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**RELAXATION OF
INTERNAL TEMPERATURE
AND VOLUME VISCOSITY**

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Relaxation of Internal Temperature and Volume Viscosity

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Abstract

We investigate the relaxation of internal temperature and the concept of volume viscosity in nonequilibrium gas models derived from the kinetic theory. We first investigate a nonequilibrium gas model with two temperatures—translational and internal—where the volume viscosity is absent. We establish that, in a relaxation regime, the temperature difference becomes proportional to the divergence of the velocity fields and define a nonequilibrium, multitemperature, volume viscosity coefficient. We next analyze the convergence of the two temperature model towards the one temperature model when the relaxation is fast. We then investigate a nonequilibrium two temperature gas model with a fast and a slow internal energy mode. We establish that, in a relaxation regime, there are four contributions to the volume viscosity, namely the fast internal mode volume viscosity, the slow internal mode volume viscosity, the relaxation pressure and the perturbed source term. In the thermodynamic equilibrium limit, the sum of these four terms converges toward the one-temperature two-mode volume viscosity. We finally perform Monte Carlo simulations of spontaneous fluctuations near thermodynamic equilibrium. The numerical results obtained from the Boltzmann equation are compared to the predictions of the one and two temperature fluid models and the agreement between theory and calculations is complete.

1 Introduction

We investigate in this paper the relaxation of internal and translational temperatures as well as the concept of volume viscosity in nonequilibrium gas models derived from the kinetic theory.

We first study a two-temperature kinetic model where elastic and resonant collisions are fast but collisions exchanging energy between the translational and the internal modes are slow. In such a framework, the translational and internal temperatures are macroscopic quantities associated with collisional invariants of the fast collision operator and there is no volume viscosity term in the viscous tensor unlike with one-temperature polyatomic models [1, 2, 3, 4, 5, 6, 7, 8, 9, 10]. In order to investigate this point, we introduce a relaxation regime where the temperature difference becomes proportional to the divergence of the velocity field and define a new volume viscosity coefficient involving the two temperatures as well as nonlinear effects associated with the kinetics of relaxation. We further discuss higher order effects associated with heat conductivity, viscous dissipation and perturbed source terms, and we evaluate the translational and internal entropies per unit volume and the corresponding Gibbs relations. In the limiting situation of fast relaxation, we recover the classical one-temperature model including the volume viscosity coefficient. Theoretical models as well as experimental measurements of the volume viscosity have confirmed that this coefficient is of the order of the shear viscosity for polyatomic gases [11, 12, 13, 14, 15] and the impact of volume viscosity in fluid mechanics—especially for fast flows—has been established [16, 17, 18, 19, 20].

We then investigate a two-temperature kinetic model with two internal energy modes, one with a slow exchange rate and one with a fast exchange rate. In this situation, there is a volume viscosity due to the fast internal energy mode as in classical one-temperature models. However, part of the thermodynamic equilibrium volume viscosity is still hidden in the slow internal modes. A detailed analysis yields that, in a relaxation regime, there are four contributions to the effective volume viscosity, namely the fast internal mode volume viscosity, the slow internal mode volume viscosity, the relaxation pressure and the perturbed source term. In the thermodynamic equilibrium limit, the sum of these four contributions coincide with the one-temperature two-mode volume viscosity.

We finally perform Monte Carlo simulations of spontaneous fluctuations near thermodynamic equilibrium to investigate the transport properties of a model polyatomic gas [21, 22]. We integrate the full Boltzmann transport equation with a Monte Carlo method [23, 24, 25, 26, 27] for a model gas

with internal degrees of freedom. The results obtained from the numerical solution of the Boltzmann equation are compared to the predictions of the one and two temperature fluid models.

When the characteristic time of internal energy relaxation is larger than the flow characteristic time, the two temperature model gives an accurate description of the system and the one temperature model fails. On the other hand, when the characteristic time of internal energy relaxation is smaller than the flow time, both the two temperature model and the one temperature model *including the volume viscosity* are adequate to describe the fluid. The agreement between theory and calculations is complete and these calculations also confirm the importance of the volume viscosity coefficient.

The nonequilibrium two-temperature model is considered in Section 2 and the two-temperature two-mode nonequilibrium model in Section 3. The numerical method and the numerical results are finally presented in Section 4.

2 A Two-Temperature Kinetic Model

We investigate in this section a nonequilibrium kinetic model for a polyatomic gas with a slow energy exchange rate between the translational and internal degrees of freedom. In such a two-temperature kinetic model, the macroscopic temperatures are defined with the kinetic energy and internal energy collisional invariants. The corresponding viscous tensor then does not contain any volume viscosity term. In order to recover such an effect, we introduce a relaxation equation of the temperature difference and define a new volume viscosity coefficient involving the two temperatures as well as nonlinear effects associated with the kinetics of relaxation. In the limiting situation of fast relaxation, we recover the one temperature model.

2.1 A multi-temperature kinetic framework

Thermodynamic nonequilibrium is of fundamental importance in reentry problems, laboratory and atmospheric plasmas, as well as discharges. 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 [28, 29, 30, 31, 32, 33, 34, 35, 36, 37]. When there are partial equilibria between some of these states, species internal energy temperatures can be defined and the complexity of the model is correspondingly reduced [30, 31, 32, 33, 34, 35, 36, 37]. Another example is that of electron temperature in plasmas [38, 39, 40, 41, 42, 43, 44]. The next reduction step then consists in equating some of the species internal temperatures [35] and it yields the two temperature models investigated in this paper.

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

$$\partial_t f + \mathbf{c} \cdot \nabla f = \frac{1}{\epsilon} \mathcal{J}^{\text{rap}} + \mathcal{J}^{\text{sl}}, \quad (2.1)$$

where t denotes time, ∂_t the time derivative operator, \mathbf{x} the spatial coordinate, ∇ the space derivative operator, \mathbf{c} the particle velocity, $f(t, \mathbf{x}, \mathbf{c}, \mathfrak{l})$ the distribution function, \mathfrak{l} the index of the quantum energy state, \mathcal{J}^{rap} the rapid collision operator, \mathcal{J}^{sl} the slow collision operator, and ϵ the formal parameter associated with the Chapman-Enskog procedure. We assume for the sake of simplicity that the particles are not influenced by an external force field.

The complete collision operator $\mathcal{J} = \mathcal{J}^{\text{rap}} + \mathcal{J}^{\text{sl}}$ is in the form

$$\mathcal{J}(f) = \sum_{\mathfrak{l}, \mathfrak{l}', \mathfrak{j}} \int (f(\mathbf{c}', \mathfrak{l}') f(\tilde{\mathbf{c}}, \mathfrak{j}) \frac{a_{\mathfrak{l}} a_{\mathfrak{j}}}{a_{\mathfrak{l}'} a_{\mathfrak{j}'}} - f(\mathbf{c}, \mathfrak{l}) f(\tilde{\mathbf{c}}, \mathfrak{j})) g \sigma^{\mathfrak{l}\mathfrak{l}'\mathfrak{j}\mathfrak{j}'} d\tilde{\mathbf{c}} d\mathbf{e}', \quad (2.2)$$

where *in a direct collision* \mathfrak{l} and \mathfrak{j} denote the indices of the quantum energy states before collision, \mathfrak{l}' and \mathfrak{j}' the corresponding numbers after collision, $\tilde{\mathbf{c}}$ the velocity of the colliding partner, \mathbf{c}' and $\tilde{\mathbf{c}}'$ the velocities after collision, $a_{\mathfrak{l}}$ the degeneracy of the \mathfrak{l} th quantum energy state, $\sigma^{\mathfrak{l}\mathfrak{l}'\mathfrak{j}\mathfrak{j}'}$ the collision cross section, g the absolute value of the relative velocity $\mathbf{c} - \tilde{\mathbf{c}}$ of the incoming particles and \mathbf{e}' the unit vector in the direction of the relative velocity $\mathbf{c}' - \tilde{\mathbf{c}}'$ after collision. Conversely, for *inverse collisions*, the primed quantities denote the state before collision and the unprimed quantities after collision. Only binary collisions are considered since the system is dilute and the cross sections satisfy the reciprocity relations [3, 7]

$$a_{\mathfrak{l}} a_{\mathfrak{j}} g \sigma^{\mathfrak{l}\mathfrak{l}'\mathfrak{j}\mathfrak{j}'} d\mathbf{c} d\tilde{\mathbf{c}} d\mathbf{e}' = a_{\mathfrak{l}'} a_{\mathfrak{j}'} g \sigma^{\mathfrak{l}'\mathfrak{j}'\mathfrak{l}\mathfrak{j}} d\mathbf{c}' d\tilde{\mathbf{c}}' d\mathbf{e}. \quad (2.3)$$

Denoting by $W^{\mathbb{W}'J'}$ the transition probability for collisions, we also have the identity $g\sigma^{\mathbb{W}'J'}d\mathbf{e}' = W^{\mathbb{W}'J'}d\mathbf{c}'d\tilde{\mathbf{c}}'$ so that the collision terms may equivalently be written in terms of transition probabilities [7].

Denoting by E_i the internal energy of the particle in the i th state, the rapid collisions are either elastic without any change of internal energy levels $E_{i'} = E_i$ and $E_{j'} = E_j$, or resonant with $E_i + E_j = E_{i'} + E_{j'}$ where $E_{i'} \neq E_i$ and $E_{j'} \neq E_j$, whereas the slow collisions are such that $\Delta E = E_{i'} + E_{j'} - E_i - E_j \neq 0$. We denote by $\mathcal{J}^{\text{tr-tr}}$ the operator associated with elastic collision, $\mathcal{J}^{\text{int-int}}$ the operator associated with resonant collisions, and $\mathcal{J}^{\text{tr-int}}$ the operator associated with collisions such that $\Delta E \neq 0$. These operators $\mathcal{J}^{\text{tr-tr}}$, $\mathcal{J}^{\text{int-int}}$, and $\mathcal{J}^{\text{tr-int}}$, are in the form (2.2) with the summation restricted to elastic, resonant, and non elastic non resonant collisions, respectively, and the fast and slow collision operators are then $\mathcal{J}^{\text{rap}} = \mathcal{J}^{\text{tr-tr}} + \mathcal{J}^{\text{int-int}}$ and $\mathcal{J}^{\text{sl}} = \mathcal{J}^{\text{tr-int}}$. The collisional invariants of the fast collision operator are now associated with particle number $\psi^1 = 1$, momentum $\psi^{1+\nu} = m\mathbf{c}_\nu$, $\nu \in \{1, 2, 3\}$, as well as kinetic energy $\psi^5 = \psi^{\text{tr}}$ and internal energy $\psi^6 = \psi^{\text{int}}$, where $\psi^{\text{tr}} = \frac{1}{2}m(\mathbf{c} - \mathbf{v}) \cdot (\mathbf{c} - \mathbf{v})$ and $\psi^{\text{int}} = E_i$.

