsymbol{c}_i' \mathrm{d}\widetilde{\boldsymbol{c}}_j'$ so that the collision terms may equivalently be written in terms of transition probabilities [33, 16].

The internal energy of the ith species in the Ith quantum state is decomposed into

$$E_{i\mathrm{I}} = E_{i\mathrm{I}}^{\mathrm{r}} + E_{i\mathrm{I}}^{\mathrm{v}}, \tag{4}$$

where I denotes the index of the quantum energy state, $E_{i\mathrm{I}}^{\mathrm{r}}$ the rotational internal energy, $E_{i\mathrm{I}}^{\mathrm{v}}$ the vibrational internal energy, and we write $\Delta E_{ij}^{\mathrm{v}} = E_{i\mathrm{I}'}^{\mathrm{v}} + E_{j\mathrm{J}'}^{\mathrm{v}} - E_{i\mathrm{I}}^{\mathrm{v}} - E_{j\mathrm{J}}^{\mathrm{v}}$ for the vibrational energy jump. The fast collision operator $\mathcal{J}_i^{\mathrm{rap}}$ for the ith species includes all collisions satisfying $\Delta E_{ij}^{\mathrm{v}} = 0$, either involving only the translational-rotational energies or resonant with respect to the vibrational energy, and the slow collision operator $\mathcal{J}_i^{\mathrm{sl}}$ describes the collisions for which $\Delta E_{ij}^{\mathrm{v}} \neq 0$. Assuming that there are sufficiently resonant collisions between the species, the collisional invariants of the fast collision operator are associated with the species particle numbers $\psi^k = (\delta_{ki})_{i \in \mathfrak{S}}$, $k \in \mathfrak{S}$, momentum $\psi^{\mathrm{N}^s + l} = (m_i c_{il})_{i \in \mathfrak{S}}$, $l \in \{1, 2, 3\}$, the energy associated with translational and rotational degrees of freedom $\psi^{\mathrm{N}^s + 4} = \psi^{\mathrm{t}} + \psi^{\mathrm{r}}$ and the vibrational energy mode $\psi^{\mathrm{N}^s + 5} = \psi^{\mathrm{v}}$, where $\psi^{\mathrm{t}} = \big(\frac{1}{2} m_i (\boldsymbol{c}_i - \boldsymbol{v}) \cdot (\boldsymbol{c}_i - \boldsymbol{v})\big)_{i \in \mathfrak{S}}$, $\psi^{\mathrm{r}} = (E_{i\mathrm{I}}^{\mathrm{r}})_{i \in \mathfrak{S}}$, and $\psi^{\mathrm{v}} = (E_{i\mathrm{I}}^{\mathrm{v}})_{i \in \mathfrak{S}}$. Tensorial quantities that have one component for each species are denoted for convenience in the form $\xi = (\xi_i)_{i \in \mathfrak{S}}$.

The Enskog expansion reads $f_i = f_i^{(0)} \big(1 + \epsilon \phi_i + \mathcal{O}(\epsilon^2)\big)$ where $f_i^{(0)}$ is the Maxwellian distribution for the ith species and we denote $f = (f_i)_{i \in \mathfrak{S}}$, $f^{(0)} = (f_i^{(0)})_{i \in \mathfrak{S}}$, and $\phi = (\phi_i)_{i \in \mathfrak{S}}$. The Maxwellian distributions are found in the form

$$f_i^{(0)} = \Big(\frac{m_i}{2\pi k_{\mathrm{B}} \overline{\overline{T}}}\Big)^{\frac{3}{2}} \frac{n_i a_{i\mathrm{I}}}{Z_i} \exp\Big(-\frac{m_i (\boldsymbol{c}_i - \boldsymbol{v}) \cdot (\boldsymbol{c}_i - \boldsymbol{v})}{2 k_{\mathrm{B}} \overline{\overline{T}}} - \frac{E_{i\mathrm{I}}^{\mathrm{r}}}{k_{\mathrm{B}} \overline{\overline{T}}} - \frac{E_{i\mathrm{I}}^{\mathrm{v}}}{k_{\mathrm{B}} T^{\mathrm{v}}}\Big), \qquad i \in \mathfrak{S}, \tag{5}$$

with

$$Z_i = \sum_{\mathrm{I}} a_{i\mathrm{I}} \exp\Big(-\frac{E^{\mathrm{r}}_{i\mathrm{I}}}{k_{\mathrm{B}}\overline{T}} - \frac{E^{\mathrm{v}}_{i\mathrm{I}}}{k_{\mathrm{B}}T^{\mathrm{v}}} \Big), \tag{6}$$

where $\overline{T}$ is the partial equilibrium temperature between the translational and rotational degrees of freedom, T^{v} the temperature associated with the vibrational degrees of freedom, and Z_i the partition function for internal energy of the ith species. Since the rotational and vibrational energies are not assumed to be independent, the internal energy partition function Z_i cannot be factorized.

2.2 Fluid equations

The equations for the conservation of mass, momentum and internal energies are obtained by taking the scalar product of the Boltzmann equation (1) with the collisional invariants of the fast collision operator. The scalar product $\langle\!\langle \xi, \zeta \rangle\!\rangle$ between two tensorial quantities $\xi = (\xi_i)_{i\in\mathfrak{S}}$ and $\zeta = (\zeta_i)_{i\in\mathfrak{S}}$ with components $\xi_i(t, \boldsymbol{x}, \boldsymbol{c}_i, \mathrm{I})$ and $\zeta_i(t, \boldsymbol{x}, \boldsymbol{c}_i, \mathrm{I})$ is defined by

$$\langle\!\langle \xi, \zeta \rangle\!\rangle = \sum_{i\in\mathfrak{S}} \sum_{\mathrm{I}} \int \xi_i \odot \zeta_i \,\mathrm{d}\boldsymbol{c}_i,$$

where $\xi_i \odot \zeta_i$ is the contracted product. The fluid variables are the particle number densities $n_k = \langle\!\langle \psi^k, f \rangle\!\rangle = \langle\!\langle \psi^k, f^{(0)} \rangle\!\rangle$ or equivalently the mass densities $\rho_k = m_k n_k$ for $k \in \mathfrak{S}$, the mass averaged velocity $\boldsymbol{v}$ such that $\rho \boldsymbol{v}_l = \langle\!\langle \psi^{\mathrm{N}^{\mathrm{s}}+l}, f \rangle\!\rangle = \langle\!\langle \psi^{\mathrm{N}^{\mathrm{s}}+l}, f^{(0)} \rangle\!\rangle$ for $l \in \{1, 2, 3\}$, the partial equilibrium temperature between the translational and rotational degrees of freedom $\overline{T}$ and the vibrational temperature T^{v}. The latter are defined by the coupled system of equations $\mathcal{E}^{\mathrm{t+r}}(\overline{T}, T^{\mathrm{v}}) = \langle\!\langle f, \psi^{\mathrm{t}} + \psi^{\mathrm{r}} \rangle\!\rangle = \langle\!\langle f^{(0)}, \psi^{\mathrm{t}} + \psi^{\mathrm{r}} \rangle\!\rangle$ and $\mathcal{E}^{\mathrm{v}}(\overline{T}, T^{\mathrm{v}}) = \langle\!\langle f, \psi^{\mathrm{v}} \rangle\!\rangle = \langle\!\langle f^{(0)}, \psi^{\mathrm{v}} \rangle\!\rangle$, the dependence on the species number densities n_i, $i \in \mathfrak{S}$, being left implicit to simplify notation.

Following the Chapman-Enskog procedure, the conservation equations for mass, momentum and internal energies are found in the form [7]

$$\partial_t \rho_k + \boldsymbol{\nabla}\cdot(\rho_k \boldsymbol{v}) + \boldsymbol{\nabla}\cdot(\rho_k \boldsymbol{V}_k) = 0, \qquad k \in \mathfrak{S}, \tag{7}$$

$$\partial_t (\rho \boldsymbol{v}) + \boldsymbol{\nabla}\cdot(\rho \boldsymbol{v}\otimes\boldsymbol{v} + p\boldsymbol{I}) + \boldsymbol{\nabla}\cdot\boldsymbol{\Pi} = 0, \tag{8}$$

$$\partial_t \mathcal{E}^{\mathrm{t+r}} + \boldsymbol{\nabla}\cdot(\boldsymbol{v}\mathcal{E}^{\mathrm{t+r}}) + \boldsymbol{\nabla}\cdot\boldsymbol{Q}^{\mathrm{t+r}} = -p\boldsymbol{\nabla}\cdot\boldsymbol{v} - \boldsymbol{\Pi}\boldsymbol{:}\boldsymbol{\nabla}\boldsymbol{v} - \omega^{\mathrm{v}}_1, \tag{9}$$

$$\partial_t \mathcal{E}^{\mathrm{v}} + \boldsymbol{\nabla}\cdot(\boldsymbol{v}\mathcal{E}^{\mathrm{v}}) + \boldsymbol{\nabla}\cdot\boldsymbol{Q}^{\mathrm{v}} = \omega^{\mathrm{v}}_1, \tag{10}$$

where $\mathcal{E}^{\mathrm{t+r}} = \mathcal{E}^{\mathrm{t}} + \mathcal{E}^{\mathrm{r}}$, $\mathcal{E}^{\mathrm{t}} = \langle\!\langle f^{(0)}, \psi^{\mathrm{t}} \rangle\!\rangle$ denotes the internal energy per unit volume of translational origin, $\mathcal{E}^{\mathrm{r}} = \langle\!\langle f^{(0)}, \psi^{\mathrm{r}} \rangle\!\rangle$ the internal energy per unit volume of rotational origin, $\mathcal{E}^{\mathrm{v}}$ the internal energy per unit volume of vibrational origin, $\boldsymbol{Q}^{\mathrm{t+r}}$ and $\boldsymbol{Q}^{\mathrm{v}}$ the corresponding heat fluxes, and ω^{v}_1 the exchange term in the Navier-Stokes regime. The transport fluxes are defined by

$$\boldsymbol{V}_i = \sum_{\mathrm{I}} \int (\boldsymbol{c}_i - \boldsymbol{v}) f^{(0)}_i \phi_i \,\mathrm{d}\boldsymbol{c}_i, \qquad i \in \mathfrak{S}, \tag{11}$$

$$\boldsymbol{\Pi} = \sum_{i\in\mathfrak{S}} \sum_{\mathrm{I}} \int (\boldsymbol{c}_i - \boldsymbol{v})\otimes(\boldsymbol{c}_i - \boldsymbol{v}) f^{(0)}_i \phi_i \,\mathrm{d}\boldsymbol{c}_i, \tag{12}$$

$$\boldsymbol{Q}^{\mathrm{t+r}} = \sum_{i\in\mathfrak{S}} \sum_{\mathrm{I}} \int \big(\tfrac{1}{2} m_i (\boldsymbol{c}_i - \boldsymbol{v})^2 + E^{\mathrm{r}}_{i\mathrm{I}}\big)(\boldsymbol{c}_i - \boldsymbol{v}) f^{(0)}_i \phi_i \,\mathrm{d}\boldsymbol{c}_i, \tag{13}$$

$$\boldsymbol{Q}^{\mathrm{v}} = \sum_{i\in\mathfrak{S}} \sum_{\mathrm{I}} \int E^{\mathrm{v}}_{i\mathrm{I}} (\boldsymbol{c}_i - \boldsymbol{v}) f^{(0)}_i \phi_i \,\mathrm{d}\boldsymbol{c}_i. \tag{14}$$

In the next sections, we investigate the thermodynamic properties p, $\mathcal{E}^{\mathrm{t}}$, $\mathcal{E}^{\mathrm{r}}$, and $\mathcal{E}^{\mathrm{v}}$, the source term ω^{v}_1, as well as the transport fluxes $\boldsymbol{V}_i$, $i \in \mathfrak{S}$, $\boldsymbol{\Pi}$, $\boldsymbol{Q}^{\mathrm{t+r}}$, and $\boldsymbol{Q}^{\mathrm{v}}$.

2.3 Thermodynamics

The state law and the internal energies are in the form

$$p = n k_{\mathrm{B}} \overline{T}, \qquad \mathcal{E}^{\mathrm{t}} = n \tfrac{3}{2} k_{\mathrm{B}} \overline{T} \qquad \mathcal{E}^{\mathrm{r}} = \sum_{i\in\mathfrak{S}} n_i \overline{E}^{\mathrm{r}}_i, \qquad \mathcal{E}^{\mathrm{v}} = \sum_{i\in\mathfrak{S}} n_i \overline{E}^{\mathrm{v}}_i, \tag{15}$$

where $n = \sum_{i \in \mathfrak{S}} n_i$ and $\overline{E}_i^{\mathrm{r}}$ and $\overline{E}_i^{\mathrm{v}}$ denote the average rotational and vibrational internal energy per particle of the ith species. The internal energies are not supposed to be independent in this work, that is, the composed index I can be written $\mathrm{I} = (\mathrm{I}^{\mathrm{r}}, \mathrm{I}^{\mathrm{v}})$ where I^{r} and I^{v} denote the rotational and vibrational quantum numbers of the state, respectively, but the energies $E_{i\mathrm{I}}^{\mathrm{r}}$ and $E_{i\mathrm{I}}^{\mathrm{v}}$ depend a priori on both indices I^{r} and I^{v}. In order to define the average energies as well as the specific heats, it is convenient to introduce the averaging operator for the ith species

$$\big\langle \xi_{i\mathrm{I}} \big\rangle_i = \sum_{\mathrm{I}} \frac{a_{i\mathrm{I}} \xi_{i\mathrm{I}}}{Z_i} \exp\Big(- \frac{E_{i\mathrm{I}}^{\mathrm{r}}}{k_{\mathrm{B}} \overline{T}} - \frac{E_{i\mathrm{I}}^{\mathrm{v}}}{k_{\mathrm{B}} T^{\mathrm{v}}} \Big). \tag{16}$$

The average rotational and vibrational internal energy per particle of the ith species $\overline{E}_i^{\mathrm{r}}$ and $\overline{E}_i^{\mathrm{v}}$ are then given by

$$\overline{E}_i^{\mathrm{r}} = \big\langle E_{i\mathrm{I}}^{\mathrm{r}} \big\rangle_i, \qquad \overline{E}_i^{\mathrm{v}} = \big\langle E_{i\mathrm{I}}^{\mathrm{v}} \big\rangle_i, \tag{17}$$

and depend a priori on both $\overline{T}$ and T^{v}. We next introduce the corresponding specific heats

$$c_i^{\mathrm{rr}} = \partial_{\overline{T}} \overline{E}_i^{\mathrm{r}} = \tfrac{1}{k_{\mathrm{B}} \overline{T}^2} \Big(\big\langle E_{i\mathrm{I}}^{\mathrm{r}\,2} \big\rangle_i - \overline{E}_i^{\mathrm{r}\,2} \Big) = \tfrac{1}{k_{\mathrm{B}} \overline{T}^2} \big\langle (E_{i\mathrm{I}}^{\mathrm{r}} - \overline{E}_i^{\mathrm{r}})^2 \big\rangle \tag{18}$$

$$c_i^{\mathrm{rv}} = \partial_{T^{\mathrm{v}}} \overline{E}_i^{\mathrm{r}} = \tfrac{1}{k_{\mathrm{B}} T^{\mathrm{v}2}} \Big(\big\langle E_{i\mathrm{I}}^{\mathrm{r}} E_{i\mathrm{I}}^{\mathrm{v}} \big\rangle_i - \overline{E}_i^{\mathrm{r}} \overline{E}_i^{\mathrm{v}} \Big) = \tfrac{1}{k_{\mathrm{B}} T^{\mathrm{v}2}} \big\langle (E_{i\mathrm{I}}^{\mathrm{r}} - \overline{E}_i^{\mathrm{r}})(E_{i\mathrm{I}}^{\mathrm{v}} - \overline{E}_i^{\mathrm{v}}) \big\rangle_i, \tag{19}$$

$$c_i^{\mathrm{vr}} = \partial_{\overline{T}} \overline{E}_i^{\mathrm{v}} = \tfrac{1}{k_{\mathrm{B}} \overline{T}^2} \Big(\big\langle E_{i\mathrm{I}}^{\mathrm{r}} E_{i\mathrm{I}}^{\mathrm{v}} \big\rangle_i - \overline{E}_i^{\mathrm{r}} \overline{E}_i^{\mathrm{v}} \Big) = \tfrac{1}{k_{\mathrm{B}} \overline{T}^2} \big\langle (E_{i\mathrm{I}}^{\mathrm{r}} - \overline{E}_i^{\mathrm{r}})(E_{i\mathrm{I}}^{\mathrm{v}} - \overline{E}_i^{\mathrm{v}}) \big\rangle_i, \tag{20}$$

and

$$c_i^{\mathrm{vv}} = \partial_{T^{\mathrm{v}}} \overline{E}_i^{\mathrm{v}} = \tfrac{1}{k_{\mathrm{B}} T^{\mathrm{v}2}} \Big(\big\langle E_{i\mathrm{I}}^{\mathrm{v}2} \big\rangle_i - \overline{E}_i^{\mathrm{v}2} \Big) = \tfrac{1}{k_{\mathrm{B}} T^{\mathrm{v}2}} \big\langle (E_{i\mathrm{I}}^{\mathrm{v}} - \overline{E}_i^{\mathrm{v}})^2 \big\rangle_i. \tag{21}$$

Note that we have $c_i^{\mathrm{rv}} T^{\mathrm{v}2} = c_i^{\mathrm{vr}} \overline{T}^2$ in such a way that at equilibrium ($T^{\mathrm{v}} = \overline{T}$) we have $c_i^{\mathrm{rv}} = c_i^{\mathrm{vr}}$. In the simpler situation where the rotational and vibrational energies are independent, then the cross specific heats c_i^{rv} and c_i^{vr} vanish. We also define the translational specific heat c^{t} as well as the combined specific heats c_i^{r}, c_i^{v}, and $c_{\mathrm{vl}\,i}$ by

$$c^{\mathrm{t}} = \tfrac{3}{2} k_{\mathrm{B}}, \qquad c_i^{\mathrm{r}} = c_i^{\mathrm{rr}} + c_i^{\mathrm{rv}}, \qquad c_i^{\mathrm{v}} = c_i^{\mathrm{vr}} + c_i^{\mathrm{vv}}, \tag{22}$$

$$c_{\mathrm{vl}\,i} = c^{\mathrm{t}} + c_i^{\mathrm{rr}} + c_i^{\mathrm{rv}} + c_i^{\mathrm{vr}} + c_i^{\mathrm{vv}}. \tag{23}$$

We introduce the corresponding mixture heats c^{rr}, c^{rv}, c^{vr}, c^{vv}, c^{r}, c^{v}, and c_{vl} given by

$$n c^{\mathrm{rr}} = \sum_i n_i c_i^{\mathrm{rr}}, \qquad n c^{\mathrm{rv}} = \sum_i n_i c_i^{\mathrm{rv}}, \qquad n c^{\mathrm{vr}} = \sum_i n_i c_i^{\mathrm{vr}}, \qquad n c^{\mathrm{vv}} = \sum_i n_i c_i^{\mathrm{vv}},$$

$$n c^{\mathrm{r}} = \sum_i n_i c_i^{\mathrm{r}}, \qquad n c^{\mathrm{v}} = \sum_i n_i c_i^{\mathrm{v}}, \qquad n c_{\mathrm{vl}} = \sum_i n_i c_{\mathrm{vl}\,i}.$$

For future use, we also introduce the modified specific heats

$$c_i^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} = c_i^{\mathrm{rr}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}} c_i^{\mathrm{vr}} = c_i^{\mathrm{rr}} - \frac{c^{\mathrm{vr}}}{c^{\mathrm{vv}}} c_i^{\mathrm{rv}}, \qquad c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} = c^{\mathrm{rr}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}} c^{\mathrm{vr}},$$

which are associated with the derivative of $\overline{E}_i^{\mathrm{r}}$ and $\overline{E}^{\mathrm{r}}$ when $\overline{E}^{\mathrm{v}}$ is kept constant, respectively, as well as the shifted rotational energies

$$E_{i\mathrm{I}}^{\tilde{\mathrm{r}}} = E_{i\mathrm{I}}^{\mathrm{r}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}} E_{i\mathrm{I}}^{\mathrm{v}}, \qquad \overline{E}_i^{\tilde{\mathrm{r}}} = \big\langle E_{i\mathrm{I}}^{\tilde{\mathrm{r}}} \big\rangle_i = \overline{E}_i^{\mathrm{r}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}} \overline{E}_i^{\mathrm{v}},$$

and it is easily checked that

$$n c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} = \sum_i n_i \tfrac{1}{k_{\mathrm{B}} \overline{T}^2} \big\langle (E_{i\mathrm{I}}^{\tilde{\mathrm{r}}} - \overline{E}_i^{\tilde{\mathrm{r}}})^2 \big\rangle_i, \qquad \sum_i n_i \big\langle (E_{i\mathrm{I}}^{\tilde{\mathrm{r}}} - \overline{E}_i^{\tilde{\mathrm{r}}})(E_{i\mathrm{I}}^{\mathrm{v}} - \overline{E}_i^{\mathrm{v}}) \big\rangle_i = 0.$$

The basis functions built from the shifted energies will notably be orthogonal to the vibrational collisional invariant ψ^{v} of the fast collision operator.

2.4 Source terms

The full source term ω^{v} may be written $\omega^{\mathrm{v}} = \langle\!\langle \psi^{\mathrm{v}}, \mathcal{J}^{\mathrm{sl}} \rangle\!\rangle = \langle\!\langle \psi^{\mathrm{v}}, \mathcal{J} \rangle\!\rangle$ since $\langle\!\langle \psi^{\mathrm{v}}, \mathcal{J}^{\mathrm{rap}} \rangle\!\rangle = 0$ and may be expanded into $\omega^{\mathrm{v}} = \omega^{\mathrm{v}}_0 + \epsilon\delta\omega^{\mathrm{v}}_1 + \mathcal{O}(\epsilon^2)$. The source term ω^{v}_1 is then given by

$$\omega^{\mathrm{v}}_1 = \omega^{\mathrm{v}}_0 + \epsilon\delta\omega^{\mathrm{v}}_1, \tag{24}$$

where ω^{v}_0 denotes the source term evaluated from the Maxwellian distribution $f^{(0)}$ and $\delta\omega^{\mathrm{v}}_1$ the correction associated with the Navier-Stokes perturbation $f^{(0)}\phi$.

