Internal Energy Relaxation Processes and Bulk Viscosities in Fluids

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We revisit internal energy relaxation processes and related bulk viscosity coefficients in fluid models derived from the kinetic theory. We discuss the apparition of bulk viscosity coefficients in relaxation regimes and the links with equilibrium one-temperature bulk viscosity coefficients. Multiple temperature models of single species fluids are investigated as well as state-to-state models for mixtures of gases. Monte Carlo numerical simulations of internal energy relaxation processes in polyatomic gases are shown to fully agree with the theoretical results. The impact of bulk viscosity in fluid mechanics is also addressed as well as various mathematical aspects of internal energy relaxation and Chapman-Enskog asymptotic expansion for a two-temperature fluid model.

I. INTRODUCTION

The relaxation of internal energy is of fundamental importance in reentry problems and laboratory plasmas [1–12]. Internal energy exchanges notably lead to the apparition of bulk viscosity coefficients in fluid models in relaxation regimes [13–26]. Theoretical results and experimental measurements have further shown that bulk viscosity coefficients of polyatomic gases are of the order of shear viscosity coefficients [27–33]. These are strong motivations for investigating internal energy relaxation processes and related bulk viscosity coefficients in nonequilibrium models derived from the kinetic theory of gases.

A hierarchy of thermodynamic nonequilibrium fluid models may be derived from the kinetic theory of polyatomic gas mixtures. 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 [1–12]. When there are partial equilibria between some of these states, species internal energy temperatures may be defined and the complexity of the model is accordingly reduced [9]. The next reduction step consists in equating some of the species internal temperatures with the equilibrium one-temperature model ultimately obtained [9]. Each relaxation step towards a simpler and more equilibrated model then yields bulk viscosity contributions—provided the characteristic energy relaxation times are smaller than the flow times, the most complete bulk viscosity coefficient being that obtained for the equilibrium one-temperature fluid [23–26].

We first consider a simplified kinetic model where elastic and resonant collisions are fast but collisions exchanging translational and internal energy are slow [23, 24]. In such a framework, the translational and internal temperatures are macroscopic quantities associated with collisional invariants of the fast collision operator. In a relaxation regime, when the characteristic time of internal energy relaxation is smaller than the flow characteristic time, the difference between the translational temperature $T^{\rm tr}$ and the equilibrium temperature T becomes proportional to the divergence of the velocity field $\boldsymbol{v}$. This leads to the apparition of a bulk viscosity coefficient κ such that $nk_{\rm B}(T^{\rm tr}-T)=-\kappa\boldsymbol{\nabla}\cdot\boldsymbol{v}$ where n is the number density and $k_{\rm B}$ the Boltzmann constant.

We then investigate a more complex situation with two internal energy modes, one with a slow exchange rate and the other one with a fast exchange rate [23, 24]. The translational-rapid mode temperature and the slow mode temperature are then collisional invariants of the fast collision operator. For such a model, there is a bulk viscosity due to the fast internal energy mode as in classical one-temperature models but part of the thermodynamic equilibrium bulk viscosity is still hidden in the slow internal mode. A detailed analysis yields that, in a relaxation regime, there are five contributions to the effective bulk viscosity, namely the fast internal mode bulk viscosity, the slow internal mode bulk viscosity, the reduced relaxation pressure and two perturbed relaxation source terms. In the thermodynamic equilibrium limit, the sum of these five contributions coincide with the one-temperature two-mode bulk viscosity. The physical interpretation of the origin of the bulk viscosity coefficient is found to be similar to that of the simplified two-temperature model [23, 24]. This analysis may also be generalized to the situation of gas mixtures as well as to the case of nonindependent energy modes [25].

We next consider the general situation of state-to-state mixture models where each quantum state of each species is independent [26]. Relaxation equations in symmetric form are derived for the quantum state population Gibbs functions and the translational temperature. Approximate solutions of the population relaxation equations compatible with the asymptotic equilibrium limit are then obtained. At zeroth order, using a relaxation approximation, the differences between the pseudo species chemical potentials and their equilibrium value are proportional to the divergence of the velocity field. The 'internal energy' bulk viscosity $\kappa_{[01]}$ is then recovered with the relation $nk_{\rm B}(T^{\rm tr}-T)=-\kappa_{[01]}\boldsymbol{\nabla}\cdot\boldsymbol{v}$.

At first order, the relaxation approximation yields a bulk viscosity that converges at thermodynamic equilibrium towards the traditional bulk viscosity.

Monte Carlo simulations of spontaneous fluctuations near thermodynamic equilibrium are then performed in order to investigate a polyatomic model gas [34–36]. The density fluctuation power spectrum of the model gas is evaluated by using Boltzmann equation as well as linearized fluid equations [23, 37–40]. The simplified one temperature model, including the bulk viscosity term, then well agrees with Boltzmann equation when the internal energy relaxation time is smaller than the flow time [23–25]. When the relaxation time is larger than the flow characteristic time, however, only the two temperature model is in agreement with Boltzmann equation.

A state-to-state model for mixtures of Helium and Hydrogen is next investigated numerically. The required collision integrals are evaluated from a complete set of state-to-state cross sections for the $\mathrm{He}+\mathrm{H}_2(v,j)$ collisional system. The latter have been obtained using an implementation of the quasiclassical method [41–45] with the accurate Muchnik-Russek potential energy surface [46–54]. The values of the bulk viscosity for the model gas, obtained from the fluctuation-dissipation theory [55–64], are then in full agreement with the theory [26].

We further address the impact of bulk viscosity in fluid mechanics that has scarcely been discussed in the literature [65–72]. The success of the erroneous Stokes approximation is mostly due to the gradient structure of the bulk viscosity term [69]. We also discuss the mathematical structure of relaxation systems of partial differential equations their and symmetrization [73–92]. We also address various mathematical aspects associated with the Chapman-Enskog method for partial-differential equations that are applied to the simplified two-temperature model and that are found to agree with the formal expansions [77, 89–92].

The simplified two-temperature model is considered in Section II, the two-temperature two-mode nonequilibrium model in Section III, and the state-to-state model in Section IV. The Monte Carlo simulations of single gases are presented in Section V and that of state-to-state mixture models in Section VI. The impact in fluid mechanics and the mathematical aspects are finally addressed in Section VII.

II. A SIMPLIFIED TWO TEMPERATURE MODEL

II.A. Kinetic framework

We consider a single polyatomic gas with the Boltzmann equation written in the form

$$\partial_t f + \boldsymbol{c}\cdot\boldsymbol{\nabla} f = \frac{1}{\epsilon}\mathcal{J}^{\mathrm{rap}} + \mathcal{J}^{\mathrm{sl}}, \tag{II.1}$$

where ∂_t denotes the time derivative operator, $\boldsymbol{c}$ the particle velocity, $\boldsymbol{\nabla}$ the space derivative operator, $f(t,\boldsymbol{x},\boldsymbol{c},\mathrm{I})$ the distribution function, $\boldsymbol{x}$ the spatial coordinate, I the index of the quantum energy state, $\mathcal{J}^{\mathrm{rap}}$ the rapid collision operator, $\mathcal{J}^{\mathrm{sl}}$ the slow collision operator, and ϵ the formal parameter associated with the Chapman-Enskog procedure. The complete collision operator $\mathcal{J}=\mathcal{J}^{\mathrm{rap}}+\mathcal{J}^{\mathrm{sl}}$ is in the form

$$\mathcal{J}(f)=\sum_{\mathrm{J},\mathrm{I}',\mathrm{J}'}\int\Big(f(\boldsymbol{c}',\mathrm{I}')f(\widetilde{\boldsymbol{c}}',\mathrm{J}')\frac{a_{\mathrm{I}}a_{\mathrm{J}}}{a_{\mathrm{I}'}a_{\mathrm{J}'}}-f(\boldsymbol{c},\mathrm{I})f(\widetilde{\boldsymbol{c}},\mathrm{J})\Big)g\sigma^{\mathrm{IJI'J'}}\mathrm{d}\widetilde{\boldsymbol{c}}\,\mathrm{d}\boldsymbol{e}', \tag{II.2}$$

where in a direct collision I and J denote the indices of the quantum energy states before collision, I′ and J′ the corresponding numbers after collision, $\widetilde{\boldsymbol{c}}$ the velocity of the colliding partner, $\boldsymbol{c}'$ and $\widetilde{\boldsymbol{c}}'$ the velocities after collision, a_{I} the degeneracy of the Ith quantum energy state, g the absolute value of the relative velocity $\boldsymbol{c}-\widetilde{\boldsymbol{c}}$, $\boldsymbol{e}'$ the unit vector in the direction of the relative velocity $\boldsymbol{c}'-\widetilde{\boldsymbol{c}}'$, and $\sigma^{\mathrm{IJI'J'}}$ the collision cross sections [15, 19]. The dependence of f on $(t,\boldsymbol{x})$ has been left implicit in (II.2) and the cross sections $g\sigma^{\mathrm{IJI'J'}}$ satisfy the reciprocity relations $a_{\mathrm{I}}a_{\mathrm{J}}g\sigma^{\mathrm{IJI'J'}}\mathrm{d}\boldsymbol{c}\,\mathrm{d}\widetilde{\boldsymbol{c}}\,\mathrm{d}\boldsymbol{e}'=a_{\mathrm{I}'}a_{\mathrm{J}'}g'\sigma^{\mathrm{I'J'IJ}}\mathrm{d}\boldsymbol{c}'\mathrm{d}\widetilde{\boldsymbol{c}}'\mathrm{d}\boldsymbol{e}$.

Denoting by E_{I} the internal energy of the particle in the Ith state, the rapid collisions are either elastic without change of internal energy or resonant with $\Delta E=E_{\mathrm{I}'}+E_{\mathrm{J}'}-E_{\mathrm{I}}-E_{\mathrm{J}}=0$, $E_{\mathrm{I}'}\neq E_{\mathrm{I}}$ and $E_{\mathrm{J}'}\neq E_{\mathrm{J}}$, whereas the slow collisions are such that $\Delta E=E_{\mathrm{I}'}+E_{\mathrm{J}'}-E_{\mathrm{I}}-E_{\mathrm{J}}\neq 0$. Denoting by $\mathcal{J}^{\mathrm{tr-tr}}$ the operator associated with elastic collision, $\mathcal{J}^{\mathrm{int-int}}$ the operator associated with resonant collisions, and $\mathcal{J}^{\mathrm{tr-int}}$ the operator associated with collisions such that $\Delta E\neq 0$, the fast and slow collision operators are then

$$\mathcal{J}^{\mathrm{rap}}=\mathcal{J}^{\mathrm{tr-tr}}+\mathcal{J}^{\mathrm{int-int}},\qquad \mathcal{J}^{\mathrm{sl}}=\mathcal{J}^{\mathrm{tr-int}}. \tag{II.3}$$

The collisional invariants of the fast collision operator $\mathcal{J}^{\rm rap}$ are associated with particle number $\psi^1=1$, momentum $\psi^{1+\nu}=mc_\nu$, $\nu\in\{1,2,3\}$ with $\boldsymbol{c}=(c_1,c_2,c_3)^t$, kinetic energy $\psi^5=\psi^{\rm tr}=\frac{1}{2}m|\boldsymbol{c}-\boldsymbol{v}|^2$ and internal energy $\psi^6=\psi^{\rm int}=E_{\rm I}$ where m denotes the particle mass and $\boldsymbol{v}$ the fluid velocity.

The Enskog expansion is in the form $f=f^{(0)}\big(1+\epsilon\phi+\mathcal{O}(\epsilon^2)\big)$ and the Maxwellian distribution $f^{(0)}$ reads

$$f^{(0)}=\Big(\frac{m}{2\pi k_{\rm B}T^{\rm tr}}\Big)^{\frac{3}{2}}\frac{na_{\rm I}}{Z^{\rm int}}\exp\Big(-\frac{m|\boldsymbol{c}-\boldsymbol{v}|^2}{2k_{\rm B}T^{\rm tr}}-\frac{E_{\rm I}}{k_{\rm B}T^{\rm int}}\Big),\tag{II.4}$$

where n denotes the number density, $k_{\rm B}$ the Boltzmann constant, $T^{\rm tr}$ the translational temperature, $T^{\rm int}$ the internal temperature, and $Z^{\rm int}=\sum_{\rm I}a_{\rm I}\exp\big(-E_{\rm I}/k_{\rm B}T^{\rm int}\big)$ the partition function. There are two different temperatures $T^{\rm tr}$ and $T^{\rm int}$ in $f^{(0)}$ since there are two different energy collisional invariants $\psi^{\rm tr}$ and $\psi^{\rm int}$. The scalar product $\langle\!\langle\xi,\zeta\rangle\!\rangle$ between two tensorial quantities $\xi(t,\boldsymbol{x},\boldsymbol{c},{\rm I})$ and $\zeta(t,\boldsymbol{x},\boldsymbol{c},{\rm I})$ is naturally defined by

$$\langle\!\langle\xi,\zeta\rangle\!\rangle=\sum_{\rm I}\int\xi\cdot\zeta\,{\rm d}\boldsymbol{c}.$$

where $\xi\cdot\zeta$ is the contracted product.

The equations for conservation of mass, momentum and internal energies are then obtained by taking the scalar product of the Boltzmann equation (II.1) with the collisional invariants of the fast collision operator. The corresponding fluid variables are the particle number density $n=\langle\!\langle\psi^1,f\rangle\!\rangle=\langle\!\langle\psi^1,f^{(0)}\rangle\!\rangle$ or equivalently the mass density $\rho=mn$, the mass averaged velocity $\boldsymbol{v}$ with $\rho\boldsymbol{v}=\langle\!\langle m\boldsymbol{c},f\rangle\!\rangle=\langle\!\langle m\boldsymbol{c},f^{(0)}\rangle\!\rangle$, the internal energy per unit volume of translational origin $\mathcal{E}^{\rm tr}=\langle\!\langle f,\psi^{\rm tr}\rangle\!\rangle=\langle\!\langle f^{(0)},\psi^{\rm tr}\rangle\!\rangle$, and the internal energy per unit volume of internal origin $\mathcal{E}^{\rm int}=\langle\!\langle f,\psi^{\rm int}\rangle\!\rangle=\langle\!\langle f^{(0)},\psi^{\rm int}\rangle\!\rangle$, or equivalently the translation and internal temperatures $T^{\rm tr}$ and $T^{\rm int}$ defined by $\mathcal{E}^{\rm tr}(T^{\rm tr},n)=\langle\!\langle f,\psi^{\rm tr}\rangle\!\rangle$ and $\mathcal{E}^{\rm int}(T^{\rm int},n)=\langle\!\langle f,\psi^{\rm int}\rangle\!\rangle$. The pressure p and the internal energies $\mathcal{E}^{\rm tr}$ and $\mathcal{E}^{\rm int}$ are found in the form

$$p=nk_{\rm B}T^{\rm tr},\qquad\mathcal{E}^{\rm tr}=n\tfrac{3}{2}k_{\rm B}T^{\rm tr},\qquad\mathcal{E}^{\rm int}=n\overline{E},\tag{II.5}$$

where $\overline{E}=\sum_{\rm I}\frac{a_{\rm I}E_{\rm I}}{Z^{\rm int}}\exp\big(-E_{\rm I}/k_{\rm B}T^{\rm int}\big)$ is the average internal energy per particle. The corresponding translational and internal entropies and Gibbs functions are presented in [23, 24]. Following the Chapman-Enskog procedure, the equations for conservation of mass, momentum, and internal energies are obtained in the form [9]

$$\partial_t\rho+\boldsymbol{\nabla}\cdot(\rho\boldsymbol{v})=0,\tag{II.6}$$

$$\partial_t(\rho\boldsymbol{v})+\boldsymbol{\nabla}\cdot(\rho\boldsymbol{v}\otimes\boldsymbol{v}+p\boldsymbol{I})+\boldsymbol{\nabla}\cdot\boldsymbol{\Pi}=0,\tag{II.7}$$

$$\partial_t\mathcal{E}^{\rm tr}+\boldsymbol{\nabla}\cdot(\boldsymbol{v}\mathcal{E}^{\rm tr})+\boldsymbol{\nabla}\cdot\boldsymbol{Q}^{\rm tr}=-p\boldsymbol{\nabla}\cdot\boldsymbol{v}-\boldsymbol{\Pi}\!:\!\boldsymbol{\nabla}\boldsymbol{v}-\omega_1^{\rm int},\tag{II.8}$$

$$\partial_t\mathcal{E}^{\rm int}+\boldsymbol{\nabla}\cdot(\boldsymbol{v}\mathcal{E}^{\rm int})+\boldsymbol{\nabla}\cdot\boldsymbol{Q}^{\rm int}=\omega_1^{\rm int},\tag{II.9}$$

where $\otimes$ denotes the tensor vector product, $\boldsymbol{I}$ the unit tensor, $\boldsymbol{\Pi}$ the viscous tensor, $\boldsymbol{Q}^{\rm tr}$ the translational energy heat flux, $\boldsymbol{Q}^{\rm int}$ the internal energy heat flux and $\omega_1^{\rm int}$ the first order energy exchange term. The transport fluxes are given by

$$\boldsymbol{\Pi}=-\eta\big(\boldsymbol{\nabla}\boldsymbol{v}+(\boldsymbol{\nabla}\boldsymbol{v})^t-\tfrac{2}{3}(\boldsymbol{\nabla}\cdot\boldsymbol{v})\boldsymbol{I}\big),\tag{II.10}$$

$$\boldsymbol{Q}^{\rm tr}=-\lambda^{\rm tr,tr}\boldsymbol{\nabla}T^{\rm tr}-\lambda^{\rm tr,int}\boldsymbol{\nabla}T^{\rm int},\tag{II.11}$$

$$\boldsymbol{Q}^{\rm int}=-\lambda^{\rm int,tr}\boldsymbol{\nabla}T^{\rm tr}-\lambda^{\rm int,int}\boldsymbol{\nabla}T^{\rm int},\tag{II.12}$$

where η denotes the shear viscosity, and $\lambda^{\rm tr,tr}$, $\lambda^{\rm tr,int}$, $\lambda^{\rm int,tr}$, and $\lambda^{\rm int,int}$ the thermal conductivities. The full source term $\omega^{\rm int}=\langle\!\langle\psi^{\rm int},\mathcal{J}^{\rm sl}\rangle\!\rangle=\langle\!\langle\psi^{\rm int},\mathcal{J}\rangle\!\rangle$ may be expanded as $\omega^{\rm int}=\omega_0^{\rm int}+\epsilon\delta\omega_1^{\rm int}+\mathcal{O}(\epsilon^2)$ where $\omega_0^{\rm int}$ is evaluated from the Maxwellian distribution $f^{(0)}$ and $\delta\omega_1^{\rm int}$ is the correction associated with the Navier-Stokes perturbation ϕ, so that the first order source term $\omega_1^{\rm int}$ is given by

$$\omega_1^{\rm int}=\omega_0^{\rm int}+\epsilon\delta\omega_1^{\rm int}.\tag{II.13}$$

Finally, the pressure tensor $\boldsymbol{\mathcal{P}}=p\boldsymbol{I}+\boldsymbol{\Pi}$ is given by

$$\boldsymbol{\mathcal{P}}=nk_{\rm B}T^{\rm tr}\boldsymbol{I}-\eta\big(\boldsymbol{\nabla}\boldsymbol{v}+(\boldsymbol{\nabla}\boldsymbol{v})^t-\tfrac{2}{3}(\boldsymbol{\nabla}\cdot\boldsymbol{v})\boldsymbol{I}\big),\tag{II.14}$$

and *does not involve a bulk viscosity term unlike one-temperature polyatomic gas models* [13–22].