The Enskog expansion is in the form $f = f^{(0)}(1 + \epsilon\phi + \mathcal{O}(\epsilon^2))$ where $f^{(0)}$ is the Maxwellian distribution. This Maxwellian distribution involves two temperatures and is in the form

$$f^{(0)} = \left(\frac{m}{2\pi k_{\text{B}} T^{\text{tr}}}\right)^{\frac{3}{2}} \frac{na_1}{Z^{\text{int}}} \exp\left(-\frac{m(\mathbf{c} - \mathbf{v}) \cdot (\mathbf{c} - \mathbf{v})}{2k_{\text{B}} T^{\text{tr}}} - \frac{E_i}{k_{\text{B}} T^{\text{int}}}\right), \quad (2.4)$$

where T^{tr} is the translational temperature, T^{int} the temperature associated with the internal energy modes, and Z^{int} the partition function $Z^{\text{int}} = \sum_i a_i \exp(-E_i/k_{\text{B}} T^{\text{int}})$ which only depends on T^{int} .

2.2 Fluid equations

The equations for conservation of mass, momentum and internal energies are obtained by taking the scalar product of the Boltzmann equation (2.1) with the collisional invariants of the fast collision operator. The scalar product $\langle\langle \xi, \zeta \rangle\rangle$ between two tensorial quantities $\xi(t, \mathbf{x}, \mathbf{c}, i)$ and $\zeta(t, \mathbf{x}, \mathbf{c}, i)$ is defined by

$$\langle\langle \xi, \zeta \rangle\rangle = \sum_i \int \xi \odot \zeta d\mathbf{c},$$

where $\xi \odot \zeta$ is the contracted product. The 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 \mathbf{v} such that $\rho\mathbf{v} = \langle\langle m\mathbf{c}, f \rangle\rangle = \langle\langle m\mathbf{c}, f^{(0)} \rangle\rangle$, and the translation and internal temperatures T^{tr} and T^{int} defined by $\mathcal{E}^{\text{tr}}(T^{\text{tr}}) = \langle\langle f, \psi^{\text{tr}} \rangle\rangle = \langle\langle f^{(0)}, \psi^{\text{tr}} \rangle\rangle$ and $\mathcal{E}^{\text{int}}(T^{\text{int}}) = \langle\langle f, \psi^{\text{int}} \rangle\rangle = \langle\langle f^{(0)}, \psi^{\text{int}} \rangle\rangle$. Note that the dependence on n is left implicit to simplify notation. Following the Chapman-Enskog procedure, the equations for conservation of mass, momentum, and internal energies are found in the form [35]

$$\partial_t \rho + \nabla \cdot (\rho\mathbf{v}) = 0, \quad (2.5)$$

$$\partial_t (\rho\mathbf{v}) + \nabla \cdot (\rho\mathbf{v} \otimes \mathbf{v} + p\mathbf{I}) + \nabla \cdot \mathbf{II} = 0, \quad (2.6)$$

$$\partial_t \mathcal{E}^{\text{tr}} + \nabla \cdot (\mathbf{v}\mathcal{E}^{\text{tr}}) + \nabla \cdot \mathbf{Q}^{\text{tr}} = -p\nabla \cdot \mathbf{v} - \mathbf{II} : \nabla \mathbf{v} - \omega_1^{\text{int}}, \quad (2.7)$$

$$\partial_t \mathcal{E}^{\text{int}} + \nabla \cdot (\mathbf{v}\mathcal{E}^{\text{int}}) + \nabla \cdot \mathbf{Q}^{\text{int}} = \omega_1^{\text{int}}, \quad (2.8)$$

where \mathcal{E}^{tr} denotes the internal energy per unit volume of translational origin, \mathcal{E}^{int} the internal energy per unit volume of internal origin, \mathbf{Q}^{tr} and \mathbf{Q}^{int} the corresponding heat fluxes and ω_1^{int} the exchange term in the Navier-Stokes regime. These equations may be added in order to recover a conservation equation for the the total internal energy $\mathcal{E}^{\text{tr}} + \mathcal{E}^{\text{int}}$ in the form

$$\partial_t (\mathcal{E}^{\text{tr}} + \mathcal{E}^{\text{int}}) + \nabla \cdot (\mathbf{v}(\mathcal{E}^{\text{tr}} + \mathcal{E}^{\text{int}})) + \nabla \cdot (\mathbf{Q}^{\text{tr}} + \mathbf{Q}^{\text{int}}) = -p\nabla \cdot \mathbf{v} - \mathbf{II} : \nabla \mathbf{v}. \quad (2.9)$$

The state law and the internal energies are in the form

$$p = nk_{\text{B}} T^{\text{tr}}, \quad \mathcal{E}^{\text{tr}} = n\frac{3}{2}k_{\text{B}} T^{\text{tr}}, \quad \mathcal{E}^{\text{int}} = n\bar{E}, \quad (2.10)$$

where \bar{E} denotes the average internal energy per particle $\bar{E} = \sum_i \frac{a_i E_i}{Z^{\text{int}}} \exp\left(-\frac{E_i}{k_{\text{B}} T^{\text{int}}}\right)$. The transport fluxes, on the other hand, are found in the form

$$\mathbf{II} = -\eta(\nabla \mathbf{v} + (\nabla \mathbf{v})^t - \frac{2}{3}(\nabla \cdot \mathbf{v})\mathbf{I}), \quad (2.11)$$

$$\mathbf{Q}^{\text{tr}} = -\lambda^{\text{tr, tr}} \nabla T^{\text{tr}} - \lambda^{\text{tr, int}} \nabla T^{\text{int}}, \quad (2.12)$$

$$\mathbf{Q}^{\text{int}} = -\lambda^{\text{int, tr}} \nabla T^{\text{tr}} - \lambda^{\text{int, int}} \nabla T^{\text{int}}, \quad (2.13)$$

where η denotes the shear viscosity, and $\lambda^{\text{tr, tr}}$, $\lambda^{\text{tr, int}}$, $\lambda^{\text{int, tr}}$, and $\lambda^{\text{int, int}}$ the thermal conductivities. The full source term ω^{int} may be written

$$\omega^{\text{int}} = \langle\langle \psi^{\text{int}}, \mathcal{J}^{\text{sl}} \rangle\rangle = \langle\langle \psi^{\text{int}}, \mathcal{J} \rangle\rangle, \quad (2.14)$$

since $\langle\langle \psi^{\text{int}}, \mathcal{J}^{\text{rap}} \rangle\rangle = 0$ and may be expanded into $\omega^{\text{int}} = \omega_0^{\text{int}} + \epsilon \delta \omega_1^{\text{int}} + \mathcal{O}(\epsilon^2)$. The source term ω_1^{int} is then given by

$$\omega_1^{\text{int}} = \omega_0^{\text{int}} + \epsilon \delta \omega_1^{\text{int}}, \quad (2.15)$$

where ω_0^{int} denotes the source term evaluated from the Maxwellian distribution $f^{(0)}$ and $\delta \omega_1^{\text{int}}$ the correction associated with the Navier-Stokes perturbation $f^{(0)}\phi$.

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

$$\mathcal{P} = nk_{\text{B}}T^{\text{tr}}\mathbf{I} - \eta(\nabla\mathbf{v} + (\nabla\mathbf{v})^t - \frac{2}{3}(\nabla\cdot\mathbf{v})\mathbf{I}), \quad (2.16)$$

which does not contain a volume viscosity contribution unlike with usual one-temperature polyatomic gas models [1, 2, 3, 4, 5, 6, 7, 8, 9, 10].

2.3 Translational and internal entropies

The two-temperature fluid entropy per unit volume is directly evaluated from

$$\mathcal{S} = -k_{\text{B}} \sum_{\mathbf{c}} \int f^{(0)} (\log(f^{(0)}\beta_{\mathbf{c}}) - 1) d\mathbf{c},$$

where $\beta_{\mathbf{c}} = h_{\text{P}}^3/(a_{\mathbf{c}}m^3)$ and h_{P} is the Planck constant. After some algebra, the entropy \mathcal{S} is found in the form

$$\mathcal{S} = \mathcal{S}^{\text{tr}} + \mathcal{S}^{\text{int}}, \quad (2.17)$$

where the translational entropy per unit volume \mathcal{S}^{tr} and the translational partition function Z^{tr} are given by

$$\mathcal{S}^{\text{tr}} = nk_{\text{B}} \left(\frac{5}{2} - \log \frac{n}{Z^{\text{tr}}} \right), \quad Z^{\text{tr}} = \left(\frac{2\pi mk_{\text{B}}T^{\text{tr}}}{h_{\text{P}}^2} \right)^{\frac{3}{2}}, \quad (2.18)$$

whereas the internal entropy per unit volume \mathcal{S}^{int} is given by

$$\mathcal{S}^{\text{int}} = nk_{\text{B}} \left(\frac{\bar{E}}{k_{\text{B}}T^{\text{int}}} - \log \frac{1}{Z^{\text{int}}} \right). \quad (2.19)$$

Defining the translational and internal Gibbs functions G^{tr} and G^{int} per particle by

$$G^{\text{tr}} = k_{\text{B}}T^{\text{tr}} \log \frac{n}{Z^{\text{tr}}}, \quad G^{\text{int}} = k_{\text{B}}T^{\text{int}} \log \frac{1}{Z^{\text{int}}}, \quad (2.20)$$

the translational and internal Gibbs' relations are in the form

$$T^{\text{tr}} d\mathcal{S}^{\text{tr}} = d\mathcal{E}^{\text{tr}} - G^{\text{tr}} dn, \quad T^{\text{int}} d\mathcal{S}^{\text{int}} = d\mathcal{E}^{\text{int}} - G^{\text{int}} dn, \quad (2.21)$$

and we obtain that

$$d\mathcal{S} = \frac{nc^{\text{tr}}}{T^{\text{tr}}} dT^{\text{tr}} + \frac{nc^{\text{int}}}{T^{\text{int}}} dT^{\text{int}} + \left(\frac{3}{2}k_{\text{B}} + \frac{\bar{E}}{T^{\text{int}}} - k_{\text{B}} \log \frac{n}{Z^{\text{tr}}Z^{\text{int}}} \right) dn, \quad (2.22)$$

where $c^{\text{tr}} = \frac{3}{2}k_{\text{B}}$ and $c^{\text{int}} = \sum_{\mathbf{c}} \frac{k_{\text{B}}a_{\mathbf{c}}}{Z^{\text{int}}} \left(\frac{E_{\mathbf{c}} - \bar{E}}{k_{\text{B}}T^{\text{int}}} \right)^2 \exp\left(-\frac{E_{\mathbf{c}}}{k_{\text{B}}T^{\text{int}}}\right)$.