We introduce the averaging operator $[\![\ ]\!]_{ij}$ for the species pair i, j

$$[\![\alpha_{ij}]\!]_{ij} = \frac{1}{8n_i n_j} \sum_{\mathrm{I,J,I',J'}} \int \alpha_{ij}^{\mathrm{IJI'J'}} f_i^{(0)} \widetilde{f}_j^{(0)} g_{ij} \sigma_{ij}^{\mathrm{IJI'J'}} \mathrm{d}\boldsymbol{c}_i \, \mathrm{d}\widetilde{\boldsymbol{c}}_j \, \mathrm{d}\boldsymbol{e}'_{ij}, \tag{25}$$

as well as the complete averaging operator

$$[\![\alpha]\!] = \sum_{ij} \frac{n_i n_j}{n^2} [\![\alpha_{ij}]\!]_{ij} = \frac{1}{8n^2} \sum_{ij} \sum_{\mathrm{I,J,I',J'}} \int \alpha_{ij}^{\mathrm{IJI'J'}} f_i^{(0)} \widetilde{f}_j^{(0)} g_{ij} \sigma_{ij}^{\mathrm{IJI'J'}} \mathrm{d}\boldsymbol{c}_i \, \mathrm{d}\widetilde{\boldsymbol{c}}_j \, \mathrm{d}\boldsymbol{e}'_{ij}. \tag{26}$$

Several important properties of this averaging operator are summarized in Appendix A.

A direct evaluation of the source term ω^{v}_0 yields that

$$\omega^{\mathrm{v}}_0 = -2n^2 \left[\!\!\left[(\Delta E^{\mathrm{v}}) \Big(\exp\big(\tfrac{\Delta E^{\mathrm{v}}}{k_{\mathrm{B}} \overline{T}} - \tfrac{\Delta E^{\mathrm{v}}}{k_{\mathrm{B}} T^{\mathrm{v}}} \big) - 1 \Big) \right]\!\!\right], \tag{27}$$

where $\Delta E^{\mathrm{v}}_{ij} = E^{\mathrm{v}}_{i\mathrm{I'}} + E^{\mathrm{v}}_{j\mathrm{J'}} - E^{\mathrm{v}}_{i\mathrm{I}} - E^{\mathrm{v}}_{j\mathrm{J}}$ and defining the nonequilibrium correction factor ζ^{v} by

$$\zeta^{\mathrm{v}}_{ij} = \int_0^1 \exp\Big(\big(\tfrac{\Delta E^{\mathrm{v}}_{ij}}{k_{\mathrm{B}} \overline{T}} - \tfrac{\Delta E^{\mathrm{v}}_{ij}}{k_{\mathrm{B}} T^{\mathrm{v}}} \big) s \Big) \, ds,$$

the source term ω^{v}_0 is recast in the convenient form

$$\omega^{\mathrm{v}}_0 = 2n^2 \frac{[\![(\Delta E^{\mathrm{v}})^2 \zeta^{\mathrm{v}}]\!]}{k_{\mathrm{B}} \overline{T} T^{\mathrm{v}}} (\overline{T} - T^{\mathrm{v}}). \tag{28}$$

Defining the nonequilibrium relaxation time by $\tau^{\mathrm{v}} = c^{\mathrm{v}} k_{\mathrm{B}} \overline{T} T^{\mathrm{v}} / (2n [\![(\Delta E^{\mathrm{v}})^2 \zeta^{\mathrm{v}}]\!])$, where $c^{\mathrm{v}} = c^{\mathrm{vr}} + c^{\mathrm{vv}}$, we obtain that

$$\omega^{\mathrm{v}}_0 = \frac{n c^{\mathrm{v}}}{\tau^{\mathrm{v}}} (\overline{T} - T^{\mathrm{v}}). \tag{29}$$

On the other hand, the perturbed source term $\delta\omega^{\mathrm{v}}_1$ is given by

$$\delta\omega^{\mathrm{v}}_1 = \sum_{ij \in \mathfrak{S}} \sum_{\mathrm{I,J,I',J'}} E^{\mathrm{v}}_{i\mathrm{I}} \int \Big(f_i^{(0)\prime} \widetilde{f}_j^{(0)\prime} \frac{a_{i\mathrm{I}} a_{j\mathrm{J}}}{a_{i\mathrm{I'}} a_{j\mathrm{J'}}} (\phi'_i + \widetilde{\phi}'_j) - f_i^{(0)} \widetilde{f}_j^{(0)} (\phi_i + \widetilde{\phi}_j) \Big) g_{ij} \sigma_{ij}^{\mathrm{IJI'J'}} \mathrm{d}\boldsymbol{c}_i \, \mathrm{d}\widetilde{\boldsymbol{c}}_j \, \mathrm{d}\boldsymbol{e}'_{ij}, \tag{30}$$

and upon defining $\mathcal{W}^{\mathrm{v}} = (\mathcal{W}^{\mathrm{v}}_i)_{i \in \mathfrak{S}}$ by

$$\mathcal{W}^{\mathrm{v}}_i = \sum_{j \in \mathfrak{S}} \sum_{\mathrm{J,I',J'}} (\Delta E^{\mathrm{v}}_{ij}) \int \widetilde{f}_j^{(0)} g_{ij} \sigma_{ij}^{\mathrm{IJI'J'}} \mathrm{d}\widetilde{\boldsymbol{c}}_j \, \mathrm{d}\boldsymbol{e}'_{ij},$$

it is checked that

$$\delta\omega^{\mathrm{v}}_1 = \langle\!\langle f^{(0)}\phi, \mathcal{W}^{\mathrm{v}} \rangle\!\rangle. \tag{31}$$

2.5 Transport coefficients

We denote by $\mathcal{I}^{\mathrm{rap}}_i$ the linearized fast collision operator for the ith species and $\mathcal{I}^{\mathrm{rap}} = (\mathcal{I}^{\mathrm{rap}}_i)_{i \in \mathfrak{S}}$ the mixture operator. The perturbed distribution function $\phi = (\phi_i)_{i \in \mathfrak{S}}$ is such that $\mathcal{I}^{\mathrm{rap}}(\phi) = \psi$ where $\psi = (\psi_i)_{i \in \mathfrak{S}}$ has the components

$$\psi_i = -\partial_t^{(0)} \log f_i^{(0)} - \boldsymbol{c}_i \cdot \boldsymbol{\nabla} \log f_i^{(0)} + \mathcal{J}_i^{\mathrm{sl},(0)} / f_i^{(0)}, \qquad i \in \mathfrak{S}.$$

The perturbed distribution function $\phi = (\phi_i)_{i\in\mathfrak{S}}$ is also such that $\langle\!\langle f^{(0)}\phi, \psi^j \rangle\!\rangle = 0$ for $1 \leqslant j \leqslant \textsc{n}^s + 5$, where ψ^j, $1 \leqslant j \leqslant \textsc{n}^s + 5$, are the collisional invariants of the fast collision operator. The ith component of ψ may be evaluated following the Chapman-Enskog procedure in the form

$$\psi_i = -\psi_i^{\eta} : \boldsymbol{\nabla}\boldsymbol{v} - \psi_i^{\lambda^{\mathrm{t+r}}}\cdot\boldsymbol{\nabla}\Big(\frac{1}{k_{\mathrm{B}}\overline{T}}\Big) - \psi_i^{\lambda^{\mathrm{v}}}\cdot\boldsymbol{\nabla}\Big(\frac{1}{k_{\mathrm{B}}T^{\mathrm{v}}}\Big) - \sum_{j\in\mathfrak{S}} \psi_i^{D_j}\cdot\boldsymbol{\nabla}p_j - \tfrac{1}{3}\psi_i^{\kappa}\,\boldsymbol{\nabla}\cdot\boldsymbol{v} + \psi_i^{\omega}\omega_0^{\mathrm{v}},$$

where ψ_i^{η} is a symmetric traceless tensor, $\psi_i^{\lambda^{\mathrm{t+r}}}$, $\psi_i^{\lambda^{\mathrm{v}}}$, and $\psi_i^{D_j}$, $j \in \mathfrak{S}$, are vectors, and ψ_i^{κ} and ψ_i^{ω} are scalars given by

$$\psi_i^{\eta} = \frac{m_i}{k_{\mathrm{B}}\overline{T}}\big((\boldsymbol{c}_i - \boldsymbol{v})\otimes(\boldsymbol{c}_i - \boldsymbol{v}) - \tfrac{1}{3}(\boldsymbol{c}_i - \boldsymbol{v})\cdot(\boldsymbol{c}_i - \boldsymbol{v})\boldsymbol{I}\big), \tag{32}$$

$$\psi_i^{\lambda^{\mathrm{t+r}}} = \big(\tfrac{5}{2}k_{\mathrm{B}}\overline{T} - \tfrac{1}{2}m_i(\boldsymbol{c}_i - \boldsymbol{v})\cdot(\boldsymbol{c}_i - \boldsymbol{v}) + \overline{E}_i^{\mathrm{r}} - E_{i\mathrm{I}}^{\mathrm{r}}\big)(\boldsymbol{c}_i - \boldsymbol{v}), \tag{33}$$

$$\psi_i^{\lambda^{\mathrm{v}}} = \big(\overline{E}_i^{\mathrm{v}} - E_{i\mathrm{I}}^{\mathrm{v}}\big)(\boldsymbol{c}_i - \boldsymbol{v}), \tag{34}$$

$$\psi_i^{D_j} = \frac{1}{p_i}\big(\delta_{ij} - Y_i\big)(\boldsymbol{c}_i - \boldsymbol{v}), \qquad j \in \mathfrak{S}, \tag{35}$$

$$\psi_i^{\kappa} = -\frac{2c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}{c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}\Big(\tfrac{3}{2} - \frac{m_i(\boldsymbol{c}_i - \boldsymbol{v})\cdot(\boldsymbol{c}_i - \boldsymbol{v})}{2k_{\mathrm{B}}\overline{T}}\Big) + \frac{2c^{\mathrm{t}}}{c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}\frac{\big(\overline{E}_i^{\mathrm{r}} - E_{i\mathrm{I}}^{\mathrm{r}}\big)}{k_{\mathrm{B}}\overline{T}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}\frac{2c^{\mathrm{t}}}{c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}\frac{\big(\overline{E}_i^{\mathrm{v}} - E_{i\mathrm{I}}^{\mathrm{v}}\big)}{k_{\mathrm{B}}\overline{T}}, \tag{36}$$

$$\psi_i^{\omega} = \frac{\widetilde{\mathcal{J}}_i^{\mathrm{sl},(0)}}{f_i^{(0)}} - \frac{\tfrac{3}{2}k_{\mathrm{B}}\overline{T} - \tfrac{1}{2}m_i(\boldsymbol{c}_i - \boldsymbol{v})\cdot(\boldsymbol{c}_i - \boldsymbol{v})}{nk_{\mathrm{B}}(c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})\overline{T}^2}\frac{c^{\mathrm{vv}} + c^{\mathrm{rv}}}{c^{\mathrm{vv}}} - \frac{\overline{E}_i^{\mathrm{r}} - E_{i\mathrm{I}}^{\mathrm{r}}}{nk_{\mathrm{B}}(c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})\overline{T}^2}\frac{c^{\mathrm{vv}} + c^{\mathrm{rv}}}{c^{\mathrm{vv}}} \tag{37}$$

$$+ \frac{\overline{E}_i^{\mathrm{v}} - E_{i\mathrm{I}}^{\mathrm{v}}}{nk_{\mathrm{B}}c^{\mathrm{vv}}T^{\mathrm{v}\,2}}\frac{c^{\mathrm{t}} + c^{\mathrm{rr}} + c^{\mathrm{vr}}}{c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}. \tag{38}$$

The source term $\mathcal{J}^{\mathrm{sl},(0)} = (\mathcal{J}^{\mathrm{sl},(0)})_{i\in\mathfrak{S}}$ has been written $\mathcal{J}_i^{\mathrm{sl},(0)} = \omega_0^{\mathrm{v}}\widetilde{\mathcal{J}}_i^{\mathrm{sl},(0)}$ where

$$\widetilde{\mathcal{J}}_i^{\mathrm{sl},(0)} = -\frac{1}{2n^2[\![(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}]\!]}\sum_{j\in\mathfrak{S}}\sum_{\mathrm{J,I',J'}}\int f_i^{(0)}\widetilde{f}_j^{(0)}(\Delta E_{ij}^{\mathrm{v}})\zeta_{ij}^{\mathrm{v}}g_{ij}\sigma_{ij}^{\mathrm{IJI'J'}}\,\mathrm{d}\widetilde{\boldsymbol{c}}_j\,\mathrm{d}\boldsymbol{e}'_{ij}. \tag{39}$$

and we have $\langle\!\langle \psi^{\mathrm{v}}, \widetilde{\mathcal{J}}^{\mathrm{sl},(0)} \rangle\!\rangle = 1$, $\langle\!\langle \psi^{\mathrm{t}} + \psi^{\mathrm{r}}, \widetilde{\mathcal{J}}^{\mathrm{sl},(0)} \rangle\!\rangle = -1$, $\langle\!\langle \psi^{\mathrm{H}_2}, \widetilde{\mathcal{J}}^{\mathrm{sl},(0)} \rangle\!\rangle = 0$, $\langle\!\langle \psi^{\mathrm{H}}, \widetilde{\mathcal{J}}^{\mathrm{sl},(0)} \rangle\!\rangle = 0$ in such a way that ψ^{ω} is orthogonal to the collisional invariants of the fast collision operator. Thanks to linearity $\phi = (\phi_i)_{i\in\mathfrak{S}}$ may be expanded in the form

$$\phi_i = -\phi_i^{\eta} : \boldsymbol{\nabla}\boldsymbol{v} - \phi_i^{\lambda^{\mathrm{t+r}}}\cdot\boldsymbol{\nabla}\Big(\frac{1}{k_{\mathrm{B}}\overline{T}}\Big) - \phi_i^{\lambda^{\mathrm{v}}}\cdot\boldsymbol{\nabla}\Big(\frac{1}{k_{\mathrm{B}}T^{\mathrm{v}}}\Big) - \sum_{j\in\mathfrak{S}} \phi_i^{D_j}\cdot\boldsymbol{\nabla}p_j - \tfrac{1}{3}\phi_i^{\kappa}\,\boldsymbol{\nabla}\cdot\boldsymbol{v} + \phi_i^{\omega}\omega_0^{\mathrm{v}}, \tag{40}$$

where ϕ_i^{η} is a symmetric traceless tensor, $\phi_i^{\lambda^{\mathrm{t+r}}}$ $\phi_i^{\lambda^{\mathrm{v}}}$, and $\phi_i^{D_j}$, $j \in \mathfrak{S}$ are vectors, ϕ_i^{κ} and ϕ_i^{ω} are scalars. These coefficients $\phi^{\mu} = (\phi_i^{\mu})_{i\in\mathfrak{S}}$, $\mu \in \{\eta, \lambda^{\mathrm{t+r}}, \lambda^{\mathrm{v}}, (D_j, j \in \mathfrak{S}), \kappa, \omega\}$, satisfy the linearized Boltzmann equations

$$\mathcal{I}^{\mathrm{rap}}(\phi^{\mu}) = \psi^{\mu}, \tag{41}$$

i.e., $\mathcal{I}_i^{\mathrm{rap}}(\phi^{\mu}) = \psi_i^{\mu}$ for $i \in \mathfrak{S}$, with the constraints

$$\langle\!\langle f^{(0)}\phi^{\mu}, \psi^j \rangle\!\rangle = 0, \qquad 1 \leqslant j \leqslant \textsc{n}^s + 5. \tag{42}$$

These integral equations (41)(42) are well posed and only involve fast collisions.

On the other hand, it may be checked that the fluxes can be written

$$\boldsymbol{V}_i = k_{\mathrm{B}}\overline{T}\langle\!\langle \psi^{D_i}, f^{(0)}\phi \rangle\!\rangle, \qquad i \in \mathfrak{S}, \tag{43}$$

$$\boldsymbol{\Pi} = k_{\mathrm{B}}\overline{T}\langle\!\langle \psi^{\eta}, f^{(0)}\phi \rangle\!\rangle + \tfrac{1}{3}k_{\mathrm{B}}\overline{T}\langle\!\langle \psi^{\kappa}, f^{(0)}\phi \rangle\!\rangle\boldsymbol{I}, \tag{44}$$

$$\boldsymbol{Q}^{\mathrm{t+r}} = -\langle\!\langle \psi^{\lambda^{\mathrm{t+r}}}, f^{(0)}\phi \rangle\!\rangle + \sum_{i\in\mathfrak{S}}(\tfrac{5}{2}k_{\mathrm{B}}\overline{T} + \overline{E}_i^{\mathrm{r}})n_i\boldsymbol{V}_i, \tag{45}$$

$$\boldsymbol{Q}^{\mathrm{v}} = -\langle\!\langle \psi^{\lambda^{\mathrm{v}}}, f^{(0)}\phi \rangle\!\rangle + \sum_{i\in\mathfrak{S}}\overline{E}_i^{\mathrm{v}}n_i\boldsymbol{V}_i. \tag{46}$$

Substituting the expansion (40) of the perturbed distribution function ϕ into the above relations, and using the isotropy of the collision operator $\mathcal{I}^{\mathrm{rap}}$, we obtain the following expressions for the transport fluxes

$$\boldsymbol{V}_i = -\sum_{j\in\mathfrak{S}} D_{ij}\boldsymbol{d}_j - \theta_i^{\mathrm{t+r}}\boldsymbol{\nabla}\log\overline{T} - \theta_i^{\mathrm{v}}\boldsymbol{\nabla}\log T^{\mathrm{v}}, \tag{47}$$

$$\boldsymbol{\Pi} = p^{\mathrm{rel}} - \kappa^{\mathrm{r}}\boldsymbol{\nabla}\cdot\boldsymbol{v}\boldsymbol{I} - \eta\big(\boldsymbol{\nabla}\boldsymbol{v} + (\boldsymbol{\nabla}\boldsymbol{v})^t - \tfrac{2}{3}(\boldsymbol{\nabla}\cdot\boldsymbol{v})\boldsymbol{I}\big), \tag{48}$$

$$\boldsymbol{Q}^{\mathrm{t+r}} = -\lambda^{\mathrm{t+r,t+r}}\boldsymbol{\nabla}\overline{T} - \lambda^{\mathrm{t+r,v}}\boldsymbol{\nabla}T^{\mathrm{v}} - p\sum_{i\in\mathfrak{S}}\theta_i^{\mathrm{t+r}}\boldsymbol{d}_i + \sum_{i\in\mathfrak{S}}(\tfrac{5}{2}k_{\mathrm{B}}\overline{T} + \overline{E}_i^{\mathrm{r}})n_i\boldsymbol{V}_i, \tag{49}$$

$$\boldsymbol{Q}^{\mathrm{v}} = -\lambda^{\mathrm{v,t+r}}\boldsymbol{\nabla}\overline{T} - \lambda^{\mathrm{v,v}}\boldsymbol{\nabla}T^{\mathrm{v}} - p\frac{T^{\mathrm{v}}}{\overline{T}}\sum_{i\in\mathfrak{S}}\theta_i^{\mathrm{v}}\boldsymbol{d}_i + \sum_{i\in\mathfrak{S}}\overline{E}_i^{\mathrm{v}}n_i\boldsymbol{V}_i, \tag{50}$$

where

$$\boldsymbol{d}_i = \frac{\boldsymbol{\nabla}p_i}{p}, \qquad i\in\mathfrak{S},$$

are the diffusion driving forces and where D_{ij} are the multicomponent diffusion coefficients, $\theta_i^{\mathrm{t+r}}$ the translational and rotational thermal diffusion coefficients, θ_i^{v} the vibrational thermal diffusion coefficients, p^{rel} the relaxation pressure, κ^{r} the rotational volume viscosity, η the shear viscosity, and $\lambda^{\mathrm{t+r,t+r}}$, $\lambda^{\mathrm{t+r,v}}$, $\lambda^{\mathrm{v,t+r}}$, and $\lambda^{\mathrm{v,v}}$ the thermal conductivities.

In order to express the corresponding transport coefficients we define the bracket operator associated with the fast linearized collision operator by

$$[\xi,\zeta] = \langle\!\langle f^{(0)}\mathcal{I}^{\mathrm{rap}}(\xi),\zeta\rangle\!\rangle = \langle\!\langle f^{(0)}\xi,\mathcal{I}^{\mathrm{rap}}(\zeta)\rangle\!\rangle = [\zeta,\xi].$$

This bracket is symmetric positive semi-definite and its nullspace is spanned by the collisional invariants, i.e., $[\xi,\xi]=0$ if and only if ξ is a linear combination of collisional invariants of the fast collision operator $\mathcal{I}^{\mathrm{rap}}$.