II.B. Relaxation and bulk viscosity

From the energy equations (II.8) and (II.9) it is obtained at zeroth order that

$$\partial_t T^{\rm tr} + \boldsymbol{v}\cdot\boldsymbol{\nabla} T^{\rm tr} = -\frac{p\boldsymbol{\nabla}\cdot\boldsymbol{v}}{nc^{\rm tr}} - \frac{\omega_0^{\rm int}}{nc^{\rm tr}}, \qquad \partial_t T^{\rm int} + \boldsymbol{v}\cdot\boldsymbol{\nabla} T^{\rm int} = \frac{\omega_0^{\rm int}}{nc^{\rm int}}, \tag{II.15}$$

where the heat capacities are given by

$$c^{\rm tr} = \tfrac{3}{2}k_{\rm B}, \qquad c^{\rm int} = \sum_{\rm I} \frac{k_{\rm B}a_{\rm I}}{Z^{\rm int}}\Big(\frac{E_{\rm I}-\overline{E}}{k_{\rm B}T^{\rm int}}\Big)^2 \exp\Big(-\frac{E_{\rm I}}{k_{\rm B}T^{\rm int}}\Big), \qquad c^{\rm vl} = c^{\rm tr} + c^{\rm int}.$$

The zeroth order source term $\omega_0^{\rm int}$ is in the form $\omega_0^{\rm int} = -2n^2\big[\!\big[(\Delta E)\big(\exp\big(\frac{\Delta E}{k_{\rm B}T^{\rm tr}} - \frac{\Delta E}{k_{\rm B}T^{\rm int}}\big)-1\big)\big]\!\big]$ where $[\![\ ]\!]$ is the averaging operator $[\![\alpha]\!] = \frac{1}{8n^2}\sum_{{\rm I},{\rm J},{\rm I}',{\rm J}'}\int \alpha_{{\rm I}{\rm J}{\rm I}'{\rm J}'} f^{(0)}\widetilde{f}^{(0)} g\sigma^{{\rm I}{\rm J}{\rm I}'{\rm J}'}\,{\rm d}\boldsymbol{c}\,{\rm d}\widetilde{\boldsymbol{c}}\,{\rm d}\boldsymbol{e}'$. Defining the nonequilibrium correction factor by $\zeta = \int_0^1 \exp\big((\frac{\Delta E}{k_{\rm B}T^{\rm tr}} - \frac{\Delta E}{k_{\rm B}T^{\rm int}})s\big)\,ds$ and the relaxation time by $\tau^{\rm int} = c^{\rm int}k_{\rm B}T^{\rm tr}T^{\rm int}/2n[\![(\Delta E)^2\zeta]\!]$, the source term $\omega_0^{\rm int}$ may be rewritten in the relaxation form

$$\omega_0^{\rm int} = \frac{nc^{\rm int}}{\tau^{\rm int}}(T^{\rm tr} - T^{\rm int}). \tag{II.16}$$

Subtracting the $T^{\rm int}$ equation from that for $T^{\rm tr}$ and using (II.16), the resulting equation for $T^{\rm tr} - T^{\rm int}$ reads

$$\partial_t(T^{\rm tr} - T^{\rm int}) + \boldsymbol{v}\cdot\boldsymbol{\nabla}(T^{\rm tr} - T^{\rm int}) = -\frac{p\boldsymbol{\nabla}\cdot\boldsymbol{v}}{nc^{\rm tr}} - \frac{c^{\rm vl}}{c^{\rm tr}}\frac{T^{\rm tr} - T^{\rm int}}{\tau^{\rm int}}. \tag{II.17}$$

This is a typical relaxation equation and when $\tau^{\rm int}$ is smaller that the flow characteristic time we obtain, after some initial layer, the relaxation relation $T^{\rm tr} - T^{\rm int} = -\tau^{\rm int}p\boldsymbol{\nabla}\cdot\boldsymbol{v}/nc^{\rm vl}$. The equilibrium temperature is naturally defined as the unique scalar T such that

$$\mathcal{E}^{\rm tr}(T) + \mathcal{E}^{\rm int}(T) = \mathcal{E}^{\rm tr}(T^{\rm tr}) + \mathcal{E}^{\rm int}(T^{\rm int}), \tag{II.18}$$

and only this temperature T is available for the limiting one-temperature fluid model. Using $\mathcal{E}^{\rm int}(T) - \mathcal{E}^{\rm int}(T^{\rm int}) = \int_{T^{\rm int}}^{T} c^{\rm int}(T')\,{\rm d}T' = \widetilde{c}^{\rm int}(T - T^{\rm int})$ where $\widetilde{c}^{\rm int} = \int_0^1 c^{\rm int}\big(T^{\rm int} + s(T - T^{\rm int})\big)\,{\rm d}s$ we have $c^{\rm tr}(T^{\rm tr} - T) = \widetilde{c}^{\rm int}(T - T^{\rm int})$. We also define the bulk viscosity by $\kappa = pk_{\rm B}\widetilde{c}^{\rm int}\tau^{\rm int}/c^{\rm vl}\widetilde{c}^{\rm vl}$ where $\widetilde{c}^{\rm vl} = c^{\rm tr} + \widetilde{c}^{\rm int}$ so that

$$\kappa = \frac{c^{\rm int}\widetilde{c}^{\rm int}}{c^{\rm vl}\,\widetilde{c}^{\rm vl}}\frac{k_{\rm B}^3(T^{\rm tr})^2T^{\rm int}}{2[\![(\Delta E)^2\zeta]\!]}, \tag{II.19}$$

and the equilibrium limit of this coefficient is $\big(\frac{c^{\rm int}}{c^{\rm vl}}\big)^2(k_{\rm B}T)^3/2[\![(\Delta E)^2]\!]$ that coincides with the bulk viscosity coefficient obtained independently from the Chapman-Enskog method for the equilibrium fluid [32, 33]. Combining the relaxation relation with $c^{\rm tr}(T^{\rm tr} - T) = \widetilde{c}^{\rm int}(T - T^{\rm int})$ and the definition of κ we obtain the fundamental relation

$$nk_{\rm B}(T^{\rm tr} - T) = -\kappa\boldsymbol{\nabla}\cdot\boldsymbol{v}. \tag{II.20}$$

We next note that the pressure tensor $\boldsymbol{\mathcal{P}}$ is in the form

$$\boldsymbol{\mathcal{P}} = nk_{\rm B}T\boldsymbol{I} - \kappa\boldsymbol{\nabla}\cdot\boldsymbol{v}\boldsymbol{I} - \eta\big(\boldsymbol{\nabla}\boldsymbol{v} + (\boldsymbol{\nabla}\boldsymbol{v})^t - \tfrac{2}{3}(\boldsymbol{\nabla}\cdot\boldsymbol{v})\boldsymbol{I}\big), \tag{II.21}$$

and *we have recovered the bulk viscosity coefficient of the one-temperature equilibrium limit fluid that only involves T*. Many authors have discussed the *near thermodynamic equilibrium* situation, where the internal temperature $T^{\rm int}$ and the translational temperature $T^{\rm tr}$ are close, notably Kohler [13], Hirschfelder Curtiss and Bird [14], Waldmann [15], Chapman and Cowling [16], Ferziger and Kapper [17], McCourt et al. [18], de Groot and Mazur [21], Keizer [22], Zhdanov [8], Nagnibeda and Kustova [9], and Brun [10].

It is also possible to establish that first order corrections to the bulk viscosity coefficient are negligible for such a simplified two temperature model. Discarding Burnett type terms, the corrections indeed involve the perturbed source term $\delta\omega_1^{\rm int}$ that is in the form $\delta\omega_1^{\rm int} = \langle\!\langle f^{(0)}\phi, \mathcal{W}^{\rm int}\rangle\!\rangle = \langle\!\langle f^{(0)}\phi^\omega, \mathcal{W}^{\rm int}\rangle\!\rangle\omega_0^{\rm int}$ where ϕ^ω is the scalar perturbed distribution function arising from the expansion [23]

$$\phi = -\phi^\eta\colon\boldsymbol{\nabla}\boldsymbol{v} - \boldsymbol{\phi}^{\lambda^{\rm tr}}\cdot\boldsymbol{\nabla}\Big(\frac{1}{k_{\rm B}T^{\rm tr}}\Big) - \boldsymbol{\phi}^{\lambda^{\rm int}}\cdot\boldsymbol{\nabla}\Big(\frac{1}{k_{\rm B}T^{\rm int}}\Big) + \phi^\omega\omega_0^{\rm int},$$

with ϕ^η denoting a symmetric traceless tensor, and $\phi^{\lambda^{\rm tr}}$ and $\phi^{\lambda^{\rm int}}$ are vectors [9, 23]. However, the standard scalar basis functions $\phi^{0010} = \frac{3}{2} - \frac{1}{2}\frac{m}{k_{\rm B}T}|\boldsymbol{c}-\boldsymbol{v}|^2$ and $\phi^{0001} = (\overline{E} - E_{\rm I})/k_{\rm B}T^{\rm int}$ used for scalar linearized kinetic equations are both collisional invariants of the rapid collision operator and are therefore in the nullspace of the linearized fast collision operator $\mathcal{I}^{\rm rap}$. Therefore the perturbed term $\phi^\omega \simeq 0$ vanishes in a first approximation, we have $\omega_1^{\rm int} \simeq \omega_0^{\rm int}$, and there are no first order corrections to the bulk viscosity coefficient [23].

III. A TWO-MODE TWO-TEMPERATURE MODEL

III.A. Kinetic framework

We consider the more complex situation of a single polyatomic gas with two independent internal energy modes having different exchange rates. A first mode is assumed to have a rapid exchange rate with the translational degrees of freedom whereas the other one is assumed to have a slow exchange rate. The internal energy in the Ith quantum state is accordingly split as

$$E_{\rm I} = E^{\rm rap}_{\rm I^{rap}} + E^{\rm sl}_{\rm I^{sl}}, \tag{III.1}$$

where I denotes the composed index $\mathrm{I} = (\mathrm{I}^{\rm rap}, \mathrm{I}^{\rm sl})$, $\mathrm{I}^{\rm rap}$ the index of the quantum energy state of the rapid mode, $\mathrm{I}^{\rm sl}$ the index of the quantum energy state of the slow mode, $E^{\rm rap}_{\rm I^{rap}}$ the rapid mode internal energy, and $E^{\rm sl}_{\rm I^{sl}}$ the slow mode internal energy. We also denote for short $E^{\rm rap}_{\rm I}$ for $E^{\rm rap}_{\rm I^{rap}}$ and $E^{\rm sl}_{\rm I}$ for $E^{\rm sl}_{\rm I^{sl}}$ so that $E_{\rm I} = E^{\rm rap}_{\rm I} + E^{\rm sl}_{\rm I}$. We also denote by $a_{\rm I}$ the degeneracy of the Ith state that may be decomposed as $a_{\rm I} = a^{\rm rap}_{\rm I^{rap}} a^{\rm sl}_{\rm I^{sl}}$ where $a^{\rm rap}_{\rm I^{rap}}$ and $a^{\rm sl}_{\rm I^{sl}}$ are the degeneracies of the fast and slow modes. We assume that the rapid collisions are all the collisions such that $\Delta E^{\rm sl} = E^{\rm sl}_{\rm I'} + E^{\rm sl}_{\rm J'} - E^{\rm sl}_{\rm I} - E^{\rm sl}_{\rm J} = 0$, either only involving the translational and rapid mode energy or resonant with respect to the slow internal mode. Denoting by $\mathcal{J}^{({\rm tr+rap})-({\rm tr+rap})}$ the collision operator involving solely the translational and fast internal degrees of freedom, $\mathcal{J}^{\rm sl-sl}$ the operator for resonant collision with respect to $E^{\rm sl}$, and $\mathcal{J}^{({\rm tr+rap})-{\rm sl}}$ the operator for collisions such that $\Delta E^{\rm sl} \neq 0$, the Boltzmann equation governing the distribution $f(t, \boldsymbol{x}, {\rm I})$ is in the form (II.1) with the fast and slow collision operators given by

$$\mathcal{J}^{\rm rap} = \mathcal{J}^{({\rm tr+rap})-({\rm tr+rap})} + \mathcal{J}^{\rm sl-sl} \qquad \mathcal{J}^{\rm sl} = \mathcal{J}^{({\rm tr+rap})-{\rm sl}}. \tag{III.2}$$

The collisional invariants of the fast collision operator are associated with particle number $\psi^1 = 1$, momentum $\psi^{1+\nu} = mc_\nu$, $\nu \in \{1,2,3\}$, translational and rapid mode energy $\psi^5 = \psi^{\rm tr} + \psi^{\rm rap}$ and slow mode energy $\psi^6 = \psi^{\rm sl}$, where $\psi^{\rm tr} = \frac{1}{2}m|\boldsymbol{c}-\boldsymbol{v}|^2$, $\psi^{\rm rap} = E^{\rm rap}_{\rm I}$, and $\psi^{\rm sl} = E^{\rm sl}_{\rm I}$.

The Enskog expansion is in the form $f = f^{(0)}\big(1 + \epsilon\phi + \mathcal{O}(\epsilon^2)\big)$ and the Maxwellian $f^{(0)}$ is found to be

$$f^{(0)} = \Big(\frac{m}{2\pi k_{\rm B}\overline{T}}\Big)^{\frac{3}{2}} \frac{n a_{\rm I}}{Z^{\rm int}} \exp\Big(-\frac{m|\boldsymbol{c}-\boldsymbol{v}|^2)}{2k_{\rm B}\overline{T}} - \frac{E^{\rm rap}_{\rm I}}{k_{\rm B}\overline{T}} - \frac{E^{\rm sl}_{\rm I}}{k_{\rm B}T^{\rm sl}}\Big), \tag{III.3}$$

where $\overline{T}$ is the partial equilibrium temperature between the translational and fast internal degrees of freedom, $T^{\rm sl}$ the temperature associated with the slow internal energy modes, and $Z^{\rm int} = \sum_{\rm I} a_{\rm I} \exp\big(-\frac{E^{\rm rap}_{\rm I}}{k_{\rm B}\overline{T}} - \frac{E^{\rm sl}_{\rm I}}{k_{\rm B}T^{\rm sl}}\big)$ the internal partition function. There are two different temperatures $\overline{T}$ and $T^{\rm sl}$ involved in $f^{(0)}$ since there are two different energy collisional invariants $\psi^{\rm tr} + \psi^{\rm rap}$ and $\psi^{\rm sl}$. The partition function may be decomposed as $Z^{\rm int} = Z^{\rm rap} Z^{\rm sl}$ where $Z^{\rm rap} = \sum_{\rm I^{rap}} a^{\rm rap}_{\rm I^{rap}} \exp\big(-E^{\rm rap}_{\rm I^{rap}}/k_{\rm B}\overline{T}\big)$ and $Z^{\rm sl} = \sum_{\rm I^{sl}} a^{\rm sl}_{\rm I^{sl}} \exp\big(-E^{\rm sl}_{\rm I^{sl}}/k_{\rm B}T^{\rm sl}\big)$ are the fast and slow mode partition functions.

The equations for conservation of mass, momentum and internal energies are obtained by taking scalar products of the Boltzmann equation with the collisional invariants of the fast collision operator. The extra fluid variables to consider, in addition to the particle number density n and the mass averaged velocity $\boldsymbol{v}$, are now the energies $\mathcal{E}^{\rm tr+rap} = \langle\!\langle f, \psi^{\rm tr} + \psi^{\rm rap}\rangle\!\rangle = \langle\!\langle f^{(0)}, \psi^{\rm tr} + \psi^{\rm rap}\rangle\!\rangle$ and $\mathcal{E}^{\rm sl} = \langle\!\langle f, \psi^{\rm sl}\rangle\!\rangle = \langle\!\langle f^{(0)}, \psi^{\rm sl}\rangle\!\rangle$ or equivalently the temperatures $\overline{T}$ and $T^{\rm sl}$ defined by $\mathcal{E}^{\rm tr+rap}(\overline{T}, n) = \langle\!\langle f, \psi^{\rm tr} + \psi^{\rm rap}\rangle\!\rangle$ and $\mathcal{E}^{\rm sl}(T^{\rm sl}, n) = \langle\!\langle f, \psi^{\rm sl}\rangle\!\rangle$. The pressure p and the internal energies $\mathcal{E}^{\rm tr+rap}$ and $\mathcal{E}^{\rm sl}$ are obtained in the form

$$p = nk_{\rm B}\overline{T}, \qquad \mathcal{E}^{\rm tr+rap} = n(\tfrac{3}{2}k_{\rm B}\overline{T} + \overline{E}^{\rm rap}), \qquad \mathcal{E}^{\rm sl} = n\overline{E}^{\rm sl}, \tag{III.4}$$

where $\overline{E}^{\rm rap} = \sum_{\rm I^{rap}} \frac{a^{\rm rap}_{\rm I^{rap}} E^{\rm rap}_{\rm I^{rap}}}{Z^{\rm rap}} \exp\big(-E^{\rm rap}_{\rm I^{rap}}/k_{\rm B}\overline{T}\big)$ and $\overline{E}^{\rm sl} = \sum_{\rm I^{sl}} \frac{a^{\rm sl}_{\rm I^{sl}} E^{\rm sl}_{\rm I^{sl}}}{Z^{\rm sl}} \exp\big(-E^{\rm sl}_{\rm I^{sl}}/k_{\rm B}T^{\rm sl}\big)$ are the average fast and slow mode internal energy per particle. The corresponding entropies and Gibbs functions are presented in [23, 24]. The

corresponding mass and momentum conservation equations are similar to (II.6) and (II.7) and are not repeated. On the other hand, the equations for conservation of internal energies are in the form

$$\partial_t \mathcal{E}^{\rm tr+rap} + \boldsymbol{\nabla}\cdot(\boldsymbol{v}\mathcal{E}^{\rm tr+rap}) + \boldsymbol{\nabla}\cdot\boldsymbol{Q}^{\rm tr+rap} = -p\boldsymbol{\nabla}\cdot\boldsymbol{v} - \boldsymbol{\Pi}\!:\!\boldsymbol{\nabla}\boldsymbol{v} - \omega_1^{\rm sl}, \tag{III.5}$$

$$\partial_t \mathcal{E}^{\rm sl} + \boldsymbol{\nabla}\cdot(\boldsymbol{v}\mathcal{E}^{\rm sl}) + \boldsymbol{\nabla}\cdot\boldsymbol{Q}^{\rm sl} = \omega_1^{\rm sl}, \tag{III.6}$$

where $\boldsymbol{Q}^{\rm tr+rap}$ denotes the translational and fast mode energy flux, $\boldsymbol{Q}^{\rm sl}$ the slow mode energy flux, and $\omega_1^{\rm sl}$ the first order energy exchange term. The transport fluxes are given by

$$\boldsymbol{\Pi} = p^{\rm rel}\boldsymbol{I} - \kappa^{\rm rap}\boldsymbol{\nabla}\cdot\boldsymbol{v}\boldsymbol{I} - \eta\big(\boldsymbol{\nabla}\boldsymbol{v} + (\boldsymbol{\nabla}\boldsymbol{v})^t - \tfrac{2}{3}(\boldsymbol{\nabla}\cdot\boldsymbol{v})\boldsymbol{I}\big), \tag{III.7}$$

$$\boldsymbol{Q}^{\rm tr+rap} = -\lambda^{\rm tr+rap,tr+rap}\boldsymbol{\nabla}\overline{T} - \lambda^{\rm tr+rap,sl}\boldsymbol{\nabla}T^{\rm sl}, \tag{III.8}$$

$$\boldsymbol{Q}^{\rm sl} = -\lambda^{\rm sl,tr+rap}\boldsymbol{\nabla}\overline{T} - \lambda^{\rm sl,sl}\boldsymbol{\nabla}T^{\rm sl}, \tag{III.9}$$

where $p^{\rm rel}$ denotes the relaxation pressure, $\kappa^{\rm rap}$ the fast internal energy mode bulk viscosity, η the shear viscosity, and $\lambda^{\rm tr+rap,tr+rap}$, $\lambda^{\rm tr+rap,sl}$, $\lambda^{\rm sl,tr+rap}$, and $\lambda^{\rm sl,sl}$ the thermal conductivities. The full source term $\omega^{\rm sl} = \langle\!\langle \psi^{\rm sl}, \mathcal{J}^{\rm sl}\rangle\!\rangle = \langle\!\langle \psi^{\rm sl}, \mathcal{J}\rangle\!\rangle$ may be expanded as $\omega^{\rm sl} = \omega_0^{\rm sl} + \epsilon\delta\omega_1^{\rm sl} + \mathcal{O}(\epsilon^2)$ where $\omega_0^{\rm sl}$ is evaluated from the Maxwellian distribution $f^{(0)}$ and $\delta\omega_1^{\rm sl}$ is the correction associated with the Navier-Stokes perturbation ϕ so that $\omega_1^{\rm sl}$ is given by

$$\omega_1^{\rm sl} = \omega_0^{\rm sl} + \epsilon\delta\omega_1^{\rm sl}. \tag{III.10}$$