From the differential of entropy (2.22), after some lengthy algebra, the following entropy governing equation is obtained

$$\partial_t \mathcal{S} + \nabla \cdot (\mathbf{v}\mathcal{S}) + \nabla \cdot \left(\frac{\mathbf{Q}^{\text{tr}}}{T^{\text{tr}}} + \frac{\mathbf{Q}^{\text{int}}}{T^{\text{int}}} \right) = -\frac{\mathbf{Q}^{\text{tr}} \cdot \nabla T^{\text{tr}}}{T^{\text{tr}2}} - \frac{\mathbf{Q}^{\text{int}} \cdot \nabla T^{\text{int}}}{T^{\text{int}2}} - \frac{\mathbf{II} : \nabla \mathbf{v}}{T^{\text{tr}}} + \frac{\omega_1^{\text{int}}(T^{\text{tr}} - T^{\text{int}})}{T^{\text{tr}}T^{\text{int}}}. \quad (2.23)$$

2.4 The thermodynamic equilibrium temperature

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

$$\mathcal{E}^{\text{tr}}(T) + \mathcal{E}^{\text{int}}(T) = \mathcal{E}^{\text{tr}}(T^{\text{tr}}) + \mathcal{E}^{\text{int}}(T^{\text{int}}), \quad (2.24)$$

keeping in mind that $\mathcal{E}^{\text{tr}}(T) + \mathcal{E}^{\text{int}}(T)$ is an increasing function of T since c^{tr} and c^{int} are positive. The function \mathcal{E}^{int} is generally nonlinear but may be written

$$\mathcal{E}^{\text{int}}(T) - \mathcal{E}^{\text{int}}(T^{\text{int}}) = \int_{T^{\text{int}}}^T c^{\text{int}}(T') dT' = \tilde{c}^{\text{int}}(T - T^{\text{int}}), \quad (2.25)$$

where we have introduced $\tilde{c}^{\text{int}}(T, T^{\text{int}}) = \int_0^1 c^{\text{int}}(T^{\text{int}} + s(T - T^{\text{int}})) ds$. The relation $\mathcal{E}^{\text{tr}}(T^{\text{tr}}) - \mathcal{E}^{\text{tr}}(T) = \mathcal{E}^{\text{int}}(T) - \mathcal{E}^{\text{int}}(T^{\text{int}})$ may then be recast in the form

$$c^{\text{tr}}(T^{\text{tr}} - T) = \tilde{c}^{\text{int}}(T - T^{\text{int}}). \quad (2.26)$$

Finally, a governing equation for T may easily be obtained from (2.24) and (2.9).

2.5 Relaxation and volume viscosity

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

$$\begin{cases} \partial_t T^{\text{tr}} + \mathbf{v} \cdot \nabla T^{\text{tr}} = -\frac{p \nabla \cdot \mathbf{v}}{nc^{\text{tr}}} - \frac{\omega_0^{\text{int}}}{nc^{\text{tr}}}, \\ \partial_t T^{\text{int}} + \mathbf{v} \cdot \nabla T^{\text{int}} = \frac{\omega_0^{\text{int}}}{nc^{\text{int}}}. \end{cases} \quad (2.27)$$

A direct evaluation of the source term ω_0^{int} yields that

$$\omega_0^{\text{int}} = -2n^2 \llbracket (\Delta E) \left(\exp\left(\frac{\Delta E}{k_B T^{\text{tr}}} - \frac{\Delta E}{k_B T^{\text{int}}}\right) - 1 \right) \rrbracket, \quad (2.28)$$

where $\llbracket \cdot \rrbracket$ denotes the averaging operator

$$\llbracket \alpha \rrbracket = \frac{1}{8n^2} \sum_{i,j,i',j'} \int \alpha_{ij i' j'} f^{(0)} \tilde{f}^{(0)} g \sigma^{ij i' j'} d\mathbf{c} d\tilde{\mathbf{c}} d\mathbf{e}'. \quad (2.29)$$

Defining the nonequilibrium correction factor ζ as

$$\zeta = \int_0^1 \exp\left(\left(\frac{\Delta E}{k_B T^{\text{tr}}} - \frac{\Delta E}{k_B T^{\text{int}}}\right)s\right) ds,$$

the source term ω_0^{int} is recast in the convenient form

$$\omega_0^{\text{int}} = 2n^2 \frac{\llbracket (\Delta E)^2 \zeta \rrbracket}{k_B T^{\text{tr}} T^{\text{int}}} (T^{\text{tr}} - T^{\text{int}}), \quad (2.30)$$

Defining naturally the nonequilibrium relaxation time by $\tau^{\text{int}} = c^{\text{int}} k_B T^{\text{tr}} T^{\text{int}} / (2n \llbracket (\Delta E)^2 \zeta \rrbracket)$, we finally obtain that

$$\omega_0^{\text{int}} = \frac{nc^{\text{int}}}{\tau^{\text{int}}} (T^{\text{tr}} - T^{\text{int}}). \quad (2.31)$$

The resulting equation for $T^{\text{tr}} - T^{\text{int}}$ is now

$$\partial_t (T^{\text{tr}} - T^{\text{int}}) + \mathbf{v} \cdot \nabla (T^{\text{tr}} - T^{\text{int}}) = -\frac{p \nabla \cdot \mathbf{v}}{nc^{\text{tr}}} - \frac{c_v}{c^{\text{tr}}} \frac{T^{\text{tr}} - T^{\text{int}}}{\tau^{\text{int}}}, \quad (2.32)$$

where we have defined $c_v = c^{\text{tr}} + c^{\text{int}}(T^{\text{int}})$. This is a typical relaxation equation and the corresponding relaxation approximation yields

$$T^{\text{tr}} - T^{\text{int}} = -\frac{\tau^{\text{int}}}{nc_v} p \nabla \cdot \mathbf{v}. \quad (2.33)$$

This is the only approximation made in this section in order to recover a volume viscosity effect and it neither requires τ^{int} being small nor T^{tr} and T^{int} being close. This relaxation approximation is

valid when the flow characteristic time is greater than τ^{int} . We now define the nonequilibrium volume viscosity by $\kappa = p k_{\text{B}} \tilde{c}^{\text{int}} \tau^{\text{int}} / (c_{\text{v}} \tilde{c}_{\text{v}})$ where $\tilde{c}_{\text{v}} = c^{\text{tr}} + \tilde{c}^{\text{int}}(T, T^{\text{int}})$. From the expression of τ^{int} , this nonequilibrium volume viscosity may be written

$$\kappa = \frac{c^{\text{int}} \tilde{c}^{\text{int}} k_{\text{B}}^3 (T^{\text{tr}})^2 T^{\text{int}}}{c_{\text{v}} \tilde{c}_{\text{v}} 2 [(\Delta E)^2 \zeta]}, \quad (2.34)$$

and we emphasize that this coefficient differs in many aspects from its thermodynamic equilibrium limit $\kappa^{\text{eq}} = (\frac{c^{\text{int}}}{c_{\text{v}}})^2 (k_{\text{B}} T)^3 / 2 [(\Delta E)^2]$ obtained independently from the Chapman-Enskog method [45, 46]. Thanks to the nonlinear relation $\tilde{c}_{\text{v}} T = c^{\text{tr}} T^{\text{tr}} + \tilde{c}^{\text{int}} T^{\text{int}}$ we further obtain in the relaxation regime

$$n k_{\text{B}} T^{\text{tr}} = n k_{\text{B}} T - \kappa \nabla \cdot \mathbf{v}, \quad (2.35)$$

as well as $n k_{\text{B}} T^{\text{int}} = n k_{\text{B}} T + c^{\text{tr}} \kappa \nabla \cdot \mathbf{v} / c^{\text{int}}$. The relation (2.35) is now similar to classical estimates of temperature deviations and we have recovered a volume viscosity effect in the relaxation regime by using the equilibrium temperature T .

Finally, close to thermodynamic equilibrium, T^{tr} and T^{int} are close to T , so that \tilde{c}_{v} tends to c_{v} , \tilde{c}^{int} tends to c^{int} , ζ tends to one, and the nonequilibrium κ tends to the corresponding one-temperature formula κ^{eq} . Many authors have discussed the *near thermodynamic equilibrium* situation, where the internal temperature and the translational temperature are close, notably Kholer [1], Hirschfelder Curtiss and Bird [2], Waldmann [3], Chapman and Cowling [4], Ferziger and Kapper [5], McCourt et al. [6], de Groot and Mazur [9], Keizer [10], Zhdanov [33], Nagnibeda and Kustova [35], and Brun [36]. Second order effects are notably discussed by Hirschfelder Curtiss and Bird [2] and Zhdanov [33].

2.6 Higher order effects

We further investigate in this section the relaxation process in the Navier-Stokes regime. From the governing equations we deduce, in the Navier-Stokes regime, the system

$$\begin{cases} \partial_t T^{\text{tr}} + \mathbf{v} \cdot \nabla T^{\text{tr}} = -\frac{p \nabla \cdot \mathbf{v}}{n c^{\text{tr}}} - \frac{\nabla \cdot \mathbf{Q}^{\text{tr}}}{n c^{\text{tr}}} - \frac{\mathbf{\Pi} : \nabla \mathbf{v}}{n c^{\text{tr}}} - \frac{\omega_1^{\text{int}}}{n c^{\text{tr}}}, \\ \partial_t T^{\text{int}} + \mathbf{v} \cdot \nabla T^{\text{int}} = -\frac{\nabla \cdot \mathbf{Q}^{\text{int}}}{n c^{\text{int}}} + \frac{\omega_1^{\text{int}}}{n c^{\text{int}}}, \end{cases} \quad (2.36)$$

and we have to investigate the first order source term ω_1^{int} .