The transport coefficients are then given by

$$D_{ij} = \frac{pk_{\mathrm{B}}\overline{T}}{3}[\phi^{D_i},\phi^{D_j}], \qquad i,j\in\mathfrak{S}, \tag{51}$$

$$\theta_i^{\mathrm{t+r}} = -\frac{1}{3}[\phi^{D_i},\phi^{\lambda^{\mathrm{t+r}}}], \qquad \theta_i^{\mathrm{v}} = -\frac{1}{3}\frac{\overline{T}}{T^{\mathrm{v}}}[\phi^{D_i},\phi^{\lambda^{\mathrm{v}}}], \qquad i\in\mathfrak{S}, \tag{52}$$

$$\eta = \tfrac{1}{10}k_{\mathrm{B}}\overline{T}[\phi^{\eta},\phi^{\eta}], \qquad \kappa = \tfrac{1}{9}k_{\mathrm{B}}\overline{T}[\phi^{\kappa},\phi^{\kappa}], \tag{53}$$

$$\lambda^{\mathrm{t+r,t+r}} = \frac{1}{3k_{\mathrm{B}}\overline{T}^2}[\phi^{\lambda^{\mathrm{t+r}}},\phi^{\lambda^{\mathrm{t+r}}}], \qquad \lambda^{\mathrm{t+r,v}} = \frac{1}{3k_{\mathrm{B}}T^{\mathrm{v}\,2}}[\phi^{\lambda^{\mathrm{t+r}}},\phi^{\lambda^{\mathrm{v}}}], \tag{54}$$

$$\lambda^{\mathrm{v,t+r}} = \frac{1}{3k_{\mathrm{B}}\overline{T}^2}[\phi^{\lambda^{\mathrm{v}}},\phi^{\lambda^{\mathrm{t+r}}}], \qquad \lambda^{\mathrm{v,v}} = \frac{1}{3k_{\mathrm{B}}T^{\mathrm{v}\,2}}[\phi^{\lambda^{\mathrm{v}}},\phi^{\lambda^{\mathrm{v}}}]. \tag{55}$$

In addition, the relaxation pressure p^{rel} and the reduced relaxation pressure $\widetilde{p}^{\mathrm{rel}}$ are given by

$$p^{\mathrm{rel}} = \widetilde{p}^{\mathrm{rel}}\omega_0^{\mathrm{v}}, \qquad \widetilde{p}^{\mathrm{rel}} = \tfrac{1}{3}k_{\mathrm{B}}\overline{T}\langle\!\langle f^{(0)}\phi^{\omega},\psi^{\kappa}\rangle\!\rangle = \tfrac{1}{3}k_{\mathrm{B}}\overline{T}\langle\!\langle f^{(0)}\phi^{\kappa},\psi^{\omega}\rangle\!\rangle. \tag{56}$$

Using now the Curie principle, we may also write

$$\delta\omega_1^{\mathrm{v}} = -\tfrac{1}{3}\langle\!\langle f^{(0)}\phi^{\kappa},\mathcal{W}^{\mathrm{v}}\rangle\!\rangle\boldsymbol{\nabla}\cdot\boldsymbol{v} + \langle\!\langle f^{(0)}\phi^{\omega},\mathcal{W}^{\mathrm{v}}\rangle\!\rangle\omega_0^{\mathrm{v}},$$

so that defining

$$w_1^{\kappa} = -\tfrac{1}{3}\langle\!\langle f^{(0)}\phi^{\kappa},\mathcal{W}^{\mathrm{v}}\rangle\!\rangle, \qquad w_1^{\mathrm{v}} = \langle\!\langle f^{(0)}\phi^{\omega},\mathcal{W}^{\mathrm{v}}\rangle\!\rangle, \tag{57}$$

we have

$$\delta\omega_1^{\mathrm{v}} = w_1^{\kappa}\,\boldsymbol{\nabla}\cdot\boldsymbol{v} + w_1^{\mathrm{v}}\,\omega_0^{\mathrm{v}}. \tag{58}$$

Finally, defining the pressure tensor as $\boldsymbol{\mathcal{P}} = p\boldsymbol{I} + \boldsymbol{\Pi}$, we have

$$\boldsymbol{\mathcal{P}} = (nk_{\mathrm{B}}\overline{T} + p^{\mathrm{rel}} - \kappa^{\mathrm{r}}\boldsymbol{\nabla}\cdot\boldsymbol{v})\boldsymbol{I} - \eta\big(\boldsymbol{\nabla}\boldsymbol{v} + (\boldsymbol{\nabla}\boldsymbol{v})^t - \tfrac{2}{3}(\boldsymbol{\nabla}\cdot\boldsymbol{v})\boldsymbol{I}\big), \tag{59}$$

with a pressure term $nk_{\mathrm{B}}\overline{T}\boldsymbol{I}$, a volume viscosity contribution associated with rotation $\kappa^{\mathrm{r}}\boldsymbol{\nabla}\cdot\boldsymbol{v}\boldsymbol{I}$, and a relaxation pressure term $p^{\mathrm{rel}}\boldsymbol{I}$.

2.6 The traditional rotational volume viscosity

We introduce the orthogonal polynomials

$$\phi^{0010k} = \Big(\tfrac{1}{k_{\mathrm{B}} \overline{T}} \big(\tfrac{3}{2} k_{\mathrm{B}} \overline{T} - \tfrac{1}{2} m_i (\boldsymbol{c}_i - \boldsymbol{v}) \cdot (\boldsymbol{c}_i - \boldsymbol{v}) \big) \delta_{ki} \Big)_{i \in \mathfrak{S}}, \qquad k \in \mathfrak{S},$$

$$\phi^{000\mathrm{r}k} = \Big(\tfrac{1}{k_{\mathrm{B}} \overline{T}} \big(\overline{E}_i^{\mathrm{r}} - E_{i\mathrm{I}}^{\mathrm{r}} \big) \delta_{ki} \Big)_{i \in \mathfrak{S}}, \qquad k \in \mathfrak{P},$$

and

$$\phi^{000\mathrm{v}k} = \Big(\tfrac{1}{k_{\mathrm{B}} T^{\mathrm{v}}} \big(\overline{E}_i^{\mathrm{v}} - E_{i\mathrm{I}}^{\mathrm{v}} \big) \delta_{ki} \Big)_{i \in \mathfrak{S}}, \qquad k \in \mathfrak{P},$$

where $\mathfrak{P}$ denotes the set of polyatomic species and N^p the number of polyatomic species. We also denote by

$$\widehat{\psi}^{\mathrm{t+r}} = \sum_{l \in \mathfrak{S}} \phi^{0010l} + \sum_{l \in \mathfrak{P}} \phi^{000\mathrm{r}l}, \qquad \widehat{\psi}^{\mathrm{v}} = \sum_{l \in \mathfrak{P}} \phi^{000\mathrm{v}l},$$

the collisional invariant of the fast collision operator and by $\widehat{\psi}^{\mathrm{t+r+v}} = \widehat{\psi}^{\mathrm{t+r}} + \frac{T^{\mathrm{v}}}{\overline{T}} \widehat{\psi}^{\mathrm{v}}$ the total energy collisional invariant.

The basis functions $\phi^{000\mathrm{r}k}$, $k \in \mathfrak{P}$, however, are not adapted to the fast collision operator since they are not guaranteed to be orthogonal to the collisional invariant $\widehat{\psi}^{\mathrm{v}}$. In order to obtain such basis functions, it is natural to use the shifted energies

$$\phi^{000\tilde{\mathrm{r}}k} = \phi^{000\mathrm{r}k} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}} \frac{T^{\mathrm{v}}}{\overline{T}} \phi^{000\mathrm{v}k} = \Big(\tfrac{1}{k_{\mathrm{B}} \overline{T}} \big(\overline{E}_i^{\tilde{\mathrm{r}}} - E_{i\mathrm{I}}^{\tilde{\mathrm{r}}} \big) \delta_{ki} \Big)_{i \in \mathfrak{S}}, \qquad k \in \mathfrak{P},$$

as well as the shifted collisional invariant

$$\widehat{\psi}^{\mathrm{t}+\tilde{\mathrm{r}}} = \widehat{\psi}^{\mathrm{t+r}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}} \frac{T^{\mathrm{v}}}{\overline{T}} \widehat{\psi}^{\mathrm{v}} = \sum_{l \in \mathfrak{S}} \phi^{0010l} + \sum_{l \in \mathfrak{P}} \phi^{000\tilde{\mathrm{r}}l},$$

that are automatically orthogonal to $\widehat{\psi}^{\mathrm{v}}$. The natural generalization of the standard linear system associated with the evaluation of the rotational volume viscosity is then obtained with the Galerkin variational approximation space spanned by the orthogonal polynomials ϕ^{0010k}, $k \in \mathfrak{S}$, and $\phi^{000\tilde{\mathrm{r}}k}$ $k \in \mathfrak{P}$. The matrix coefficients of the corresponding transport linear system of size $\mathrm{N}^s + \mathrm{N}^p$ are similar to that of the independent energy situation since fast collisions are such that $\Delta E^{\mathrm{v}} = \Delta \widetilde{E}^{\mathrm{v}}$ but the right hand side vectors differ.

In the special situation where $\mathfrak{S} = \{\mathrm{H}_2, \mathrm{H}\}$, we have $\mathfrak{P} = \{\mathrm{H}_2\}$, $\mathrm{N}^s = 2$, $\mathrm{N}^p = 1$, $\widehat{\psi}^{\mathrm{t+r}} = \phi^{0010\mathrm{H}_2} + \phi^{0010\mathrm{H}} + \phi^{000\mathrm{r}\mathrm{H}_2}$, and $\widehat{\psi}^{\mathrm{v}} = \phi^{000\mathrm{v}\mathrm{H}_2}$. The variational space is spanned by $\phi^{0010\mathrm{H}_2}$, $\phi^{0010\mathrm{H}}$, and $\phi^{000\tilde{\mathrm{r}}\mathrm{H}_2}$ and the transport linear system is of size $\mathrm{N}^s + \mathrm{N}^p = 3$. Expanding ϕ^{κ} in the form

$$\phi^{\kappa} = -\frac{3}{p} \Big(\alpha_{\mathrm{H}_2}^{10\kappa} \phi^{0010\mathrm{H}_2} + \alpha_{\mathrm{H}}^{10\kappa} \phi^{0010\mathrm{H}} + \alpha_{\mathrm{H}_2}^{0\tilde{\mathrm{r}}\kappa} \phi^{000\tilde{\mathrm{r}}\mathrm{H}_2} \Big),$$

we obtain

$$K \alpha^{\kappa} = \beta^{\kappa}, \tag{60}$$

and the constraint

$$< \mathcal{K}, \alpha^{\kappa} >= 0, \tag{61}$$

and the linear system (60)(61) is well posed. The right member β^{κ} is given by

$$\beta_{\mathrm{H}_2}^{10\kappa} = \frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}{c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}} X_{\mathrm{H}_2}, \qquad \beta_{\mathrm{H}}^{10\kappa} = \frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}{c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}} X_{\mathrm{H}}, \qquad \beta_{\mathrm{H}_2}^{0\tilde{\mathrm{r}}\kappa} = -\frac{c_{\mathrm{H}_2}^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}{c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}} X_{\mathrm{H}_2},$$

where $c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} = \sum_{i \in \mathfrak{S}} X_i c_i^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} = X_{\mathrm{H}_2} c_{\mathrm{H}_2}^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}$. The constraint vector $\mathcal{K}$ ensures the orthogonality with the collisional invariant $\widehat{\psi}^{\mathrm{t}+\tilde{\mathrm{r}}}$ and is given by

$$\mathcal{K}_{\mathrm{H}_2}^{10} = c^{\mathrm{t}} X_{\mathrm{H}_2}, \qquad \mathcal{K}_{\mathrm{H}}^{10} = c^{\mathrm{t}} X_{\mathrm{H}}, \qquad \mathcal{K}_{\mathrm{H}_2}^{0\tilde{\mathrm{r}}} = c_{\mathrm{H}_2}^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} X_{\mathrm{H}_2}.$$

The coefficients of the matrix K, taking into account that H is not polyatomic, are given by [33, 34]

$$K_{\mathrm{H}_2\mathrm{H}_2}^{1010} = \frac{4 X_{\mathrm{H}} X_{\mathrm{H}_2}}{k_{\mathrm{B}} \overline{T}} \Big(\frac{4 m_{\mathrm{H}} m_{\mathrm{H}_2}}{(m_{\mathrm{H}} + m_{\mathrm{H}_2})^2} \Omega_{\mathrm{H}\mathrm{H}_2}^{(1,1)} + \frac{m_{\mathrm{H}}^2}{(m_{\mathrm{H}} + m_{\mathrm{H}_2})^2} \frac{[\![(\Delta E^{\mathrm{r}})^2]\!]_{\mathrm{H}\mathrm{H}_2}^{\mathrm{r}}}{(k_{\mathrm{B}} \overline{T})^2} \Big) + \frac{2 X_{\mathrm{H}_2}^2}{k_{\mathrm{B}} \overline{T}} \frac{[\![(\Delta E^{\mathrm{r}})^2]\!]_{\mathrm{H}_2\mathrm{H}_2}^{\mathrm{r}}}{(k_{\mathrm{B}} \overline{T})^2},$$

$$K^{1010}_{\rm HH_2} = K^{1010}_{\rm H_2H} = \frac{4X_{\rm H}X_{\rm H_2}}{k_{\rm B}\overline{T}}\,\frac{m_{\rm H}m_{\rm H_2}}{(m_{\rm H}+m_{\rm H_2})^2}\Big(-4\Omega^{(1,1)}_{\rm HH_2} + \frac{\llbracket(\Delta E^{\rm r})^2\rrbracket^{\rm r}_{\rm HH_2}}{(k_{\rm B}\overline{T})^2}\Big),$$

$$K^{1010}_{\rm HH} = \frac{4X_{\rm H}X_{\rm H_2}}{k_{\rm B}\overline{T}}\Big(\frac{4m_{\rm H}m_{\rm H_2}}{(m_{\rm H}+m_{\rm H_2})^2}\Omega^{(1,1)}_{\rm HH_2} + \frac{m^2_{\rm H_2}}{(m_{\rm H}+m_{\rm H_2})^2}\,\frac{\llbracket(\Delta E^{\rm r})^2\rrbracket^{\rm r}_{\rm HH_2}}{(k_{\rm B}\overline{T})^2}\Big),$$

$$K^{100\tilde{\rm r}}_{\rm H_2H_2} = K^{0\tilde{\rm r}10}_{\rm H_2H_2} = -\frac{4X_{\rm H}X_{\rm H_2}}{k_{\rm B}\overline{T}}\,\frac{m_{\rm H}}{m_{\rm H}+m_{\rm H_2}}\,\frac{\llbracket(\Delta E^{\rm r})^2\rrbracket^{\rm r}_{\rm HH_2}}{(k_{\rm B}\overline{T})^2} - \frac{2X^2_{\rm H_2}}{k_{\rm B}\overline{T}}\,\frac{\llbracket(\Delta E^{\rm r})^2\rrbracket^{\rm r}_{\rm H_2H_2}}{(k_{\rm B}\overline{T})^2},$$

$$K^{100\tilde{\rm r}}_{\rm HH_2} = K^{0\tilde{\rm r}10}_{\rm H_2H} = -\frac{4X_{\rm H}X_{\rm H_2}}{k_{\rm B}\overline{T}}\,\frac{m_{\rm H_2}}{m_{\rm H}+m_{\rm H_2}}\,\frac{\llbracket(\Delta E^{\rm r})^2\rrbracket^{\rm r}_{\rm HH_2}}{(k_{\rm B}\overline{T})^2},$$

$$K^{0\tilde{\rm r}0\tilde{\rm r}}_{\rm H_2H_2} = \frac{4X_{\rm H}X_{\rm H_2}}{k_{\rm B}\overline{T}}\,\frac{\llbracket(\Delta E^{\rm r})^2\rrbracket^{\rm r}_{\rm HH_2}}{(k_{\rm B}\overline{T})^2} + \frac{2X^2_{\rm H_2}}{k_{\rm B}\overline{T}}\,\frac{\llbracket(\Delta E^{\rm r})^2\rrbracket^{\rm r}_{\rm H_2H_2}}{(k_{\rm B}\overline{T})^2}.$$

keeping in mind that $\Delta E^{\tilde{\rm r}} = \Delta E^{\rm r} - \frac{c^{\rm rv}}{c^{\rm vv}}\Delta E^{\rm v} = \Delta E^{\rm r}$ for rapid collisions. Note that the averaging operator $\llbracket\ \rrbracket^{\rm r}$ only involve fast collisions and has been denoted by adding the superscript $^{\rm r}$. More details on the transport linear systems associated with the calculation of volume viscosities are given in References [33, 34]. The special systems associated with the mixture $\mathfrak{S} = \{{\rm H_2}, {\rm H}\}$ admit simplified notation for the averaged brackets since there is only one polyatomic species and only one monatomic species.

2.7 The reduced rotational volume viscosity

The traditional variational approximation space used to evaluate the rotational volume viscosity may conveniently be replaced by the reduced Galerkin variational approximation space spanned by the functions

$$\widehat{\phi}^{000\tilde{\rm r}k} = \phi^{000\tilde{\rm r}k} - \frac{X_k c^{\tilde{\rm r}\tilde{\rm r}}_k}{c^{\rm t}+c^{\tilde{\rm r}\tilde{\rm r}}}\widehat{\psi}^{{\rm t}+\tilde{\rm r}}, \qquad k \in \mathfrak{P},$$

leading to a transport linear system of size N^p. The term proportional to the collisional invariant $\widehat{\psi}^{{\rm t}+\tilde{\rm r}}$ guarantees that $\widehat{\phi}^{000\tilde{\rm r}k}$, $k \in \mathfrak{P}$, are orthogonal to $\widehat{\psi}^{{\rm t}+\tilde{\rm r}}$, and since they are also automatically orthogonal to $\widehat{\psi}^{\rm v}$ by construction, they are thus orthogonal to both collisional invariants $\widehat{\psi}^{\rm t+r}$ and $\widehat{\psi}^{\rm v}$ of the fast collision operator. The idea behind this basis function is that the most important part of the dynamics is associated with internal energy exchanges and not with the kinetic energy [33, 34]. The influence of the later is simply taken into account with a global energy conservation constraint. The corresponding volume viscosity has been shown to be accurate in various situations with at most a few percent errors [33, 34].

Proceeding as for one-temperature systems [33], the corresponding matrix and right member are shown to be the $0\tilde{\rm r}0\tilde{\rm r}$ components of the more traditional approximation discussed in the previous section and there is no constraint [33, 34]. Under this approximation, for the $\mathfrak{S} = \{{\rm H_2}, {\rm H}\}$ system, there remains a *single* basis function $\widehat{\phi}^{000\tilde{\rm r}{\rm H_2}}$ and we expand ϕ^κ in the form

$$\phi^\kappa = -\frac{3}{p}\alpha^{0\tilde{\rm r}\kappa}_{\rm H_2}\widehat{\phi}^{000\tilde{\rm r}{\rm H_2}},$$

with

$$K_{[0\tilde{\rm r}]}\alpha^\kappa_{[0\tilde{\rm r}]} = \beta^\kappa_{[0\tilde{\rm r}]}. \tag{62}$$

The right member $\beta^{0\tilde{\rm r}\kappa}$ is given by

$$\beta^{0\tilde{\rm r}\kappa}_{\rm H_2} = -\frac{c^{\tilde{\rm r}\tilde{\rm r}}_{\rm H_2}X_{\rm H_2}}{c^{\rm t}+c^{\tilde{\rm r}\tilde{\rm r}}} = -\frac{c^{\tilde{\rm r}\tilde{\rm r}}}{c^{\rm t}+c^{\tilde{\rm r}\tilde{\rm r}}},$$

and the coefficient of $K_{[0\tilde{\rm r}]}$ is given by

$$K^{0\tilde{\rm r}0\tilde{\rm r}}_{\rm H_2H_2} = \frac{4X_{\rm H}X_{\rm H_2}}{k_{\rm B}\overline{T}}\,\frac{\llbracket(\Delta E^{\rm r})^2\rrbracket^{\rm r}_{\rm HH_2}}{(k_{\rm B}\overline{T})^2} + \frac{2X^2_{\rm H_2}}{k_{\rm B}\overline{T}}\,\frac{\llbracket(\Delta E^{\rm r})^2\rrbracket^{\rm r}_{\rm H_2H_2}}{(k_{\rm B}\overline{T})^2} = \frac{2\llbracket(\Delta E^{\rm r})^2\rrbracket^{\rm r}}{(k_{\rm B}\overline{T})^3}.$$

From these relations, it is directly obtained that

$$\phi^\kappa = \frac{3}{p}\Big(\frac{c^{\tilde{\rm r}\tilde{\rm r}}}{c^{\rm t}+c^{\tilde{\rm r}\tilde{\rm r}}}\Big)\,\frac{(k_{\rm B}\overline{T})^3}{2\llbracket(\Delta E^{\rm r})^2\rrbracket^{\rm r}}\widehat{\phi}^{000\tilde{\rm r}{\rm H_2}}, \tag{63}$$

and

$$\kappa^{\mathrm{r}} = \Big(\frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}{c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}\Big)^2 \frac{(k_{\mathrm{B}}\overline{T})^3}{2[\![(\Delta E^{\mathrm{r}})^2]\!]^{\mathrm{r}}}. \tag{64}$$

Note that the bracket $[\![(\Delta E^{\mathrm{r}})^2]\!]^{\mathrm{r}}$ is distinct from $[\![(\Delta E^{\mathrm{r}})^2]\!]$ since only rapid collisions are involved.