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

$$\boldsymbol{\mathcal{P}} = nk_{\rm B}\overline{T}\boldsymbol{I} + p^{\rm rel}\boldsymbol{I} - \kappa^{\rm rap}\boldsymbol{\nabla}\cdot\boldsymbol{v}\,\boldsymbol{I} - \eta\big(\boldsymbol{\nabla}\boldsymbol{v} + (\boldsymbol{\nabla}\boldsymbol{v})^t - \tfrac{2}{3}(\boldsymbol{\nabla}\cdot\boldsymbol{v})\boldsymbol{I}\big), \tag{III.11}$$

with a pressure term $nk_{\rm B}\overline{T}\boldsymbol{I}$, a relaxation pressure term $p^{\rm rel}\boldsymbol{I}$, a bulk viscosity contribution solely associated with the fast internal modes $\kappa^{\rm rap}\boldsymbol{\nabla}\cdot\boldsymbol{v}\boldsymbol{I}$ and a shear viscosity term. In particular, the resulting bulk viscosity $\kappa^{\rm rap}$ *differ from that obtained at equilibrium that involves the two internal energy modes* [32, 33].

III.B. Relaxation and the slow mode bulk viscosity

From the energy equations (III.5) and (III.6) we obtain at zeroth order that

$$\partial_t\overline{T} + \boldsymbol{v}\cdot\boldsymbol{\nabla}\overline{T} = -\frac{p\boldsymbol{\nabla}\cdot\boldsymbol{v}}{n(c^{\rm tr}+c^{\rm rap})} - \frac{\omega_0^{\rm sl}}{n(c^{\rm tr}+c^{\rm rap})}, \qquad \partial_t T^{\rm sl} + \boldsymbol{v}\cdot\boldsymbol{\nabla}T^{\rm sl} = \frac{\omega_0^{\rm sl}}{nc^{\rm sl}}, \tag{III.12}$$

where the heat capacities are given by

$$c^{\rm tr} = \tfrac{3}{2}k_{\rm B}, \qquad c^{\rm rap} = \sum_{{\rm I}^{\rm rap}} \frac{k_{\rm B}a_{{\rm I}^{\rm rap}}^{\rm rap}}{Z^{\rm rap}}\Big(\frac{E_{{\rm I}^{\rm rap}}^{\rm rap} - \overline{E}^{\rm rap}}{k_{\rm B}\overline{T}}\Big)^2\exp\Big(-\frac{E_{{\rm I}^{\rm rap}}^{\rm rap}}{k_{\rm B}\overline{T}}\Big), \qquad c^{\rm sl} = \sum_{{\rm I}^{\rm sl}} \frac{k_{\rm B}a_{{\rm I}^{\rm sl}}^{\rm sl}}{Z^{\rm sl}}\Big(\frac{E_{{\rm I}^{\rm sl}}^{\rm sl} - \overline{E}^{\rm sl}}{k_{\rm B}\overline{T}}\Big)^2\exp\Big(-\frac{E_{{\rm I}^{\rm sl}}^{\rm sl}}{k_{\rm B}\overline{T}}\Big),$$

and $c^{\rm vl} = c^{\rm tr} + c^{\rm rap} + c^{\rm sl}$. The source term $\omega_0^{\rm sl}$ is in the form $\omega_0^{\rm sl} = -2n^2\big[\!\big[(\Delta E^{\rm sl})\big(\exp\big(\frac{\Delta E^{\rm sl}}{k_{\rm B}\overline{T}} - \frac{\Delta E^{\rm sl}}{k_{\rm B}T^{\rm sl}}\big) - 1\big)\big]\!\big]$ where $[\![\ ]\!]$ is the averaging operator. Defining the nonequilibrium correction factor as $\zeta^{\rm sl} = \int_0^1 \exp\big(\big(\frac{\Delta E^{\rm sl}}{k_{\rm B}\overline{T}} - \frac{\Delta E^{\rm sl}}{k_{\rm B}T^{\rm sl}}\big)s\big)\,ds$ and the relaxation time by $\tau^{\rm sl} = c^{\rm sl}k_{\rm B}\overline{T}T^{\rm sl}/2n[\![(\Delta E^{\rm sl})^2\zeta^{\rm sl}]\!]$, the source term $\omega_0^{\rm sl}$ may be recast in the relaxation form

$$\omega_0^{\rm sl} = \frac{nc^{\rm sl}}{\tau^{\rm sl}}(\overline{T} - T^{\rm sl}). \tag{III.13}$$

Subtracting the $T^{\rm sl}$ equation from that of $\overline{T}$ and using (III.13), the resulting equation for $\overline{T} - T^{\rm sl}$ is then

$$\partial_t(\overline{T} - T^{\rm sl}) + \boldsymbol{v}\cdot\boldsymbol{\nabla}(\overline{T} - T^{\rm sl}) = -\frac{p\boldsymbol{\nabla}\cdot\boldsymbol{v}}{n(c^{\rm tr}+c^{\rm rap})} - \frac{c^{\rm vl}}{(c^{\rm tr}+c^{\rm rap})}\frac{\overline{T} - T^{\rm sl}}{\tau^{\rm sl}}. \tag{III.14}$$

This is a typical relaxation equation and, assuming that $\tau^{\rm sl}$ is smaller than the flow characteristic time, we obtain after some initial layer the relaxation relation at zeroth order $\overline{T} - T^{\rm sl} = -\tau^{\rm sl}p\boldsymbol{\nabla}\cdot\boldsymbol{v}/nc^{\rm vl}$. The equilibrium temperature T is naturally defined such that

$$\mathcal{E}^{\rm tr}(T,n) + \mathcal{E}^{\rm rap}(T,n) + \mathcal{E}^{\rm sl}(T,n) = \mathcal{E}^{\rm tr}(\overline{T},n) + \mathcal{E}^{\rm rap}(\overline{T},n) + \mathcal{E}^{\rm sl}(T^{\rm sl},n), \tag{III.15}$$

and letting $\mathcal{E}^{\rm sl}(T,n)-\mathcal{E}^{\rm sl}(T^{\rm sl},n)=n\int_{T^{\rm sl}}^{T}c^{\rm sl}(T')\,{\rm d}T'=n\,\widetilde{c}^{\rm sl}(T-T^{\rm sl})$ with $\widetilde{c}^{\rm sl}=\int_0^1 c^{\rm sl}\big(T^{\rm sl}+s(T-T^{\rm sl})\big)\,{\rm d}s$ and similarly $\mathcal{E}^{\rm rap}(T,n)-\mathcal{E}^{\rm rap}(\overline{T},n)=n\int_{\overline{T}}^{T}c^{\rm rap}(T')\,{\rm d}T'=n\,\widetilde{c}^{\rm rap}(T-\overline{T})$ with $\widetilde{c}^{\rm rap}=\int_0^1 c^{\rm rap}\big(\overline{T}+s(T-\overline{T})\big)\,{\rm d}s$, we have $(c^{\rm tr}+\widetilde{c}^{\rm rap})(\overline{T}-T)=\widetilde{c}^{\rm sl}(T-T^{\rm sl})$. We also define the slow mode bulk viscosity by $\kappa^{\rm sl}=pk_{\rm B}\widetilde{c}^{\rm sl}\tau^{\rm sl}/c^{\rm vl}\widetilde{c}^{\rm vl}$, where $\widetilde{c}^{\rm vl}=c^{\rm tr}+\widetilde{c}^{\rm rap}+\widetilde{c}^{\rm sl}$ and $\kappa^{\rm sl}$ may also be written

$$\kappa^{\rm sl}=\frac{c^{\rm sl}\widetilde{c}^{\rm sl}}{c^{\rm vl}\,\widetilde{c}^{\rm vl}}\frac{k_{\rm B}^3\overline{T}^2T^{\rm sl}}{2[\![(\Delta E^{\rm sl})^2\zeta^{\rm sl}]\!]}. \tag{III.16}$$

Combining the relaxation relation with the later definitions we obtain at zeroth order that

$$nk_{\rm B}\overline{T}=nk_{\rm B}T-\kappa^{\rm sl}\boldsymbol{\nabla}\cdot\boldsymbol{v}. \tag{III.17}$$

Using the state law (III.4) and the expression of the pressure tensor (III.11), we then deduce an effective bulk viscosity in the form $\kappa^{\rm rap}+\kappa^{\rm sl}$ *that differ from the one-temperature two-mode bulk viscosity directly obtained at equilibrium* [32, 33] also presented in Appendix A. It is thus necessary to investigate first order effects in order to recover the full one-temperature two-mode equilibrium bulk viscosity.

III.C. The effective bulk viscosity

We need to take into account first order corrections to the relaxation relation in order to recover the proper one-temperature two-mode bulk viscosity at equilibrium. From the governing equations (III.5) and (III.6) we deduce that at first order

$$\begin{cases}\partial_t\overline{T}+\boldsymbol{v}\cdot\boldsymbol{\nabla}\overline{T}=-\dfrac{p\boldsymbol{\nabla}\cdot\boldsymbol{v}}{n(c^{\rm tr}+c^{\rm rap})}-\dfrac{\boldsymbol{\nabla}\cdot\boldsymbol{Q}^{\rm tr+rap}}{n(c^{\rm tr}+c^{\rm rap})}-\dfrac{\boldsymbol{\Pi}:\boldsymbol{\nabla}\boldsymbol{v}}{n(c^{\rm tr}+c^{\rm rap})}-\dfrac{\omega_1^{\rm sl}}{n(c^{\rm tr}+c^{\rm rap})},\\[2ex]\partial_tT^{\rm sl}+\boldsymbol{v}\cdot\boldsymbol{\nabla}T^{\rm sl}=-\dfrac{\boldsymbol{\nabla}\cdot\boldsymbol{Q}^{\rm sl}}{nc^{\rm sl}}+\dfrac{\omega_1^{\rm sl}}{nc^{\rm sl}},\end{cases} \tag{III.18}$$

so that we have to investigate the structure of the first order source term $\omega_1^{\rm sl}=\omega_0^{\rm sl}+\delta\omega_1^{\rm sl}$. From the structure of the linearized Boltzmann equation the perturbed distribution function ϕ may be expanded as

$$\phi=-\phi^{\eta}\colon\boldsymbol{\nabla}\boldsymbol{v}-\phi^{\lambda^{\rm tr+rap}}\cdot\boldsymbol{\nabla}\Big(\frac{1}{k_{\rm B}\overline{T}}\Big)-\phi^{\lambda^{\rm sl}}\cdot\boldsymbol{\nabla}\Big(\frac{1}{k_{\rm B}T^{\rm sl}}\Big)-\tfrac{1}{3}\phi^{\kappa}\,\boldsymbol{\nabla}\cdot\boldsymbol{v}+\phi^{\omega}\omega_0^{\rm sl},$$

where ϕ^{η} is a symmetric traceless tensor, $\phi^{\lambda^{\rm tr+rap}}$ and $\phi^{\lambda^{\rm sl}}$ are vectors, ϕ^{κ} and ϕ^{ω} are scalars. The coefficients ϕ^{μ}, $\mu\in\{\eta,\lambda^{\rm tr+rap},\lambda^{\rm sl},\kappa,{\rm sl}\}$, satisfy linearized Boltzmann equations $\mathcal{I}^{\rm rap}(\phi^{\mu})=\psi^{\mu}$ with the constraints $\langle\!\langle f^{(0)}\phi^{\mu},\psi^{j}\rangle\!\rangle=0$, $1\leqslant j\leqslant 6$, where $\mathcal{I}^{\rm rap}$ is the linearized fast collision operator and the right hand sides ψ^{μ} are presented in [23]. Defining $\mathcal{W}^{\rm sl}=\sum_{\rm J,I',J'}(\Delta E^{\rm sl})\iint\widetilde{f}^{(0)}g\sigma^{\rm IJI'J'}{\rm d}\widetilde{\boldsymbol{c}}\,{\rm d}\boldsymbol{e}'$ the perturbed source term is then in the form $\delta\omega_1^{\rm sl}=\langle\!\langle f^{(0)}\phi,\mathcal{W}^{\rm sl}\rangle\!\rangle$ and from the Curie principle, we have $\delta\omega_1^{\rm sl}=-\frac{1}{3}\langle\!\langle f^{(0)}\phi^{\kappa},\mathcal{W}^{\rm sl}\rangle\!\rangle\boldsymbol{\nabla}\cdot\boldsymbol{v}+\langle\!\langle f^{(0)}\phi^{\omega},\mathcal{W}^{\rm sl}\rangle\!\rangle\omega_0^{\rm sl}$. Defining $w_1^{\kappa}=-\frac{1}{3}\langle\!\langle f^{(0)}\phi^{\kappa},\mathcal{W}^{\rm sl}\rangle\!\rangle$ and $w_1^{\rm sl}=\langle\!\langle f^{(0)}\phi^{\omega},\mathcal{W}^{\rm sl}\rangle\!\rangle$ we have obtained that the perturbed term $\delta\omega_1^{\rm sl}$ is in the form

$$\delta\omega_1^{\rm sl}=w_1^{\kappa}\,\boldsymbol{\nabla}\cdot\boldsymbol{v}+w_1^{\rm sl}\,\omega_0^{\rm sl}. \tag{III.19}$$

In the relaxation approximation, at first order, we may also replace $\omega_0^{\rm sl}$ by its zeroth order approximation $\omega_0^{\rm sl}\approx-c^{\rm sl}p\boldsymbol{\nabla}\cdot\boldsymbol{v}/c^{\rm vl}$ in the first order term $\delta\omega_1^{\rm sl}$. The perturbed source terms w_1^{κ} and $w_1^{\rm sl}$ then yield corrections to the temperature difference $\overline{T}-T^{\rm sl}$ in such a way that [23, 24]

$$nk_{\rm B}(\overline{T}-T)=-\big(\kappa^{\rm sl}+\kappa^{\rm sl}\frac{c^{\rm vl}w_1^{\kappa}}{c^{\rm sl}p}-\kappa^{\rm sl}w_1^{\rm sl}\big)\boldsymbol{\nabla}\cdot\boldsymbol{v}. \tag{III.20}$$

In addition, the relaxation pressure $p^{\rm rel}$ is given by

$$p^{\rm rel}=\widetilde{p}^{\rm rel}\omega_0^{\rm sl},\qquad\widetilde{p}^{\rm rel}=\tfrac{1}{3}k_{\rm B}\overline{T}\langle\!\langle f^{(0)}\phi^{\omega},\psi^{\kappa}\rangle\!\rangle=\tfrac{1}{3}k_{\rm B}\overline{T}\langle\!\langle f^{(0)}\phi^{\kappa},\psi^{\omega}\rangle\!\rangle, \tag{III.21}$$

where $\widetilde{p}^{\rm rel}$ is the reduced relaxation pressure so that $p^{\rm rel}$ is also proportional to $\boldsymbol{\nabla}\cdot\boldsymbol{v}$ and further yields a bulk viscosity contribution. Finally, using the general expression of the pressure tensor (III.11), the definition of $\widetilde{p}^{\rm rel}$, as well as (III.20), it is found that the effective bulk viscosity in the Navier-Stokes regime is in the form [23, 24]

$$\kappa^{\rm eff}=\kappa^{\rm rap}-\widetilde{p}^{\rm rel}\frac{c^{\rm sl}p}{c^{\rm vl}}+\kappa^{\rm sl}+\kappa^{\rm sl}\frac{c^{\rm vl}w_1^{\kappa}}{c^{\rm sl}p}-\kappa^{\rm sl}w_1^{\rm sl}. \tag{III.22}$$

The detailed calculation of each term finally yields *after lengthy algebra* that [23]

$$\begin{aligned}\kappa^{\rm eff} = &\Big(\frac{c^{\rm rap}}{c^{\rm tr}+c^{\rm rap}}\Big)^2\frac{(k_{\rm B}\overline{T})^3}{2[\![(\Delta E^{\rm rap})^2]\!]}-\frac{c^{\rm sl}}{c^{\rm vl}}\Big(\frac{c^{\rm rap}}{c^{\rm tr}+c^{\rm rap}}\Big)^2\frac{(k_{\rm B}\overline{T})^3c^{\rm sl}c^{\rm rap}}{2[\![(\Delta E^{\rm rap})^2]\!]}-\frac{c^{\rm rap}c^{\rm sl}}{(c^{\rm tr}+c^{\rm rap})c^{\rm vl}}\frac{(k_{\rm B}\overline{T})^3[\![(\Delta E^{\rm rap})(\Delta E^{\rm sl})\zeta^{\rm sl}]\!]}{2[\![(\Delta E^{\rm rap})^2\zeta^{\rm sl}]\!][\![(\Delta E^{\rm sl})^2\zeta^{\rm sl}]\!]}\\
&+\frac{c^{\rm sl}\widetilde{c}^{\rm sl}}{c^{\rm vl}\widetilde{c}_{\rm vl}}\frac{{k_{\rm B}}^3(\overline{T})^2T^{\rm sl}}{2[\![\Delta E^{\rm sl})^2\zeta^{\rm sl}]\!]}-\frac{\widetilde{c}^{\rm sl}}{\widetilde{c}_{\rm vl}}\Big(\frac{c^{\rm rap}}{c^{\rm tr}+c^{\rm rap}}\Big)^2\frac{k_{\rm B}^3\overline{T}^2T^{\rm sl}}{2[\![(\Delta E^{\rm rap})^2]\!]}-\frac{c^{\rm rap}\widetilde{c}^{\rm sl}}{(c^{\rm tr}+c^{\rm rap})\widetilde{c}_{\rm vl}}\frac{k_{\rm B}^3\overline{T}^2T^{\rm sl}[\![(\Delta E^{\rm sl})(\Delta E^{\rm rap})]\!]}{2[\![(\Delta E^{\rm rap})^2]\!][\![(\Delta E^{\rm sl})^2\zeta^{\rm sl}]\!]}\\
&+\frac{c^{\rm sl}\widetilde{c}^{\rm sl}}{c^{\rm vl}\widetilde{c}_{\rm vl}}\Big(\frac{c^{\rm rap}}{c^{\rm tr}+c^{\rm rap}}\Big)^2\frac{k_{\rm B}^3\overline{T}^2T^{\rm sl}}{2[\![(\Delta E^{\rm rap})^2]\!]}+2\frac{c^{\rm rap}c^{\rm sl}\widetilde{c}^{\rm sl}}{(c^{\rm tr}+c^{\rm rap})c^{\rm vl}\widetilde{c}_{\rm vl}}\frac{k_{\rm B}^3\overline{T}^2T^{\rm sl}[\![(\Delta E^{\rm sl})(\Delta E^{\rm rap})]\!]}{2[\![(\Delta E^{\rm rap})^2]\!][\![(\Delta E^{\rm sl})^2\zeta^{\rm sl}]\!]}.\end{aligned}\tag{III.23}$$

The effective bulk viscosity at thermodynamic equilibrium $\overline{T}=T^{\rm sl}=T$ then coincides with the one-temperature two-mode bulk viscosity derived from the Chapman-Enskog method and presented in Appendix A.