The perturbed distribution function ϕ is such that $\mathcal{I}^{\text{rap}}(\phi) = \psi$ and $\langle \langle f^{(0)} \phi, \psi^j \rangle \rangle = 0$ for $1 \leq j \leq 6$, where \mathcal{I}^{rap} denotes the linearized Boltzmann rapid collision operator, ψ the functional $\psi = -\partial_t^{(0)} \log f^{(0)} - \mathbf{c} \cdot \nabla \log f^{(0)} + \mathcal{J}^{\text{sl},(0)} / f^{(0)}$, and ψ^j , $1 \leq j \leq 6$, the collisional invariants of the fast collision operator. The functional $\psi = -\partial_t^{(0)} \log f^{(0)} - \mathbf{c} \cdot \nabla \log f^{(0)} + \mathcal{J}^{\text{sl},(0)} / f^{(0)}$ may be evaluated in the form

$$\psi = -\psi^\eta : \nabla \mathbf{v} - \psi^{\lambda^{\text{tr}}} \cdot \nabla \left(\frac{1}{k_{\text{B}} T^{\text{tr}}} \right) - \psi^{\lambda^{\text{int}}} \cdot \nabla \left(\frac{1}{k_{\text{B}} T^{\text{int}}} \right) + \psi^\omega \omega_0^{\text{int}},$$

where ψ^η is a symmetric traceless tensor, $\psi^{\lambda^{\text{tr}}}$ and $\psi^{\lambda^{\text{int}}}$ are vectors, and ψ^ω is a scalar

$$\psi^\eta = \frac{m}{k_{\text{B}} T^{\text{tr}}} \left((\mathbf{c} - \mathbf{v}) \otimes (\mathbf{c} - \mathbf{v}) - \frac{1}{3} (\mathbf{c} - \mathbf{v}) \cdot (\mathbf{c} - \mathbf{v}) \right), \quad (2.37)$$

$$\psi^{\lambda^{\text{tr}}} = \left(\frac{5}{2} k_{\text{B}} T^{\text{tr}} - \frac{1}{2} m (\mathbf{c} - \mathbf{v}) \cdot (\mathbf{c} - \mathbf{v}) \right) (\mathbf{c} - \mathbf{v}), \quad (2.38)$$

$$\psi^{\lambda^{\text{int}}} = (\bar{E} - E_1) (\mathbf{c} - \mathbf{v}), \quad (2.39)$$

$$\psi^\omega = \frac{\tilde{\mathcal{J}}^{\text{sl},(0)}}{f^{(0)}} - \frac{\frac{3}{2} k_{\text{B}} T^{\text{tr}} - \frac{1}{2} m (\mathbf{c} - \mathbf{v}) \cdot (\mathbf{c} - \mathbf{v})}{n k_{\text{B}} c^{\text{tr}} T^{\text{tr}2}} + \frac{\bar{E} - E_1}{n k_{\text{B}} c^{\text{int}} T^{\text{int}2}}. \quad (2.40)$$

The source term evaluated from the Maxwellian distribution $\mathcal{J}^{\text{sl},(0)}$ has been decomposed in the form $\mathcal{J}^{\text{sl},(0)} = \omega_0^{\text{int}} \tilde{\mathcal{J}}^{\text{sl},(0)}$ where

$$\tilde{\mathcal{J}}^{\text{sl},(0)} = \frac{1}{2n^2 [(\Delta E)^2 \zeta]} \sum_{j, j', j''} \int f^{(0)} \tilde{f}^{(0)} (\Delta E) \zeta g \sigma^{\text{ll}'j''} d\tilde{\mathbf{c}} d\mathbf{e}', \quad (2.41)$$

and we have $\langle\langle \psi^{\text{int}}, \tilde{\mathcal{J}}^{\text{sl},(0)} \rangle\rangle = 1$ as well as $\langle\langle \psi^{\text{tr}}, \tilde{\mathcal{J}}^{\text{sl},(0)} \rangle\rangle = -1$ and $\langle\langle 1, \tilde{\mathcal{J}}^{\text{sl},(0)} \rangle\rangle = 0$ in such a way that ψ^ω is orthogonal to the collisional invariants of the fast collision operator. Thanks to linearity ϕ may be written in the form

$$\phi = -\phi^\eta: \nabla \mathbf{v} - \phi^{\lambda^{\text{tr}}} \cdot \nabla \left(\frac{1}{k_{\text{B}} T^{\text{tr}}} \right) - \phi^{\lambda^{\text{int}}} \cdot \nabla \left(\frac{1}{k_{\text{B}} T^{\text{int}}} \right) + \phi^\omega \omega_0^{\text{int}},$$

where ϕ^η is a symmetric traceless tensor, $\phi^{\lambda^{\text{tr}}}$ and $\phi^{\lambda^{\text{int}}}$ are vectors and ϕ^ω is a scalar [35]. These coefficients satisfy for $\mu \in \{\eta, \lambda^{\text{tr}}, \lambda^{\text{int}}, \text{sl}\}$ the linearized Boltzmann equations $\mathcal{I}^{\text{rap}}(\phi^\mu) = \psi^\mu$ with the constraints $\langle\langle f^{(0)} \phi^\mu, \psi^j \rangle\rangle = 0$ for $1 \leq j \leq 6$.

The shear viscosity may be written $\eta = \frac{1}{10} k_{\text{B}} T \llbracket \phi^\eta, \phi^\eta \rrbracket$, the translational thermal conductivities in the form $\lambda^{\text{tr},\text{tr}} = \frac{1}{3} \llbracket \phi^{\lambda^{\text{tr}}}, \phi^{\lambda^{\text{tr}}} \rrbracket / k_{\text{B}} (T^{\text{tr}})^2$, $\lambda^{\text{tr},\text{int}} = \frac{1}{3} \llbracket \phi^{\lambda^{\text{tr}}}, \phi^{\lambda^{\text{int}}} \rrbracket / k_{\text{B}} (T^{\text{int}})^2$, and the internal thermal conductivities in the form $\lambda^{\text{int},\text{tr}} = \frac{1}{3} \llbracket \phi^{\lambda^{\text{int}}}, \phi^{\lambda^{\text{tr}}} \rrbracket / k_{\text{B}} (T^{\text{tr}})^2$, $\lambda^{\text{int},\text{int}} = \frac{1}{3} \llbracket \phi^{\lambda^{\text{int}}}, \phi^{\lambda^{\text{int}}} \rrbracket / k_{\text{B}} (T^{\text{int}})^2$.

The source term ω_1^{int} can next be written

$$\omega_1^{\text{int}} = \omega_0^{\text{int}} + \delta\omega_1^{\text{int}}, \quad (2.42)$$

where the perturbed source term $\delta\omega_1^{\text{int}}$ is given by

$$\delta\omega_1^{\text{int}} = \sum_{i,j,i',j'} E_i \int \left(f^{(0)'} \tilde{f}^{(0)'} \frac{a_i a_j}{a_{i'} a_{j'}} (\phi' + \tilde{\phi}') - f^{(0)} \tilde{f}^{(0)} (\phi + \tilde{\phi}) \right) g \sigma^{\text{ll}'j'} d\tilde{c} d\tilde{c}' de'. \quad (2.43)$$

Upon defining $\mathcal{W}^{\text{int}} = \sum_{j,i',j'} (\Delta E) \int \tilde{f}^{(0)} g \sigma^{\text{ll}'j'} d\tilde{c} d\tilde{c}'$ it is shown that $\delta\omega_1^{\text{int}} = \langle\langle f^{(0)} \phi, \mathcal{W}^{\text{int}} \rangle\rangle$. Using now the Curie principle, we have $\delta\omega_1^{\text{int}} = \omega_0^{\text{int}} \langle\langle f^{(0)} \phi^\omega, \mathcal{W}^{\text{int}} \rangle\rangle$ and we may define

$$w_1^{\text{int}} = \langle\langle f^{(0)} \phi^\omega, \mathcal{W}^{\text{int}} \rangle\rangle, \quad (2.44)$$

in such a way that $\delta\omega_1^{\text{int}}$ may be written in the form

$$\delta\omega_1^{\text{int}} = \omega_0^{\text{int}} w_1^{\text{int}}. \quad (2.45)$$

In the Navier-Stokes regime, the relaxation approximation then yields that

$$nk_{\text{B}} T^{\text{tr}} - nk_{\text{B}} T = -\kappa (1 - w_1^{\text{int}}) \nabla \cdot \mathbf{v} - \frac{\kappa}{p} \left(\mathbf{\Pi} : \nabla \mathbf{v} + \nabla \cdot \mathbf{Q}^{\text{tr}} - \frac{c^{\text{tr}}}{c^{\text{int}}} \nabla \cdot \mathbf{Q}^{\text{int}} \right). \quad (2.46)$$

The correction terms in (2.46) either involve the product of κ by another transport coefficient or the perturbed source term w_1^{int} . Near thermodynamic equilibrium, all terms involving the product of two transport coefficients must be discarded as pertaining to the Burnett regime, and only the term $-\kappa (1 - w_1^{\text{int}}) \nabla \cdot \mathbf{v}$ may play a rôle. We note, however, that the perturbed term ϕ^ω vanishes in a first approximation and thus the perturbation w_1^{int} also vanishes. Indeed, the standard Galerkin variational approximation space for scalar functions is spanned by $\phi^{0010} = \frac{3}{2} - \frac{1}{2} \frac{m}{k_{\text{B}} T} (\mathbf{c} - \mathbf{v}) \cdot (\mathbf{c} - \mathbf{v})$ and $\phi^{0001} = (\bar{E} - E_1) / k_{\text{B}} T^{\text{int}}$, which are both collisional invariants of the rapid collision operator, and are therefore in the nullspace of \mathcal{I}^{rap} .

2.7 The thermodynamic equilibrium asymptotic limit

We investigate more closely in this section the asymptotic convergence of the two-temperature model towards the one-temperature model when the characteristic time for energy exchange becomes of the order of magnitude of the elastic collision time, that is, when $\tau^{\text{int}} = \mathcal{O}(\epsilon)$. It is fundamental to observe here that the one temperature model is only valid under the condition $\tau^{\text{int}} = \mathcal{O}(\epsilon)$ as confirmed by the results of the numerical experiments of Section 4.

When $\tau^{\text{int}} = \mathcal{O}(\epsilon)$ we are certainly in the relaxation regime and we further deduce from $nk_{\text{B}} (T^{\text{tr}} - T) = -\kappa \nabla \cdot \mathbf{v}$ that $T^{\text{tr}} - T = \mathcal{O}(\epsilon)$ and $T^{\text{int}} - T = \mathcal{O}(\epsilon)$ since then $\kappa = \mathcal{O}(\epsilon)$. Denoting by $\kappa^{\text{eq}} = (c^{\text{int}}/c_{\text{v}})^2 (k_{\text{B}} T)^3 / 2 \llbracket (\Delta E)^2 \rrbracket$ the limiting one-temperature value of the volume viscosity κ , we also have $\kappa^{\text{eq}} = \mathcal{O}(\epsilon)$ and $\kappa - \kappa^{\text{eq}} = \mathcal{O}(\epsilon^2)$, so that $nk_{\text{B}} T^{\text{tr}} = nk_{\text{B}} T - \kappa^{\text{eq}} \nabla \cdot \mathbf{v} + \mathcal{O}(\epsilon^2)$ and $nk_{\text{B}} T^{\text{int}} = nk_{\text{B}} T + c^{\text{tr}} \kappa^{\text{eq}} \nabla \cdot \mathbf{v} / c^{\text{int}} + \mathcal{O}(\epsilon^2)$.

Considering first the momentum equation, only the pressure term $nk_{\text{B}} T^{\text{tr}}$ need to be rewritten into $nk_{\text{B}} T - \kappa^{\text{eq}} \nabla \cdot \mathbf{v}$ and the resulting pressure tensor at thermodynamic equilibrium is in the form

$$\mathcal{P}^{\text{eq}} = (nk_{\text{B}} T - \kappa^{\text{eq}} (\nabla \cdot \mathbf{v})) \mathbf{I} - \eta^{\text{eq}} (\nabla \mathbf{v} + (\nabla \mathbf{v})^t - \frac{2}{3} (\nabla \cdot \mathbf{v}) \mathbf{I}). \quad (2.47)$$

This is in agreement with the one-temperature model where the state law reads $p^{\text{eq}} = nk_{\text{B}}T$ and the viscous tensor is $\mathbf{\Pi}^{\text{eq}} = -\kappa^{\text{eq}}(\nabla \cdot \mathbf{v})\mathbf{I} - \eta^{\text{eq}}(\nabla \mathbf{v} + (\nabla \mathbf{v})^t - \frac{2}{3}(\nabla \cdot \mathbf{v})\mathbf{I})$. The two-temperature momentum equation thus coincide with the one-temperature momentum equation up to Burnett type $\mathcal{O}(\epsilon^2)$ terms.