3 Relaxation and Volume Viscosities

3.1 The thermodynamic equilibrium temperature

We *define* the equilibrium temperature as the unique scalar T such that

$$\mathcal{E}^{\mathrm{t}}(T) + \mathcal{E}^{\mathrm{r}}(T,T) + \mathcal{E}^{\mathrm{v}}(T,T) = \mathcal{E}^{\mathrm{t}}(\overline{T}) + \mathcal{E}^{\mathrm{r}}(\overline{T},T^{\mathrm{v}}) + \mathcal{E}^{\mathrm{v}}(\overline{T},T^{\mathrm{v}}), \tag{65}$$

keeping in mind that $\mathcal{E}^{\mathrm{t}}(T)+\mathcal{E}^{\mathrm{r}}(T,T)+\mathcal{E}^{\mathrm{v}}(T,T)$ is an increasing function of T and where the dependence on the species number densities n_i, $i \in \mathfrak{S}$, is left implicit to simplify notation. Since for any smooth function $\varphi(\overline{T},T^{\mathrm{v}})$ we have the identity

$$\varphi(\overline{T},T^{\mathrm{v}}) - \varphi(T,T) = \int_T^{\overline{T}} \partial_{\overline{T}}\varphi(\theta,T^{\mathrm{v}})\mathrm{d}\theta + \int_T^{T^{\mathrm{v}}} \partial_{T^{\mathrm{v}}}\varphi(T,\theta)\mathrm{d}\theta,$$

we define for each species

$$\overline{c}_i^{\mathrm{rr}} = \int_0^1 c_i^{\mathrm{rr}}\big(T + s(\overline{T}-T),T^{\mathrm{v}}\big)\,\mathrm{d}s, \qquad \overline{c}_i^{\mathrm{vr}} = \int_0^1 c_i^{\mathrm{vr}}\big(T + s(\overline{T}-T),T^{\mathrm{v}}\big)\,\mathrm{d}s, \qquad i \in \mathfrak{S},$$

$$\overline{c}_i^{\mathrm{rv}} = \int_0^1 c_i^{\mathrm{rv}}\big(T,T + s(T^{\mathrm{v}}-T)\big)\,\mathrm{d}s, \qquad \overline{c}_i^{\mathrm{vv}} = \int_0^1 c_i^{\mathrm{vv}}\big(T,T + s(T^{\mathrm{v}}-T)\big)\,\mathrm{d}s, \qquad i \in \mathfrak{S},$$

as well as

$$\overline{c}_i^{\mathrm{r}} = \overline{c}_i^{\mathrm{rr}} + \overline{c}_i^{\mathrm{vr}}, \qquad \overline{c}_i^{\mathrm{v}} = \overline{c}_i^{\mathrm{rv}} + \overline{c}_i^{\mathrm{vv}}, \qquad \overline{c}_{\mathrm{vl}\,i} = c^{\mathrm{t}} + \overline{c}_i^{\mathrm{rr}} + \overline{c}_i^{\mathrm{rv}} + \overline{c}_i^{\mathrm{vr}} + \overline{c}_i^{\mathrm{vv}}.$$

We also introduce the corresponding mixture properties

$$n\overline{c}^{\mathrm{rr}} = \sum_{i\in\mathfrak{S}} n_i\overline{c}_i^{\mathrm{rr}}, \qquad n\overline{c}^{\mathrm{rv}} = \sum_{i\in\mathfrak{S}} n_i\overline{c}_i^{\mathrm{rv}}, \qquad n\overline{c}^{\mathrm{vr}} = \sum_{i\in\mathfrak{S}} n_i\overline{c}_i^{\mathrm{vr}}. \qquad n\overline{c}^{\mathrm{vv}} = \sum_{i\in\mathfrak{S}} n_i\overline{c}_i^{\mathrm{vv}}.$$

$$n\overline{c}^{\mathrm{r}} = \sum_{i\in\mathfrak{S}} n_i\overline{c}_i^{\mathrm{r}}. \qquad n\overline{c}^{\mathrm{v}} = \sum_{i\in\mathfrak{S}} n_i\overline{c}_i^{\mathrm{v}}, \qquad n\overline{c}_{\mathrm{vl}} = \sum_{i\in\mathfrak{S}} n_i\overline{c}_{\mathrm{vl}\,i}.$$

Note the difference in the definitions of $c^{\mathrm{r}} = c^{\mathrm{rr}} + c^{\mathrm{rv}}$ and $\overline{c}^{\mathrm{r}} = \overline{c}^{\mathrm{rr}} + \overline{c}^{\mathrm{vr}}$ as well as between $c^{\mathrm{v}} = c^{\mathrm{vr}} + c^{\mathrm{vv}}$ and $\overline{c}^{\mathrm{v}} = \overline{c}^{\mathrm{rv}} + \overline{c}^{\mathrm{vv}}$. We then have the identities

$$\mathcal{E}^{\mathrm{t}}(\overline{T}) - \mathcal{E}^{\mathrm{t}}(T) = n\overline{c}^{\mathrm{t}}(\overline{T}-T),$$

$$\mathcal{E}^{\mathrm{r}}(\overline{T},T^{\mathrm{v}}) - \mathcal{E}^{\mathrm{r}}(T,T) = n\overline{c}^{\mathrm{rr}}(\overline{T}-T) + n\overline{c}^{\mathrm{rv}}(T^{\mathrm{v}}-T),$$

$$\mathcal{E}^{\mathrm{v}}(\overline{T},T^{\mathrm{v}}) - \mathcal{E}^{\mathrm{v}}(T,T) = n\overline{c}^{\mathrm{vr}}(\overline{T}-T) + n\overline{c}^{\mathrm{vv}}(T^{\mathrm{v}}-T),$$

The relation $\mathcal{E}^{\mathrm{t+r}}(\overline{T},T^{\mathrm{v}}) - \mathcal{E}^{\mathrm{t+r}}(T,T) = \mathcal{E}^{\mathrm{v}}(T,T) - \mathcal{E}^{\mathrm{v}}(\overline{T},T^{\mathrm{v}})$ may then be recast in the form

$$(c^{\mathrm{t}} + \overline{c}^{\mathrm{r}})(\overline{T}-T) = \overline{c}^{\mathrm{v}}(T-T^{\mathrm{v}}), \tag{66}$$

and also implies that

$$\overline{c}_{\mathrm{vl}}(\overline{T}-T) = \overline{c}^{\mathrm{v}}(\overline{T}-T^{\mathrm{v}}). \tag{67}$$

3.2 The vibrational volume viscosity

From the equations governing the internal energies we deduce at the zeroth order the system

$$\begin{cases} n(c^{\mathrm{t}}+c^{\mathrm{rr}})(\partial_t\overline{T}+\boldsymbol{v}\cdot\boldsymbol{\nabla}\overline{T})+nc^{\mathrm{rv}}(\partial_t T^{\mathrm{v}}+\boldsymbol{v}\cdot\boldsymbol{\nabla}T^{\mathrm{v}}) = -p\boldsymbol{\nabla}\cdot\boldsymbol{v}-\omega_0^{\mathrm{v}}, \\ nc^{\mathrm{vr}}(\partial_t\overline{T}+\boldsymbol{v}\cdot\boldsymbol{\nabla}\overline{T})+nc^{\mathrm{vv}}(\partial_t T^{\mathrm{v}}+\boldsymbol{v}\cdot\boldsymbol{\nabla}T^{\mathrm{v}}) = \omega_0^{\mathrm{v}}. \end{cases} \tag{68}$$

Using the identity $c^{\mathrm{t}}c^{\mathrm{vv}}+c^{\mathrm{rr}}c^{\mathrm{vv}}-c^{\mathrm{rv}}c^{\mathrm{vr}}=(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})c^{\mathrm{vv}}$ the governing equations for $\overline{T}$ and T^{v} are found in the form

$$\begin{cases} \partial_t\overline{T}+\boldsymbol{v}\cdot\boldsymbol{\nabla}\overline{T} = -\dfrac{c^{\mathrm{vv}}p\boldsymbol{\nabla}\cdot\boldsymbol{v}+(c^{\mathrm{vv}}+c^{\mathrm{rv}})\omega_0^{\mathrm{v}}}{n(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})c^{\mathrm{vv}}}, \\ \partial_t T^{\mathrm{v}}+\boldsymbol{v}\cdot\boldsymbol{\nabla}T^{\mathrm{v}} = \dfrac{c^{\mathrm{vr}}p\boldsymbol{\nabla}\cdot\boldsymbol{v}+(c^{\mathrm{t}}+c^{\mathrm{rr}}+c^{\mathrm{vr}})\omega_0^{\mathrm{v}}}{n(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})c^{\mathrm{vv}}}. \end{cases} \tag{69}$$

The resulting equation for $\overline{T}-T^{\mathrm{v}}$ is then

$$\partial_t(\overline{T}-T^{\mathrm{v}})+\boldsymbol{v}\cdot\boldsymbol{\nabla}(\overline{T}-T^{\mathrm{v}}) = -\frac{c^{\mathrm{v}}p\boldsymbol{\nabla}\cdot\boldsymbol{v}+c_{\mathrm{vl}}\omega_0^{\mathrm{v}}}{n(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})c^{\mathrm{vv}}},$$

and from the expression (29) we obtain

$$\partial_t(\overline{T}-T^{\mathrm{v}})+\boldsymbol{v}\cdot\boldsymbol{\nabla}(\overline{T}-T^{\mathrm{v}}) = -\frac{c^{\mathrm{v}}p\boldsymbol{\nabla}\cdot\boldsymbol{v}}{n(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})c^{\mathrm{vv}}} - \frac{c_{\mathrm{vl}}\,c^{\mathrm{v}}}{(c^{\mathrm{t}}+c^{\mathrm{r}})c^{\mathrm{vv}}}\frac{\overline{T}-T^{\mathrm{v}}}{\tau^{\mathrm{v}}}. \tag{70}$$

This is a typical relaxation equation and the corresponding relaxation approximation yields at the zeroth order

$$\overline{T}-T^{\mathrm{v}} = -\frac{\tau^{\mathrm{v}}}{nc_{\mathrm{vl}}}p\boldsymbol{\nabla}\cdot\boldsymbol{v}, \qquad \omega_0^{\mathrm{v}} = -\frac{c^{\mathrm{v}}}{c_{\mathrm{vl}}}p\boldsymbol{\nabla}\cdot\boldsymbol{v}. \tag{71}$$

This approximation neither require τ^{v} to be small nor $\overline{T}$ and T^{v} to be close and is indeed valid when the flow characteristic time is greater than τ^{v}. We now define the vibrational nonequilibrium volume viscosity by $\kappa^{\mathrm{v}}=pk_{\mathrm{B}}\overline{c}^{\mathrm{v}}\tau^{\mathrm{v}}/(c_{\mathrm{vl}}\overline{c}_{\mathrm{vl}})$, where $\overline{c}^{\mathrm{v}}=\overline{c}^{\mathrm{rv}}+\overline{c}^{\mathrm{vv}}$ and $\overline{c}_{\mathrm{vl}}=c^{\mathrm{t}}+\overline{c}^{\mathrm{rr}}+\overline{c}^{\mathrm{rv}}+\overline{c}^{\mathrm{vr}}+\overline{c}^{\mathrm{vv}}$ and κ^{v} may then be written

$$\kappa^{\mathrm{v}} = \frac{c^{\mathrm{v}}\overline{c}^{\mathrm{v}}}{c_{\mathrm{vl}}\,\overline{c}_{\mathrm{vl}}}\frac{k_{\mathrm{B}}{}^3\overline{T}^2T^{\mathrm{v}}}{2[\![(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}]\!]}. \tag{72}$$

Thanks to the relation (67) we further obtain—after some algebra—that at zeroth order

$$nk_{\mathrm{B}}\overline{T} = nk_{\mathrm{B}}T-\kappa^{\mathrm{v}}\boldsymbol{\nabla}\cdot\boldsymbol{v}, \tag{73}$$

which generalizes a similar relation established in the single species case [8]. Note incidentally that the coefficient κ^{v} differs in many aspects from its thermodynamic equilibrium limit since both $\overline{T}$ and T^{v} play a role as well as the nonequilibrium factor ζ^{v} and the averaged coefficients $\overline{c}^{\mathrm{v}}$ and $\overline{c}_{\mathrm{vl}}$.

3.3 First order corrections

Since we need to add the vibrational volume viscosity κ^{v}, which is $\mathcal{O}(\tau^{\mathrm{v}})$, to the rotational volume viscosity κ^{r} in the Navier-Stokes regime, which is $\mathcal{O}(\epsilon)$, we need to take into account first order corrections to the temperature difference $\overline{T}-T^{\mathrm{v}}$. From the governing equations we deduce in the Navier-Stokes regime the conservation equations

$$\begin{cases} n(c^{\mathrm{t}}+c^{\mathrm{rr}})(\partial_t\overline{T}+\boldsymbol{v}\cdot\boldsymbol{\nabla}\overline{T})+nc^{\mathrm{rv}}(\partial_t T^{\mathrm{v}}+\boldsymbol{v}\cdot\boldsymbol{\nabla}T^{\mathrm{v}}) = -p\boldsymbol{\nabla}\cdot\boldsymbol{v} \\ \qquad\qquad -\boldsymbol{\nabla}\cdot\boldsymbol{Q}^{\mathrm{t+r}}-\boldsymbol{\Pi}\boldsymbol{:}\boldsymbol{\nabla}\boldsymbol{v}-\omega_0^{\mathrm{v}}-\delta\omega_1^{\mathrm{v}}, \\ nc^{\mathrm{vr}}(\partial_t\overline{T}+\boldsymbol{v}\cdot\boldsymbol{\nabla}\overline{T})+nc^{\mathrm{vv}}(\partial_t T^{\mathrm{v}}+\boldsymbol{v}\cdot\boldsymbol{\nabla}T^{\mathrm{v}}) = -\boldsymbol{\nabla}\cdot\boldsymbol{Q}^{\mathrm{v}}+\omega_0^{\mathrm{v}}+\delta\omega_1^{\mathrm{v}}, \end{cases} \tag{74}$$

and we have to investigate the perturbed first order source term $\delta\omega_1^{\mathrm{v}}=\omega_1^{\mathrm{v}}-\omega_0^{\mathrm{v}}$. Furthermore, in the relaxation approximation, and in the Navier-Stokes regime, we may replace ω_0^{v} by its zeroth order approximation $\omega_0^{\mathrm{v}}\approx -c^{\mathrm{v}}p\boldsymbol{\nabla}\cdot\boldsymbol{v}/c_{\mathrm{vl}}$ in the first order term $\delta\omega_1^{\mathrm{v}}$. The resulting effective first order correction *in the relaxation regime* is therefore

$$\delta\omega_1^{\mathrm{v}} = \big(w_1^{\kappa}-\frac{pc^{\mathrm{v}}}{c_{\mathrm{vl}}}w_1^{\mathrm{v}}\big)\boldsymbol{\nabla}\cdot\boldsymbol{v}. \tag{75}$$

After some algebra, the first order relaxation approximation then yields that

$$n k_{\mathrm{B}} \overline{T} - n k_{\mathrm{B}} T = -\kappa^{\mathrm{v}}\, \boldsymbol{\nabla}\!\cdot\! \boldsymbol{v} \Big(1 + \frac{c_{\mathrm{vl}}}{c^{\mathrm{v}} p} w_1^{\kappa} - w_1^{\mathrm{v}} \Big) - \frac{\kappa^{\mathrm{v}}}{p} \Big(\boldsymbol{\Pi} \boldsymbol{:} \boldsymbol{\nabla} \boldsymbol{v} + \boldsymbol{\nabla}\!\cdot\! \boldsymbol{Q}^{\mathrm{t+r}} - \frac{c^{\mathrm{t}} + c^{\mathrm{r}}}{c^{\mathrm{v}}} \boldsymbol{\nabla}\!\cdot\! \boldsymbol{Q}^{\mathrm{v}} \Big). \tag{76}$$

The new terms in (76) involve either the product of κ^{v} by another transport coefficient or the perturbed source terms w_1^{κ} and w_1^{v}. Near equilibrium only the term $-\kappa^{\mathrm{v}}\, \boldsymbol{\nabla}\!\cdot\! \boldsymbol{v} \big(1 + c_{\mathrm{vl}} w_1^{\kappa} / p c^{\mathrm{v}} - w_1^{\mathrm{v}} \big)$ plays a role since all terms involving the product of two transport coefficients are associated with the Burnett regime.

Combining these results with the expression of the viscous tensor, and keeping in mind that in the relaxation approximation the source term ω_0^{v} is proportional to $\boldsymbol{\nabla}\!\cdot\! \boldsymbol{v}$, we conclude that the effective first order volume viscosity is given by

$$\kappa^{\mathrm{eff}} = \kappa^{\mathrm{r}} + \frac{c^{\mathrm{v}} p}{c_{\mathrm{vl}}} \widetilde{p}^{\mathrm{rel}} + \kappa^{\mathrm{v}} \Big(1 + \frac{c_{\mathrm{vl}}}{c^{\mathrm{v}} p} w_1^{\kappa} - w_1^{\mathrm{v}} \Big), \tag{77}$$

so that we need to evaluate the relaxation pressure as well as the perturbed source terms.

3.4 Translational and rapid mode temperatures

The partial equilibrium temperature $\overline{T}$ between the translational and rotational degrees of freedom and the vibrational temperatures T^{v} are defined from the system of equations $\mathcal{E}^{\mathrm{t}}(\overline{T}) + \mathcal{E}^{\mathrm{r}}(\overline{T}, T^{\mathrm{v}}) = \langle\!\langle f^{(0)}, \psi^{\mathrm{t}} + \psi^{\mathrm{r}} \rangle\!\rangle = \langle\!\langle f, \psi^{\mathrm{t}} + \psi^{\mathrm{r}} \rangle\!\rangle$ and $\mathcal{E}^{\mathrm{v}}(\overline{T}, T^{\mathrm{v}}) = \langle\!\langle f^{(0)}, \psi^{\mathrm{v}} \rangle\!\rangle = \langle\!\langle f, \psi^{\mathrm{v}} \rangle\!\rangle$ and are macroscopic quantities since $\psi^{\mathrm{t}} + \psi^{\mathrm{r}}$ and ψ^{v} are collisional invariants of the fast collision operator. The translational T^{t} and the rotational temperature T^{r} are now *defined* from

$$\mathcal{E}^{\mathrm{t}}(T^{\mathrm{t}}) = \langle\!\langle f, \psi^{\mathrm{t}} \rangle\!\rangle \qquad \mathcal{E}^{\mathrm{r}}(T^{\mathrm{r}}, T^{\mathrm{v}}) = \langle\!\langle f, \psi^{\mathrm{r}} \rangle\!\rangle, \tag{78}$$

where the dependence on the species number densities is left implicit to simplify notation. Note that both $\overline{T}$ and T^{v} are treated as constants in these definitions—since they are defined from collisional invariants—and we have in particular $\mathcal{E}^{\mathrm{t}}(T^{\mathrm{t}}) + \mathcal{E}^{\mathrm{r}}(T^{\mathrm{r}}, T^{\mathrm{v}}) = \mathcal{E}^{\mathrm{t}}(\overline{T}) + \mathcal{E}^{\mathrm{r}}(\overline{T}, T^{\mathrm{v}})$. Since neither ψ^{t} nor ψ^{r} is a collision invariant of the fast collision operator, these temperatures cannot solely be expressed in terms of zeroth order quantities and have to be expanded in the form

$$T^{\mathrm{t}} = T_0^{\mathrm{t}} + \epsilon\, \delta T_1^{\mathrm{t}} + \mathcal{O}(\epsilon^2), \qquad T^{\mathrm{r}} = T_0^{\mathrm{r}} + \epsilon\, \delta T_1^{\mathrm{r}} + \mathcal{O}(\epsilon^2), \tag{79}$$

where T_0^{t} and T_0^{r} are the zeroth order terms and δT_1^{t} and δT_1^{r} the first order corrections associated with the Navier-Stokes regime.

From the definition (78) and the expansions (79) we deduce that at the zeroth order we have $\mathcal{E}^{\mathrm{t}}(T_0^{\mathrm{t}}) = \langle\!\langle f^{(0)}, \psi^{\mathrm{t}} \rangle\!\rangle$ and $\mathcal{E}^{\mathrm{r}}(T_0^{\mathrm{r}}, T^{\mathrm{v}}) = \langle\!\langle f^{(0)}, \psi^{\mathrm{r}} \rangle\!\rangle$, so that $\mathcal{E}^{\mathrm{t}}(T_0^{\mathrm{t}}) = \mathcal{E}^{\mathrm{t}}(\overline{T})$, and $\mathcal{E}^{\mathrm{r}}(T_0^{\mathrm{r}}, T^{\mathrm{v}}) = \mathcal{E}^{\mathrm{r}}(\overline{T}, T^{\mathrm{v}})$ in such a way that at the zeroth order

$$T_0^{\mathrm{t}} = T_0^{\mathrm{r}} = \overline{T}, \tag{80}$$

in agreement with the fast mode assumption.

We introduce for convenience the notation

$$T_1^{\mathrm{t}} = T_0^{\mathrm{t}} + \epsilon\, \delta T_1^{\mathrm{t}}, \qquad T_1^{\mathrm{r}} = T_0^{\mathrm{r}} + \epsilon\, \delta T_1^{\mathrm{r}}, \tag{81}$$

in such a way that $T^{\mathrm{t}} = T_1^{\mathrm{t}} + \mathcal{O}(\epsilon^2)$ and $T^{\mathrm{r}} = T_1^{\mathrm{r}} + \mathcal{O}(\epsilon^2)$. In other words T^{t} and T_1^{t} coincide in the Navier-Stokes regime as well as T^{r} and T_1^{r}. From the general relations

$$\mathcal{E}^{\mathrm{t}}(T^{\mathrm{t}}) - \mathcal{E}^{\mathrm{t}}(\overline{T}) = \langle\!\langle f - f^{(0)}, \psi^{\mathrm{t}} \rangle\!\rangle, \qquad \mathcal{E}^{\mathrm{r}}(T^{\mathrm{r}}, T^{\mathrm{v}}) - \mathcal{E}^{\mathrm{r}}(\overline{T}, T^{\mathrm{v}}) = \langle\!\langle f - f^{(0)}, \psi^{\mathrm{r}} \rangle\!\rangle,$$

we next obtain the linearized expressions

$$n c^{\mathrm{t}} (T_1^{\mathrm{t}} - \overline{T}) = \langle\!\langle f^{(0)} \phi, \psi^{\mathrm{t}} \rangle\!\rangle, \qquad n c^{\mathrm{rr}} (T_1^{\mathrm{r}} - \overline{T}) = \langle\!\langle f^{(0)} \phi, \psi^{\mathrm{r}} \rangle\!\rangle. \tag{82}$$

It is important to note that only c^{rr} plays a role since T^{v} is fixed, being defined from collisional invariants. In addition, c^{rr} may be evaluated at $(\overline{T}, T^{\mathrm{v}})$ since T^{r} is a deviation from $\overline{T}$ in the Navier-Stokes regime. We also know that $\psi^{\mathrm{t}} + \psi^{\mathrm{r}}$ is a collisional invariant so that $\langle\!\langle f^{(0)} \phi, \psi^{\mathrm{t}} + \psi^{\mathrm{r}} \rangle\!\rangle = 0$ and

$$(c^{\mathrm{t}} + c^{\mathrm{rr}}) \overline{T} = c^{\mathrm{t}} T_1^{\mathrm{t}} + c^{\mathrm{rr}} T_1^{\mathrm{r}}. \tag{83}$$

We next need to evaluate the first order perturbations $T_1^{\mathrm{t}}-\overline{T}$ and $T_1^{\mathrm{r}}-\overline{T}$ in terms of the divergence of the velocity field and the relaxation pressure.