Finally, it is possible to introduce a translational temperature $T^{\rm tr}$ from the relation $\mathcal{E}^{\rm tr}(T^{\rm tr},n)=\langle\!\langle f,\psi^{\rm tr}\rangle\!\rangle$. This temperature is not a collisional invariant and must be expanded in the form $T^{\rm tr}=T_1^{\rm tr}+\mathcal{O}(\epsilon^2)$. It is then established that

$$nk_{\rm B}(T_1^{\rm tr}-\overline{T})=-\big(\kappa^{\rm rap}-\widetilde{p}^{\rm rel}\frac{c^{\rm sl}p}{c^{\rm vl}}\big)\boldsymbol{\nabla}\cdot\boldsymbol{v}.\tag{III.24}$$

Combining (III.20) and (III.24) it is finally obtained that $T_1^{\rm tr}$ and $\kappa^{\rm eff}$, defined by (III.22) and given by (III.23), are such that

$$nk_{\rm B}(T_1^{\rm tr}-T)=-\kappa^{\rm eff}\boldsymbol{\nabla}\cdot\boldsymbol{v}.\tag{III.25}$$

Therefore, the physical interpretation gained with the previous simplified model (II.20) is also valid in the more complex situation where there are two energy modes with different dynamics [23, 24]. All these results may further be extended to mixtures of gases as well as to the situation where the fast and slow energy modes are not independent [25].

IV. A STATE-TO-STATE MODEL FOR GAS MIXTURES

IV.A. Kinetic framework

We consider a state-to-state model for a mixture of polyatomic gases [1–12]. We denote by $i{\rm I}$ the pseuso species index for the ith species in the Iith quantum state, $\mathfrak{S}=\{1,\dots,{\rm N}^s\}$ the species indexing set, ${\rm N}^s$ the number of species, $\mathfrak{Q}_i$ the ith species quantum state indexing set, $\mathfrak{Q}=\cup_{i\in\mathfrak{S}}\{i\}\times\mathfrak{Q}_i$ the pseudo species indexing set, and ${\rm N}^q$ the number of pseudo species. The pseudo species Boltzmann equations are written as

$$\partial_t f_{i{\rm I}}+\boldsymbol{c}_{i{\rm I}}\cdot\boldsymbol{\nabla}f_{i{\rm I}}=\frac{1}{\epsilon}\mathcal{J}_{i{\rm I}}^{\rm rap}+\mathcal{J}_{i{\rm I}}^{\rm sl},\qquad i{\rm I}\in\mathfrak{Q},\tag{IV.1}$$

where $\boldsymbol{c}_{i{\rm I}}$ denotes the velocity of the particle of the iIith pseudo species, $f_{i{\rm I}}(t,\boldsymbol{x},\boldsymbol{c}_{i{\rm I}})$ the distribution function for the iIith pseudo species, $\mathcal{J}_{i{\rm I}}^{\rm rap}$ the rapid collision operator, $\mathcal{J}_{i{\rm I}}^{\rm sl}$ the slow collision operator, and ϵ the formal parameter associated with the Chapman-Enskog procedure. We will also denote by denoting by $E_{i{\rm I}}$ the internal energy of the iIith pseudo species and by $a_{i{\rm I}}$ the corresponding degeneracy. Using similar notation as in previous sections, the fast and slow collision operators are given by

$$\mathcal{J}_{i{\rm I}}^{\rm rap}=\mathcal{J}_{i{\rm I}}^{\rm tr-tr},\qquad \mathcal{J}_{i{\rm I}}^{\rm sl}=\mathcal{J}_{i{\rm I}}^{\rm tr-int}+\mathcal{J}_{i{\rm I}}^{\rm int-int}.\tag{IV.2}$$

The collisional invariants of the fast collision operator $\mathcal{J}^{\rm rap}=(\mathcal{J}_{i{\rm I}}^{\rm rap})_{i{\rm I}\in\mathfrak{Q}}$ are associated with the pseudo species particle numbers $\psi^{k{\rm K}}=(\delta_{ki}\delta_{{\rm I}{\rm K}})_{i{\rm I}\in\mathfrak{Q}}$, $k{\rm K}\in\mathfrak{Q}$, momentum $\psi^{{\rm N}^q+\nu}=(m_ic_{i\nu})_{i{\rm I}\in\mathfrak{Q}}$, $\nu\in\{1,2,3\}$, where m_i denotes the mass of the particles of the ith species and $\boldsymbol{c}_{i{\rm I}}=(c_{i{\rm I}1},c_{i{\rm I}2},c_{i{\rm I}3})^t$, and kinetic energy $\psi^{{\rm N}^q+4}=\psi^{\rm tr}=\big(\frac{1}{2}m_i|\boldsymbol{c}_{i{\rm I}}-\boldsymbol{v}|^2\big)_{i{\rm I}\in\mathfrak{Q}}$ where $\boldsymbol{v}$ denotes the mass average mixture velocity.

The Enskog expansion reads $f_{i{\rm I}}=f_{i{\rm I}}^{(0)}\big(1+\epsilon\phi_{i{\rm I}}+\mathcal{O}(\epsilon^2)\big)$ with the Maxwellian distribution of the iIith pseudo species $f_{i{\rm I}}^{(0)}$ in the form

$$f_{i{\rm I}}^{(0)}=\Big(\frac{m_i}{2\pi k_{\rm B}T^{\rm tr}}\Big)^{3/2}n_{i{\rm I}}\exp\Big(-\frac{m_i|\boldsymbol{c}_{i{\rm I}}-\boldsymbol{v}|^2}{2k_{\rm B}T^{\rm tr}}\Big),\tag{IV.3}$$

where $T^{\rm tr}$ is the translational temperature of the mixture. Assuming that there are sufficiently inelastic collisions, the collision invariants of the slow collision operator $\mathcal{J}^{\rm sl}=(\mathcal{J}^{\rm sl}_{i\mathrm{I}})_{i\mathrm{I}\in\mathfrak{Q}}$, are associated with the species particle numbers $\psi^k=(\delta_{ki})_{i\mathrm{I}\in\mathfrak{Q}}=\sum_{\mathrm{K}\in\mathfrak{Q}_k}\psi^{k\mathrm{K}}$, $k\in\mathfrak{S}$, momentum $\psi^{\mathrm{N}^q+\nu}$, $\nu\in\{1,2,3\}$, and mixture total energy $\psi^{\rm en}=\psi^{\mathrm{N}^q+4}=\big(\frac{1}{2}m_i|\boldsymbol{c}_{i\mathrm{I}}-\boldsymbol{v}|^2+E_{i\mathrm{I}}\big)_{i\mathrm{I}\in\mathfrak{Q}}$. The scalar product $\langle\!\langle\xi,\zeta\rangle\!\rangle$ between two tensorial quantities $\xi=(\xi_{i\mathrm{I}})_{i\mathrm{I}\in\mathfrak{Q}}$ and $\zeta=(\zeta_{i\mathrm{I}})_{i\mathrm{I}\in\mathfrak{Q}}$ is naturally defined by

$$\langle\!\langle\xi,\zeta\rangle\!\rangle=\sum_{i\mathrm{I}\in\mathfrak{Q}}\int\xi_{i\mathrm{I}}{\cdot}\zeta_{i\mathrm{I}}\,\mathrm{d}\boldsymbol{c}_{i\mathrm{I}},$$

where $\xi_{i\mathrm{I}}{\cdot}\zeta_{i\mathrm{I}}$ is the contracted product.

The fluid equations are obtained by taking the scalar product of Boltzmann equations (IV.1) with the collisional invariants of the fast collision operator. The fluid variables are the pseudo species number densities $n_{k\mathrm{K}}=\langle\!\langle\psi^{k\mathrm{K}},f\rangle\!\rangle=\langle\!\langle\psi^{k\mathrm{K}},f^{(0)}\rangle\!\rangle$ or equivalently the mass densities $\rho_{k\mathrm{K}}=m_kn_{k\mathrm{K}}$ for $k\mathrm{K}\in\mathfrak{Q}$, the mass averaged velocity $\boldsymbol{v}=(v_1,v_2,v_3)^t$ with $\rho v_\nu=\langle\!\langle\psi^{\mathrm{N}^q+\nu},f\rangle\!\rangle=\langle\!\langle\psi^{\mathrm{N}^q+\nu},f^{(0)}\rangle\!\rangle$ for $\nu\in\{1,2,3\}$ and $\rho=\sum_{k\mathrm{K}\in\mathfrak{Q}}\rho_{k\mathrm{K}}$, and the translational temperature defined by $\frac{3}{2}nk_{\rm B}T^{\rm tr}=\langle\!\langle f,\psi^{\rm tr}\rangle\!\rangle=\langle\!\langle f^{(0)},\psi^{\rm tr}\rangle\!\rangle$ with $n=\sum_{k\mathrm{K}\in\mathfrak{Q}}n_{k\mathrm{K}}$ denoting the total number density. The pressure p, the translational energy $\mathcal{E}^{\rm tr}$ and the total internal energy $\mathcal{E}$ are found in the form

$$p=nk_{\rm B}T^{\rm tr},\qquad\mathcal{E}^{\rm tr}=n\tfrac{3}{2}k_{\rm B}T^{\rm tr}\qquad\mathcal{E}=\mathcal{E}^{\rm tr}+\sum_{i\mathrm{I}\in\mathfrak{Q}}n_{i\mathrm{I}}E_{i\mathrm{I}}.\tag{IV.4}$$

Introducing the partition functions $Z_{i\mathrm{I}}=Z^{\rm tr}_iZ^{\rm int}_{i\mathrm{I}}$ with

$$Z^{\rm tr}_i=\Big(\frac{2\pi m_ik_{\rm B}T^{\rm tr}}{h_{\rm P}^2}\Big)^{3/2},\qquad Z^{\rm int}_{i\mathrm{I}}=a_{i\mathrm{I}}\exp\Big(-\frac{E_{i\mathrm{I}}}{k_{\rm B}T^{\rm tr}}\Big),$$

where $h_{\rm P}$ is the Planck constant, we may then rewrite the Maxwellian distribution of the $i\mathrm{I}$th pseudo-species in the form $f^{(0)}_{i\mathrm{I}}=\frac{1}{\beta_{i\mathrm{I}}}\frac{n_{i\mathrm{I}}}{Z_{i\mathrm{I}}}\exp\big(-m_i|\boldsymbol{c}_{i\mathrm{I}}-\boldsymbol{v}|^2/2k_{\rm B}T^{\rm tr}-E_{i\mathrm{I}}/k_{\rm B}T^{\rm tr}\big)$ where $\beta_{i\mathrm{I}}=h_{\rm P}^3/(a_{i\mathrm{I}}m_i^3)$. The entropy per particle of the $i\mathrm{I}$th pseudo species is given by $\mathcal{S}_{i\mathrm{I}}=\frac{5}{2}k_{\rm B}-k_{\rm B}\log\frac{n_{i\mathrm{I}}}{a_{i\mathrm{I}}Z^{\rm tr}_i}=\frac{5}{2}k_{\rm B}+\frac{E_{i\mathrm{I}}}{T^{\rm tr}}-k_{\rm B}\log\frac{n_{i\mathrm{I}}}{Z_{i\mathrm{I}}}$ for $i\mathrm{I}\in\mathfrak{Q}$ and the mixture fluid entropy by $\mathcal{S}=\sum_{i\mathrm{I}\in\mathfrak{Q}}n_{i\mathrm{I}}\mathcal{S}_{i\mathrm{I}}$. The Gibbs function $\mathcal{G}_{i\mathrm{I}}$ of the $i\mathrm{I}$th pseudo particle isalso given by $\mathcal{G}_{i\mathrm{I}}=k_{\rm B}T^{\rm tr}\log\frac{n_{i\mathrm{I}}}{Z_{i\mathrm{I}}}$ and the reduced chemical potential $\mu_{i\mathrm{I}}$ and $\mu_{\rm tr}$ by

$$\mu_{i\mathrm{I}}=\log\frac{n_{i\mathrm{I}}}{Z_{i\mathrm{I}}},\qquad i\mathrm{I}\in\mathfrak{Q},\qquad\qquad\mu_{\rm tr}=-\frac{1}{T_{\rm tr}},\tag{IV.5}$$

and will be used are symmetrizing variables.

Following the Chapman-Enskog procedure, the conservation equations are found in the form [9]

$$\partial_tn_{k\mathrm{K}}+\boldsymbol{\nabla}{\cdot}(n_{k\mathrm{K}}\boldsymbol{v})+\boldsymbol{\nabla}{\cdot}(n_{k\mathrm{K}}\boldsymbol{V}_{k\mathrm{K}})=\omega^{(1)}_{k\mathrm{K}},\qquad k\mathrm{K}\in\mathfrak{Q},\tag{IV.6}$$

$$\partial_t(\rho\boldsymbol{v})+\boldsymbol{\nabla}{\cdot}(\rho\boldsymbol{v}{\otimes}\boldsymbol{v}+p\boldsymbol{I})+\boldsymbol{\nabla}{\cdot}\boldsymbol{\Pi}=0,\tag{IV.7}$$

$$\partial_t\mathcal{E}+\boldsymbol{\nabla}{\cdot}(\boldsymbol{v}\mathcal{E})+\boldsymbol{\nabla}{\cdot}\boldsymbol{Q}=-p\boldsymbol{\nabla}{\cdot}\boldsymbol{v}-\boldsymbol{\Pi}\boldsymbol{:}\boldsymbol{\nabla}\boldsymbol{v},\tag{IV.8}$$

where $\boldsymbol{V}_{k\mathrm{K}}$ denotes the diffusion velocity of the $k\mathrm{K}$th pseudo species, $\omega^{(1)}_{k\mathrm{K}}$ the first order production term of the $k\mathrm{K}$th pseudo species, $\boldsymbol{\Pi}$ the viscous tensor, and $\boldsymbol{Q}$ the heat flux.

The inelastic collisions are written for convenience as chemical reactions

$$\sum_{i\mathrm{I}\in\mathfrak{Q}}\nu^{\rm f}_{i\mathrm{I}r}\mathfrak{M}_{i\mathrm{I}}\rightleftarrows\sum_{i\mathrm{I}\in\mathfrak{Q}}\nu^{\rm b}_{i\mathrm{I}r}\mathfrak{M}_{i\mathrm{I}},\qquad\qquad r\in\mathfrak{R},\tag{IV.9}$$

where $\mathfrak{M}_{i\mathrm{I}}$ is the symbol of the $i\mathrm{I}$ pseudo species, r the reaction number, $\mathfrak{R}$ the reaction indexing set and $\nu^{\rm f}_{i\mathrm{I}r}$ and $\nu^{\rm b}_{i\mathrm{I}r}$ the forward and backward stoichiometric coefficients of pseudo species $i\mathrm{I}$ in reaction r. The source term may be expanded as $\omega^{(1)}_{k\mathrm{K}}=\omega^{(0)}_{k\mathrm{K}}+\epsilon\delta\omega^{(1)}_{k\mathrm{K}}$ where $\omega^{(0)}_{k\mathrm{K}}$ is evaluated with Maxwellian distributions and $\delta\omega^{(1)}_{k\mathrm{K}}$ is the first order perturbation. The zeroth order source terms are first obtained in the form $\omega^{(0)}_{k\mathrm{K}}=\sum_{r\in\mathfrak{R}}\nu_{k\mathrm{K}r}\bar\tau_r$, with the stoichiometric coefficients defined by $\nu_{k\mathrm{K}r}=\nu^{\rm b}_{k\mathrm{K}r}-\nu^{\rm f}_{k\mathrm{K}r}$, and the rates of progress in the form $\bar\tau_r=\mathfrak{C}_r\big\{\prod_{i\mathrm{I}\in\mathfrak{Q}}(n_{i\mathrm{I}}/Z_{i\mathrm{I}})^{\nu^{\rm f}_{i\mathrm{I}r}}-\prod_{i\mathrm{I}\in\mathfrak{Q}}(n_{i\mathrm{I}}/Z_{i\mathrm{I}})^{\nu^{\rm b}_{i\mathrm{I}r}}\big\}$ where $\mathfrak{C}_r$ is an average quantity associated with chemical transition probabilities of reaction r [9, 19]. Letting $\omega^{(0)}=(\omega^{(0)}_{i\mathrm{I}})_{i\mathrm{I}\in\mathfrak{Q}}$, $\nu^{\rm f}_r=(\nu^{\rm f}_{i\mathrm{I}r})_{i\mathrm{I}\in\mathfrak{Q}}$, $\nu^{\rm b}_r=(\nu^{\rm b}_{i\mathrm{I}r})_{i\mathrm{I}\in\mathfrak{Q}}$, $\nu_r=(\nu_{i\mathrm{I}r})_{i\mathrm{I}\in\mathfrak{Q}}$ the zeroth order source term may then be written as $\omega^{(0)}=\sum_{r\in\mathfrak{R}}\nu_r\bar\tau_r$ with $\bar\tau_r=\mathfrak{C}_r\big(\exp\langle\mu,\nu^{\rm f}_r\rangle-\exp\langle\mu,\nu^{\rm b}_r\rangle\big)$ and defining $\zeta_r=\int_0^1\exp\big(\langle\mu,\nu_r\rangle s\big)\,\mathrm{d}s$ we obtain that

$$\omega^{(0)}=-\Lambda\mu=-\Lambda(\mu-\mu^{\rm e}),\qquad\Lambda=\sum_{r\in\mathfrak{R}}\Lambda_r\,\nu_r{\otimes}\nu_r,\qquad\Lambda_r=\mathfrak{C}_r\zeta_r\,\exp\langle\mu,\nu^{\rm b}_r\rangle,\tag{IV.10}$$

where $\mu^{\rm e} = (\mu^{\rm e}_{i\imath})_{i\imath\in\mathfrak{O}}$ denotes the equilibrium value of μ and where we have used that $\langle \nu_r, \mu^{\rm e}\rangle = 0$, $r \in \mathfrak{R}$. The perturbed source terms $\delta\omega^{(1)}_{k\kappa}$ may also be expressed in terms of the perturbed distribution ϕ [19, 23, 25].