Similarly, in the total internal energy conservation equation (2.9), we may replace $\mathcal{E}^{\text{tr}}(T^{\text{tr}}) + \mathcal{E}^{\text{int}}(T^{\text{int}})$ by $\mathcal{E}(T) + \mathcal{E}^{\text{int}}(T)$ by definition of T , and we may also replace T^{tr} and T^{int} by T in the fluxes since all thermal conductivities are $\mathcal{O}(\epsilon)$ perturbations and since $\mathcal{O}(\epsilon^2)$ terms must be discarded in the Navier-Stokes regime. This yields in particular $\mathbf{Q}^{\text{eq}} = \mathbf{Q}^{\text{tr}} + \mathbf{Q}^{\text{int}} = -\lambda^{\text{eq}}\nabla T$ with $\lambda^{\text{eq}} = \lambda^{\text{tr, tr}} + \lambda^{\text{tr, int}} + \lambda^{\text{int, tr}} + \lambda^{\text{int, int}}$. The only left term is the pressure term $p\nabla \cdot \mathbf{v} = nk_{\text{B}}T^{\text{tr}}\nabla \cdot \mathbf{v}$ which must be rewritten in into $nk_{\text{B}}T\nabla \cdot \mathbf{v} - \kappa^{\text{eq}}(\nabla \cdot \mathbf{v})^2$. The term $-\kappa^{\text{eq}}(\nabla \cdot \mathbf{v})^2$ then completes the friction term associated with the shear viscosity to form the full viscous dissipation term. We have then recovered the classical one-temperature energy equation

$$\partial_t \mathcal{E} + \nabla \cdot (\mathcal{E}\mathbf{v}) + \nabla \cdot \mathbf{Q}^{\text{eq}} = -p^{\text{eq}}\nabla \cdot \mathbf{v} - \mathbf{\Pi}^{\text{eq}} : \nabla \mathbf{v}. \quad (2.48)$$

where $\mathcal{E}(T) = \mathcal{E}^{\text{tr}}(T) + \mathcal{E}^{\text{int}}(T)$ and thus the full set of one-temperature Navier-Stokes conservation equations discarding Burnett type $\mathcal{O}(\epsilon^2)$ terms.

We further investigate the entropy per unit volume as well as the entropy conservation equation. From the differential (2.22) and the energy constraint $\mathcal{E}(T) = \mathcal{E}^{\text{tr}}(T^{\text{tr}}) + \mathcal{E}^{\text{int}}(T^{\text{int}})$, it is easily deduced that when $\tau^{\text{int}} = \mathcal{O}(\epsilon)$ then

$$\mathcal{S}^{\text{eq}}(T) = \mathcal{S}^{\text{tr}}(T^{\text{tr}}) + \mathcal{S}^{\text{int}}(T^{\text{int}}) + \mathcal{O}(\epsilon^2),$$

where $\mathcal{S}^{\text{eq}}(T)$ denotes the equilibrium one-temperature entropy [7]. Furthermore, the chemical term involving ω_1^{int} in the entropy conservation equation (2.23) is such that

$$\frac{\omega_1^{\text{int}}(T^{\text{tr}} - T^{\text{int}})}{T^{\text{tr}}T^{\text{int}}} = \frac{\kappa^{\text{eq}}}{T}(\nabla \cdot \mathbf{v})^2 + \mathcal{O}(\epsilon^2),$$

since $\omega_1^{\text{int}} = \omega_0^{\text{int}} + \mathcal{O}(\epsilon)$, so that the two-temperature entropy governing equation finally converges term by term towards the one-temperature entropy governing equation discarding Burnett type $\mathcal{O}(\epsilon^2)$ terms.

Finally, we note that theoretical models as well as experimental measurements of the volume viscosity have confirmed that this coefficient is of the order of the shear viscosity for polyatomic gases [11, 12, 13, 14, 15] and the impact of volume viscosity in fluid mechanics—especially for fast flows—has been established [16, 17, 18, 19, 20]. More generally, recent numerical investigations have brought further support for the importance of accurate transport property in various multicomponent reactive flows calculations [47, 48, 49, 50, 51, 52, 53].

3 A Two-temperature Two-Mode Kinetic Model

We investigate in this section a kinetic model with two internal energy modes. A first mode has a rapid exchange rate with the translational degrees of freedom whereas the other one has a slow exchange rate. In this situation, there is a volume viscosity due to the rapid internal energy mode as in one-temperature models. Nevertheless, part of the equilibrium viscosity is still hidden in the slow internal energy mode. In a relaxation regime, there are indeed four contributions to the effective volume viscosity, namely the fast energy mode volume viscosity, the slow energy mode volume viscosity, the relaxation pressure and the perturbed source term. In the near equilibrium limit, the sum of these four contributions coincides with the one-temperature two-mode volume viscosity.

3.1 A multi-temperature multi-mode kinetic framework

We consider a kinetic framework of a single polyatomic gas with two independent internal energy modes. The internal energy in the i th quantum state is decomposed into

$$E_{\mathbf{I}} = E_{\mathbf{I}^{\text{rap}}}^{\text{rap}} + E_{\mathbf{I}^{\text{sl}}}^{\text{sl}}, \quad (3.1)$$

where \mathbf{I} denotes the composed index $\mathbf{I} = (\mathbf{I}^{\text{rap}}, \mathbf{I}^{\text{sl}})$, \mathbf{I}^{rap} the index of the quantum energy state of the rapid mode, \mathbf{I}^{sl} the index of the quantum energy state of the slow mode, $E_{\mathbf{I}^{\text{rap}}}^{\text{rap}}$ the rapid mode internal energy, and $E_{\mathbf{I}^{\text{sl}}}^{\text{sl}}$ the slow mode internal energy. We will often denote for short $E_{\mathbf{I}}^{\text{rap}}$ for $E_{\mathbf{I}^{\text{rap}}}^{\text{rap}}$ and $E_{\mathbf{I}}^{\text{sl}}$ for $E_{\mathbf{I}^{\text{sl}}}^{\text{sl}}$ so that $E_{\mathbf{I}} = E_{\mathbf{I}}^{\text{rap}} + E_{\mathbf{I}}^{\text{sl}}$. We assume that the rapid collisions are all the collisions such that $\Delta E^{\text{sl}} = E_{\mathbf{I}'}^{\text{sl}} + E_{\mathbf{J}'}^{\text{sl}} - E_{\mathbf{I}}^{\text{sl}} - E_{\mathbf{J}}^{\text{sl}} = 0$, either only involving the translational energy and rapid

mode internal energy or resonant with respect to the slow internal energy mode. The corresponding Boltzmann equation is in the form

$$\partial_t f + \mathbf{c} \cdot \nabla_{\mathbf{x}} f = \frac{1}{\epsilon} \mathcal{J}^{\text{rap}} + \mathcal{J}^{\text{sl}} \quad (3.2)$$

where $f(t, \mathbf{x}, \mathbf{c}, \mathbf{i})$ denotes the distribution function, $\mathcal{J}^{\text{rap}} = \mathcal{J}^{(\text{tr}+\text{rap})-(\text{tr}+\text{rap})} + \mathcal{J}^{\text{sl}-\text{sl}}$ the rapid collision operator, and $\mathcal{J}^{\text{sl}} = \mathcal{J}^{(\text{tr}+\text{rap})-\text{sl}}$ the slow collision operator. We have denoted by $\mathcal{J}^{(\text{tr}+\text{rap})-(\text{tr}+\text{rap})}$ the collision operator involving solely the translational and fast internal degrees of freedom, $\mathcal{J}^{\text{sl}-\text{sl}}$ the operator for resonant collision with respect to E^{sl} , and $\mathcal{J}^{(\text{tr}+\text{rap})-\text{sl}}$ the operator for collisions such that $\Delta E^{\text{sl}} \neq 0$. The collisional invariants of the fast collision operator are now associated with particle number $\psi^1 = 1$, momentum $\psi^{1+\nu} = mc_{\nu}$, $\nu \in \{1, 2, 3\}$, the energy associated with translational and fast internal degrees of freedom $\psi^5 = \psi^{\text{tr}} + \psi^{\text{rap}}$ and the slow internal energy mode $\psi^6 = \psi^{\text{sl}}$, where $\psi^{\text{tr}} = \frac{1}{2}m(\mathbf{c} - \mathbf{v}) \cdot (\mathbf{c} - \mathbf{v})$, $\psi^{\text{rap}} = E_i^{\text{rap}}$, and $\psi^{\text{sl}} = E_i^{\text{sl}}$.

The Enskog expansion is in the form $f = f^{(0)}(1 + \epsilon\phi + \mathcal{O}(\epsilon^2))$ where $f^{(0)}$ is the Maxwellian distribution. This Maxwellian distribution is found in the form

$$f^{(0)} = \left(\frac{m}{2\pi k_{\text{B}} \bar{T}} \right)^{\frac{3}{2}} \frac{na_1}{Z^{\text{int}}} \exp\left(-\frac{m(\mathbf{c} - \mathbf{v}) \cdot (\mathbf{c} - \mathbf{v})}{2k_{\text{B}} \bar{T}} - \frac{E_i^{\text{rap}}}{k_{\text{B}} \bar{T}} - \frac{E_i^{\text{sl}}}{k_{\text{B}} T^{\text{sl}}} \right), \quad (3.3)$$

where the degeneracy a_1 is given by $a_1 = a_{\text{tr+rap}}^{\text{rap}} a_{\text{sl}}^{\text{sl}}$ and

$$Z^{\text{int}} = \sum_1 a_1 \exp\left(-\frac{E_i^{\text{rap}}}{k_{\text{B}} \bar{T}} - \frac{E_i^{\text{sl}}}{k_{\text{B}} T^{\text{sl}}} \right), \quad Z^{\text{int}} = Z^{\text{rap}} Z^{\text{sl}}, \quad (3.4)$$

$$Z^{\text{rap}} = \sum_{\text{rap}} a_{\text{rap}}^{\text{rap}} \exp\left(-\frac{E_i^{\text{rap}}}{k_{\text{B}} \bar{T}} \right), \quad Z^{\text{sl}} = \sum_{\text{sl}} a_{\text{sl}}^{\text{sl}} \exp\left(-\frac{E_i^{\text{sl}}}{k_{\text{B}} T^{\text{sl}}} \right), \quad (3.5)$$

\bar{T} is the thermodynamic partial equilibrium temperature between the translational and fast internal degrees of freedom, and T^{sl} the temperature associated with the slow internal energy modes.