Since ψ^{t} and ψ^{r} are scalars, from the Curie principle, only the scalar part of ϕ yields nonzero contribution in the products $\langle\!\langle f^{(0)}\phi,\psi^{\mathrm{t}}\rangle\!\rangle$ and $\langle\!\langle f^{(0)}\phi,\psi^{\mathrm{r}}\rangle\!\rangle$, in such a way that

$$nc^{\mathrm{t}}(T_1^{\mathrm{t}}-\overline{T}) = -\tfrac{1}{3}\langle\!\langle f^{(0)}\phi^{\kappa},\psi^{\mathrm{t}}\rangle\!\rangle\boldsymbol{\nabla}\cdot\boldsymbol{v} + \langle\!\langle f^{(0)}\phi^{\omega},\psi^{\mathrm{t}}\rangle\!\rangle\omega_0^{\mathrm{v}}, \tag{84}$$

$$nc^{\mathrm{rr}}(T_1^{\mathrm{r}}-\overline{T}) = -\tfrac{1}{3}\langle\!\langle f^{(0)}\phi^{\kappa},\psi^{\mathrm{r}}\rangle\!\rangle\boldsymbol{\nabla}\cdot\boldsymbol{v} + \langle\!\langle f^{(0)}\phi^{\omega},\psi^{\mathrm{r}}\rangle\!\rangle\omega_0^{\mathrm{v}}. \tag{85}$$

Since $\psi^{\mathrm{t}}+\psi^{\mathrm{r}}$ is a collisional invariant, the scalar products $\langle\!\langle f^{(0)}\phi^{\kappa},\psi^{\mathrm{t}}\rangle\!\rangle$ and $\langle\!\langle f^{(0)}\phi^{\kappa},\psi^{\mathrm{r}}\rangle\!\rangle$ are such that $\langle\!\langle f^{(0)}\phi^{\kappa},\psi^{\mathrm{t}}\rangle\!\rangle+\langle\!\langle f^{(0)}\phi^{\kappa},\psi^{\mathrm{r}}\rangle\!\rangle=0$. On the other hand, we have the relation

$$\kappa^{\mathrm{r}} = \tfrac{1}{9}k_{\mathrm{B}}\overline{T}\langle\!\langle f^{(0)}\phi^{\kappa},\psi^{\kappa}\rangle\!\rangle = \tfrac{1}{9}k_{\mathrm{B}}\overline{T}[\phi^{\kappa},\phi^{\kappa}].$$

Noting that $\psi^{\kappa}-\frac{2c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})k_{\mathrm{B}}\overline{T}}\psi^{\mathrm{t}}+\frac{2c^{\mathrm{t}}}{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})k_{\mathrm{B}}\overline{T}}\psi^{\mathrm{r}}$ is a fast collisional invariant, we obtain upon taking the scalar product with $f^{(0)}\phi^{\kappa}$ a second relation between $\langle\!\langle f^{(0)}\phi^{\kappa},\psi^{\mathrm{t}}\rangle\!\rangle$ and $\langle\!\langle f^{(0)}\phi^{\kappa},\psi^{\mathrm{r}}\rangle\!\rangle$. Combining these relations yields after some algebra the identity $\langle\!\langle f^{(0)}\phi^{\kappa},\psi^{\mathrm{t}}\rangle\!\rangle=\frac{9}{2}\kappa^{\mathrm{r}}$. Similarly, the scalar products $\langle\!\langle f^{(0)}\phi^{\omega},\psi^{\mathrm{t}}\rangle\!\rangle$ and $\langle\!\langle f^{(0)}\phi^{\omega},\psi^{\mathrm{r}}\rangle\!\rangle$ are such that $\langle\!\langle f^{(0)}\phi^{\omega},\psi^{\mathrm{t}}\rangle\!\rangle+\langle\!\langle f^{(0)}\phi^{\omega},\psi^{\mathrm{r}}\rangle\!\rangle=0$ and we know that

$$\widetilde{p}^{\mathrm{rel}} = \tfrac{1}{3}k_{\mathrm{B}}\overline{T}\langle\!\langle f^{(0)}\phi^{\omega},\psi^{\kappa}\rangle\!\rangle.$$

Upon expressing ψ^{κ} in terms of ψ^{t}, ψ^{r} and a fast collisional invariant, taking the scalar product with $f^{(0)}\phi^{\omega}$, we obtain a second relation between $\langle\!\langle f^{(0)}\phi^{\omega},\psi^{\mathrm{t}}\rangle\!\rangle$ and $\langle\!\langle f^{(0)}\phi^{\omega},\psi^{\mathrm{r}}\rangle\!\rangle$ and finally get that $\langle\!\langle f^{(0)}\phi^{\omega},\psi^{\mathrm{t}}\rangle\!\rangle=\frac{3}{2}\widetilde{p}^{\mathrm{rel}}$. Combining these results we obtain that

$$nk_{\mathrm{B}}T_1^{\mathrm{t}} = nk_{\mathrm{B}}\overline{T} - \kappa^{\mathrm{r}}\boldsymbol{\nabla}\cdot\boldsymbol{v} + \widetilde{p}^{\mathrm{rel}}\omega_0^{\mathrm{v}}, \tag{86}$$

$$nk_{\mathrm{B}}T_1^{\mathrm{r}} = nk_{\mathrm{B}}\overline{T} + \frac{c^{\mathrm{t}}}{c^{\mathrm{rr}}}\big(\kappa^{\mathrm{r}}\boldsymbol{\nabla}\cdot\boldsymbol{v} - \widetilde{p}^{\mathrm{rel}}\omega_0^{\mathrm{v}}\big). \tag{87}$$

We notably deduce that the expression $nk_{\mathrm{B}}\overline{T}-\kappa^{\mathrm{r}}\boldsymbol{\nabla}\cdot\boldsymbol{v}+p^{\mathrm{rel}}$ appearing in the pressure tensor may be written $nk_{\mathrm{B}}T_1^{\mathrm{t}}$ in the Navier-Stokes regime. The volume viscosity term $-\kappa^{\mathrm{r}}\boldsymbol{\nabla}\cdot\boldsymbol{v}$ and the relaxation pressure $p^{\mathrm{rel}}=\widetilde{p}^{\mathrm{rel}}\omega_0^{\mathrm{v}}$ modify the partial equilibrium temperature pressure term $nk_{\mathrm{B}}\overline{T}$ into a—first order accurate—translational temperature pressure term $nk_{\mathrm{B}}T_1^{\mathrm{t}}$.

3.5 The relaxation pressure

In order to evaluate the reduced relaxation pressure $\widetilde{p}^{\mathrm{rel}}$ we use the expression

$$\widetilde{p}^{\mathrm{rel}} = \tfrac{1}{3}k_{\mathrm{B}}\overline{T}\langle\!\langle f^{(0)}\phi^{\kappa},\psi^{\omega}\rangle\!\rangle = \tfrac{1}{3}k_{\mathrm{B}}\overline{T}\langle\!\langle \phi^{\kappa},\widetilde{\mathcal{J}}^{\mathrm{sl},(0)}\rangle\!\rangle,$$

and we have already evaluated ϕ^{κ} in (63)

$$\phi^{\kappa} = \frac{3}{p}\Big(\frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}{c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}\Big)\,\frac{(k_{\mathrm{B}}\overline{T})^3}{2\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}}\widehat{\phi}^{000\tilde{\mathrm{r}}\mathrm{H}_2}.$$

Since we also have

$$\widehat{\phi}^{000\tilde{\mathrm{r}}\mathrm{H}_2} = \phi^{000\tilde{\mathrm{r}}\mathrm{H}_2} - \frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}{c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}\widehat{\psi}^{\mathrm{t}+\tilde{\mathrm{r}}},$$

as well as $\phi^{000\tilde{\mathrm{r}}\mathrm{H}_2}=\phi^{000\mathrm{rH}_2}-\frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}\frac{T^{\mathrm{v}}}{\overline{T}}\phi^{000\mathrm{vH}_2}$, $\widehat{\psi}^{\mathrm{t}+\tilde{\mathrm{r}}}=\widehat{\psi}^{\mathrm{t}+\mathrm{r}}-\frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}\frac{T^{\mathrm{v}}}{\overline{T}}\widehat{\psi}^{\mathrm{v}}$, and $\phi^{000\mathrm{vH}_2}=\widehat{\psi}^{\mathrm{v}}$, we only have to evaluate the scalar products

$$\langle\!\langle \phi^{000\mathrm{rH}_2},\widetilde{\mathcal{J}}^{\mathrm{sl},(0)}\rangle\!\rangle, \qquad \langle\!\langle \widehat{\psi}^{\mathrm{t}+\mathrm{r}},\widetilde{\mathcal{J}}^{\mathrm{sl},(0)}\rangle\!\rangle, \qquad \langle\!\langle \widehat{\psi}^{\mathrm{v}},\widetilde{\mathcal{J}}^{\mathrm{sl},(0)}\rangle\!\rangle. \tag{88}$$

After some algebra, it is found that

$$\langle\!\langle \phi^{000\mathrm{rH}_2},\widetilde{\mathcal{J}}^{\mathrm{sl},(0)}\rangle\!\rangle = -\frac{\llbracket(\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}})\zeta^{\mathrm{v}}\rrbracket}{\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket k_{\mathrm{B}}\overline{T}}, \tag{89}$$

$$\langle\!\langle \widehat{\psi}^{\mathrm{t}+\mathrm{r}},\widetilde{\mathcal{J}}^{\mathrm{sl},(0)}\rangle\!\rangle = \frac{\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket}{\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket k_{\mathrm{B}}\overline{T}} = \frac{1}{k_{\mathrm{B}}\overline{T}}, \tag{90}$$

$$\frac{T^{\mathrm{v}}}{\overline{T}}\langle\!\langle \widehat{\psi}^{\mathrm{v}},\widetilde{\mathcal{J}}^{\mathrm{sl},(0)}\rangle\!\rangle = -\frac{\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket}{\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket k_{\mathrm{B}}\overline{T}} = -\frac{1}{k_{\mathrm{B}}\overline{T}}. \tag{91}$$

As a consequence, we obtain that

$$\langle\!\langle \phi^{000\tilde{\mathrm{r}}\mathrm{H}_2}, \widetilde{\mathcal{J}}^{\mathrm{sl},(0)} \rangle\!\rangle = -\frac{1}{k_{\mathrm{B}}\overline{T}} \frac{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})[\![(\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}})\zeta^{\mathrm{v}}]\!] + (c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}c^{\mathrm{t}})[\![(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}]\!]}{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})[\![(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}]\!]}. \tag{92}$$

The resulting rescaled relaxation pressure $\widetilde{p}^{\mathrm{rel}}$ is then given by

$$\widetilde{p}^{\mathrm{rel}} = -\frac{(k_{\mathrm{B}}\overline{T})^3 c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}{p(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})^2} \frac{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})[\![(\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}})\zeta^{\mathrm{v}}]\!] + (c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}c^{\mathrm{t}})[\![(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}]\!]}{2[\![(\Delta E^{\mathrm{r}})^2]\!]^{\mathrm{r}}[\![(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}]\!]}. \tag{93}$$

3.6 The perturbed source term

We further have to evaluate the perturbed source term $\delta\omega_1^{\mathrm{v}}$ or equivalently the scalar products

$$w_1^{\kappa} = -\tfrac{1}{3}\langle\!\langle f^{(0)}\phi^{\kappa}, \mathcal{W}^{\mathrm{v}} \rangle\!\rangle, \qquad w_1^{\mathrm{v}} = \langle\!\langle f^{(0)}\phi^{\omega}, \mathcal{W}^{\mathrm{v}} \rangle\!\rangle,$$

since we may next form $\delta\omega_1^{\mathrm{v}} = w_1^{\kappa}\,\boldsymbol{\nabla}\cdot\boldsymbol{v} + w_1^{\mathrm{v}}\,\omega_0^{\mathrm{v}}$. We first investigate the product w_1^{κ} and then the product w_1^{v}.

The perturbed distribution function ϕ^{κ} has been evaluated in terms of $\phi^{000\tilde{\mathrm{r}}\mathrm{H}_2} = \phi^{000\mathrm{rH}_2} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}\frac{T^{\mathrm{v}}}{\overline{T}}\phi^{000\mathrm{vH}_2}$ and $\widehat{\psi}^{\mathrm{t}+\tilde{\mathrm{r}}} = \widehat{\psi}^{\mathrm{t}+\mathrm{r}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}\frac{T^{\mathrm{v}}}{\overline{T}}\widehat{\psi}^{\mathrm{v}}$, and we also have $\phi^{000\mathrm{vH}_2} = \widehat{\psi}^{\mathrm{v}}$, so that we are left with the calculation of the products $\langle\!\langle f^{(0)}\phi^{000\mathrm{rH}_2}, \mathcal{W}^{\mathrm{v}} \rangle\!\rangle$, $\langle\!\langle f^{(0)}\widehat{\psi}^{\mathrm{t}+\mathrm{r}}, \mathcal{W}^{\mathrm{v}} \rangle\!\rangle$ and $\langle\!\langle f^{(0)}\widehat{\psi}^{\mathrm{v}}, \mathcal{W}^{\mathrm{v}} \rangle\!\rangle$ in order to evaluate w_1^{κ}. From the calculations presented in Appendix A, these scalar products may be expressed in the form

$$\langle\!\langle f^{(0)}\phi^{000\mathrm{rH}_2}, \mathcal{W}^{\mathrm{v}} \rangle\!\rangle = \frac{2n^2}{k_{\mathrm{B}}\overline{T}}\Big([\![(\Delta E^{\mathrm{v}})(\Delta E^{\mathrm{r}})]\!] + 2[\![(\Delta E^{\mathrm{v}})^2\phi^{000\mathrm{rH}_2}\zeta^{\mathrm{v}}]\!]\frac{\overline{T}-T^{\mathrm{v}}}{T^{\mathrm{v}}}\Big), \tag{94}$$

$$\langle\!\langle f^{(0)}\widehat{\psi}^{\mathrm{t}+\mathrm{r}}, \mathcal{W}^{\mathrm{v}} \rangle\!\rangle = -\frac{2n^2}{k_{\mathrm{B}}\overline{T}}\Big([\![(\Delta E^{\mathrm{v}})^2]\!] - 2[\![(\Delta E^{\mathrm{v}})^2\widehat{\psi}^{\mathrm{t}+\mathrm{r}}\zeta^{\mathrm{v}}]\!]\frac{\overline{T}-T^{\mathrm{v}}}{T^{\mathrm{v}}}\Big). \tag{95}$$

$$\frac{T^{\mathrm{v}}}{\overline{T}}\langle\!\langle f^{(0)}\widehat{\psi}^{\mathrm{v}}, \mathcal{W}^{\mathrm{v}} \rangle\!\rangle = \frac{2n^2}{k_{\mathrm{B}}\overline{T}}\Big([\![(\Delta E^{\mathrm{v}})^2]\!] + 2[\![(\Delta E^{\mathrm{v}})^2\widehat{\psi}^{\mathrm{v}}\zeta^{\mathrm{v}}]\!]\frac{\overline{T}-T^{\mathrm{v}}}{\overline{T}}\Big). \tag{96}$$

As discussed in Appendix A, we may also evaluate the difference between $[\![(\Delta E^{\mathrm{v}})(\Delta E^{\mathrm{r}})]\!]$ and $[\![(\Delta E^{\mathrm{v}})(\Delta E^{\mathrm{r}})\zeta^{\mathrm{v}}]\!]$ and the difference between $[\![(\Delta E^{\mathrm{v}})^2]\!]$ and $[\![(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}]\!]$ in the form

$$[\![(\Delta E^{\mathrm{v}})(\Delta E^{\mathrm{r}})]\!] = [\![(\Delta E^{\mathrm{v}})(\Delta E^{\mathrm{r}})\zeta^{\mathrm{v}}]\!] + [\![(\Delta E^{\mathrm{v}})^2(\Delta E^{\mathrm{r}})\widehat{\zeta}^{\mathrm{v}}]\!]\frac{\overline{T}-T^{\mathrm{v}}}{k_{\mathrm{B}}\overline{T}T^{\mathrm{v}}},$$

$$[\![(\Delta E^{\mathrm{v}})^2]\!] = [\![(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}]\!] + [\![(\Delta E^{\mathrm{v}})^3\widehat{\zeta}^{\mathrm{v}}]\!]\frac{\overline{T}-T^{\mathrm{v}}}{k_{\mathrm{B}}\overline{T}T^{\mathrm{v}}}$$

where

$$\widehat{\zeta}^{\mathrm{v}} = \int_0^1\!\!\int_0^s \exp\Big(\big(\tfrac{\Delta E^{\mathrm{v}}}{k_{\mathrm{B}}\overline{T}} - \tfrac{\Delta E^{\mathrm{v}}}{k_{\mathrm{B}}T^{\mathrm{v}}}\big)r\Big)\,\mathrm{d}r\,\mathrm{d}s. \tag{97}$$

In the relaxation approximation and in the Navier-Stokes regime, we have to discard gradients terms squared associated with the Burnett regime, and we are left with the approximations

$$\langle\!\langle f^{(0)}\phi^{000\mathrm{rH}_2}, \mathcal{W}^{\mathrm{v}} \rangle\!\rangle \approx \frac{2n^2}{k_{\mathrm{B}}\overline{T}}[\![(\Delta E^{\mathrm{v}})(\Delta E^{\mathrm{r}})\zeta^{\mathrm{v}}]\!], \tag{98}$$

$$\langle\!\langle f^{(0)}\widehat{\psi}^{\mathrm{t}+\mathrm{r}}, \mathcal{W}^{\mathrm{v}} \rangle\!\rangle \approx -\frac{2n^2}{k_{\mathrm{B}}\overline{T}}[\![(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}]\!], \tag{99}$$

$$\frac{T^{\mathrm{v}}}{\overline{T}}\langle\!\langle f^{(0)}\widehat{\psi}^{\mathrm{v}}, \mathcal{W}^{\mathrm{v}} \rangle\!\rangle \approx \frac{2n^2}{k_{\mathrm{B}}\overline{T}}[\![(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}]\!]. \tag{100}$$

The resulting perturbed source term is then in the form

$$w_1^{\kappa} = -\frac{p\,c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})^2} \frac{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})[\![(\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}})\zeta^{\mathrm{v}}]\!] + (c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}c^{\mathrm{t}})[\![(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}]\!]}{[\![(\Delta E^{\mathrm{r}})^2]\!]^{\mathrm{r}}}. \tag{101}$$

On the other hand, in order to evaluate the perturbed distribution function ϕ^{ω}, we use the same Galerkin variational approximation space as for ϕ^{κ}. Upon expanding ϕ^{ω} in the form

$$\phi^{\omega} = -\frac{3}{p}\alpha_{\mathrm{H}_2}^{0\tilde{\mathrm{r}}\omega}\widehat{\phi}^{000\tilde{\mathrm{r}}\mathrm{H}_2}, \tag{102}$$

we obtain a linear system $K_{[0\tilde{\mathrm{r}}]}\alpha^{\omega}_{[0\tilde{\mathrm{r}}]} = \beta^{\omega}_{[0\tilde{\mathrm{r}}]}$ where $K_{[0\tilde{\mathrm{r}}]}$ is is presented in Section 2.7, and the right hand side β^{ω} is evaluated from

$$\beta_{\mathrm{H}_2}^{0\tilde{\mathrm{r}}\omega} = -\frac{1}{3n}\langle\!\langle f^{(0)}\widehat{\phi}^{000\tilde{\mathrm{r}}\mathrm{H}_2}, \psi^{\omega}\rangle\!\rangle.$$

However, since $\langle\!\langle f^{(0)}\widehat{\phi}^{000\tilde{\mathrm{r}}\mathrm{H}_2}, \psi^{\omega}\rangle\!\rangle = \langle\!\langle \widehat{\phi}^{000\tilde{\mathrm{r}}\mathrm{H}_2}, \widetilde{\mathcal{J}}^{\mathrm{sl},(0)}\rangle\!\rangle$, this scalar product has already been evaluated in Section 3.5. After some algebra, we obtain that

$$\beta_{\mathrm{H}_2}^{0\tilde{\mathrm{r}}\omega} = \frac{1}{3p}\,\frac{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})\llbracket(\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}})\zeta^{\mathrm{v}}\rrbracket + (c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}c^{\mathrm{t}})\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket}{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket},$$

and

$$\phi^{\omega} = -\frac{(k_{\mathrm{B}}\overline{T})^3}{p^2}\,\frac{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})\llbracket(\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}})\zeta^{\mathrm{v}}\rrbracket + (c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}c^{\mathrm{t}})\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket}{2(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket}\,\widehat{\phi}^{000\tilde{\mathrm{r}}\mathrm{H}_2}. \tag{103}$$