Denoting by $\mathcal{I}^{\rm rap}_{i\imath}$ the linearized fast collision operator for the $i\imath$th pseudo species and by $\mathcal{I}^{\rm rap} = (\mathcal{I}^{\rm rap}_{i\imath})_{i\imath\in\mathfrak{O}}$ the linearized operator of the mixture, the perturbed distribution function $\phi = (\phi_{i\imath})_{i\imath\in\mathfrak{O}}$ is such that $\mathcal{I}^{\rm rap}(\phi) = \psi$ where $\psi = (\psi_{i\imath})_{i\imath\in\mathfrak{O}}$ has components

$$\psi_{i\imath} = -\partial_t^{(0)} \log f^{(0)}_{i\imath} - \boldsymbol{c}_{i\imath}\cdot\boldsymbol{\nabla} \log f^{(0)}_{i\imath} + \mathcal{J}^{{\rm sl},(0)}_{i\imath}/f^{(0)}_{i\imath},$$

and ϕ must satisfy the Enskog constraints $\langle\!\langle f^{(0)}\phi, \psi^j\rangle\!\rangle = 0$ for $1 \le j \le {\rm N}^q + 4$. Expanding the perturbed distribution function in terms of the gradients of the macroscopic variables, the dissipative fluxes are found in the classical form [9, 19, 23]. In particular, the viscous tensor reads $\boldsymbol{\Pi} = -\eta\big(\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^t - \frac{2}{3}(\boldsymbol{\nabla}\cdot\boldsymbol{v})\boldsymbol{I}\big)$ and there is neither a bulk viscosity term nor a relaxation pressure since all pseudo species have a single internal state [9, 19]. Defining the pressure tensor as $\boldsymbol{\mathcal{P}} = p\boldsymbol{I} + \boldsymbol{\Pi}$ we finally have

$$\boldsymbol{\mathcal{P}} = n k_{\rm B} T^{\rm tr}\boldsymbol{I} - \eta\big(\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^t - \tfrac{2}{3}(\boldsymbol{\nabla}\cdot\boldsymbol{v})\boldsymbol{I}\big) \tag{IV.11}$$

so that $\boldsymbol{\mathcal{P}}$ *does not contain a bulk viscosity term unlike with one-temperature polyatomic gas mixtures* [13–22].

IV.B. Equilibrium population and bulk viscosities

The equilibrium limit of the state-to-state model is obtained by zeroing the chemistry sources $\omega^{(0)}$ while maintaining constant the slow variables associated with the collision invariants of the full collision operator $\mathcal{J}^{\rm rap} + \mathcal{J}^{\rm sl}$, namely the species number densities $n_k = \sum_{\kappa\in\mathfrak{O}_k} n_{k\kappa}$, $k \in \mathfrak{S}$, momentum $\rho\boldsymbol{v}$ and the total internal energy $n\frac{3}{2}k_{\rm B}T^{\rm tr} + \sum_{i\imath\in\mathfrak{O}} n_{i\imath}E_{i\imath}$. Denoting by T the thermodynamic equilibrium temperature, the species equilibrium population is given by the Boltzmann distribution

$$n^{\rm e}_{i\imath} = \frac{a_{i\imath}n_i}{Z^{\rm int}_i}\exp\big(-\frac{E_{i\imath}}{k_{\rm B}T}\big), \qquad i\imath \in \mathfrak{O}, \tag{IV.12}$$

where $Z^{\rm int}_i = \sum_{\imath\in\mathfrak{O}_i} a_{i\imath}\exp\big(-E_{i\imath}/k_{\rm B}T\big)$ is the equilibrium internal partition function of the ith species and where $\sum_{\imath\in\mathfrak{O}_i} n_{i\imath} = \sum_{\imath\in\mathfrak{O}_i} n^{\rm e}_{i\imath} = n_i$, for $i \in \mathfrak{S}$. The corresponding equilibrium species average energies are then $\overline{E}_i = \sum_{\imath\in\mathfrak{O}_i}(a_{i\imath}E_{i\imath}/Z^{\rm int}_i)\exp(-E_{i\imath}/k_{\rm B}T)$, the internal heat capacities are given by

$$c^{\rm int}_i = \partial_T\overline{E}_i = \sum_{\imath\in\mathfrak{O}_i} a_{i\imath}\frac{(E_{i\imath}-\overline{E}_i)^2}{k_{\rm B}T^2 Z^{\rm int}_i}\exp\big(-E_{i\imath}/k_{\rm B}T\big),$$

and the equilibrium temperature is the unique scalar T such that

$$n\tfrac{3}{2}k_{\rm B}T + \sum_{i\in\mathfrak{S}} n_i\overline{E}_i = \sum_{i\imath\in\mathfrak{O}} n_{i\imath}(\tfrac{3}{2}k_{\rm B}T^{\rm tr} + E_{i\imath}). \tag{IV.13}$$

With the chemistry analogy we may further introduce $\psi^k = (\delta_{ik})_{i\imath\in\mathfrak{O}} = \sum_{\kappa\in\mathfrak{O}_k}\psi^{k\kappa}$, for $k \in \mathfrak{S}$, and $\nu_r = (\nu_{i\imath r})_{i\imath\in\mathfrak{O}}$, for $r \in \mathfrak{R}$, and define

$$\mathcal{R} = {\rm span}\{\ \nu_r,\ r\in\mathfrak{R}\ \}, \qquad \mathcal{A} = {\rm span}\{\ \psi^k,\ k\in\mathfrak{S}\ \}.$$

Using a chemistry vocabulary, we may then say that the species are the atoms of the pseudo species. Assuming naturally that there are sufficiently energy exchanges we further have $\mathcal{R}^\perp = \mathcal{A}$, that is, the reaction vectors ν_r, $r \in \mathfrak{R}$ are sufficiently numerous in order to span the maximum space $\mathcal{A}^\perp$, keeping in mind that there is no dissociation or recombination. The equilibrium pseudo species number densities $\mu^{\rm e} = (\mu^{\rm e}_{i\imath})_{i\imath\in\mathfrak{O}}$ are then the unique solution of the equilibrium conditions $\mu^{\rm e} \in \mathcal{R}^\perp$ or equivalently $\mu^{\rm e} \in \mathcal{A}$ under the constraints that n_k for $k \in \mathfrak{S}$ and $\mathcal{E}$ are invariants. The reduced chemical potentials at equilibrium are indeed such that $\mu^{\rm e}_{i\imath} = \log(n^{\rm e}_{i\imath}/Z^{\rm e}_{i\imath}) = \log(n_i/Z^{\rm int}_i)$ where $Z^{\rm e}_{i\imath} = Z_{i\imath}(T)$ so that $\mu^{\rm e} = \sum_{i\in\mathfrak{S}}\log(n_i/Z^{\rm int}_i)\,\psi^i$ and $\langle\mu^{\rm e}, \nu_r\rangle = 0$, $r \in \mathfrak{R}$.

The usual scalar species basis functions *at equilibrium* are given by $\phi^{0001k} = \big((\overline{E}_i - E_{i\imath})\delta_{ik}/k_{\rm B}T\big)_{i\imath\in\mathfrak{O}}$ and $\phi^{0010k} = \big((\frac{3}{2} - \frac{1}{2}\frac{m_i}{k_{\rm B}T}|\boldsymbol{c}-\boldsymbol{v}|^2)\delta_{ki}\big)_{i\imath\in\mathfrak{O}}$ for the kth species. The basis function ϕ^{0010k} are defined for any $k \in \mathfrak{S}$ while ϕ^{0001k} are defined for any $k \in \mathfrak{S}^p$ where $\mathfrak{S}^p$ denotes the set of polyatomic species. We also consider the projected basis functions

$\widehat{\phi}^{0001k} = \phi^{0001k} - \psi^{\rm en} c_k^{\rm int}/c^{\rm vl}$, $k \in \mathfrak{S}^p$, where the term proportional to $\psi^{\rm en}$ ensures that $\widehat{\phi}^{0001k}$ is orthogonal to the collisional invariant $\psi^{\rm en}$ of the complete collision operator in the equilibrium kinetic framework. Two bulk viscosities at equilibrium may then be defined, namely the 'internal energy' bulk viscosity $\kappa_{[01]}$ as well as the 'standard bulk viscosity' κ. The linear system associated with the evaluation of the 'internal energy' bulk viscosity $\kappa_{[01]}$ at equilibrium is obtained by using the Galerkin variational approximation space spanned by $\widehat{\phi}^{0001k}$, $k \in \mathfrak{S}^p$. The idea behind this basis function is that the most important part of the dynamics is that associated with internal energy exchanges and not with kinetic energy [32, 33]. The 'internal energy' bulk viscosity $\kappa_{[01]}$ is obtained by solving the tranport linear system $K_{[01]}\gamma = \beta_{[01]}$ of size N^p, where N^p is the number of polyatomic species, where $K_{[01]kl} = [\phi^{0001k}, \phi^{0001l}]/np$, $\beta_{[01]i} = -\mathsf{x}_i c_i^{\rm int}/c^{\rm vl}$, and $[,]$ is the classical bracket product [32, 33]. The matrix $K_{[01]}$ is symmetric positive definite and letting $\gamma = (\gamma_i)_{i\in\mathfrak{S}}$, the 'internal energy' bulk viscosity is given by $\kappa_{[01]} = -\sum_{i\in\mathfrak{S}} p\gamma_i \mathsf{x}_i c_i^{\rm int}/c^{\rm vl}$ and has been found to be accurate [32, 33]. On the other hand, the standard bulk viscosity is obtained with the Galerkin variational approximation space spanned by ϕ^{0001k} and ϕ^{0010k}, $k \in \mathfrak{S}$.

IV.C. Symmetric zeroth order relaxation equations

The system of partial differential equations governing the pseudo species Gibbs functions and the translational temperature at zeroth order is written in symmetric form. Symmetrized forms are convenient for analyzing systems of partial differential equations modeling fluids and are generally obtained by using entropic type variable $-(\partial_{\mathsf{u}}\mathcal{S})^t$ where u denotes the vector of conservative variables. Since we are interested in the relaxation of thermodynamic variables we use for convenience the variables $(\delta\mu, \delta\mu_{\rm tr})^t = (\mu - \mu^{\rm e}, \mu_{\rm tr} - \mu_{\rm tr}^{\rm e})^t$ where $\mu = (\mu_{i\imath})_{i\imath\in\mathfrak{Q}}$, $\mu^{\rm e} = (\mu_{i\imath}^{\rm e})_{i\imath\in\mathfrak{Q}}$, $\mu_{\rm tr} = -1/(k_{\rm B}T^{\rm tr})$, and $\mu_{\rm tr}^{\rm e} = -1/(k_{\rm B}T)$. Denoting for short $\mathrm{d}_t = \partial_t + \boldsymbol{v}\cdot\boldsymbol{\nabla}$ the convective derivative, the governing equations at zeroth order are found in the form

$$n_{i\imath}\mathrm{d}_t\delta\mu_{i\imath} + n_{i\imath}(\tfrac{3}{2}k_{\rm B}T^{\rm tr} + E_{i\imath})\mathrm{d}_t\delta\mu_{\rm tr} = \omega_{i\imath}^{(0)} + \frac{n_{i\imath}^{\rm e}(E_{i\imath} - \overline{E}_i)}{Tc^{\rm vl}}\,\boldsymbol{\nabla}\cdot\boldsymbol{v}, \qquad i\imath \in \mathfrak{Q}, \tag{IV.14}$$

$$\sum_{i\imath\in\mathfrak{Q}} n_{i\imath}(\tfrac{3}{2}k_{\rm B}T^{\rm tr} + E_{i\imath})\mathrm{d}_t\delta\mu_{i\imath} + \mathsf{a}_{\rm tr}\mathrm{d}_t\delta\mu_{\rm tr} = 0, \tag{IV.15}$$

where $\mathsf{a}_{\rm tr} = \sum_{i\imath\in\mathfrak{Q}} n_{i\imath}(\frac{3}{2}k_{\rm B}T^{\rm tr} + E_{i\imath})^2 + \frac{3}{2}pk_{\rm B}T^{\rm tr}$. Denoting by $\mathcal{N}$ the diagonal matrix $\mathcal{N} = \mathrm{diag}\big((n_{i\imath})_{i\imath\in\mathfrak{Q}}\big)$ and a the vector with components $\mathsf{a}_{i\imath} = n_{i\imath}(\frac{3}{2}k_{\rm B}T^{\rm tr} + E_{i\imath})$, $i\imath \in \mathfrak{Q}$, these equations involve the symmetric positive definite matrix $\widetilde{A} = \left(\begin{smallmatrix} \mathcal{N} & \mathsf{a} \\ \mathsf{a}^t & \mathsf{a}_{\rm tr}\end{smallmatrix}\right)$.

The equations (IV.14)(IV.15) imply that $\delta\mu = \mu - \mu^{\rm e}$ satisfies the vector partial differential equation

$$\widetilde{\mathcal{N}}\,\mathrm{d}_t\delta\mu = -\Lambda\delta\mu + \mathsf{b}\boldsymbol{\nabla}\cdot\boldsymbol{v}, \tag{IV.16}$$

where $\widetilde{\mathcal{N}} = \mathcal{N} - \mathsf{a}\otimes\mathsf{a}/\mathsf{a}_{\rm tr}$ is symmetric positive definite, Λ symmetric positive semi-definite, and $\mathsf{b} = (\mathsf{b}_{i\imath})_{i\imath\in\mathfrak{Q}}$ is given by $\mathsf{b}_{i\imath} = n_{i\imath}^{\rm e}(E_{i\imath} - \overline{E}_i)/Tc^{\rm vl}$, $i\imath \in \mathfrak{Q}$. Since $\widetilde{\mathcal{N}}$ is positive definite and Λ is positive semidefinite, (IV.16) is a typical vector relaxation equation and the corresponding vector relaxation relation is then in the form

$$\Lambda^{\rm e}\delta\mu = \mathsf{b}\boldsymbol{\nabla}\cdot\boldsymbol{v}, \tag{IV.17}$$

where $\Lambda^{\rm e}$ is the matrix Λ at equilibrium $\Lambda^{\rm e} = \sum_{r\in\mathfrak{R}} \Lambda_r^{\rm e}\nu_r\otimes\nu_r$ with $\Lambda_r^{\rm e} = \mathfrak{C}_r^{\rm e}\exp\langle\mu^{\rm e}, \nu_r^{\rm f}\rangle = \mathfrak{C}_r^{\rm e}\exp\langle\mu^{\rm e}, \nu_r^{\rm b}\rangle$ and $\zeta_r^{\rm e} = 1$. Since the nullspace of $\Lambda^{\rm e}$ is $\mathcal{A}$ we also need constraints to determine uniquely $\delta\mu$, using $\sum_{\imath\in\mathfrak{Q}_i}(n_{i\imath} - n_{i\imath}^{\rm e}) = 0$, $i \in \mathfrak{S}$. In the relaxation approximation, we may linearize the constraints around equilibrium and after some algebra it is obtained that $\langle\mathcal{N}^{\rm e}\delta\mu, \psi^i\rangle = \sum_{\imath\in\mathfrak{Q}_i} n_{i\imath}^{\rm e}(\mu_{i\imath} - \mu_{i\imath}^{\rm e}) = -n_i(\frac{3}{2}k_{\rm B}T^{\rm tr} + \overline{E}_i)(T^{\rm tr} - T)/k_{\rm B}T^2$ for $i \in \mathfrak{S}$.

IV.D. Bulk viscosity at zeroth order

Taking into account the relaxation relation (IV.17) and the mass constraints, we are lead to decompose $\delta\mu$ in the vector form

$$\delta\mu = \delta\mu^{\mathcal{R}}\,\boldsymbol{\nabla}\cdot\boldsymbol{v} + \delta\mu^{\mathcal{A}}, \qquad \delta\mu^{\mathcal{R}} \in (\mathcal{N}^{\rm e})^{-1}\mathcal{A}^{\perp}, \qquad \delta\mu^{\mathcal{A}} \in N(\Lambda^{\rm e}) = \mathcal{A}. \tag{IV.18}$$

The term $\delta\mu^{\mathcal{R}}$ is such that $\Lambda^{\rm e}\delta\mu^{\mathcal{R}} = \mathsf{b}$ and b is in the range $R(\Lambda^{\rm e})$ since $\sum_{\imath\in\mathfrak{Q}_i} n^{\rm e}_{i\imath}(E_{i\imath} - \overline{E}_i) = 0$. We now seek an approximate solution of the constrained relaxation equations that is *compatible with the equilibrium limit mixture* so that $\delta\mu^{\mathcal{R}} = \sum_{i\in\mathfrak{S}} \gamma'_i \phi^{0001i}$ and $\delta\mu^{\mathcal{A}} = \sum_{i\in\mathfrak{S}} \gamma''_i \psi^i$. Using that $\delta\mu^{\mathcal{R}} \in (\mathcal{N}^{\rm e})^{-1}\mathcal{A}^\perp$ we first obtain from the mass constraints that $\langle \mathcal{N}^{\rm e}\delta\mu^{\mathcal{A}}, \psi^i\rangle = -n^{\rm e}_i(\frac{3}{2}k_{\rm B}T^{\rm tr} + \overline{E}_i)(T^{\rm tr} - T)/k_{\rm B}T^2$ for $i \in \mathfrak{S}$ so that $\gamma''_i = -(\frac{3}{2}k_{\rm B}T + \overline{E}_i)\frac{T^{\rm tr}-T}{k_{\rm B}T^2}$, for $i \in \mathfrak{S}$. In order to determine the coefficients vector $\gamma' = (\gamma'_i)_{i\in\mathfrak{S}}$, we use a least square approximation of the relaxation equations upon writing that $\sum_{l\in\mathfrak{S}}\langle \phi^{0001i}, \Lambda^{\rm e}\phi^{0001l}\rangle\gamma'_l = \langle \phi^{0001i}, \mathsf{b}\rangle$ for $i \in \mathfrak{S}$. The matrix $\mathcal{K} = \big(\langle \phi^{0001i}, \Lambda^{\rm e}\phi^{0001j}\rangle\big)_{i,j\in\mathfrak{S}}$ is found to be positive definite and a direct comparison yields that the coefficients of the both matrices $K_{[01]}$ and $\Lambda^{\rm e}$ are proportional $\langle \Lambda^{\rm e}\phi^{0001i}, \phi^{0001j}\rangle = npK_{[01]ij}$ and $\langle \phi^{0001i}, \mathsf{b}\rangle = -n\mathsf{x}_i c_i^{\rm int}/c^{\rm vl}$ so that $\langle \phi^{0001i}, \mathsf{b}\rangle = n\beta_{[01]i}$ and $\gamma = p\gamma'_{[01]}$. We have thus established that the least square solution to the relaxation equations under the linearized constraints is given by

$$\mu_{i\imath} - \mu^{\rm e}_{i\imath} = \gamma_i \frac{\overline{E}_i - E_{i\imath}}{k_{\rm B}T}\boldsymbol{\nabla}\cdot\boldsymbol{v} - (\tfrac{3}{2}k_{\rm B}T + \overline{E}_i)\frac{T^{\rm tr} - T}{k_{\rm B}T^2}, \qquad i\imath \in \mathfrak{Q}, \tag{IV.19}$$

where where $\gamma = (\gamma_i)_{i\in\mathfrak{S}}$ is the solution of the transport linear system $K_{[01]}\gamma = n\beta_{[01]i}$ associated with the internal mode bulk viscosity $\kappa_{[01]}$.