3.2 Fluid equations

The equations for conservation of mass, momentum and internal energies are classically 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 \mathbf{v} , are now the partial equilibrium temperature between the translational and fast internal degrees of freedom \bar{T} and the slow mode internal temperature T^{sl} defined by $\mathcal{E}^{\text{tr+rap}}(\bar{T}) = \langle\langle f, \psi^{\text{tr}} + \psi^{\text{rap}} \rangle\rangle = \langle\langle f^{(0)}, \psi^{\text{tr}} + \psi^{\text{rap}} \rangle\rangle$ and $\mathcal{E}^{\text{sl}}(T^{\text{sl}}) = \langle\langle f, \psi^{\text{sl}} \rangle\rangle = \langle\langle f^{(0)}, \psi^{\text{sl}} \rangle\rangle$. The corresponding mass and momentum conservation equations are similar to (2.5) and (2.6) and are not repeated. On the other hand, the equations for conservation of internal energies are in the form

$$\partial_t \mathcal{E}^{\text{tr+rap}} + \nabla \cdot (\mathbf{v} \mathcal{E}^{\text{tr+rap}}) + \nabla \cdot \mathbf{Q}^{\text{tr+rap}} = -p \nabla \cdot \mathbf{v} - \mathbf{\Pi} : \nabla \mathbf{v} - \omega_1^{\text{sl}}, \quad (3.6)$$

$$\partial_t \mathcal{E}^{\text{sl}} + \nabla \cdot (\mathbf{v} \mathcal{E}^{\text{sl}}) + \nabla \cdot \mathbf{Q}^{\text{sl}} = \omega_1^{\text{sl}}, \quad (3.7)$$

where $\mathcal{E}^{\text{tr+rap}} = \mathcal{E}^{\text{tr}}(\bar{T}) + \mathcal{E}^{\text{rap}}(\bar{T})$ denotes the internal energy per unit volume of translational and fast internal mode origin with $\mathcal{E}^{\text{tr}}(\bar{T}) = \langle\langle f^{(0)}, \psi^{\text{tr}} \rangle\rangle$ and $\mathcal{E}^{\text{rap}}(\bar{T}) = \langle\langle f^{(0)}, \psi^{\text{rap}} \rangle\rangle$, \mathcal{E}^{sl} the internal energy per unit volume of slow internal mode origin, $\mathbf{Q}^{\text{tr+rap}}$ and \mathbf{Q}^{sl} the corresponding heat fluxes, and ω_1^{sl} the exchange term in the Navier-Stokes regime.

The state law and the internal energies are in the form

$$p = nk_{\text{B}} \bar{T}, \quad \mathcal{E}^{\text{tr+rap}} = n\left(\frac{3}{2}k_{\text{B}} \bar{T} + \bar{E}^{\text{rap}}\right), \quad \mathcal{E}^{\text{sl}} = n\bar{E}^{\text{sl}}, \quad (3.8)$$

where \bar{E}^{rap} and \bar{E}^{sl} denote the average fast and slow mode internal energy per particle $\bar{E}^{\text{rap}} = \sum_{\text{rap}} \frac{a_{\text{rap}}^{\text{rap}} E_i^{\text{rap}}}{Z^{\text{rap}}} \exp\left(-\frac{E_i^{\text{rap}}}{k_{\text{B}} \bar{T}}\right)$ and $\bar{E}^{\text{sl}} = \sum_{\text{sl}} \frac{a_{\text{sl}}^{\text{sl}} E_i^{\text{sl}}}{Z^{\text{sl}}} \exp\left(-\frac{E_i^{\text{sl}}}{k_{\text{B}} T^{\text{sl}}}\right)$. The transport fluxes, on the other hand, are found in the form

$$\mathbf{\Pi} = p^{\text{rel}} - \kappa^{\text{rap}} \nabla \cdot \mathbf{v} \mathbf{I} - \eta(\nabla \mathbf{v} + (\nabla \mathbf{v})^t - \frac{2}{3}(\nabla \cdot \mathbf{v}) \mathbf{I}), \quad (3.9)$$

$$\mathbf{Q}^{\text{tr+rap}} = -\lambda^{\text{tr+rap, tr+rap}} \nabla \bar{T} - \lambda^{\text{tr+rap, sl}} \nabla T^{\text{sl}}, \quad (3.10)$$

$$\mathbf{Q}^{\text{sl}} = -\lambda^{\text{sl, tr+rap}} \nabla \bar{T} - \lambda^{\text{sl, sl}} \nabla T^{\text{sl}}, \quad (3.11)$$

where p^{rel} denotes the relaxation pressure, κ^{rap} the volume viscosity associated with the fast internal energy modes, η the shear viscosity, and $\lambda^{\text{tr+rap, tr+rap}}$, $\lambda^{\text{tr+rap, sl}}$, $\lambda^{\text{sl, tr+rap}}$, and $\lambda^{\text{sl, sl}}$ the thermal conductivities. The full source term ω^{sl} may be written

$$\omega^{\text{sl}} = \langle\langle \psi^{\text{sl}}, \mathcal{J}^{\text{sl}} \rangle\rangle = \langle\langle \psi^{\text{sl}}, \mathcal{J} \rangle\rangle, \quad (3.12)$$

since $\langle\langle \psi^{\text{sl}}, \mathcal{J}^{\text{rap}} \rangle\rangle = 0$ and may be expanded into $\omega^{\text{sl}} = \omega_0^{\text{sl}} + \epsilon \delta \omega_1^{\text{sl}} + \mathcal{O}(\epsilon^2)$. The source term ω_1^{sl} is then given by

$$\omega_1^{\text{sl}} = \omega_0^{\text{sl}} + \epsilon \delta \omega_1^{\text{sl}}, \quad (3.13)$$

where ω_0^{sl} denotes the source term evaluated from the Maxwellian distribution $f^{(0)}$ and $\delta \omega_1^{\text{sl}}$ the correction associated with the Navier-Stokes perturbation $f^{(0)} \phi$.

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

$$\mathcal{P} = (nk_{\text{B}}\bar{T} + p^{\text{rel}} - \kappa^{\text{rap}}\nabla \cdot \mathbf{v})\mathbf{I} - \eta(\nabla \mathbf{v} + (\nabla \mathbf{v})^t - \frac{2}{3}(\nabla \cdot \mathbf{v})\mathbf{I}), \quad (3.14)$$

with a pressure term $nk_{\text{B}}\bar{T}\mathbf{I}$, a volume viscosity contribution associated with the fast internal modes $\kappa^{\text{rap}}\nabla \cdot \mathbf{v}\mathbf{I}$, and a relaxation pressure term $p^{\text{rel}}\mathbf{I}$.

3.3 The thermodynamic equilibrium temperature

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

$$\mathcal{E}^{\text{tr}}(T) + \mathcal{E}^{\text{rap}}(T) + \mathcal{E}^{\text{sl}}(T) = \mathcal{E}^{\text{tr}}(\bar{T}) + \mathcal{E}^{\text{rap}}(\bar{T}) + \mathcal{E}^{\text{sl}}(T^{\text{sl}}), \quad (3.15)$$

keeping in mind that $\mathcal{E}^{\text{tr}}(T) + \mathcal{E}^{\text{rap}}(T) + \mathcal{E}^{\text{sl}}(T)$ is an increasing function of T since since $c^{\text{tr}} = \frac{3}{2}k_{\text{B}}$, $c^{\text{rap}} = \sum_{\text{rap}} \frac{k_{\text{B}} a_{\text{rap}}^{\text{rap}}}{Z^{\text{rap}}} \left(\frac{E_{\text{rap}}^{\text{rap}} - \bar{E}^{\text{rap}}}{k_{\text{B}} \bar{T}} \right)^2 \exp\left(-\frac{E_{\text{rap}}^{\text{rap}}}{k_{\text{B}} \bar{T}}\right)$, and $c^{\text{sl}} = \sum_{\text{sl}} \frac{k_{\text{B}} a_{\text{sl}}^{\text{sl}}}{Z^{\text{sl}}} \left(\frac{E_{\text{sl}}^{\text{sl}} - \bar{E}^{\text{sl}}}{k_{\text{B}} \bar{T}} \right)^2 \exp\left(-\frac{E_{\text{sl}}^{\text{sl}}}{k_{\text{B}} \bar{T}}\right)$ are positive. The function \mathcal{E}^{sl} is generally nonlinear but may be written

$$\mathcal{E}^{\text{sl}}(T) - \mathcal{E}^{\text{sl}}(T^{\text{sl}}) = \int_{T^{\text{sl}}}^T c^{\text{sl}}(T') dT' = \tilde{c}^{\text{sl}}(T - T^{\text{sl}}), \quad (3.16)$$

where we have introduced $\tilde{c}^{\text{sl}}(T, T^{\text{sl}}) = \int_0^1 c^{\text{sl}}(T^{\text{sl}} + s(T - T^{\text{sl}})) ds$. Similarly, we write the nonlinear function \mathcal{E}^{rap} in the form

$$\mathcal{E}^{\text{rap}}(T) - \mathcal{E}^{\text{rap}}(\bar{T}) = \int_{\bar{T}}^T c^{\text{rap}}(T') dT' = \tilde{c}^{\text{rap}}(T - \bar{T}), \quad (3.17)$$

where $\tilde{c}^{\text{rap}}(T, \bar{T}) = \int_0^1 c^{\text{rap}}(\bar{T} + s(T - \bar{T})) ds$. The relation $\mathcal{E}^{\text{tr+rap}}(\bar{T}) - \mathcal{E}^{\text{tr+rap}}(T) = \mathcal{E}^{\text{sl}}(T) - \mathcal{E}^{\text{sl}}(T^{\text{sl}})$ may then be recast in the form

$$(c^{\text{tr}} + \tilde{c}^{\text{rap}})(\bar{T} - T) = \tilde{c}^{\text{sl}}(T - T^{\text{sl}}). \quad (3.18)$$

Finally, a governing equation for T may easily be obtained from (3.15) and by adding (3.6) and (3.7).