Using (98) and (99), the perturbed source term w_1^{v} is obtained in the form

$$w_1^{\mathrm{v}} = -\frac{1}{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})^2}\,\frac{\big((c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})\llbracket(\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}})\zeta^{\mathrm{v}}\rrbracket + (c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}c^{\mathrm{t}})\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket\big)^2}{\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket}. \tag{104}$$

3.7 The effective volume viscosity

The general expression of the effective volume viscosity in the Navier-Stokes regime and *in the relaxation approximation* is in the form

$$\kappa^{\mathrm{eff}} = \kappa^{\mathrm{r}} + \frac{c^{\mathrm{v}}p}{c_{\mathrm{vl}}}\widetilde{p}^{\mathrm{rel}} + \kappa^{\mathrm{v}} + \kappa^{\mathrm{v}}\frac{c_{\mathrm{vl}}}{c^{\mathrm{v}}p}w_1^{\kappa} - \kappa^{\mathrm{v}}w_1^{\mathrm{v}}. \tag{105}$$

Collecting from the previous sections we have

$$\kappa^{\mathrm{r}} = \Big(\frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}{c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}\Big)^2\frac{(k_{\mathrm{B}}\overline{T})^3}{2\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}},$$

$$\frac{c^{\mathrm{v}}}{c_{\mathrm{vl}}}p\,\widetilde{p}^{\mathrm{rel}} = -\frac{c^{\mathrm{v}}}{c_{\mathrm{vl}}}\,\frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}(k_{\mathrm{B}}\overline{T})^3}{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})^2}\,\frac{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})\llbracket(\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}})\zeta^{\mathrm{v}}\rrbracket + (c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}c^{\mathrm{t}})\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket}{2\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket},$$

$$\kappa^{\mathrm{v}} = \frac{c^{\mathrm{v}}\overline{c}^{\mathrm{v}}}{c_{\mathrm{vl}}\,\overline{c}_{\mathrm{vl}}}\,\frac{{k_{\mathrm{B}}}^3\overline{T}^2T^{\mathrm{v}}}{2\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket},$$

$$\kappa^{\mathrm{v}}\frac{c_{\mathrm{vl}}w_1^{\kappa}}{c^{\mathrm{v}}p} = -\frac{\overline{c}^{\mathrm{v}}}{\overline{c}_{\mathrm{vl}}}\,\frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}{k_{\mathrm{B}}}^3\overline{T}^2T^{\mathrm{v}}}{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})^2}\,\frac{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})\llbracket(\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}})\zeta^{\mathrm{v}}\rrbracket + (c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}c^{\mathrm{t}})\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket}{2\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket},$$

$$-\kappa^{\mathrm{v}}w_1^{\mathrm{v}} = \frac{c^{\mathrm{v}}\,\overline{c}^{\mathrm{v}}}{c_{\mathrm{vl}}\,\overline{c}_{\mathrm{vl}}}\,\frac{{k_{\mathrm{B}}}^3\overline{T}^2T^{\mathrm{v}}}{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})^2}\,\frac{\big((c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})\llbracket(\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}})\zeta^{\mathrm{v}}\rrbracket + (c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}c^{\mathrm{t}})\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket\big)^2}{2\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket^2}.$$

Finally, the nonequilibrium effective volume viscosity in the relaxation approximation is found in the form

$$\begin{aligned}
\kappa^{\mathrm{eff}} = {} & \Big(\frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}{c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}\Big)^2\frac{(k_{\mathrm{B}}\overline{T})^3}{2\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}} \\
& - \frac{c^{\mathrm{v}}}{c_{\mathrm{vl}}}\,\frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}(k_{\mathrm{B}}\overline{T})^3}{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})^2}\,\frac{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})\llbracket(\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}})\zeta^{\mathrm{v}}\rrbracket + (c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}c^{\mathrm{t}})\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket}{2\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket} \\
& + \frac{c^{\mathrm{v}}\overline{c}^{\mathrm{v}}}{c_{\mathrm{vl}}\,\overline{c}_{\mathrm{vl}}}\,\frac{{k_{\mathrm{B}}}^3\overline{T}^2T^{\mathrm{v}}}{2\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket} \\
& - \frac{\overline{c}^{\mathrm{v}}}{\overline{c}_{\mathrm{vl}}}\,\frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}{k_{\mathrm{B}}}^3\overline{T}^2T^{\mathrm{v}}}{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})^2}\,\frac{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})\llbracket(\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}})\zeta^{\mathrm{v}}\rrbracket + (c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}c^{\mathrm{t}})\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket}{2\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket} \\
& + \frac{c^{\mathrm{v}}\,\overline{c}^{\mathrm{v}}}{c_{\mathrm{vl}}\,\overline{c}_{\mathrm{vl}}}\,\frac{{k_{\mathrm{B}}}^3\overline{T}^2T^{\mathrm{v}}}{(c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})^2}\,\frac{\big((c^{\mathrm{t}}+c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})\llbracket(\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}})\zeta^{\mathrm{v}}\rrbracket + (c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}c^{\mathrm{t}})\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket\big)^2}{2\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}\llbracket(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}}\rrbracket^2}.
\end{aligned} \tag{106}$$

4 The Equilibrium Limit

4.1 The one-temperature two-mode volume viscosity

We investigate in this section the volume viscosity associated with a one-temperature $T = \overline{T} = T^{\mathrm{v}}$ two-mode gas mixture of H and H_2. The 'internal energy' approach linear system associated with the evaluation of the two-mode volume viscosity is obtained with the Galerkin variational approximation space spanned by

$$\widehat{\phi}^{000\mathrm{rH}_2} = \phi^{000\mathrm{rH}_2} - \frac{c^{\mathrm{r}}}{c_{\mathrm{vl}}}\widehat{\psi}^{\mathrm{t+r+v}},$$

$$\widehat{\phi}^{000\mathrm{vH}_2} = \phi^{000\mathrm{vH}_2} - \frac{c^{\mathrm{v}}}{c_{\mathrm{vl}}}\widehat{\psi}^{\mathrm{t+r+v}},$$

where $\phi^{000\mathrm{rH}_2} = (\overline{E}^{\mathrm{r}}_{\mathrm{H}_2} - E^{\mathrm{r}}_{\mathrm{H}_2\mathrm{I}})/k_{\mathrm{B}}T$, $\phi^{000\mathrm{vH}_2} = (\overline{E}^{\mathrm{v}}_{\mathrm{H}_2} - E^{\mathrm{v}}_{\mathrm{H}_2\mathrm{I}})/k_{\mathrm{B}}T$, $c^{\mathrm{r}} = c^{\mathrm{rr}} + c^{\mathrm{rv}}$ and $c^{\mathrm{v}} = c^{\mathrm{vr}} + c^{\mathrm{vv}}$. Note incidentally that $c^{\mathrm{vr}} = c^{\mathrm{rv}}$ since we have $T = \overline{T} = T^{\mathrm{v}}$. The terms proportional to $\widehat{\psi}^{\mathrm{t+r+v}}$ are here to ensure that $\widehat{\phi}^{000\mathrm{r}k}$ and $\widehat{\phi}^{000\mathrm{v}k}$ are orthogonal to the collisional invariant $\widehat{\psi}^{\mathrm{t+r+v}}$ of the *full* collision operator

$$\widehat{\psi}^{\mathrm{t+r+v}} = \sum_{l\in\mathfrak{S}} \phi^{0010l} + \sum_{l\in\mathfrak{P}} \phi^{000\mathrm{r}l} + \sum_{l\in\mathfrak{P}} \phi^{000\mathrm{v}l}.$$

The idea behind this basis function is that the most important part of the dynamics is the one associated with energy exchanges and not with the kinetic energy. The influence of the latter is simply taken into account with a global energy conservation constraint [33, 34].

A second important observation is that the usual expressions derived for the transport linear systems *may readily be used with nonorthogonal basis functions* like $\widehat{\phi}^{000\mathrm{rH}_2}$ and $\widehat{\phi}^{000\mathrm{vH}_2}$. The transport linear system associated with the volume viscosity comes indeed from a variational formulation of the corresponding integral equation and its derivation does not require orthogonality properties (the right hand side member β being covariant and the unknown vector contravariant). This also applies to the final expression of the volume viscosity.

The general solution of the transport linear systems associated with the volume viscosities as well as their mathematical structure have been already investigated [33, 34].

The corresponding linear system of size 2 is in the form

$$K_{[01]}\alpha_{[01]} = \beta_{[01]}, \tag{107}$$

where $K_{[01]}$ denotes the system matrix, $\alpha_{[01]} = (\alpha^{0\mathrm{r}\kappa}_{\mathrm{H}_2}, \alpha^{0\mathrm{v}\kappa}_{\mathrm{H}_2})^t$ the unknown vector, $\beta_{[01]} = (\beta^{0\mathrm{r}\kappa}_{\mathrm{H}_2}, \beta^{0\mathrm{v}\kappa}_{\mathrm{H}_2})^t$ the right hand side vector. The volume viscosity is $\kappa^{\mathrm{eq}} = \alpha^{0\mathrm{r}\kappa}_{\mathrm{H}_2}\beta^{0\mathrm{r}\kappa}_{\mathrm{H}_2} + \alpha^{0\mathrm{v}\kappa}_{\mathrm{H}_2}\beta^{0\mathrm{v}\kappa}_{\mathrm{H}_2}$. The matrix $K_{[01]}$ is positive definite and the right hand side vector is given by $\beta = (-c^{\mathrm{r}}, -c^{\mathrm{v}})^t/c_{\mathrm{vl}}$ where $c^{\mathrm{r}} = c^{\mathrm{rr}} + c^{\mathrm{rv}}$, $c^{\mathrm{v}} = c^{\mathrm{vr}} + c^{\mathrm{vv}}$, $c_{\mathrm{vl}} = c^{\mathrm{t}} + c^{\mathrm{r}} + c^{\mathrm{v}}$, noting that at equilibrium ($\overline{T} = T^{\mathrm{v}}$) we also have $c^{\mathrm{rv}} = c^{\mathrm{vr}}$.

After some algebra, using the reduced linear system (107) of size 2, it is obtained that

$$\kappa^{\mathrm{eq}} = \frac{1}{c_{\mathrm{vl}}^2}\,\frac{(c^{\mathrm{r}})^2K^{\mathrm{v,v}} - 2c^{\mathrm{r}}c^{\mathrm{v}}K^{\mathrm{r,v}} + (c^{\mathrm{v}})^2K^{\mathrm{r,r}}}{K^{\mathrm{r,r}}K^{\mathrm{v,v}} - K^{\mathrm{r,v}}K^{\mathrm{r,v}}}. \tag{108}$$

We also have the relations $K^{\mathrm{r,r}} = 2\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket/(k_{\mathrm{B}}T)^3$, $K^{\mathrm{r,v}} = 2\llbracket(\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}})\rrbracket/(k_{\mathrm{B}}T)^3$, and $K^{\mathrm{v,v}} = 2\llbracket(\Delta E^{\mathrm{v}})^2\rrbracket/(k_{\mathrm{B}}T)^3$. We investigate in the next section how to identify the rotational integral $\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}$ associated with the fast collision operator within the variational framework.

4.2 Variational approximation of $\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}$

We have to derive an approximation $\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}\prime}$ of the bracket $\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}$ associated with the fast collision operator within the variational approximation space spanned by $\widehat{\phi}^{000\mathrm{rH}_2}$ and $\widehat{\phi}^{000\mathrm{vH}_2}$ and using the collision integrals associated with the full collision operator.

Since we investigate the equilibrium limit in a regime where one mode is fast and the other is slow, and since $\mathcal{J} = \mathcal{J}^{\mathrm{rap}} + \mathcal{J}^{\mathrm{sl}}$, a first idea is to write that $\mathcal{J} \simeq \mathcal{J}^{\mathrm{rap}}$ so that $\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}\prime} \simeq \llbracket(\Delta E^{\mathrm{r}})^2\rrbracket$. In this situation, the coefficient $K^{\mathrm{r,r}}$ is large and the cross terms $K^{\mathrm{r,v}} = K^{\mathrm{v,r}}$ are small. A good approximation in the regime under consideration is thus to write that $\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}\prime} \simeq \llbracket(\Delta E^{\mathrm{r}})^2\rrbracket$ and to neglect the square term $K^{\mathrm{v,r}}K^{\mathrm{r,v}}$ in the expression of the equilibrium volume viscosity as already done in Reference [8].

However, a better approximation is obtained by noting that $\widehat{\phi}^{000\mathrm{vH}_2}$ is in the nullspace of $\mathcal{J}^{\mathrm{rap}}$ in such a way that $\mathcal{J}(\widehat{\phi}^{000\mathrm{vH}_2}) = \mathcal{J}^{\mathrm{sl}}(\widehat{\phi}^{000\mathrm{vH}_2})$. We may thus approximate $\mathcal{J}^{\mathrm{sl}}$ by its orthogonal projection onto span$\{\, \widehat{\phi}^{000\mathrm{vH}_2} \,\}$ and so approximate $\mathcal{J}^{\mathrm{rap}}$ in the form

$$\mathcal{J}^{\mathrm{rap}}(\psi) \simeq \mathcal{J}(\psi) - \frac{\langle\!\langle f^{(0)} \mathcal{J}(\widehat{\phi}^{000\mathrm{vH}_2}), \psi \rangle\!\rangle}{\langle\!\langle f^{(0)} \mathcal{J}(\widehat{\phi}^{000\mathrm{vH}_2}), \widehat{\phi}^{000\mathrm{vH}_2} \rangle\!\rangle} \mathcal{J}(\widehat{\phi}^{000\mathrm{vH}_2}).$$

Letting $\psi = \widehat{\phi}^{000\mathrm{rH}_2}$ and taking the scalar product with $\widehat{\phi}^{000\mathrm{rH}_2}$ we obtain now the more accurate approximation

$$\llbracket (\Delta E^{\mathrm{r}})^2 \rrbracket^{\mathrm{r}\prime} = \llbracket (\Delta E^{\mathrm{r}})^2 \rrbracket - \frac{\llbracket (\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}}) \rrbracket^2}{\llbracket (\Delta E^{\mathrm{v}})^2 \rrbracket}. \tag{109}$$

Combining this approximation (109) with the expression (108) we have established that the equilibrium viscosity may be written

$$\begin{aligned}\kappa^{\mathrm{eq}} =& \Big(\frac{c^{\mathrm{r}}}{c_{\mathrm{vl}}}\Big)^2 \frac{(k_{\mathrm{B}}T)^3}{2\llbracket (\Delta E^{\mathrm{r}})^2 \rrbracket^{\mathrm{r}\prime}} - \frac{c^{\mathrm{r}} c^{\mathrm{v}}}{c_{\mathrm{vl}}^2} \frac{(k_{\mathrm{B}}T)^3 \llbracket (\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}}) \rrbracket}{\llbracket (\Delta E^{\mathrm{r}})^2 \rrbracket^{\mathrm{r}\prime} \llbracket (\Delta E^{\mathrm{v}})^2 \rrbracket} \\ &+ \Big(\frac{c^{\mathrm{v}}}{c_{\mathrm{vl}}}\Big)^2 \frac{(k_{\mathrm{B}}T)^3}{2\llbracket (\Delta E^{\mathrm{v}})^2 \rrbracket} + \Big(\frac{c^{\mathrm{v}}}{c_{\mathrm{vl}}}\Big)^2 \frac{(k_{\mathrm{B}}T)^3 \llbracket (\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}}) \rrbracket^2}{2\llbracket (\Delta E^{\mathrm{r}})^2 \rrbracket^{\mathrm{r}\prime} \llbracket (\Delta E^{\mathrm{v}})^2 \rrbracket^2},\end{aligned} \tag{110}$$

where the last term arises from the $K^{\mathrm{r,r}}$ term at the numerator of (108) and from (109).

An elementary estimate also confirm the estimate (109). Indeed, we may roughly write that *during slow collisions*, we have average energy jumps $\overline{\Delta E}^{\mathrm{r}}$ and $\overline{\Delta E}^{\mathrm{v}}$ and that there are N^{v} such collisions. Then we may evaluate the bracket ratio in the form

$$\frac{\llbracket (\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}}) \rrbracket^2}{\llbracket (\Delta E^{\mathrm{v}})^2 \rrbracket} \simeq \frac{(N^{\mathrm{v}} \overline{\Delta E}^{\mathrm{r}} \overline{\Delta E}^{\mathrm{v}})^2}{N^{\mathrm{v}} (\overline{\Delta E}^{\mathrm{v}})^2} = N^{\mathrm{v}} (\overline{\Delta E}^{\mathrm{r}})^2,$$

so that $\llbracket (\Delta E^{\mathrm{r}})^2 \rrbracket - \frac{\llbracket (\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}}) \rrbracket^2}{\llbracket (\Delta E^{\mathrm{v}})^2 \rrbracket} \simeq N^{\mathrm{r}} (\overline{\Delta E}^{\mathrm{r}})^2 \simeq \llbracket (\Delta E^{\mathrm{r}})^2 \rrbracket^{\mathrm{r}}$.

4.3 Identification of the equilibrium limit

The equilibrium limit of the effective volume viscosity $\kappa^{\mathrm{eff,eq}}$ is directly deduced from (106) by letting $\overline{T} = T^{\mathrm{v}}$, $\zeta^{\mathrm{v}} = 1$, $\overline{c}^{\mathrm{v}} = c^{\mathrm{v}}$, and $\overline{c}_{\mathrm{vl}} = c_{\mathrm{vl}}$. Note in particular that, at equilibrium, $\overline{c}^{\mathrm{v}}$ and c^{v} coincide since then $c^{\mathrm{rv}} = c^{\mathrm{vr}}$ and $c^{\mathrm{rr}} = \overline{c}^{\mathrm{rr}}$, $c^{\mathrm{rv}} = \overline{c}^{\mathrm{rv}}$, $c^{\mathrm{vr}} = \overline{c}^{\mathrm{vr}}$, and $c^{\mathrm{vv}} = \overline{c}^{\mathrm{vv}}$. The resulting limit is in the form

$$\begin{aligned}\kappa^{\mathrm{eff,eq}} =& \quad \Big(\frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}{c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}\Big)^2 \frac{(k_{\mathrm{B}}T)^3}{2\llbracket (\Delta E^{\mathrm{r}})^2 \rrbracket^{\mathrm{r}}} \\ &- \frac{c^{\mathrm{v}}}{c_{\mathrm{vl}}} \frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} (k_{\mathrm{B}}T)^3}{(c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})^2} \frac{(c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}) \llbracket (\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}}) \rrbracket + (c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}} c^{\mathrm{t}}) \llbracket (\Delta E^{\mathrm{v}})^2 \rrbracket}{2\llbracket (\Delta E^{\mathrm{r}})^2 \rrbracket^{\mathrm{r}} \llbracket (\Delta E^{\mathrm{v}})^2 \rrbracket} \\ &+ \frac{(c^{\mathrm{v}})^2}{(c_{\mathrm{vl}})^2} \frac{(k_{\mathrm{B}}T)^3}{2\llbracket (\Delta E^{\mathrm{v}})^2 \rrbracket} \\ &- \frac{c^{\mathrm{v}}}{c_{\mathrm{vl}}} \frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} (k_{\mathrm{B}}T)^3}{(c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})^2} \frac{(c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}) \llbracket (\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}}) \rrbracket + (c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}} c^{\mathrm{t}}) \llbracket (\Delta E^{\mathrm{v}})^2 \rrbracket}{2\llbracket (\Delta E^{\mathrm{r}})^2 \rrbracket^{\mathrm{r}} \llbracket (\Delta E^{\mathrm{v}})^2 \rrbracket} \\ &+ \frac{(c^{\mathrm{v}})^2}{(c_{\mathrm{vl}})^2} \frac{(k_{\mathrm{B}}T)^3}{(c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})^2} \frac{\big((c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}) \llbracket (\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}}) \rrbracket + (c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}} - \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}} c^{\mathrm{t}}) \llbracket (\Delta E^{\mathrm{v}})^2 \rrbracket\big)^2}{2\llbracket (\Delta E^{\mathrm{r}})^2 \rrbracket^{\mathrm{r}} \llbracket (\Delta E^{\mathrm{v}})^2 \rrbracket^2}.\end{aligned} \tag{111}$$

We will now show that this expression coincides with the one-temperature volume viscosity (110), evaluated independently in Section 4.2, provided the approximation $\llbracket (\Delta E^{\mathrm{r}})^2 \rrbracket^{\mathrm{r}\prime}$ is used in place of the fast collision operator collision integral, $\llbracket (\Delta E^{\mathrm{r}})^2 \rrbracket^{\mathrm{r}}$.

We first consider the terms in (111) proportional to $(k_{\mathrm{B}}T)^3 / \big(2\llbracket (\Delta E^{\mathrm{r}})^2 \rrbracket^{\mathrm{r}}\big)$.

Adding the contributions arising from the first, the second, the fourth and the fifth terms of (111), we get

$$\Big(\frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}{c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}\Big)^2 \Big(1 - \frac{c^{\mathrm{v}}}{c_{\mathrm{vl}}} \Big(1 - \frac{c^{\mathrm{t}}}{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}} \frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}\Big)\Big)^2.$$

Making use of the identity $c_{\mathrm{vl}} - c^{\mathrm{v}}\big(1 - \frac{c^{\mathrm{t}}}{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}\frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}\big) = \frac{c^{\mathrm{r}}}{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}(c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}})$, derived in Appendix B, we arrive at

$$\Big(\frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}{c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}\Big)^2 \bigg(1 - \frac{c^{\mathrm{v}}}{c_{\mathrm{vl}}}\Big(1 - \frac{c^{\mathrm{t}}}{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}\frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}\Big)\bigg)^2 = \Big(\frac{c^{\mathrm{r}}}{c_{\mathrm{vl}}}\Big)^2,$$

so that the sum of all contributions proportional to $(k_{\mathrm{B}}T)^3/\big(2\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}\big)$ in (111) exactly yields the first term of (110).