By definition of the equilibrium temperature T we have $c^{\rm tr}(T^{\rm tr} - T) + \sum_{i\imath\in\mathfrak{Q}} n_{i\imath}(E_{i\imath} - \overline{E}_i) = 0$ and linearizing the expression of the reduced potential (IV.19) we obtain

$$\frac{n_{i\imath} - n^{\rm e}_{i\imath}}{n^{\rm e}_{i\imath}} = \gamma_i \frac{\overline{E}_i - E_{i\imath}}{k_{\rm B}T}\boldsymbol{\nabla}\cdot\boldsymbol{v} + (E_{i\imath} - \overline{E}_i)\frac{T^{\rm tr} - T}{k_{\rm B}T^2}. \tag{IV.20}$$

Multiplying by $n^{\rm e}_{i\imath}(E_{i\imath} - \overline{E}_i)$ and summing over $\imath \in \mathfrak{Q}_i$ yields $\sum_{\imath\in\mathfrak{Q}_i} n_{i\imath}(E_{i\imath} - \overline{E}_i) = -nT\gamma_i\mathsf{x}_i c_i^{\rm int}\boldsymbol{\nabla}\cdot\boldsymbol{v} + n\mathsf{x}_i c_i^{\rm int}(T^{\rm tr} - T)$ and summing over $i \in \mathfrak{S}$ we finally obtain that [26]

$$k_{\rm B}n(T^{\rm tr} - T) = -\kappa_{[01]}\boldsymbol{\nabla}\cdot\boldsymbol{v}. \tag{IV.21}$$

We have thus recovered the 'internal energy mode' equilibrium bulk viscosity $\kappa_{[01]}$ and established the relaxation relation (IV.21) [26]. Although the kinetic framework for state-to-state mixtures of gases is much more complex than that of previous two-temperature models, a similar physical interpretation of the bulk viscosity coefficient has been obtained with (II.20), (III.25), and (IV.21).

IV.E. Bulk viscosity at first order

A similar analysis may be conducted for first order equations but is much more intricate analytically. The first order relaxation equations for the pseudo species are in the form $\omega^{(0)}_{i\imath} + \delta\omega^{(1)}_{i\imath} = -\mathsf{b}_{i\imath}\boldsymbol{\nabla}\cdot\boldsymbol{v}$, for $i\imath \in \mathfrak{Q}$, and require to evaluate the perturbed source term $\delta\omega^{(1)}$ in the neighborhood of equilibrium. The resulting analytical expressions and the resulting relaxation approximation have been obtained as well as identification of the equilibrium limit with the traditional bulk viscosity using notably the basis vectors ϕ^{0010k}, $k \in \mathfrak{S}$, and ϕ^{0001k}, $k \in \mathfrak{S}^p$, the blocks $K_{[01]} = K^{0101}$ K^{0110}, K^{1010} and K^{1001} of the K matrix as well as the Schur complement $\widehat{K}_{[01]} = K^{0101} - K^{0110}(K^{1010})^{-1}K^{1001}$.

V. NUMERICAL EXPERIMENTS FOR THE SIMPLIFIED TWO-TEMPERATURE MODEL

The results derived in Section II are assessed against numerical experiments for a model gas. Results are obtained by solving the appropriate Boltzmann transport equation via Monte Carlo methods [23, 35, 37–40]. The transport properties of the model system are investigated by looking at the spontaneous fluctuations at thermal equilibrium [35, 55–57]. Interestingly, the dynamics of spontaneous fluctuations can actually be probed by light scattering experiments [57–59].

V.A. Kinetic theory of spontaneous fluctuations

We consider a fluctuating gas near equilibrium and the dynamics of the fluctuations of a variable $A(\mathbf{r},t)$ is investigated by using the space-time correlation function

$$\delta A^2(\mathbf{r},t;\mathbf{r}',t') =< \delta A(\mathbf{r},t)\delta A(\mathbf{r}',t') >, \tag{V.1}$$

where $< ... >$ means ensemble average and $\delta A(\mathbf{r},t) = A(\mathbf{r},t) - < A(\mathbf{r},t) >$ is the fluctuation of the dynamic variable. For an isotropic system in thermodynamic equilibrium the correlation function depends only on the space-time distance

$$\delta A^2(\mathbf{r},t;\mathbf{r}',t') = \delta A^2(|\mathbf{r}-\mathbf{r}'|,t-t'). \tag{V.2}$$

In particular, the quantity actually measured in light (or neutron) scattering experiments is the Laplace-Fourier transform of the correlation function of density fluctuations, the spectral density (or power spectrum) of these fluctuations [57]

$$\delta n^2(k,\omega) = \int e^{\mathrm{i}(\boldsymbol{k}\cdot\mathbf{r}-\omega t)}\delta n^2(\mathrm{r},t)d\mathbf{r}dt. \tag{V.3}$$

Since the equilibrium fluctuations of the fluid variables are small compared to the average values, their dynamics is governed by the same equations that govern the dynamics of the system, but linearized around the equilibrium solution. These linearized equations are then doubly Laplace-Fourier transformed to the (k,ω) space and are solved for $\widetilde{\delta\rho_k}(s=\epsilon+i\omega)$. The latter is used to construct the space time correlation function $< \delta\rho_k^*(0)\widetilde{\delta\rho_k}(s) >$.

Finally, this correlation function may be connected with the density fluctuation power spectrum $S(k,\omega)$ that is a quantity experimentally measurable in light scattering experiments

$$\frac{S(k,\omega)}{S(k)} = 2Re\lim_{\epsilon\to 0}\frac{< \delta\rho_k^*(0)\widetilde{\delta\rho_k}(s) >}{< \delta\rho_k^*(0)\delta\rho_k(0) >}. \tag{V.4}$$

For thermal fluctuations in gases, the ratio of the fluctuation wavelength to the mean free path defines the flow regime (from high to low ratios: hydrodynamic, kinetic, collisionless). Different regimes are described by different values of the parameter $y = (8/3\sqrt{2}\pi)\rho_0\sqrt{k_BT/m}/\eta k$ where ρ_0 is the equilibrium density, η is the shear viscosity and k is the fluctuation wavenumber. The collisionless limit corresponds to $y \to 0$, whereas the hydrodynamic limit ($k \to 0$) is approached for $y \geqslant 5$. In the following we derive the thermal fluctuation power spectra in the hydrodynamic regime as obtained by the one temperature model and the two temperature model fluid equations.

V.B. Simulation of spontaneous fluctuations in a dilute gas

The fluctuation power spectrum for a one-temperature fluid described Navier Stokes equations is reported in the book by J.P. Boon and S. Yip [55] whereas for the simplified two temperature model it is reported in [23]. The general method to derive such fluctuation power spectrum is to start from the fluid equation, to linearize near equilibrium, to take the Fourier transform in space and then the Laplace transform in time and the results are typically in the form

$$< \delta\rho_k^*(0)\widetilde{\delta\rho_k}(s) >= \frac{N(k,s)}{M(k,s)} < \delta\rho_k^*(0)\delta\rho_k(0) > . \tag{V.5}$$

where $M(k,s)$ and $N(k,s)$ are polynomials in s.

On the other hand, at the molecular level, thermodynamic fluctuations in gases, provided the density is low enough that only bimolecular collisions are effective, are described by the Boltzmann equation. In the case of the Boltzmann equation, the system is described in terms of the one-particle distribution function. By linearizing the equation around the equilibrium distribution a integro-differential equation for the space-time correlation of the fluctuations of the distribution function is obtained [60]. The density fluctuations are then readily obtained by integration over the velocity space.

For the simulation of the spontaneous fluctuations in a gas in thermodynamic equilibrium we use the Direct Simulation Monte Carlo method [34–36]. DSMC is a particle simulation method that solves the nonlinear Boltzmann equation. As such, it can simulate flows in the rarefied and/or hypersonic regime that cannot be dealt with in the framework of a fluid-dynamic treatment. Besides, it can handle situations of strong thermal nonequilibrium where

a clear hierarchy of relaxation times cannot be established and rate equation methods fail [40]. The principle of the method is the decoupling, over a small time-step, of the processes of free flight and of collisional relaxation. A number of simulated particles are moved in the simulation domain according to their velocities and to prescribed boundary conditions. In the collision step, particles are made to collide inside spatially homogeneous cells. A Monte Carlo method is used to realize collision events with the appropriate frequency. The details of the molecular processes occurring in the gas system are specified by assigning the appropriate set of collision cross sections. The viscosity and diffusion coefficients of the gas can be modeled by the Variable Soft Sphere model of Koura [61].

The power spectrum of the fluctuations of the dynamic variable $n(\mathbf{r},t)$ is evaluated as follows. The variable fluctuations at all sampled space-time points, $\delta n_{ij} = n_{ij} - n_0$, are recorded during the simulation, n_0 being the equilibrium value. This discrete set is then Fourier transformed and squared to get the discrete power spectrum. For an isotropic medium, it is sufficient to simulate a one-dimensional spatial domain. Also, for obvious reasons, the number of simulated particles is much less than the number of real particles present in the physical volume. The ratio of real to simulated particle number is called the weight w of the simulated particle and it is a constant throughout the simulation. Now, since the density fluctuations are proportional to the gas density [62], i.e., given the volume, to the number of particles, the simulated fluctuations are equal to the real fluctuations to within a factor w. Therefore, the spectrum sampled by the simulation is exactly equivalent, to within normalization factors, to the spectrum measured in light scattering experiments. In order to reduce the statistical scatter inherent in the particle simulation method ensemble averaging of the results is performed by averaging the results of many independent runs. This procedure allows also to estimate the variance of the results with respect to the statistical scatter. It is worth mentioning that this procedure is amenable to implementation on a computational grid. The GRID infrastructure allows hundreds of runs to be performed simultaneously, thus reducing drastically the global computational time. The simulations of this work, in particular, have been done under the Compchem Virtual Organisation and more details on the computational procedures may be found in [23].

V.C. Simulations for a model gas

A single gas of Hard Spheres is considered with $mass = 28.9641\ amu$, $\sigma = 7.2 \cdot 10^{-19}\ m^2$. The gas has two internal energy levels with degeneracies and energies given by

$$a_0 = 1, \qquad E_0 = 0\ J, \tag{V.6}$$

$$a_1 = 9, \qquad E_1 = k_{\text{B}} \cdot 1000\ J. \tag{V.7}$$

Molecules exchange internal energy in collision according to the simplest single-quantum, line-of-centers model

$$p(0 \leftarrow 1) = p_0, \tag{V.8}$$

$$p(1 \leftarrow 0) = \begin{cases} 0 & \epsilon_k < E_1 \\ a_1 p_0 (1 - \frac{E_1}{\epsilon_k}) & \epsilon_k \geq E_1 \end{cases} \tag{V.9}$$

where $\epsilon_k = \frac{1}{2}\mu g^2$ is the kinetic energy in collision. The temperature and density are chosen to be $T = 285.71\ K$ and $n = 2.4 \cdot 10^{21}\ m^{-3}$. The fluctuation spectra are sampled at the wavelength $2\pi/k = 0.02\ m$ that gives $y = 5.97$ so that the probed fluctuations fall into the hydrodynamic regime.

Two situations are analyzed. In the first case, we have chosen $p_0 = 0.01$, that gives for the relaxation time $\tau_0 \approx 7.0 \cdot 10^{-5}\ s$ ($Z \equiv \tau_0/\tau_c = 49$). Figure 1 shows the fluctuation power spectra for this case. The spectra are normalized to unit maximum value. In this case, the relaxation is slow enough that a relaxation approximation does not hold and the one-temperature model fails to describe the transport properties of the system correctly. The two-temperature model, instead, gives an adequate description of the system behaviour and the agreement with the DSMC simulations is satisfactory. Also reported for comparison is the spectrum predicted for the same gas when the internal energy relaxation is forbidden (*frozen* relaxation).

Next, we analyse a situation where relaxation of internal energy is fast enough as compared to the flow characteristic time (as determined by the speed of sound). In these conditions we expect the one-temperature model to be accurate and that the two-temperature model reduce to the former. We have chosen $p_0 = 0.1$ that gives for the relaxation time $\tau_0 = 7.0 \cdot 10^{-6}\ s$ ($Z \equiv \tau_0/\tau_c = 4.9$). Figure 2 shows the fluctuation power spectra as obtained from DSMC simulations and from the one-temperature and two-temperature models, respectively. Also shown for comparison are the spectra predicted for the same gas when the bulk viscosity contribution is neglected (i.e., $\kappa = 0$). We see that, in this case, both models describe the DSMC results accurately. Comparison with the $\kappa = 0$ case also shows that this agreement is

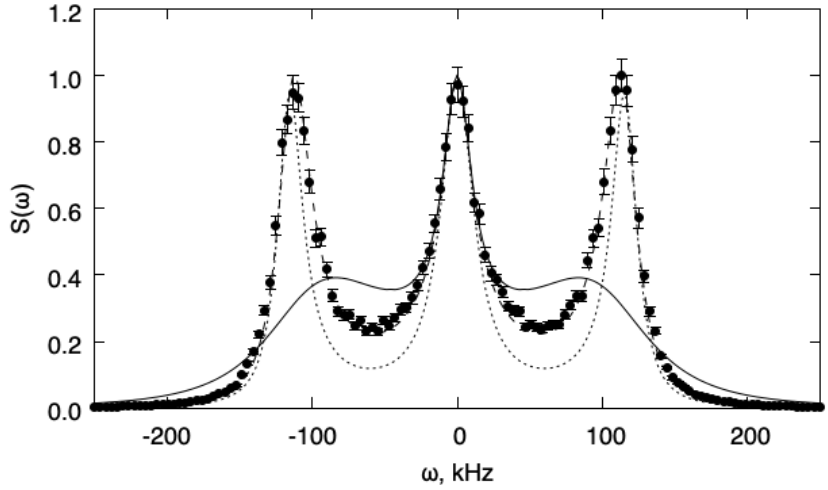

FIG. 1. Fluctuation power spectra for the slow relaxation case ($p_0 = 0.01$). The spectra are normalized to unit maximum value. Full line: 1T model; dotted line: frozen; dashed line: 2T model; symbols: DSMC.

not trivial since there is an important contribution of the bulk viscosity to the spectrum with $\frac{\kappa}{\eta} \approx 1$. Note, however, that the one-temperature model cannot describe the (small) change in the speed of sound that is a consequence of the finite relaxation time for internal energy.

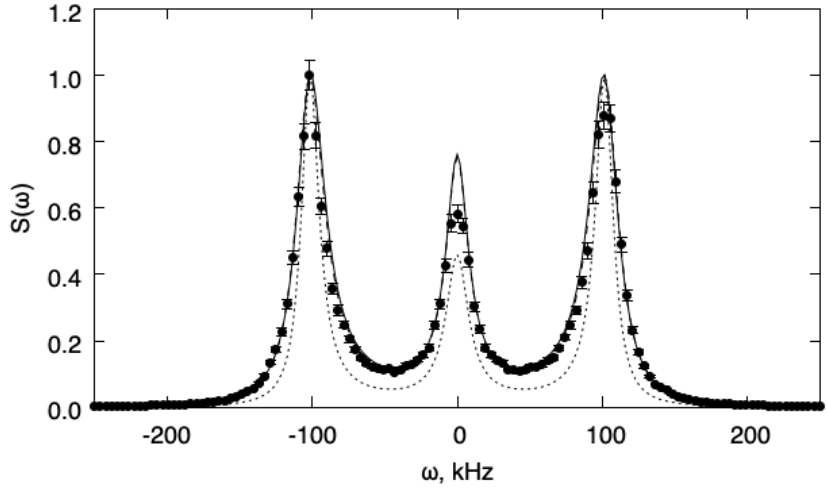

FIG. 2. Fluctuation power spectra for the fast relaxation case ($p_0 = 0.1$). The spectra are normalized to unit maximum value. Full line: 1T model; dotted line: 1T model without bulk viscosity; dashed line: 2T model; symbols: DSMC.

The statistical error in the simulation results is around 4% for the slow relaxation and 12% for the fast relaxation case, respectively. We conclude that multi-temperature hydrodynamic equations, as derived from the Boltzmann transport equation, provide an adequate description of internal energy relaxation for all values of the relaxation time. Therefore there is no need to invoke frequency dependent transport coefficients that introduce unnecessary complications. Further, the results support the conclusion, obtained by kinetic theoretical arguments in the previous sections, that the multi-temperature model reduces to the one-temperature model when the relaxation time is small enough and that only in this case a bulk viscosity formalism is adequate.

These results are also relevant in view of the renewed interest in Rayleigh-Brillouin scattering in gases made possible by the use of nonlinear optical techniques [64]. Coherent Rayleigh-Brillouin scattering is a technique capable of making localized and high signal-to-noise ratio measurements of gases from the collisionless limit to the hydrodynamic regime. CRBS data are therefore expected to become a valuable source for the study of kinetic processes in molecular gases.

VI. NUMERICAL EXPERIMENTS FOR A QUANTUM STATE POPULATION

VI.A. Internal energy spectrum and energy-exchange collisions

The kinetic model is developed for arbitrary gas mixtures $\mathfrak{S}$ and specialized to $\mathfrak{S} = \{\mathrm{He}, \mathrm{H}_2\}$ for applications. The required 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 [41–45]. 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 $\mathrm{He} + \mathrm{H}_2(v, j) \rightarrow \mathrm{He} + \mathrm{H}_2(w, k)$ 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. Particular care has been put in accuracy of trajectory calculation, with a strict checking at each step of each trajectory, in order to accurately determine the optimal time step and improve the overall computational efficiency [44]. The potential energy surface (PES) adopted in this study is the well known Muchnik-Russek [46], instead of the more recent BMP [47], used for example in a similar work by Kim *et al.* [48]. This choice is motivated by the important discrepancies found with respect to experimental data in Lee *et al.* [49]. Six billions of trajectories, using 9.5 years of CPU, have been calculated in this way on the Muchnik-Russek potential energy surface [46], using a constant density of 50000 trajectories per eV of collisional energy (uniformly distributed) and per Å of impact parameter, in the range $1\ meV - 10\ eV$, with stratified sampling applied. Comparisons with available accurate quantum-mechanical theoretical data [50] put in evidence a very good reliability starting from $0.1 - 0.5\ eV$, depending on the initial states, corresponding to a minimal temperature of about 2000 K for rate coefficients [51]. For lower values of translational energies cross sections tend to be less reliable, due to problems typical of non-reactive low energy processes treated with QCT. A specific paper on this topic is in preparation. Finally, elastic collision integrals have been taken from ref. [52].