3.4 Relaxation and the slow mode volume viscosity

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

$$\begin{cases} \partial_t \bar{T} + \mathbf{v} \cdot \nabla \bar{T} = -\frac{p \nabla \cdot \mathbf{v}}{n(c^{\text{tr}} + c^{\text{rap}})} - \frac{\omega_0^{\text{sl}}}{n(c^{\text{tr}} + c^{\text{rap}})} \\ \partial_t T^{\text{sl}} + \mathbf{v} \cdot \nabla T^{\text{sl}} = \frac{\omega_0^{\text{sl}}}{nc^{\text{sl}}}, \end{cases} \quad (3.19)$$

and a direct evaluation of the source term ω_0^{sl} also yields that

$$\omega_0^{\text{sl}} = -2n^2 \left[(\Delta E^{\text{sl}}) \left(\exp\left(\frac{\Delta E^{\text{sl}}}{k_{\text{B}} T} - \frac{\Delta E^{\text{sl}}}{k_{\text{B}} T^{\text{sl}}}\right) - 1 \right) \right]. \quad (3.20)$$

Defining the nonequilibrium correction factor ζ^{sl} as in the previous section

$$\zeta^{\text{sl}} = \int_0^1 \exp\left(\left(\frac{\Delta E^{\text{sl}}}{k_{\text{B}} T} - \frac{\Delta E^{\text{sl}}}{k_{\text{B}} T^{\text{sl}}}\right)s\right) ds,$$

the source term ω_0^{sl} is recast in the convenient form

$$\omega_0^{\text{sl}} = 2n^2 \frac{[(\Delta E^{\text{sl}})^2 \zeta^{\text{sl}}]}{k_{\text{B}} \bar{T} T^{\text{sl}}} (\bar{T} - T^{\text{sl}}). \quad (3.21)$$

Defining naturally the nonequilibrium relaxation time by $\tau^{\text{sl}} = c^{\text{sl}} k_{\text{B}} \bar{T} T^{\text{sl}} / (2n[(\Delta E^{\text{sl}})^2 \zeta^{\text{sl}}])$, we finally obtain that

$$\omega_0^{\text{sl}} = \frac{nc^{\text{sl}}}{\tau^{\text{sl}}} (\bar{T} - T^{\text{sl}}). \quad (3.22)$$

The resulting equation for $\bar{T} - T^{\text{sl}}$ is then

$$\partial_t (\bar{T} - T^{\text{sl}}) + \mathbf{v} \cdot \nabla (\bar{T} - T^{\text{sl}}) = -\frac{p \nabla \cdot \mathbf{v}}{n(c^{\text{tr}} + c^{\text{rap}})} - \frac{c_{\text{v}}}{(c^{\text{tr}} + c^{\text{rap}})} \frac{\bar{T} - T^{\text{sl}}}{\tau^{\text{sl}}}, \quad (3.23)$$

where we have defined $c_{\text{v}} = c^{\text{tr}} + c^{\text{rap}}(\bar{T}) + c^{\text{sl}}(T^{\text{sl}})$. This is a typical relaxation equation and the corresponding relaxation approximation yields at the zeroth order

$$\bar{T} - T^{\text{sl}} = -\frac{\tau^{\text{sl}}}{nc_{\text{v}}} p \nabla \cdot \mathbf{v}. \quad (3.24)$$

This approximation neither require τ^{sl} to be small nor \bar{T} and T^{sl} to be close and is indeed valid when the flow characteristic time is greater than τ^{sl} . We next define the slow mode nonequilibrium volume viscosity by $\kappa^{\text{sl}} = pk_{\text{B}} \tilde{c}^{\text{sl}} \tau^{\text{sl}} / (c_{\text{v}} \tilde{c}_{\text{v}})$, where $\tilde{c}_{\text{v}} = c^{\text{tr}} + \tilde{c}^{\text{rap}}(T, \bar{T}) + \tilde{c}^{\text{sl}}(T, T^{\text{sl}})$ and κ^{sl} may also be written

$$\kappa^{\text{sl}} = \frac{c^{\text{sl}} \tilde{c}^{\text{sl}}}{c_{\text{v}} \tilde{c}_{\text{v}}} \frac{k_{\text{B}}^3 \bar{T}^2 T^{\text{sl}}}{2[(\Delta E^{\text{sl}})^2 \zeta^{\text{sl}}]}. \quad (3.25)$$

Thanks to the nonlinear relation $\tilde{c}_{\text{v}} T = (c^{\text{tr}} + c^{\text{rap}}) \bar{T} + \tilde{c}^{\text{sl}} T^{\text{sl}}$ we further obtain—after some algebra—that at zeroth order

$$nk_{\text{B}} \bar{T} = nk_{\text{B}} T - \kappa^{\text{sl}} \nabla \cdot \mathbf{v}. \quad (3.26)$$

3.5 First order corrections

Since we will need to add the slow mode volume viscosity κ^{sl} , which is $\mathcal{O}(\tau^{\text{sl}})$, to the volume viscosity κ^{rap} , associated with the fast energy mode in the Navier-Stokes regime, which is $\mathcal{O}(\epsilon)$, we eventually need to take into account first order corrections to the temperature difference $\bar{T} - T^{\text{sl}}$. From the governing equations we deduce in the Navier-Stokes regime the conservation equations

$$\begin{cases} \partial_t \bar{T} + \mathbf{v} \cdot \nabla \bar{T} = -\frac{p \nabla \cdot \mathbf{v}}{n(c^{\text{tr}} + c^{\text{rap}})} - \frac{\nabla \cdot \mathbf{Q}^{\text{tr+rap}}}{n(c^{\text{tr}} + c^{\text{rap}})} - \frac{\mathbf{H} : \nabla \mathbf{v}}{n(c^{\text{tr}} + c^{\text{rap}})} - \frac{\omega_1^{\text{sl}}}{n(c^{\text{tr}} + c^{\text{rap}})}, \\ \partial_t T^{\text{sl}} + \mathbf{v} \cdot \nabla T^{\text{sl}} = -\frac{\nabla \cdot \mathbf{Q}^{\text{sl}}}{nc^{\text{sl}}} + \frac{\omega_1^{\text{sl}}}{nc^{\text{sl}}}, \end{cases} \quad (3.27)$$

and we thus have to investigate the structure of the first order source term $\omega_1^{\text{sl}} = \omega_0^{\text{sl}} + \delta\omega_1^{\text{sl}}$.

The perturbed distribution function ϕ is such that $\mathcal{I}^{\text{rap}}(\phi) = \psi$ and $\langle\langle f^{(0)} \phi, \psi^j \rangle\rangle = 0$ for $1 \leq j \leq 6$, where \mathcal{I}^{rap} denotes the linearized Boltzmann rapid collision operator, and ψ the functional $\psi = -\partial_t^{(0)} \log f^{(0)} - \mathbf{c} \cdot \nabla \log f^{(0)} + \mathcal{J}^{\text{sl},(0)} / f^{(0)}$, and ψ^j , $1 \leq j \leq 6$, the collisional invariants of the fast collision operator. The functional $\psi = -\partial_t^{(0)} \log f^{(0)} - \mathbf{c} \cdot \nabla \log f^{(0)} + \mathcal{J}^{\text{sl},(0)} / f^{(0)}$ may be evaluated in the form

$$\psi = -\psi^\eta : \nabla \mathbf{v} - \psi^\lambda{}^{\text{tr+rap}} \cdot \nabla \left(\frac{1}{k_{\text{B}} \bar{T}} \right) - \psi^\lambda{}^{\text{sl}} \cdot \nabla \left(\frac{1}{k_{\text{B}} T^{\text{sl}}} \right) - \frac{1}{3} \psi^\kappa \nabla \cdot \mathbf{v} + \psi^\omega \omega_0^{\text{sl}},$$

where ψ^η is a symmetric traceless tensor, $\psi^\lambda{}^{\text{tr+rap}}$ and $\psi^\lambda{}^{\text{sl}}$ are vectors, ψ^κ and ψ^ω are scalars given by

[35]

$$\psi^\eta = \frac{m}{k_{\text{B}}\bar{T}} \left((\mathbf{c} - \mathbf{v}) \otimes (\mathbf{c} - \mathbf{v}) - \frac{1}{3} (\mathbf{c} - \mathbf{v}) \cdot (\mathbf{c} - \mathbf{v}) \right), \quad (3.28)$$

$$\psi^{\lambda^{\text{tr}+\text{rap}}} = \left(\frac{5}{2} k_{\text{B}} \bar{T} - \frac{1}{2} m (\mathbf{c} - \mathbf{v}) \cdot (\mathbf{c} - \mathbf{v}) \right) (\mathbf{c} - \mathbf{v}), \quad (3.29)$$

$$\psi^{\lambda^{\text{sl}}} = (\bar{E}^{\text{sl}} - E_1^{\text{sl}}) (\mathbf{c} - \mathbf{v}), \quad (3.30)$$

$$\psi^\kappa = -\frac{2c^{\text{rap}}}{c^{\text{tr}} + c^{\text{rap}}} \left(\frac{3}{2} - \frac{m(\mathbf{c} - \mathbf{v}) \cdot (\mathbf{c} - \mathbf{v})}{2k_{\text{B}}\bar{T}} \right) + \frac{2c^{\text{tr}}}{c^{\text{tr}} + c^{\text{rap}}} \frac{(\bar{E}^{\text{rap}} - E_1^{\text{rap}})}{k_{\text{B}}\bar{T}}, \quad (3.31)$$

$$\psi^\omega = \frac{\tilde{\mathcal{J}}^{\text{sl},(0)}}{f^{(0)}} - \frac{\frac{3}{2}k_{\text{B}}\bar{T} - \frac{1}{2}m(\mathbf{c} - \mathbf{v}) \cdot (\mathbf{c} - \mathbf{v})}{nk_{\text{B}}(c^{\text{tr}} + c^{\text{rap}})\bar{T}^2} - \frac{\bar{E}^{\text{rap}} - E_1^{\text{rap}}}{nk_{\text{B}}(c^{\text{tr}} + c^{\text{rap}})\bar{T}^2} + \frac{\bar{E}^{\text{sl}} - E_1^{\text{sl}}}{nk_{\text{B}}c^{\text{sl}}T^{\text{sl}2}}. \quad (3.32)$$

The source term $\mathcal{J}^{\text{sl},(0)}$ has been written $\mathcal{J}^{\text{sl},(0)} = \omega_0^{\text{sl}} \tilde{\mathcal{J}}^{\text{sl},(0)}$ where

$$\tilde{\mathcal{J}}^{\text{sl},(0)} = \frac{1}{2n^2 \llbracket (\Delta E^{\text{sl}})^2 \zeta^{\text{sl}} \rrbracket} \sum_{j,j',j''} \int f^{(0)} \tilde{f}^{(0)} (\Delta E^{\text{sl}})_{\zeta^{\text{sl}}} g \sigma^{\text{ll}'j''} d\tilde{\mathbf{c}} d\mathbf{e}', \quad (3.33)$$

and we have $\langle\langle \psi^{\text{sl}}, \tilde{\mathcal{J}}^{\text{sl},(0)} \rangle\rangle = 1$, $\langle\langle \psi^{\text{tr}} + \psi^{\text{rap}}, \tilde{\mathcal{J}}^{\text{sl},(0)} \rangle\rangle = -1$, and $\langle\langle 1, \tilde{\mathcal{J}}^{\text{sl},(0)} \rangle\rangle = 0$ in such a way that ψ^ω is orthogonal to the collisional invariants of the fast collision operator. Thanks to linearity ϕ may be expanded in the form

$$\phi = -\phi^\eta: \nabla \mathbf{v} - \phi^{\lambda^{\text{tr}+\text{rap}}} \cdot \nabla \left(\frac{1}{k_{\text{B}}\bar{T}} \right) - \phi^{\lambda^{\text{sl}}} \cdot \nabla \left(\frac{1}{k_{\text{B}}T^{\text{sl}}} \right) - \frac{1}{3} \phi^\kappa \nabla \cdot \mathbf{v} + \phi^\omega \omega_0^{\text{sl}},$$

where ϕ^η is a symmetric traceless tensor, $\phi^{\lambda^{\text{tr}+\text{rap}}}$ and $\phi^{\lambda^{\text{sl}}}$ are vectors, ϕ^κ and ϕ^ω are scalars. These coefficients ϕ^μ , $\mu \in \{\eta, \lambda^{\text{tr}+\text{rap}}, \lambda^{\text{sl}}, \kappa, \text{sl}\}$, satisfy the linearized Boltzmann equations $\mathcal{I}^{\text{rap}}(\phi^\mu) = \psi^\mu$ with the constraints $\langle\langle f^{(0)} \phi^\mu, \psi^j \rangle\rangle = 0$, $1 \leq j \leq 6$.