Contributions proportional to $(k_{\mathrm{B}}T)^3\llbracket(\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}})\rrbracket/\big(2\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}\llbracket(\Delta E^{\mathrm{v}})^2\rrbracket\big)$ come from the second, the fourth and the fifth terms of (111)

$$-2\Big(\frac{c^{\mathrm{v}}}{c_{\mathrm{vl}}}\Big)\Big(\frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}{c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}\Big)\bigg(1 - \frac{c^{\mathrm{v}}}{c_{\mathrm{vl}}}\Big(1 - \frac{c^{\mathrm{t}}}{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}\frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}\Big)\bigg).$$

Again, the identity derived in Appendix B can be used to conclude that

$$-2\Big(\frac{c^{\mathrm{v}}}{c_{\mathrm{vl}}}\Big)\Big(\frac{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}{c^{\mathrm{t}} + c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}\Big)\bigg(1 - \frac{c^{\mathrm{v}}}{c_{\mathrm{vl}}}\Big(1 - \frac{c^{\mathrm{t}}}{c^{\tilde{\mathrm{r}}\tilde{\mathrm{r}}}}\frac{c^{\mathrm{rv}}}{c^{\mathrm{vv}}}\Big)\bigg) = -2\frac{c^{\mathrm{r}}c^{\mathrm{v}}}{(c_{\mathrm{vl}})^2},$$

so that the sum of all contributions proportional to $(k_{\mathrm{B}}T)^3\llbracket(\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}})\rrbracket/(2\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}\llbracket(\Delta E^{\mathrm{v}})^2\rrbracket)$ in (111) exactly yields the second term of (110).

The third term in (111) exactly coincides with the third term of (110).

Similarly, the single term proportional to $(k_{\mathrm{B}}T)^3\llbracket(\Delta E^{\mathrm{r}})(\Delta E^{\mathrm{v}})\rrbracket^2/\big(2\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}\llbracket(\Delta E^{\mathrm{v}})^2\rrbracket^2\big)$, arising from the fifth term in (111), exactly coincides with the fourth term of (110).

We have thus established that the equilibrium limit of the effective volume viscosity in the relaxation regime coincides with the one-temperature two-mode volume viscosity evaluated independently, provided the approximation $\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}\prime}$ is substituted in place of the fast collision operator collision integral $\llbracket(\Delta E^{\mathrm{r}})^2\rrbracket^{\mathrm{r}}$.

5 Application to the $\mathrm{H} - \mathrm{H}_2$ system

The kinetic model discussed in the previous sections is here applied to the calculation of the volume viscosities of $\mathrm{H} - \mathrm{H}_2$ mixtures in the trace limit. To this end we start by introducing the cross section data that will be used to describe the H_2 roto-vibrational energy relaxation.

5.1 Internal energy spectrum and energy exchange collisions

The calculation of volume viscosities and other quantities needed for the description of the relaxation of the internal (rotational and vibrational) degrees of freedom of H_2 requires the evaluation of several collision integrals. To this end, information on the cross sections for internal energy exchange collisions is needed. The set of roto-vibrationally detailed cross sections used in this work has been calculated by the quasiclassical method, with an in-house developed code, that has been tested repeatedly against accurate results from the literature [35, 36, 37, 38, 39]. The set is complete, since all the H_2 rovibrational states of the electronic ground state have been considered as initial and final states. Quasibound states and dissociation processes have also been considered in the trajectory calculations, even though they have not been used in the present study.

Cross sections for the processes $\mathrm{H} + \mathrm{H}_2(v, j) \to \mathrm{H}_2(w, k) + \mathrm{H}$ with v/w initial/final vibrational states, j/k initial/final rotational states, have been calculated including both reactive (i.e. exchange) and non-reactive processes. Collision kinetic energy in the center-of-mass frame ranges from 0.001 to 9 eV allowing for accurate calculation of rate constants and collision integrals in the temperature range from 1000 K to 10000 K.

The embarrassingly parallel nature of quasiclassical calculations allowed the enormous amount of required trajectories to be calculated exploiting large distributed computational resources. The integration time step used is dynamically adapted [37, 38] in order to achieve an optimal compromise between accuracy and computational load. The Potential Energy Surface (PES) adopted is the well known BKMP2 [40], that is believed to have better accuracy both in the high energy range and for rotational transitions in the low temperature regime, with respect to the LSTH PES [41], used, for example, in the work of Martin and Mandy [42]. Results from the latter work compare well with the present calculations, differences being limited to high lying roto-vibrational states, as expected [39].

The full set of rate coefficients, as obtained from the calculated cross sections, is available upon request, and will also be available in the database of the European Project *Phys4Entry* [43]. Further details, results and comparisons with the literature can be found in References [35, 36, 39, 44, 45].

The potential energy surface used [40] supports 301 bound rovibrational states for the isolated H_2 molecule, distributed over 15 vibrational levels, each with a varying number of rotational states. The energy spectrum is depicted in fig. 1 and the internal specific heats $c^{\mathrm{rr}}_{\mathrm{H}_2}$, $c^{\mathrm{rv}}_{\mathrm{H}_2}$, and $c^{\mathrm{vv}}_{\mathrm{H}_2}$ at thermal equilibrium ($T^{\mathrm{v}} = \overline{T} = T$) are depicted in fig. 2 as a function of temperature. It is apparent that the coupling between the rotational and the vibrational energies cannot be neglected.

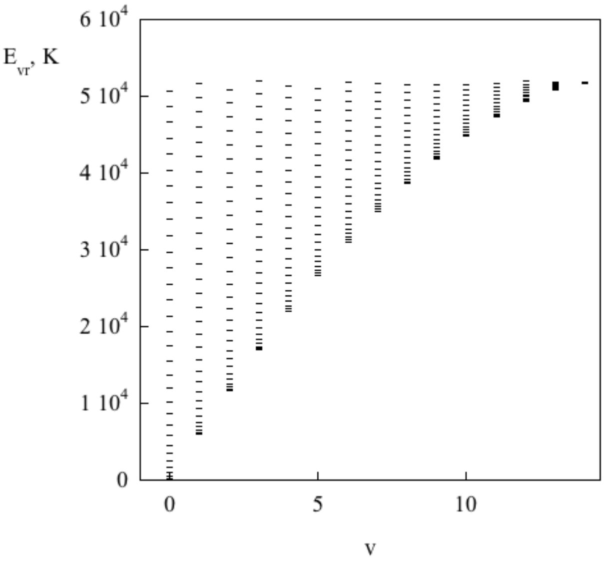

Figure 1: H_2 internal energy levels.

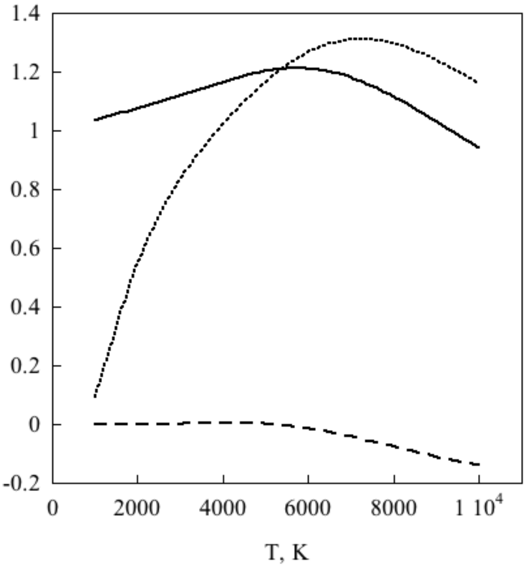

Figure 2: H_2 adimensional internal specific heats as a function of temperature; solid line: $c^{\mathrm{rr}}_{\mathrm{H}_2}$; dashed line: $c^{\mathrm{rv}}_{\mathrm{H}_2}$; dotted line: $c^{\mathrm{vv}}_{\mathrm{H}_2}$.

Finally, elastic collision integrals for the $\mathrm{H} - \mathrm{H}_2$ interaction have been taken from the work of Stallcop and coauthors [46].

5.2 Results

The theoretical results of the previous sections are here specialised to the $H - H_2$ mixture in thermal equilibrium conditions.

We have evaluated numerically the various contributions in (106) as a function of temperature. Since a complete set of inelastic cross sections is available for the atom-diatom collisional system only, all properties are calculated in the trace limit ($x_{\mathrm{H}} \to 1$, $x_{\mathrm{H}_2} \to 0$). Altough this is a strong limitation and is hardly justifiable on physical grounds, it still allows the estimation of the theoretical kinetic model for a realistic system. In addition, relevant information on the H_2 internal energy relaxation by atom impact can be obtained, as we shall see in the following. For quantities a that vanish with the hydrogen mole fraction, x_{H_2}, we have evaluated the limit ratio $\hat{a} = \lim_{x_{\mathrm{H}_2} \to 0}(a/x_{\mathrm{H}_2})$.

First we discuss the choice of the variational approximation space used for the derivation of transport linear systems from the linearized Boltzmann equations (41). The use of a reduced Galerkin variational approximation space, as described in Section 2.7, is justified for the calculation of κ^{r} since this approximation only brings differences limited to 2% as already observed in different situations [34, 33].

However, the assumptions underlying the choice of a reduced approximation space, namely that kinetic energy is not relevant for the characterization of the collision dynamics, may be improved when calculating the relaxation pressure and the perturbed source term. In these cases the relevant collision integrals include contributions from *slow* collisions where the energy exchanges between kinetic and internal energy modes can be large.

Figure 3 shows the reduced relaxation pressure $\widetilde{p}^{\mathrm{rel}}$ evaluated with the *traditional* basis functions $\phi^{0010\mathrm{H}}$, $\phi^{0010\mathrm{H}_2}$, and $\phi^{000\tilde{\mathrm{r}}\mathrm{H}_2}$ and the *reduced* basis $\widehat{\phi}^{000\tilde{\mathrm{r}}\mathrm{H}_2}$. The former is about 40% smaller in the whole temperature range.

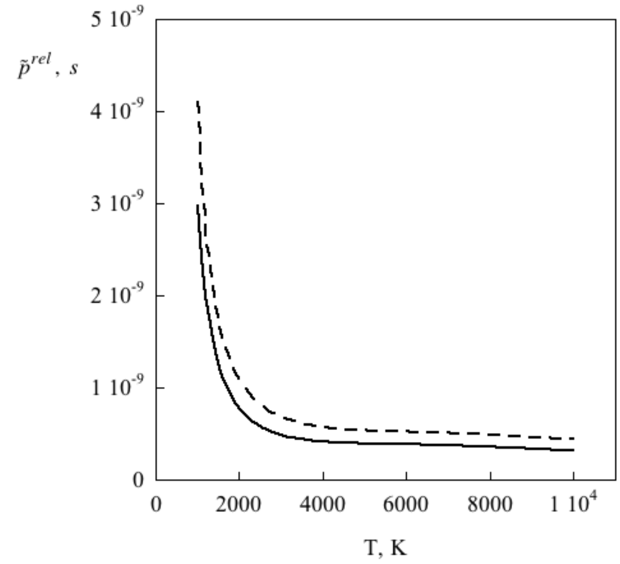

Figure 3: Comparison of $\widetilde{p}^{\mathrm{rel}}$ as obtained with the *traditional* (solid line) and *reduced* (dashed line) Galerkin variational approximation spaces.

The same is true for the perturbed source terms as depicted in figs. 4, 5.

As a result, the traditional basis functions are preferred for the calculations presented in this paper; they involve the solution of appropriate transport linear systems whose structure is analyzed in References [47, 48, 49].

Note also that larger variational approximation spaces may be required to reach convergent results. This point has been raised e.g. in Reference [22] for the case of Nitrogen. These calculations, however, would require the knowledge of higher moments of the differential scattering cross sections.

We next turn to the evaluation of the different contributions in (77). Figure 6 shows the temperature dependance of the limiting quantities $\widehat{\kappa^{\mathrm{r}}}$, $\widehat{\frac{c^{\mathrm{v}}p}{c_{\mathrm{vl}}}\widetilde{p}^{\mathrm{rel}}}$, and $\widehat{\kappa^{\mathrm{v}}}$. The shear viscosity $\eta_{\mathrm{HH}_2} = 5k_{\mathrm{B}}T/8\Omega^{(2,2)}_{\mathrm{HH}_2}$ is also plotted for comparison. All volume viscosities are comparable to or larger than the shear viscosity.

The first order source terms $\frac{c_{\mathrm{vl}}}{c^{\mathrm{v}}p}w_1^{\kappa}$ and $-w_1^{\mathrm{v}}$ which are the Navier-Stokes perturbations of the

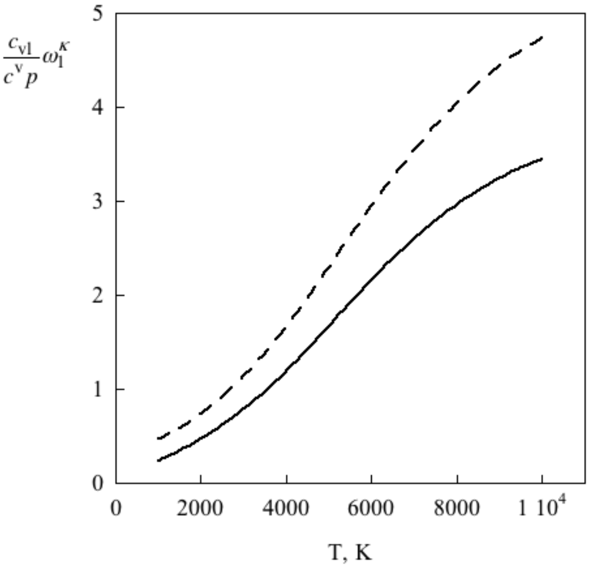

Figure 4: Comparison of $\frac{c_{\rm v1}}{c^{\rm v}p}w_1^\kappa$ as obtained with the *traditional* (solid line) and *reduced* (dashed line) Galerkin variational approximation spaces.

zeroth order relaxation term $\omega_0^{\rm v}$ are depicted in fig. 7. Since these terms are to be compared to 1, this plot shows that their contribution is by no means negligible.

Finally, a comparison of $\hat{\kappa}^{\rm eff,eq}$ and $\hat{\kappa}^{\rm eq}$ is presented in fig. 8. This plot shows that the one-temperature kinetic model described in Section 4.1 works well in the low temperature region only. Indeed, as the temperature rises, the approximation $[\![(\Delta E^{\rm r})^2]\!]^{\rm r} \approx [\![(\Delta E^{\rm r})^2]\!]^{\rm r\prime} \equiv [\![(\Delta E^{\rm r})^2]\!] - [\![(\Delta E^{\rm r})(\Delta E^{\rm v})]\!]^2/[\![(\Delta E^{\rm v})^2]\!]$ progressively degrades as depicted in fig. 9. In this conditions, the assumption of the one-temperature kinetic model, i.e. that *all* collisions are fast, breaks down and the model is not a valid description. The fast volume viscosity, $\hat{\kappa}^{\rm r}$, is also plotted for comparison: this is the limiting value of $\hat{\kappa}^{\rm eff}$ as the slow collisions are inhibited. We then conclude that, when slow collisions start playing a role a nonequilibrium description of the internal energy relaxation is required even in conditions of thermal equilibrium. Quantitative estimations of the limits are also obtained, as shown in fig. 9.

6 Conclusions

The theory developed in [8] has been extended to gas mixtures and to gases with two coupled degrees of freedom. This has allowed to test it with the real physical system $\rm H - H_2$ for which a complete set of inelastic cross sections is now available. Although the model has been investigated in the limit where $\rm H_2$ is in trace amount in a gas of H atoms, a physically unrealistic situation, it gives interesting indications on the behavior of a real diatomic molecule, for which the rotational and vibrational modes cannot be decoupled, colliding with an atomic species, as in the classical ultrasound absorption measurements discussed in References [21, 22].

It has been shown that a kinetic model that decomposes the inelastic collisions in two separate sets of *slow* and *rapid* collisions produces a nonequilibrium description of the gas where both a bulk viscosity and relaxation pressure appear. The former, $\kappa^{\rm r}$, depends on the average energy exchanged during *rapid* collisions; the latter, $p^{\rm rel}$ carries information on the *slow* collisions. Under the appropriate relaxation approximation, i.e., when the flow characteristic times are larger than the slow mode characteristic time, the slow mode relaxation also gives rise to a nonequilibrium bulk viscosity $\kappa^{\rm v}$ and to perturbed source terms. A complete expression has been derived that describes the volume viscosity effect for a gas mixture in thermal equilibrium in the frame of the two-temperature kinetic model. The theory also shows that the nonequilibrium description reduces to the equilibrium-two modes kinetic model under the appropriate relaxation assumptions, as it should be.

Calculations performed on the $\rm H - H_2$ mixture, however, have shown that the $\kappa^{\rm eff,eq} = \kappa^{\rm eq}$ equality has a limited range of applicability. Discrepancies arise when slow collisions start playing a role in the volume viscosity effect since they are not accounted for correctly in the one-temperature model. This

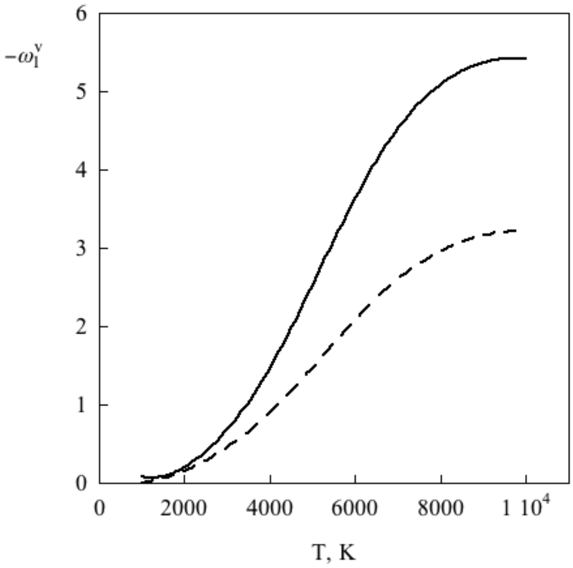

Figure 5: Comparison of $-w_1^v$ as obtained with the *traditional* (solid line) and *reduced* (dashed line) Galerkin variational approximation spaces.

is to be expected, since the equilibrium kinetic model predicts a linear dependance of the bulk viscosity coefficient on the internal mode relaxation time, as in (64), a result that cannot hold when the energy exchanges become slow and the relaxation time tends to diverge. This result, already shown in Ref. [8] for a model system, is here obtained for the molecular hydrogen internal energy relaxation by atom impact, together with the limits of validity of the one-temperature formulation.

For the very same reasons, the question arises on the limits of validity of the nonequilibrium model discussed here. The model is based on the assumption that there is a rapid rotational mode and a slow vibrational mode, an extension of the classical two temperature approach to coupled modes. Preliminary calculations on the relaxation kinetics (not presented here) show, however, that this model is not adequate to describe a system where the rate coefficients for inelastic processes seem to be ordered according to the *value* of the energy jump, as opposed to its *nature* (rotational or vibrational).

It is also worth mentioning that rotational relaxation in molecular hydrogen is known to be slow [24, 23, 27, 25] and that it is coupled to vibrational relaxation [26], so that these conclusions may not be readily extended to other diatomic molecules.

A quantitative estimation of the limits of the two-temperature model can only be obtained by the comparison to a full state-to-state model. Results of the latter could then be validated with Monte Carlo kinetic simulations as in Ref. [8].

It is also useful here to recall that any kinetic model will require the knowledge of diatom-diatom inelastic cross sections in order to be amenable to experimental verification.

More generally, the acknowledgement that reduced kinetic models have a limited domain of validity calls for the development of more accurate reduced descriptions of the molecular internal kinetics. These models have a wider scope than the determination of the bulk viscosity and are the subject of current active discussions. Since detailed state-selected energy exchange cross sections are becoming available, and the kinetic description on a state-to-state basis is complex and computationally too expensive, except in few simple cases, the development of accurate reduced models is an important task.

acknowledgments

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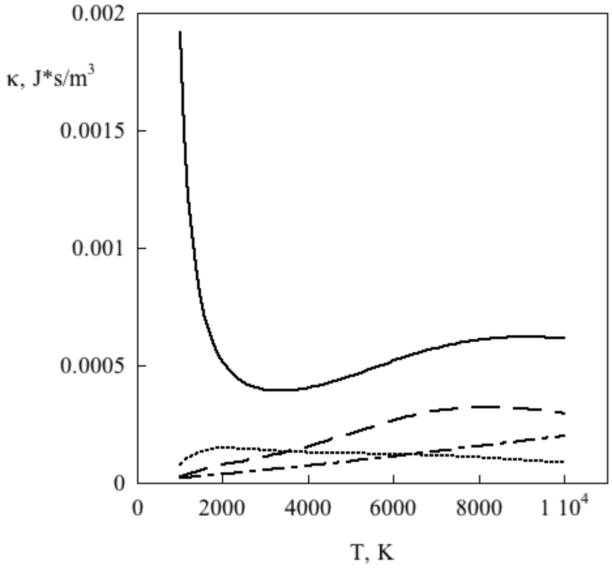

Figure 6: Different terms as they appear in (77) as a function of temperature. Solid line: $\widehat{\kappa}^{\mathrm{r}}$; dashed line: $\widehat{\frac{c^{\mathrm{v}}p}{c_{\mathrm{v}1}}\widetilde{p}^{\mathrm{rel}}}$; dotted line: $\widehat{\kappa^{\mathrm{v}}}$; dash-dotted line: η_{HH_2}.