The theoretical results of the previous sections are here specialized to the $\mathrm{He} - \mathrm{H}_2$ mixture in thermal equilibrium conditions. We have evaluated numerically the various contributions of the quantum state population as a function of temperature. The procedure is analogous to that used in a previous study on the $\mathrm{H} - \mathrm{H}_2$ mixture [25] to which the reader is referred for further details. Since a complete set of inelastic cross sections is available for the atom-diatom collisional system only, we investigated a simulated gas where $\mathrm{H}_2 - \mathrm{H}_2$ collisions are elastic. Since the resulting theoretical predictions are not amenable to experimental measurements, we resort to DSMC simulation and use Green-Kubo formulas for estimating the transport coefficients of the simulated gas.

We have simulated a $\mathrm{He} - \mathrm{H}_2$ mixture in thermal equilibrium conditions with a standard DSMC code using a majorant frequency scheme [7]. The VSS model has been used for the elastic collision cross sections, with parameters chosen to reproduce the transport coefficients in ref. [52]. The number of simulated particles is 2000 for all cases discussed. Results have been averaged over a number of independent runs in order to reduce the statistical scatter. The latter is reported in the results as the simulation's error bar.

VI.B. Green-Kubo bulk viscosity in DSMC simulations

Linear response theory is a powerful tool for the description of the relaxation towards thermodynamic equilibrium of *any* system subject to small perturbations. The fluctuation-dissipation theorem, in particular, connects the time correlation functions of mechanical quantities to the system transport properties. These relations are known as the Green-Kubo expressions for the transport coefficients [56]. This theory being independent of the mechanical model describing the system, it has been primarily applied to the evaluation of transport properties in Equilibrium Molecular Dynamics simulations of liquids [53] and solids (see, e.g. [54] and references therein). In this study we apply the Green-Kubo formulas to the evaluation of transport coefficients in DSMC simulations of dilute (i.e. ideal) gases.

For a system of volume V in equilibrium at temperature T and pressure p, the Green-Kubo formula for the bulk viscosity reads [55]:

$$\frac{4}{3}\eta + \kappa = \frac{1}{V}\frac{1}{k_{\mathrm{B}}T}\int_0^{+\infty} < (J^p_{xx}(0) - pV)(J^p_{xx}(\tau) - pV) > \, d\tau, \tag{VI.1}$$

where $< \cdots >$ denotes ensemble average, whereas that of the shear viscosity reads

$$\eta = \frac{1}{V}\frac{1}{k_{\mathrm{B}}T}\int_0^{+\infty} < J^p_{xy}(0) J^p_{xy}(\tau) > \, d\tau. \tag{VI.2}$$

The quantities J^p_{xx} or J^p_{xy}, the *currents*, are respectively any of the diagonal or off-diagonal components of the spatially-averaged, time-dependent, rank-two pressure tensor:

$$\mathbf{J}^p = \sum_i m_i \boldsymbol{C}_i \otimes \boldsymbol{C}_i - pV\boldsymbol{I}, \tag{VI.3}$$

where the sum runs over simulated particles and $\boldsymbol{C} = \boldsymbol{c}_i - \boldsymbol{v}$.

The equilibrium condition allows (via the ergodic hypothesis and stationarity) to express the integral in eq. (VI.1) as the zero-frequency limit of the current power spectrum:

$$2\int_0^{+\infty} d\tau < (J^p_{xx}(0) - pV)(J^p_{xx}(\tau) - pV) >= \lim_{T\to+\infty} \frac{1}{T}|A^p_{xx}(0)|^2, \tag{VI.4}$$

$A^p_{xx}(\omega)$ being the current Fourier transform.

In DSMC simulation, the current J^p is sampled at discrete time points then Fourier transformed with standard FFT algorithms and squared. Let P^{η_v} be the resulting zero-frequency value:

$$\frac{4}{3}\eta + \kappa = \frac{1}{V}\frac{1}{k_{\mathrm{B}}T}\frac{1}{2t_{sim}}P^{\eta_v} w \Delta_t^2. \tag{VI.5}$$

t_{sim} being the simulation duration, Δ_t the sampling time interval and w the weight of simulated particles (each particle representing w real particles). The factor w arises because the fluctuation amplitude is proportional to the square root of the number of simulated particles; the factor Δ_t^2 comes from the discrete Fourier transform.

VI.C. Results

The DSMC simulations have been performed for an equimolar mixture of helium and hydrogen with $n = 10^{20}\ m^{-3}$. The resulting bulk viscosity obtained from DSMC is presented in fig. 3 together with the equilibrium viscosity as function of temperature. The equilibrium bulk viscosity has been evaluated by using the expression

$$\kappa = \left(\frac{c^{\mathrm{int}}}{c^{\mathrm{vl}}}\right)^2 \frac{(k_{\mathrm{B}}T)^3}{2[\![(\Delta E)^2]\!]},$$

where $[\![\ ]\!]$ is the usual averaging operator and ΔE the energy jump during a collision of the simulated gas [9, 23, 25]. The DSMC calculations have been performed at temperatures $T = 6000$ K, $T = 9000$ K, and $T = 10000$ K.

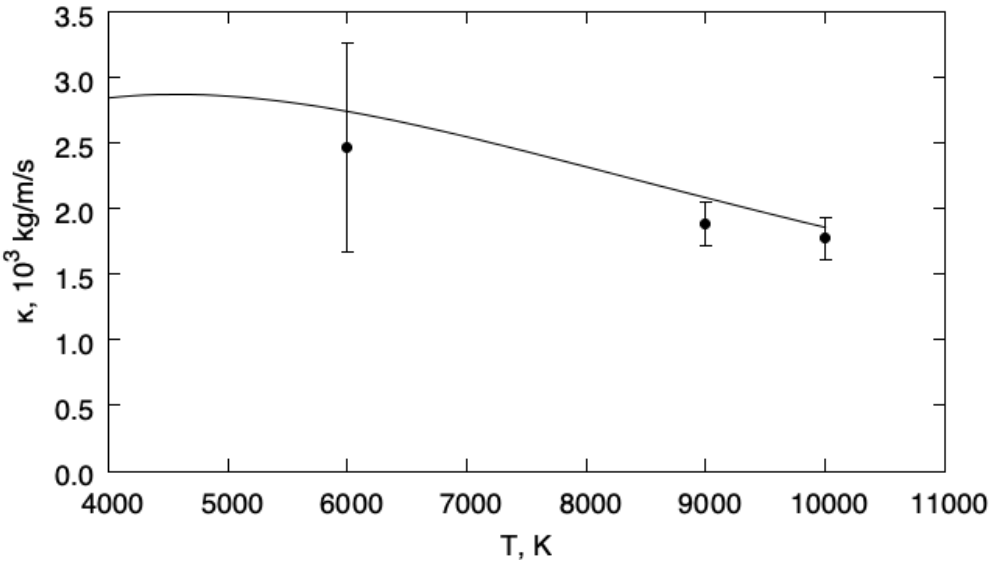

FIG. 3. Bulk viscosities. Solid line: κ^{e}; symbols: DSMC.

This figure reveals the very good agreement between the bulk viscosity of the fluctuating quantum population and the equilibrium limit, illustrating the accuracy of the least square formulation with a variational space 'compatible with the equilibrium mixture'.

VII. FLUID AND MATHEMATICAL ASPECTS

VII.A. Impact in fluid mechanics

The impact of the viscosity has scarcely been adressed in the past literature [65–68]. Karim [65] pointed out the importance of bulk viscosity coefficients and underlined that Stokes relation is only justified for *monatomic gases*. The impact of bulk viscosity on hypersonic boundary layers has also been investigated in depth by Emmanuel [66, 67]. A review of the concept of bulk viscosity and its implications for fluids over the twentieth century has been given by Graves and Argrow [68].

More recently, Billet et al. have investigated the interaction of a shock wave with an hydrogen bubble [69]. The bulk viscosity coefficient has been found to have a *major influence* on both the fluid and thermal aspects. This impact originates in particular from the thickening of pressure waves by bulk viscosity and from vorticity production when pressure and density gradients are not aligned. The artificial success of the Stokes approximation has also been related to the gradient structure of the term of $\boldsymbol{\nabla}\cdot(\kappa\boldsymbol{\nabla}\cdot\boldsymbol{v}\,\boldsymbol{I}) = \boldsymbol{\nabla}(\kappa\boldsymbol{\nabla}\cdot\boldsymbol{v})$. This term is indeed absent in boundary layers at second order and *only has a* Ma^2 influence over fluid variables. As a typical example, in a steady hydrogen-air flame, κ/η is not small, $\boldsymbol{\nabla}\cdot\boldsymbol{v}$ is not small either, but the gradient structure essentially leads to replace the hydrodynamic perturbed pressure $\widetilde{p}$ by $\widetilde{p}-\kappa\boldsymbol{\nabla}\cdot\boldsymbol{v}$ as discussed in Billet et al. [69]. Fru et al. have further investigated the small Mach situation and established that *for a long time integration* the bulk viscosity regains its major influence [70]. Two and three dimensional simulations of the interaction of a shock wave with a shear layer have further been investigated by Boukharfane et al. [71]. Finally, the interaction of a shock wave with a droplet has recently been studied by Singh et al. and bulk viscosity has again been found to play a major role [72].

Recent investigations have also shown that large values of bulk viscosity coefficients in dilute carbon dioxyde mixtures result from *erroneous applications* of relaxation relations out of their domain of validity [11, 12].

VII.B. Chapman-Enskog method for the simplified two temperature model

The system of partial differential equations (II.6)–(II.9) modeling two temperature fluids derived in Section II may be written in the convenient vector form

$$\partial_t \mathsf{u}_\epsilon + \sum_{i\in\mathcal{D}} \mathsf{A}_i(\mathsf{u})\partial_i \mathsf{u}_\epsilon - \epsilon \sum_{i,j\in\mathcal{D}} \partial_i\big(\mathsf{B}_{ij}(\mathsf{u}_\epsilon)\partial_j \mathsf{u}_\epsilon\big) - \frac{1}{\epsilon}\Omega(\mathsf{u}_\epsilon) = 0, \tag{VII.1}$$

where ∂_i is the partial derivation in the ith spatial direction, $\mathcal{D}$ the indexing ser of spatial directions, and u_ϵ the conservative variable given by

$$\mathsf{u}_\epsilon = \big(\rho,\, \rho\boldsymbol{v},\, \mathcal{E}_{\rm tr} + \mathcal{E}_{\rm int} + \tfrac{1}{2}\rho|\boldsymbol{v}|^2,\, \mathcal{E}_{\rm int}\big)^t. \tag{VII.2}$$

In these equation (VII.1), the matrix A_i is the Jacobian $\mathsf{A}_i = \partial_{\mathsf{u}}\mathsf{F}_i$ of the convective flux in the ith spatial direction F_i whereas the dissipative matrices B_{ij} are related to the dissipative fluxes $\epsilon\mathsf{F}_i^{\rm diss}$ with $\epsilon\mathsf{F}_i^{\rm diss} = -\epsilon\sum_{j\in\mathcal{D}}\mathsf{B}_{ij}(\mathsf{u}_\epsilon)\partial_j\mathsf{u}_\epsilon$. The convective flux F_i and dissipative flux $\epsilon\mathsf{F}_i^{\rm diss}$ in the ith spatial direction and source term Ω are given by

$$\mathsf{F}_i = \big(\rho v_i,\ \rho\boldsymbol{v}v_i + p\mathbf{e}_i,\ (\mathcal{E}^{\rm tr} + \mathcal{E}^{\rm int} + \tfrac{1}{2}\rho|\boldsymbol{v}|^2 + p)v_i,\ \mathcal{E}^{\rm int}v_i\big)^t, \tag{VII.3}$$

$$\epsilon\mathsf{F}_i^{\rm diss} = \big(0,\ \boldsymbol{\Pi}_i,\ Q_i^{\rm tr} + Q_i^{\rm int} + \boldsymbol{\Pi}_i\cdot\boldsymbol{v},\ Q_i^{\rm int}\big)^t = -\epsilon\sum_{j\in\mathcal{D}}\mathsf{B}_{ij}(\mathsf{u}_\epsilon)\partial_j\mathsf{u}_\epsilon, \tag{VII.4}$$

$$\frac{1}{\epsilon}\Omega = \big(0,\,\mathbf{0},\,0,\,\omega^{\rm int}\big)^t = \frac{1}{\epsilon}\big(0,\,\mathbf{0},\,0,\,\frac{\rho c^{\rm int}(T^{\rm tr}-T^{\rm int})}{\bar{\tau}^{\rm int}}\big)^t, \tag{VII.5}$$

where $\boldsymbol{\Pi}_i = (\Pi_{1i}, \Pi_{2i}, \Pi_{3i})^t$, $\boldsymbol{Q}^{\rm int} = (Q_1^{\rm int}, Q_2^{\rm int}, Q_3^{\rm int})^t$, and $\boldsymbol{Q}^{\rm tr} = (Q_1^{\rm tr}, Q_2^{\rm tr}, Q_3^{\rm tr})^t$. The convective matrices A_i, $i \in \mathcal{D}$, and the the dissipation matrices B_{ij}, that contain all the transport coefficients, are investigated in [89–91]. Both the diffusion terms and the internal energy relaxation time have naturally been rescaled in the form $\epsilon\mathsf{B}_{ij}$ and $\tau^{\rm int} = \epsilon\bar{\tau}^{\rm int}$ where ϵ is a typical Knudsen number. Two different small parameters could more generally be introduced with ϵ_d in front of the dissipation terms and ϵ for the relaxation of internal energy in (VII.1) and an independent limit with ϵ_d and ϵ may also be investihgated [89–91]. However, it is also legitimate and convenient to investigate the simpler situation where $\epsilon_d = \epsilon$ [89–92]. The dependence of the solution on the parameter ϵ has been emphasized by denoting the conservative variable in the form u_ϵ.

Symmetrized forms have been shown to be of fundamental important for analyzing the mathematical structure of hyperbolic-parabolic systems of partial differential equations modeling fluids [19, 73–88]. They are useful for a priori estimates, existence theorems [19, 73–88] as well as finite element formulations [93]. Existence of a symmetrized form is related to the existence of a mathematical entropy compatible with convective terms, dissipative terms and relaxation of energy. Symmetrized forms for the system of partial differential equations modeling two-temperature fluid (VII.1) have been comprehensively investigated under natural mathematical assumptions on thermodynamics and transport in [89–91]. Entropic as well as normal symmetrized forms have been obtained with an entropy compatible with convective, diffusive as well as source terms [89–91].

The concept of Chapman-Enskog expansion has also been extended to hyperbolic systems of partial differential equations by Liu [77] and Liu, Chen, Levermore [79] and later to hyperbolic-parabolic systems by Giovangigli and Yong [89–92]. The natural structural conditions are that there exists a mathematical entropy taken to be for convenience $\sigma = -S/R$ that is compatible with convection, diffusion as well as source terms [77, 79, 89–92]. It is also required that there exists an *equilibrium manifold* or *slow manifold* $\mathcal{E}$, characterized by the relation $T^{\rm tr} = T^{\rm int}$ for the two temperature problem, and the *slow variable* corresponding to (VII.2) reads $u_{\rm eq} = \big(\rho, \rho\boldsymbol{v}, \mathcal{E} + \frac{1}{2}\rho|\boldsymbol{v}|^2\big)^t$. For each slow variable $u_{\rm eq}$ there exists a unique $\mathsf{u}_{\rm eq}$ such that $\Pi_{\rm eq}^t\mathsf{u}_{\rm eq} = u_{\rm eq}$ where $\Pi_{\rm eq}$ is the projector operator on the slow manifold with matrix $\Pi_{\rm eq} = [\boldsymbol{e}_1, \dots, \boldsymbol{e}_4]$ with $\boldsymbol{e}_i$, $1 \le i \le 5$, denoting the canonical basis vectors of $\mathbb{R}^5$ and we also introduce for later use the projector with matrix $\Pi_{\rm rap} = [\boldsymbol{e}_5]$. The slow manifold is thus parameterized by $u_{\rm eq}$ and a careful analysis shows that the equilibrium one-temperature fluid model exactly corresponds to a second order Chapman-Enskog [89–91] of the partial differentail equations (VII.1). We thus have the following schematic diagram

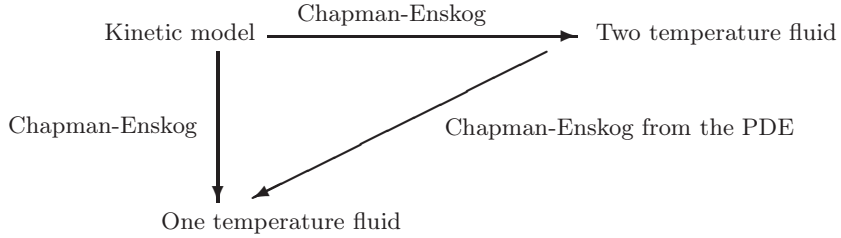

FIG. 4. Schematic diagram of the double Chapman-Enskog procedure.