A Properties of the averaging operator

The averaging operator $\llbracket\ \rrbracket$ has interesting properties which are useful to simplify analytic expressions. Letting

$$a_{ij} = \tfrac{\Delta E^{\mathrm{v}}_{ij}}{k_{\mathrm{B}}\overline{T}} - \tfrac{\Delta E^{\mathrm{v}}_{ij}}{k_{\mathrm{B}}T^{\mathrm{v}}}, \tag{112}$$

we have

$$\zeta^{\mathrm{v}}_{ij} = \int_0^1 \exp(a_{ij}s)\,ds, \qquad \exp(a_{ij}) - 1 = a_{ij}\zeta^{\mathrm{v}}_{ij},$$

and manipulating the collision integrals, it may be checked that

$$\llbracket \alpha_{ij} \rrbracket_{ij} = \llbracket \alpha'_{ij}\exp(a_{ij}) \rrbracket_{ij}, \tag{113}$$

where the prime indicates the inverse collisions, and this, in turn, implies that

$$\llbracket \alpha \rrbracket = \llbracket \alpha' \exp(a) \rrbracket. \tag{114}$$

Applying this to $\alpha = \Delta E^{\mathrm{v}}_{ij}$ we obtain that

$$\llbracket \Delta E^{\mathrm{v}} \rrbracket = -\llbracket \Delta E^{\mathrm{v}}\exp(a) \rrbracket = -\tfrac{1}{2}\llbracket \Delta E^{\mathrm{v}}\big(\exp(a)-1\big) \rrbracket = -\tfrac{1}{2}\llbracket \Delta E^{\mathrm{v}} a\zeta^{\mathrm{v}} \rrbracket,$$

and using (112) the zeroth order source term may be written

$$\omega^{\mathrm{v}}_0 = 4n^2\llbracket \Delta E^{\mathrm{v}} \rrbracket = -2n^2\llbracket (\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}} \rrbracket\Big(\tfrac{1}{k_{\mathrm{B}}\overline{T}} - \tfrac{1}{k_{\mathrm{B}}T^{\mathrm{v}}}\Big).$$

In addition, the factor ζ^{v} is very practical for nonequilibrium mixtures in order to use inverse collisions. We have for instance

$$\llbracket \alpha a\zeta^{\mathrm{v}} \rrbracket = \llbracket \alpha\big(\exp(a)-1\big) \rrbracket = \llbracket \alpha'\big(\exp(-a)-1\big)\exp(a) \rrbracket = -\llbracket \alpha'\big(\exp(a)-1\big) \rrbracket = -\llbracket \alpha' a\zeta^{\mathrm{v}} \rrbracket,$$

so that in particular

$$\llbracket \alpha\Delta E^{\mathrm{v}}\zeta^{\mathrm{v}} \rrbracket = -\llbracket \alpha'\Delta E^{\mathrm{v}}\zeta^{\mathrm{v}} \rrbracket.$$

For example, for $\alpha = \beta(\Delta E^{\mathrm{v}})$, we get $\llbracket \beta(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}} \rrbracket = \llbracket \beta'(\Delta E^{\mathrm{v}})^2\zeta^{\mathrm{v}} \rrbracket$.

The difference between $\llbracket \alpha\Delta E^{\mathrm{v}}\zeta^{\mathrm{v}} \rrbracket$ and $\llbracket \alpha\Delta E^{\mathrm{v}} \rrbracket$ may be estimated by using

$$\llbracket \alpha(\Delta E^{\mathrm{v}}) \rrbracket = \llbracket \alpha(\Delta E^{\mathrm{v}})\zeta^{\mathrm{v}} \rrbracket + \llbracket \alpha(\Delta E^{\mathrm{v}})^2\widehat{\zeta}^{\mathrm{v}} \rrbracket\frac{\overline{T} - T^{\mathrm{v}}}{k_{\mathrm{B}}\overline{T}T^{\mathrm{v}}},$$

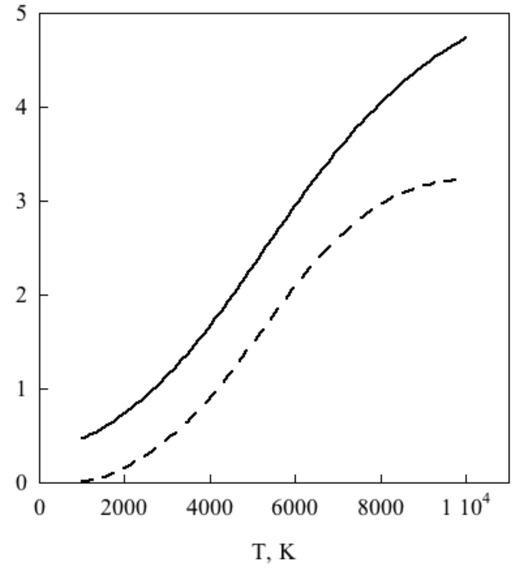

Figure 7: Comparison of first order source terms as a function of temperature. Solid line: $\frac{c_{\rm vl}}{c^{\rm v}p} w_1^{\kappa}$; dashed line: $-w_1^{\rm v}$.

where

$$\widehat{\zeta}^{\rm v} = \int_0^1 \int_0^s \exp\Big(\big(\tfrac{\Delta E^{\rm v}}{k_{\rm B}\overline{T}} - \tfrac{\Delta E^{\rm v}}{k_{\rm B}T^{\rm v}} \big) r \Big) \, {\rm d}r \, {\rm d}s. \tag{115}$$

This is indeed a direct consequence of the identity $\exp(a_{ij}) = 1 + a_{ij} + a_{ij}^2 \, \widehat{\zeta}^{\rm v}$ which is established in much the same way as the identity $\exp(a_{ij}) = 1 + a_{ij} \, \zeta^{\rm v}$.

These relations are convenient in order to evaluate some kinetic expressions. For instance, the products $\langle\!\langle f^{(0)}\alpha, \mathcal{W}^{\rm v} \rangle\!\rangle$ may be written

$$\langle\!\langle f^{(0)}\alpha, \mathcal{W}^{\rm v} \rangle\!\rangle = 8n^2 [\![\alpha \Delta E^{\rm v}]\!] = -8n^2 [\![\alpha (\Delta E^{\rm v}) \exp(a)]\!] = 4n^2 [\![(\alpha - \exp(a)\alpha') \Delta E^{\rm v}]\!],$$

and next

$$\langle\!\langle f^{(0)}\alpha, \mathcal{W}^{\rm v} \rangle\!\rangle = 4n^2 \Big([\![(\alpha - \alpha') \Delta E^{\rm v}]\!] + [\![\alpha' \big(1 - \exp(a) \big) \Delta E^{\rm v}]\!] \Big),$$

$$\langle\!\langle f^{(0)}\alpha, \mathcal{W}^{\rm v} \rangle\!\rangle = -2n^2 \Big([\![\Delta\alpha \Delta E^{\rm v}]\!] + 2 [\![\alpha \big(\exp(a) - 1 \big) \Delta E^{\rm v}]\!] \Big),$$

so that finally

$$\langle\!\langle f^{(0)}\alpha, \mathcal{W}^{\rm v} \rangle\!\rangle = -2n^2 [\![\Delta\alpha \Delta E^{\rm v}]\!] + \frac{4n^2}{k_{\rm B}\overline{T}} [\![\alpha (\Delta E^{\rm v})^2 \zeta^{\rm v}]\!] \frac{\overline{T} - T^{\rm v}}{T^{\rm v}}.$$

B Relation among the specific heats

We derive in this section the formula

$$c_{\rm vl} - c^{\rm v} \Big(1 - \frac{c^{\rm t}}{c^{\tilde{\rm r}\tilde{\rm r}}} \frac{c^{\rm rv}}{c^{\rm vv}} \Big) = \frac{c^{\rm r}}{c^{\tilde{\rm r}\tilde{\rm r}}} (c^{\rm t} + c^{\tilde{\rm r}\tilde{\rm r}}).$$

We start by developing the product and by using $c^{\rm v} = c^{\rm vr} + c^{\rm vv}$ and $c_{\rm vl} = c^{\rm t} + c^{\rm rr} + c^{\rm rv} + c^{\rm vr} + c^{\rm vv}$ to get

$$\mathfrak{v} = c_{\rm vl} - c^{\rm v} + \frac{c^{\rm v} c^{\rm t}}{c^{\tilde{\rm r}\tilde{\rm r}}} \frac{c^{\rm rv}}{c^{\rm vv}} = c^{\rm t} + c^{\rm rr} + c^{\rm rv} + \frac{c^{\rm v} c^{\rm t}}{c^{\tilde{\rm r}\tilde{\rm r}}} \frac{c^{\rm rv}}{c^{\rm vv}}.$$

Regrouping the $c^{\rm t}$ contributions and using $c^{\tilde{\rm r}\tilde{\rm r}} = c^{\rm rr} - c^{\rm rv} c^{\rm vr} / c^{\rm vv}$ we obtain after some algebra

$$\mathfrak{v} = c^{\rm t} \Big(1 + \frac{c^{\rm v}}{c^{\tilde{\rm r}\tilde{\rm r}}} \frac{c^{\rm rv}}{c^{\rm vv}} \Big) + c^{\rm rr} + c^{\rm rv} = \frac{c^{\rm t}}{c^{\tilde{\rm r}\tilde{\rm r}} c^{\rm vv}} \Big(c^{\rm rr} c^{\rm vv} - c^{\rm vr} c^{\rm rv} + (c^{\rm vr} + c^{\rm vv}) c^{\rm rv} \Big) + c^{\rm rr} + c^{\rm rv} = \ldots$$

$$\ldots = \frac{c^{\rm t}}{c^{\tilde{\rm r}\tilde{\rm r}} c^{\rm vv}} \Big(c^{\rm rr} c^{\rm vv} + c^{\rm vv} c^{\rm rv} \Big) + c^{\rm rr} + c^{\rm rv} = (c^{\rm rr} + c^{\rm rv}) \Big(\frac{c^{\rm t}}{c^{\tilde{\rm r}\tilde{\rm r}} c^{\rm vv}} c^{\rm vv} + 1 \Big) = \frac{c^{\rm r}}{c^{\tilde{\rm r}\tilde{\rm r}}} (c^{\rm t} + c^{\tilde{\rm r}\tilde{\rm r}}),$$

and this completes the proof.

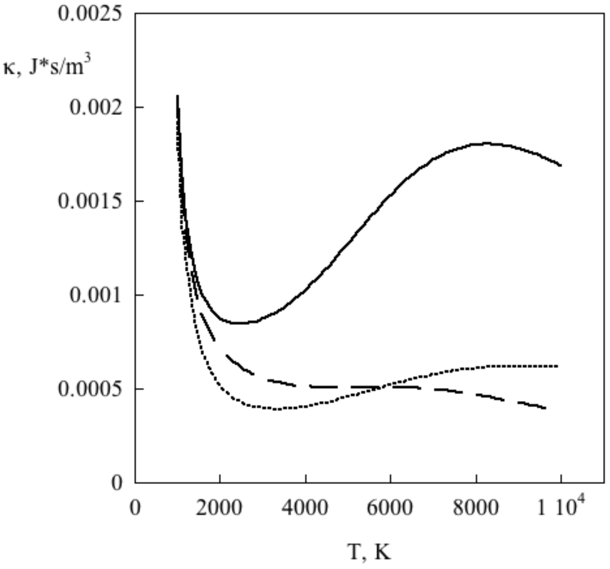

Figure 8: Comparison of volume viscosities. Solid line: $\widehat{\kappa}^{\rm eff}$; dashed line: $\widehat{\kappa}^{\rm eq}$; dotted line: $\widehat{\kappa}^{\rm r}$.

C Erratum for Reference [8]

This appendix collects some typographic errors overlooked by the authors in Reference [8]. First, equations (19), (20), (22), and (23) should be

$$\mathcal{S}^{\rm int} = n k_{\rm B}\Big(\frac{\overline{E}}{k_{\rm B}T^{\rm int}} - \log\frac{1}{Z^{\rm int}}\Big). \tag{19}$$

$$G^{\rm tr} = k_{\rm B}T^{\rm tr}\log\frac{n}{Z^{\rm tr}}, \qquad G^{\rm int} = k_{\rm B}T^{\rm int}\log\frac{1}{Z^{\rm int}}, \tag{20}$$

$$d\mathcal{S} = \frac{nc^{\rm tr}}{T^{\rm tr}}dT^{\rm tr} + \frac{nc^{\rm int}}{T^{\rm int}}dT^{\rm int} + \Big(\frac{3}{2}k_{\rm B} + \frac{\overline{E}}{T^{\rm int}} - k_{\rm B}\log\frac{n}{Z^{\rm tr}Z^{\rm int}}\Big)dn, \tag{22}$$

$$\partial_t\mathcal{S} + \boldsymbol{\nabla}\cdot(\boldsymbol{v}\mathcal{S}) + \boldsymbol{\nabla}\cdot\Big(\frac{\boldsymbol{Q}^{\rm tr}}{T^{\rm tr}} + \frac{\boldsymbol{Q}^{\rm int}}{T^{\rm int}}\Big) = -\frac{\boldsymbol{Q}^{\rm tr}\cdot\boldsymbol{\nabla}T^{\rm tr}}{{T^{\rm tr}}^2} - \frac{\boldsymbol{Q}^{\rm int}\cdot\boldsymbol{\nabla}T^{\rm int}}{{T^{\rm int}}^2} - \frac{\boldsymbol{\Pi}\boldsymbol{:}\boldsymbol{\nabla}\boldsymbol{v}}{T^{\rm tr}} + \frac{\omega_1^{\rm int}(T^{\rm tr} - T^{\rm int})}{T^{\rm tr}T^{\rm int}}. \tag{23}$$

Equations (41), (76), (77), and (81) should be

$$\widetilde{\mathcal{J}}^{\rm sl,(0)} = -\frac{1}{2n^2[\![(\Delta E)^2\zeta]\!]}\sum_{\rm J,I',J'}\int f^{(0)}\widetilde{f}^{(0)}(\Delta E)\zeta g\sigma^{\rm IJI'J'}\,d\widetilde{\boldsymbol{c}}\,d\boldsymbol{e}', \tag{41}$$

$$\psi^{\eta} = \frac{m}{k_{\rm B}\overline{T}}\big((\boldsymbol{c}-\boldsymbol{v})\otimes(\boldsymbol{c}-\boldsymbol{v}) - \tfrac{1}{3}(\boldsymbol{c}-\boldsymbol{v})\cdot(\boldsymbol{c}-\boldsymbol{v})\boldsymbol{I}\big), \tag{76}$$

$$\psi^{\lambda^{\rm tr+rap}} = \big(\tfrac{5}{2}k_{\rm B}\overline{T} - \tfrac{1}{2}m(\boldsymbol{c}-\boldsymbol{v})\cdot(\boldsymbol{c}-\boldsymbol{v}) + \overline{E}^{\rm rap} - E_{\rm I}^{\rm rap}\big)(\boldsymbol{c}-\boldsymbol{v}), \tag{77}$$

$$\widetilde{\mathcal{J}}^{\rm sl,(0)} = -\frac{1}{2n^2[\![(\Delta E^{\rm sl})^2\zeta^{\rm sl}]\!]}\sum_{\rm J,I',J'}\int f^{(0)}\widetilde{f}^{(0)}(\Delta E^{\rm sl})\zeta^{\rm sl} g\sigma^{\rm IJI'J'}\,d\widetilde{\boldsymbol{c}}\,d\boldsymbol{e}', \tag{81}$$

Equation (104), (106), (107), (108), (110), (111), and (117) should be

$$\widetilde{p}^{\rm rel} = -\frac{(k_{\rm B}\overline{T})^3c^{\rm rap}}{p(c^{\rm tr}+c^{\rm rap})^2}\,\frac{c^{\rm rap}[\![(\Delta E^{\rm sl})^2\zeta^{\rm sl}]\!] + (c^{\rm tr}+c^{\rm rap})[\![(\Delta E^{\rm rap})(\Delta E^{\rm sl})\zeta^{\rm sl}]\!]}{2[\![(\Delta E^{\rm rap})^2]\!][\![(\Delta E^{\rm sl})^2\zeta^{\rm sl}]\!]}. \tag{104}$$

$$\widehat{p}^{\rm rel} = \frac{(k_{\rm B}\overline{T})^3c^{\rm sl}c^{\rm rap}}{(c^{\rm tr}+c^{\rm rap})^2c_{\rm vl}}\,\frac{c^{\rm rap}[\![(\Delta E^{\rm sl})^2\zeta^{\rm sl}]\!] + (c^{\rm tr}+c^{\rm rap})[\![(\Delta E^{\rm rap})(\Delta E^{\rm sl})\zeta^{\rm sl}]\!]}{2[\![(\Delta E^{\rm rap})^2]\!][\![(\Delta E^{\rm sl})^2\zeta^{\rm sl}]\!]}, \tag{106}$$

$$\langle\!\langle f^{(0)}\phi^{0010}, \mathcal{W}^{\rm sl}\rangle\!\rangle = -\frac{2n^2}{k_{\rm B}\overline{T}}\Big([\![(\Delta E^{\rm sl})(\Delta E^{\rm sl}+\Delta E^{\rm rap})]\!] - 2[\![(\Delta E^{\rm sl})^2\phi^{0010}\zeta^{\rm sl}]\!]\frac{\overline{T}-T^{\rm sl}}{T^{\rm sl}}\Big), \tag{107}$$

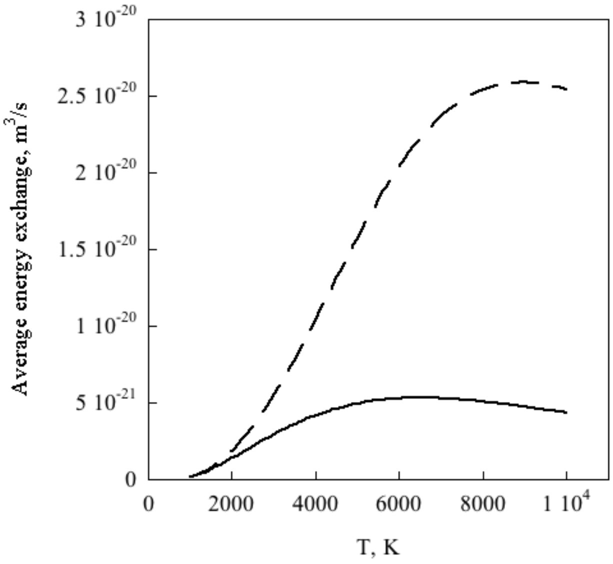

Figure 9: Average rotational energy exchange as a function of temperature. Solid line: $\llbracket(\frac{\Delta E^{\mathrm{r}}}{k_{\mathrm{B}}T})^2\rrbracket^{\mathrm{r}}$; dashed line: $\llbracket(\frac{\Delta E^{\mathrm{r}}}{k_{\mathrm{B}}T})^2\rrbracket^{\mathrm{r}\prime}$.

$$\langle\!\langle f^{(0)}\phi^{0001\mathrm{rap}}, \mathcal{W}^{\mathrm{sl}}\rangle\!\rangle = \frac{2n^2}{k_{\mathrm{B}}\overline{T}}\Big(\llbracket(\Delta E^{\mathrm{sl}})(\Delta E^{\mathrm{rap}})\rrbracket + 2\llbracket(\Delta E^{\mathrm{sl}})^2\phi^{0001\mathrm{rap}}\zeta^{\mathrm{sl}}\rrbracket\frac{\overline{T}-T^{\mathrm{sl}}}{T^{\mathrm{sl}}}\Big). \tag{108}$$

$$\langle\!\langle f^{(0)}\phi^{0010}, \mathcal{W}^{\mathrm{sl}}\rangle\!\rangle \approx -\frac{2n^2}{k_{\mathrm{B}}\overline{T}}\llbracket(\Delta E^{\mathrm{sl}})(\Delta E^{\mathrm{sl}}+\Delta E^{\mathrm{rap}})\zeta^{\mathrm{sl}}\rrbracket, \tag{110}$$

$$\langle\!\langle f^{(0)}\phi^{0001\mathrm{rap}}, \mathcal{W}^{\mathrm{sl}}\rangle\!\rangle \approx \frac{2n^2}{k_{\mathrm{B}}\overline{T}}\llbracket(\Delta E^{\mathrm{sl}})(\Delta E^{\mathrm{rap}})\zeta^{\mathrm{sl}}\rrbracket. \tag{111}$$

$$\phi^{\omega} = \frac{1}{p^2}\frac{1}{c^{\mathrm{tr}}+c^{\mathrm{rap}}}\frac{(k_{\mathrm{B}}\overline{T})^3}{2\llbracket(\Delta E^{\mathrm{rap}})^2\rrbracket}\Big(\frac{\llbracket(\Delta E^{\mathrm{sl}})(\Delta E^{\mathrm{rap}})\zeta^{\mathrm{sl}}\rrbracket}{\llbracket(\Delta E^{\mathrm{sl}})^2\zeta^{\mathrm{sl}}\rrbracket} + \frac{c^{\mathrm{rap}}}{c^{\mathrm{tr}}+c^{\mathrm{rap}}}\Big)(c^{\mathrm{rap}}\,\phi^{0010} - c^{\mathrm{tr}}\,\phi^{0001\mathrm{rap}}). \tag{117}$$

Finally, the second line of Equation (121) should be

$$-\frac{c^{\mathrm{sl}}}{c_{\mathrm{vl}}}\Big(\frac{c^{\mathrm{rap}}}{c^{\mathrm{tr}}+c^{\mathrm{rap}}}\Big)^2\frac{(k_{\mathrm{B}}\overline{T})^3}{2\llbracket(\Delta E^{\mathrm{rap}})^2\rrbracket} - \frac{c^{\mathrm{rap}}c^{\mathrm{sl}}}{(c^{\mathrm{tr}}+c^{\mathrm{rap}})c_{\mathrm{vl}}}\frac{(k_{\mathrm{B}}\overline{T})^3\llbracket(\Delta E^{\mathrm{rap}})(\Delta E^{\mathrm{sl}})\zeta^{\mathrm{sl}}\rrbracket}{2\llbracket(\Delta E^{\mathrm{rap}})^2\rrbracket\llbracket(\Delta E^{\mathrm{sl}})^2\zeta^{\mathrm{sl}}\rrbracket}$$

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