The Chapman-Enskog expansion for the solution u_ϵ to the system of partial differential equation (VII.1) is notably in the form

$$\mathsf{u}_\epsilon = \sum_{i\ge 0} \epsilon^i \overline{\mathsf{u}}_i = \overline{\mathsf{u}}_0 + \epsilon\overline{\mathsf{u}}_1 + \mathcal{O}(\epsilon^2) \tag{VII.6}$$

where the zeroth order term $\overline{\mathsf{u}}_0$ coincide with u_ϵ on the slow manifold $\Pi_{\rm eq}^t\mathsf{u}_\epsilon = \Pi_{\rm eq}^t\overline{\mathsf{u}}_0 = u_{\rm eq}$, where the Enskog constraints are in the form $\Pi_{\rm eq}^t\overline{\mathsf{u}}_i = 0$ for $i \ge 1$ and where $\overline{\mathsf{u}}_i$ only depends on $\partial^\alpha\mathsf{u}_{\rm eq}$ for $|\alpha| \le i$. Combining (VII.1) with (VII.6) the equations for $\overline{\mathsf{u}}_i$, $i \ge 0$, are given by

$$\partial_t(\overline{\mathsf{u}}_0 + \epsilon\overline{\mathsf{u}}_1 + \cdots) + \sum_{i\in\mathcal{D}} \partial_i\big(\mathsf{F}_i(\overline{\mathsf{u}}_0) + \epsilon\partial_{\mathsf{u}}\mathsf{F}_i(\overline{\mathsf{u}}_0)\overline{\mathsf{u}}_1 + \cdots\big)$$
$$- \epsilon \sum_{i,j\in\mathcal{D}} \partial_i\big(\mathsf{B}_{ij}(\overline{\mathsf{u}}_0)\partial_j\overline{\mathsf{u}}_0 + \cdots\big) = \frac{1}{\epsilon}\big(\Omega(\overline{\mathsf{u}}_0) + \epsilon\partial_{\mathsf{u}}\Omega(\overline{\mathsf{u}}_0)\overline{\mathsf{u}}_1 + \cdots\big).$$

At the order -1 it is found that $\Omega(\overline{\mathsf{u}}_0) = 0$ so that $\overline{\mathsf{u}}_0$ is an equilibrium point $\overline{\mathsf{u}}_0 = \mathsf{u}_{\rm eq}(u_{\rm eq})$ and the slow variable equations are given by

$$\partial_t u_{\rm eq} + \sum_{i\in\mathcal{D}} \partial_i\big(\Pi_{\rm eq}^t\mathsf{F}_i(\overline{\mathsf{u}}_0) + \epsilon\Pi_{\rm eq}^t\partial_{\mathsf{u}}\mathsf{F}_i(\overline{\mathsf{u}}_0)\overline{\mathsf{u}}_1 + \cdots\big) - \epsilon \sum_{i,j\in\mathcal{D}} \partial_i\big(\Pi_{\rm eq}^t\mathsf{B}_{ij}(\overline{\mathsf{u}}_0)\partial_j\overline{\mathsf{u}}_0 + \cdots\big) = 0.$$

The equation at zeroth order governing $\overline{\mathsf{u}}_0$ are found to be a symmetrizable hyperbolic system, indeed Euler equations for the one-temperature fluid. The perturbed term $\overline{\mathsf{u}}_1$ is next solution of linearized equations with the Enskog constraints in the form

$$\begin{cases} \partial_{\mathsf{u}}\Omega(\overline{\mathsf{u}}_0)\overline{\mathsf{u}}_1 = \partial_t\overline{\mathsf{u}}_0 + \sum_{i\in\mathcal{D}}\partial_i\big(\mathsf{F}_i(\overline{\mathsf{u}}_0)\big), \\ \Pi^t_{\rm eq}\overline{\mathsf{u}}_1 = 0, \end{cases} \tag{VII.7}$$

and using Euler equation in order to express $\partial_t\overline{\mathsf{u}}_0$, the first order perturbation $\overline{\mathsf{u}}_1$ is found in the form

$$\overline{\mathsf{u}}_1 = -\sum_{j\in\mathcal{D}} \mathrm{M}_j\partial_j u_{\rm eq},$$

where M_j, $j\in\mathcal{D}$, are 5x4 matrices and we refer to [89–92] for more details. The first order Navier-Stokes type equations are then obtained as

$$\partial_t u_{\rm eq} + \sum_{i\in\mathcal{D}}\mathsf{A}^{\rm eq}_i(u_{\rm eq})\partial_i u_{\rm eq} - \epsilon\sum_{i,j\in\mathcal{D}}\partial_i\big(\mathsf{B}^{\rm eq}_{ij}(u_{\rm eq})\partial_j u_{\rm eq}\big) \tag{VII.8}$$

with the diffusion coefficients in the form

$$\mathsf{B}^{\rm eq}_{ij}(u_{\rm eq}) = \Pi^t_{\rm eq}\mathsf{B}_{ij}\,\partial_{u_{\rm eq}}\mathsf{u}_{\rm eq} + \Pi^t_{\rm eq}\mathsf{A}^{\rm eq}_i\mathrm{M}_j. \tag{VII.9}$$

The resulting first order accurate governing equations for the slow variable thus involves dissipative coefficients arising from perturbed convective terms $\Pi^t_{\rm eq}\mathsf{A}^{\rm eq}_i\mathrm{M}_j$ as well as inherited directly from the system out of equilibrium $\Pi^t_{\rm eq}\mathsf{B}_{ij}$. Both the bulk viscosity term arising from the perturbed convective fluxes and the shear viscosity term inherited from the out of equilibrium viscous tensor are finally involved in the equilibrium viscous tensor. For the two temperature model it is indeed found that

$$\epsilon\sum_{i\in\mathcal{D}}\partial_i\big(\Pi^t_{\rm eq}\partial_{\mathsf{u}}\mathsf{F}_i\overline{\mathsf{u}}_1\big) = -\big(0, \boldsymbol{\nabla}\cdot(\kappa\boldsymbol{\nabla}\cdot\boldsymbol{v}\boldsymbol{I}), \boldsymbol{\nabla}\cdot(\kappa\boldsymbol{\nabla}\cdot\boldsymbol{v}\,\boldsymbol{v})\big)^t, \tag{VII.10}$$

so that the bulk viscosity coefficients is exactly obtained from the perturbed out of equilibrium convective terms in the Chapman-Enskog method whereas the shear viscosity and thermal conductivity contributions are directly inherited from the out of equilibrium model [89–92].

VII.C. Multiple time expansions for the simplified two-temperature model

Exact mathematical convergence results have further been obtained for the simplified two-temperature system of equations in the form (VII.1) over the full space $\mathbb{R}^d$ for $1\leq d\leq 3$ [91, 92]. The results and the method of proof differ depending if the inital data is well prepared with $T^{\rm tr}_{\rm data} = T^{\rm int}_{\rm data}$ or ill prepared with $T^{\rm tr}_{\rm data}\neq T^{\rm int}_{\rm data}$ where $(\rho_{\rm data}, \boldsymbol{v}_{\rm data}, T^{\rm tr}_{\rm data}, T^{\rm int}_{\rm data})^t$ denotes the variable at initial time $t=0$. Both the well prepared situation [91] and the ill prepared situations [92] have been investigated and only the ill prepared situation results are summarized in this section.

Existence of solutions to the Cauchy problem with ill prepared initial data has been established as well as the validity of asymptotic composite expansions including initial-layer correctors. The results may conveniently been presented using the variable

$$w_\epsilon = \Big(\rho,\, \rho\boldsymbol{v},\, \mathcal{E}_{\rm tr}+\mathcal{E}_{\rm int}+\tfrac{1}{2}\rho|\boldsymbol{v}|^2,\, \frac{1}{T^{\rm tr}} - \frac{1}{T^{\rm int}}\Big)^t = (u_\epsilon, q_\epsilon)^t, \tag{VII.11}$$

with the slow u_ϵ and fast q_ϵ components given by

$$u_\epsilon = \Pi^t_{\rm eq}w_\epsilon = \Pi^t_{\rm eq}\mathsf{u}_\epsilon = \Big(\rho, \rho\boldsymbol{v}, \mathcal{E}_{\rm tr}+\mathcal{E}_{\rm int}+\tfrac{1}{2}\rho|\boldsymbol{v}|^2\Big)^t$$

$$q_\epsilon = \Pi^t_{\rm rap}w_\epsilon = \frac{1}{T^{\rm tr}} - \frac{1}{T^{\rm int}}.$$

Multiple time expansions have been introduced in the form

$$w_\epsilon = w_0(t,\boldsymbol{x}) + \epsilon w_1(t,\boldsymbol{x}) + w^{\rm il}_0(t/\epsilon,\boldsymbol{x}) + \epsilon w^{\rm il}_1(t/\epsilon,\boldsymbol{x}) + \mathcal{O}(\epsilon^2), \tag{VII.12}$$

with an *outer expansion* involving the *standard time* t

$$\boldsymbol{w}_0(t,x)+\epsilon\boldsymbol{w}_1(t,x)+\mathcal{O}(\epsilon^2), \tag{VII.13}$$

as well as *initial layer correctors* involving the fast time $\tau=t/\epsilon$ in the form

$$\boldsymbol{w}_0^{\rm il}(\tau,x)+\epsilon\boldsymbol{w}_1^{\rm il}(\tau,x)+\mathcal{O}(\epsilon^2), \tag{VII.14}$$

and such that $\boldsymbol{w}_0^{\rm il}$ and $\boldsymbol{w}_1^{\rm il}$ are *exponentially decreasing* with respect to the fast time $\tau=t/\epsilon$. The equations governing each of the asymptotic expansion coefficients u_0, u_1, q_0, q_1 and q_2 where $\boldsymbol{w}_0=(u_0,q_0)^t$, $\boldsymbol{w}_1=(u_1,q_1)^t$, $\boldsymbol{w}_2'=(0,q_2)^t$ may be obtained. The proper initial and boundary conditions may also be written by first expanding the initial conditions

$$\boldsymbol{w}_{\rm data}=\boldsymbol{w}_{\rm data0}+\epsilon\boldsymbol{w}_{\rm data1}+\mathcal{O}(\epsilon^2),$$

where $\boldsymbol{w}_{\rm data}=(u_{\rm data},q_{\rm data})^t$ and then identifying $\boldsymbol{w}_0(\cdot,0)+\boldsymbol{w}_0^{\rm il}(\cdot,0)=\boldsymbol{w}_{\rm data0}$ and $\boldsymbol{w}_1(\cdot,0)+\boldsymbol{w}_1^{\rm il}(\cdot,0)=\boldsymbol{w}_{\rm data1}$ so that in particular $u_0(\cdot,0)=u_{\rm data0}$, $q_0(\cdot,0)=0$, $u_0^{\rm il}(\cdot,0)=0$, and $q_0^{\rm il}(\cdot,0)=q_{\rm data0}$. The mathematical structure of the hyperbolic type equations governing u_0 and u_1 then guarantee the existence of solutions over a finite time interval $[0,\bar t\,]$ under natural regularity assumptions [89–92]. An important role is notably played by the mathematical entropy that allows symmetrization of the corresponding systems of partial differential equations that is taken in the form $\sigma=-\mathcal{S}/R$ for convenience. In addition, the initial layer correctors are shown to satisfy systems of differential equations with respect to the fast time. Existence of exponentially decreasing global solution is then obtained by using the entropy as a Lyapunov function [92]. An important tool has also been the use of an improved truncated approximation in the form

$$\boldsymbol{w}_\epsilon^{\rm a}=\boldsymbol{w}_0+\epsilon\boldsymbol{w}_1+\epsilon^2\boldsymbol{w}_2'+\boldsymbol{w}_0^{\rm il}+\epsilon\boldsymbol{w}_1^{\rm il}, \tag{VII.15}$$

including a fast component of the second order term $\boldsymbol{w}_2'=(0,q_2)^t$

It is then established that the out of equilibrium solution exists avec a finite time interval $[0,\bar t\,]$ and the truncated approximation is second order accurate with $\sup_{t\in[0,\bar t\,]}|\boldsymbol{w}_\epsilon(t)-\boldsymbol{w}_\epsilon^{\rm a}(t)|_{L^\infty}\le C\epsilon^2$ where C is a finite constant and $|\mathsf{f}|_{L^\infty}=\sup_{\boldsymbol{x}\in\mathbb{R}^d}|\mathsf{f}(\boldsymbol{x})|$ denotes the L^∞ norm of a function f over $\mathbb{R}^d$.

It may also be established that the Hilbert type expansion $u_0+\epsilon u_1$ and the Chapman-Enskog solution at equilibrium $u_{\rm eq}$ are $\mathcal{O}(\epsilon^2)$ close so that

$$\sup_{t\in[0,\bar t\,]}\big|u_{\rm eq}(t)-\big(u_0(t)+\epsilon u_1(t)\big)\big|_{L^\infty}\le C\epsilon^2.$$

Combining these results it is then obtained that if $u_\epsilon=\Pi^t_{\rm eq}\boldsymbol{w}_\epsilon=\Pi^t_{\rm eq}\mathsf{u}_\epsilon$ then for ϵ small enough

$$\sup_{t\in[0,\bar t\,]}\big|u_\epsilon(\cdot,t)-(u_{\rm eq}(\cdot,t)+\epsilon u_1^{\rm il}(\cdot,t/\epsilon))\big|_{L^\infty}\le C\epsilon^2.$$

In other words, the out of equilibrium slow variable u_ϵ is $\mathcal{O}(\epsilon^2)$ close to the Chapman-Enskog solution at equilibrium $u_{\rm eq}$ up to a first order term $\epsilon u_1^{\rm il}(\cdot,t/\epsilon))$ that is exponentially decreasing with respect to the fast time $\tau=t/\epsilon$ [92]. The zeroth order initial layer corrector is also governed by the ordinary differential equation in the form $\partial_\tau(T^{\rm tr}-T^{\rm int})=-\frac{c_{\rm vl}}{c_{\rm tr}\tau^{\rm int}}(T^{\rm tr}-T^{\rm int})$ so that assuming for the sake of illustration that $c_{\rm int}$ and $\tau^{\rm int}$ constant we obtain that

$$T^{\rm tr}(\tau)=T+\big(T^{\rm tr}(0)-T(0)\big)\exp\Big(-\frac{c_{\rm vl}}{c_{\rm tr}}\,\frac{\tau}{\tau^{\rm int}}\Big),$$

and we also have $q_1=\frac{T^{\rm int}\tau^{\rm int}}{c_{\rm tr}(T^{\rm tr})^2+c_{\rm int}(T^{\rm int})^2}\,\boldsymbol{\nabla}\cdot\boldsymbol{v}$ that yields the bulk viscosity contributions of (VII.10).

The mathematical theoretical results obtained concerning the Chapman-Enskog solution are thus in full agreement with the physical framework. Making a parallel with the traditional Chapman-Enskog, we may say that the slow or fluid variable is the one-temperature fluid variable $u_{\rm eq}$, the Mawellian distribution is thecorresponding equilibrium two-temperature fluid variable $\mathsf{u}_{\rm eq}$, the linearized Boltzmann equations are replaced by (VII.7), and the resulting dissipative coefficients have two different sources with (VII.9).

VIII. CONCLUSION

We have investigated the relaxation of internal temperature and the concept of bulk viscosity in nonequilibrium gas models derived from the kinetic theory. When the rates for internal energy exchanges are smaller than the fluid time, a common interpretation of the apparition of the bulk viscosity coefficient has been obtained with (II.20), (III.25), and (IV.21). The Monte Carlo simulations of spontaneous fluctuations near thermal equilibrium obtained by solving the Boltzmann equation have been shown to be in full agreement with the theoretical results. Mathematical aspects of internal energy elaxation have also been discussed for a two-temperature fluid mopdel and found to agree with the formal expansions. Future work should consider numerical simulations with multiple internal energy modes and more generally states far from thermodynamic equilibrium.

Appendix A: The one-temperature two-mode bulk viscosity

We investigate in this section the bulk viscosity associated with a one-temperature two-mode polyatomic gas. The standard linear system associated with the evaluation of the two-mode bulk viscosity is obtained with the Galerkin variational approximation space spanned by the orthogonal polynomials $\phi^{0010} = \frac{3}{2} - \frac{1}{2}\frac{m}{k_{\rm B}T}|\boldsymbol{c}-\boldsymbol{v}|^2$, $\phi^{0001{\rm rap}} = (\overline{E}^{\rm rap} - E_{\rm I}^{\rm rap})/k_{\rm B}T$, and $\phi^{0001{\rm sl}} = (\overline{E}^{\rm sl} - E_{\rm I}^{\rm sl})/k_{\rm B}T$. The general solution of the Transport Linear Systems as well as their mathematical structure has been investigated [32, 33]. The modes are termed 'rapid' and 'slow' for notational consistency with the nonequilibrium framework of Section III, but in the thermodynamic equilibrium framework they are all fast. The corresponding linear system of size 3 is in the form [33]

$$\left\{\begin{array}{l} K\alpha = \beta, \\ \langle \mathcal{K}, \alpha\rangle = 0, \end{array}\right. \tag{A.1}$$

where K denotes the system matrix, $\mathcal{K}$ the constraint vector, $\alpha = (\alpha^{10}, \alpha^{01{\rm rap}}, \alpha^{01{\rm sl}})^t$ the unknown vector, $\beta = (\beta^{10}, \beta^{01{\rm rap}}, \beta^{01{\rm sl}})^t$ the right hand side vector, and the bulk viscosity is finally given by $\kappa = \alpha^{10}\beta^{10} + \alpha^{01{\rm rap}}\beta^{01{\rm rap}} + \alpha^{01{\rm sl}}\beta^{01{\rm sl}}$. The matrix K is positive semi-definite with nullspace $N(K) = \mathbb{R}\mathcal{V}$ where $\mathcal{V} = (1,1,1)^t$, the constraint vector is given by $\mathcal{K} = (c^{\rm tr}, c^{\rm rap}, c^{\rm sl})^t$, and the right hand side vector by $\beta = (c^{\rm rap} + c^{\rm sl}, -c^{\rm rap}, -c^{\rm sl})^t/c^{\rm vl}$.

We deduce from the constraint $\langle \mathcal{K}, \alpha\rangle = 0$ that $c^{\rm tr}\alpha^{10} + c^{\rm rap}\alpha^{01{\rm rap}} + c^{\rm sl}\alpha^{01{\rm sl}} = 0$ and $\kappa = -(c^{\rm rap}\alpha^{01{\rm rap}} + c^{\rm sl}\alpha^{01{\rm sl}})/c^{\rm tr}$. We may thus recast the singular linear system of size 3 into a regular linear system of size 2 involving only the unknowns $\alpha^{01{\rm rap}}$ and $\alpha^{01{\rm sl}}$. Thanks to the vector relation $K\mathcal{V} = 0$, the coefficients of this linear system may also be expressed solely in terms of $K^{\rm rap,rap}$, $K^{\rm rap,sl}$, and $K^{\rm sl,sl}$. We also have the relations $K^{\rm rap,rap} = 2[\![(\Delta E^{\rm rap})^2]\!]/(k_{\rm B}T)^3$, $K^{\rm rap,sl} = 2[\![(\Delta E^{\rm rap})(\Delta E^{\rm sl})]\!]/(k_{\rm B}T)^3$, and $K^{\rm sl,sl} = 2[\![(\Delta E^{\rm sl})^2]\!]/(k_{\rm B}T)^3$, where $\Delta E^{\rm rap} = E_{\rm I'}^{\rm rap} + E_{\rm J'}^{\rm rap} - E_{\rm I}^{\rm rap} - E_{\rm J}^{\rm rap}$ and $\Delta E^{\rm sl} = E_{\rm I'}^{\rm sl} + E_{\rm J'}^{\rm sl} - E_{\rm I}^{\rm sl} - E_{\rm J}^{\rm sl}$.

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

$$\kappa = \frac{1}{(c^{\rm vl})^2}\frac{(c^{\rm rap})^2K^{\rm sl,sl} - 2c^{\rm rap}c^{\rm sl}K^{\rm rap,sl} + (c^{\rm sl})^2K^{\rm rap,rap}}{K^{\rm rap,rap}K^{\rm sl,sl} - K^{\rm rap,sl}K^{\rm rap,sl}}. \tag{A.2}$$

Since we have to investigate the equilibrium limit of a two temperature model where one mode is fast and another one slow, we deduce that the coefficient $K^{\rm rap,rap}$ is large and that the cross terms $K^{\rm rap,sl} = K^{\rm sl,rap}$ are also small. We therefore neglect the square term $K^{\rm sl,rap}K^{\rm rap,sl}$ in the previous expression and the limiting value of the effective nonequilibrium bulk viscosity should thus be

$$\kappa = \Big(\frac{c^{\rm rap}}{c^{\rm vl}}\Big)^2\frac{(k_{\rm B}T)^3}{2[\![(\Delta E^{\rm rap})^2]\!]} - \frac{c^{\rm rap}c^{\rm sl}}{(c^{\rm vl})^2}\frac{(k_{\rm B}T)^3[\![(\Delta E^{\rm rap})(\Delta E^{\rm sl})]\!]}{[\![(\Delta E^{\rm rap})^2]\!][\![(\Delta E^{\rm sl})^2]\!]} + \Big(\frac{c^{\rm sl}}{c^{\rm vl}}\Big)^2\frac{(k_{\rm B}T)^3}{2[\![(\Delta E^{\rm sl})^2]\!]}. \tag{A.3}$$

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