The shear viscosity may be written $\eta = \frac{1}{10} k_{\text{B}} T \llbracket \phi^\eta, \phi^\eta \rrbracket$, the translational and fast mode thermal conductivities in the form $\lambda^{\text{tr}+\text{rap}, \text{tr}+\text{rap}} = \frac{1}{3} \llbracket \phi^{\lambda^{\text{tr}+\text{rap}}}, \phi^{\lambda^{\text{tr}+\text{rap}}} \rrbracket / k_{\text{B}} \bar{T}^2$, $\lambda^{\text{tr}+\text{rap}, \text{sl}} = \frac{1}{3} \llbracket \phi^{\lambda^{\text{tr}+\text{rap}}}, \phi^{\lambda^{\text{sl}}} \rrbracket / k_{\text{B}} T^{\text{sl}2}$, and the slow mode thermal conductivities in the form $\lambda^{\text{sl}, \text{tr}+\text{rap}} = \frac{1}{3} \llbracket \phi^{\lambda^{\text{sl}}}, \phi^{\lambda^{\text{tr}+\text{rap}}} \rrbracket / k_{\text{B}} \bar{T}^2$, $\lambda^{\text{sl}, \text{sl}} = \frac{1}{3} \llbracket \phi^{\lambda^{\text{sl}}}, \phi^{\lambda^{\text{sl}}} \rrbracket / k_{\text{B}} T^{\text{sl}2}$. In addition, the relaxation pressure p^{rel} and the reduced relaxation pressure \tilde{p}^{rel} are given by

$$p^{\text{rel}} = \tilde{p}^{\text{rel}} \omega_0^{\text{sl}}, \quad \tilde{p}^{\text{rel}} = \frac{1}{3} k_{\text{B}} \bar{T} \langle\langle f^{(0)} \phi^\omega, \psi^\kappa \rangle\rangle = \frac{1}{3} k_{\text{B}} \bar{T} \langle\langle f^{(0)} \phi^\kappa, \psi^\omega \rangle\rangle, \quad (3.34)$$

The source term ω_1^{sl} can be written

$$\omega_1^{\text{sl}} = \omega_0^{\text{sl}} + \delta\omega_1^{\text{sl}}, \quad (3.35)$$

where the perturbed source term $\delta\omega_1^{\text{sl}}$ is given by

$$\delta\omega_1^{\text{sl}} = \sum_{i,j,i',j'} E_i^{\text{sl}} \int \left(f^{(0)'} \tilde{f}^{(0)'} \frac{a_i a_j}{a_{i'} a_{j'}} (\phi' + \tilde{\phi}') - f^{(0)} \tilde{f}^{(0)} (\phi + \tilde{\phi}) \right) g \sigma^{\text{ll}'j'} d\mathbf{c} d\tilde{\mathbf{c}} d\mathbf{e}', \quad (3.36)$$

and upon defining $\mathcal{W}^{\text{sl}} = \sum_{j,i',j''} (\Delta E^{\text{sl}}) \int \tilde{f}^{(0)} g \sigma^{\text{ll}'j''} d\tilde{\mathbf{c}} d\mathbf{e}'$ it is shown that

$$\delta\omega_1^{\text{sl}} = \langle\langle f^{(0)} \phi, \mathcal{W}^{\text{sl}} \rangle\rangle. \quad (3.37)$$

Using now the Curie principle, we have $\delta\omega_1^{\text{sl}} = -\frac{1}{3} \langle\langle f^{(0)} \phi^\kappa, \mathcal{W}^{\text{sl}} \rangle\rangle \nabla \cdot \mathbf{v} + \langle\langle f^{(0)} \phi^\omega, \mathcal{W}^{\text{sl}} \rangle\rangle \omega_0^{\text{sl}}$ and we may define

$$w_1^\kappa = -\frac{1}{3} \langle\langle f^{(0)} \phi^\kappa, \mathcal{W}^{\text{sl}} \rangle\rangle, \quad w_1^{\text{sl}} = \langle\langle f^{(0)} \phi^\omega, \mathcal{W}^{\text{sl}} \rangle\rangle, \quad (3.38)$$

in such a way that

$$\delta\omega_1^{\text{sl}} = w_1^\kappa \nabla \cdot \mathbf{v} + w_1^{\text{sl}} \omega_0^{\text{sl}}. \quad (3.39)$$

Furthermore, in the relaxation approximation, and in the Navier-Stokes regime, we may replace ω_0^{sl} by its zeroth order approximation $\omega_0^{\text{sl}} \approx -c^{\text{sl}} p \nabla \cdot \mathbf{v} / c_v$ in the first order term $\delta\omega_1^{\text{sl}}$. The resulting effective first order correction *in the relaxation regime* is therefore

$$\delta\omega_1^{\text{sl}} = \left(w_1^\kappa - \frac{pc^{\text{sl}}}{c_v} w_1^{\text{sl}} \right) \nabla \cdot \mathbf{v}. \quad (3.40)$$

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

$$nk_{\text{B}}\bar{T} - nk_{\text{B}}T = -\kappa^{\text{sl}} \nabla \cdot \mathbf{v} \left(1 - w_1^{\text{sl}} + \frac{c_{\text{v}} w_1^{\kappa}}{c^{\text{sl}} p} \right) - \frac{\kappa^{\text{sl}}}{p} \left(\mathbf{\Pi} : \nabla \mathbf{v} + \nabla \cdot \mathbf{Q}^{\text{tr+rap}} - \frac{c^{\text{tr}} + c^{\text{rap}}}{c^{\text{sl}}} \nabla \cdot \mathbf{Q}^{\text{sl}} \right). \quad (3.41)$$

The new terms in (3.41) involve either the product of κ^{sl} by another transport coefficient or the perturbed source term w_1^{κ} and w_1^{sl} . Near equilibrium only the term $-\kappa^{\text{sl}} \nabla \cdot \mathbf{v} (1 - w_1^{\text{sl}} + c_{\text{v}} w_1^{\kappa} / p c^{\text{sl}})$ plays a rôle since all terms involving the product of two transport coefficients are associated with the Burnett regime.

3.6 Kinetic definition of the translational and rapid mode temperatures

The thermodynamic partial equilibrium temperature \bar{T} between the translational and the fast internal energy modes is defined from $\mathcal{E}^{\text{tr}}(\bar{T}) + \mathcal{E}^{\text{rap}}(\bar{T}) = \langle\langle f^{(0)}, \psi^{\text{tr}} + \psi^{\text{rap}} \rangle\rangle = \langle\langle f, \psi^{\text{tr}} + \psi^{\text{rap}} \rangle\rangle$ and it is a macroscopic quantity since $\psi^{\text{tr}} + \psi^{\text{rap}}$ is a collisional invariant. The translational T^{tr} and the fast mode internal temperature T^{rap} are now defined from

$$\mathcal{E}^{\text{tr}}(T^{\text{tr}}) = \langle\langle f, \psi^{\text{tr}} \rangle\rangle \quad \mathcal{E}^{\text{rap}}(T^{\text{rap}}) = \langle\langle f, \psi^{\text{rap}} \rangle\rangle. \quad (3.42)$$

Since neither ψ^{tr} nor ψ^{rap} is a collision invariant of the fast collision operator, these temperatures cannot solely be expressed in terms of zeroth order quantities and have to be expanded in the form

$$T^{\text{tr}} = T_0^{\text{tr}} + \epsilon \delta T_1^{\text{tr}} + \mathcal{O}(\epsilon^2), \quad T^{\text{rap}} = T_0^{\text{rap}} + \epsilon \delta T_1^{\text{rap}} + \mathcal{O}(\epsilon^2), \quad (3.43)$$

where T_0^{tr} and T_0^{rap} are the zeroth order terms and δT_1^{tr} and δT_1^{rap} the first order correctors associated with the Navier-Stokes regime.

From the definition (3.42) and the expansions (3.43) we deduce that at the zeroth order we have $\mathcal{E}^{\text{tr}}(T_0^{\text{tr}}) = \langle\langle f^{(0)}, \psi^{\text{tr}} \rangle\rangle$ and $\mathcal{E}^{\text{rap}}(T_0^{\text{rap}}) = \langle\langle f^{(0)}, \psi^{\text{rap}} \rangle\rangle$, so that $\mathcal{E}^{\text{tr}}(T_0^{\text{tr}}) = \mathcal{E}^{\text{tr}}(\bar{T})$, and $\mathcal{E}^{\text{rap}}(T_0^{\text{rap}}) = \mathcal{E}^{\text{rap}}(\bar{T})$ in such a way that at the zeroth order

$$T_0^{\text{tr}} = T_0^{\text{rap}} = \bar{T}, \quad (3.44)$$

in agreement with the fast mode assumption.

We introduce for convenience the notation

$$T_1^{\text{tr}} = T_0^{\text{tr}} + \epsilon \delta T_1^{\text{tr}}, \quad T_1^{\text{rap}} = T_0^{\text{rap}} + \epsilon \delta T_1^{\text{rap}}, \quad (3.45)$$

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

$$\mathcal{E}^{\text{tr}}(T^{\text{tr}}) - \mathcal{E}^{\text{tr}}(\bar{T}) = \langle\langle f - f^{(0)}, \psi^{\text{tr}} \rangle\rangle, \quad \mathcal{E}^{\text{rap}}(T^{\text{rap}}) - \mathcal{E}^{\text{rap}}(\bar{T}) = \langle\langle f - f^{(0)}, \psi^{\text{rap}} \rangle\rangle,$$

we next obtain the linearized expressions

$$nc^{\text{tr}}(T_1^{\text{tr}} - \bar{T}) = \langle\langle f^{(0)} \phi, \psi^{\text{tr}} \rangle\rangle, \quad nc^{\text{rap}}(T_1^{\text{rap}} - \bar{T}) = \langle\langle f^{(0)} \phi, \psi^{\text{rap}} \rangle\rangle. \quad (3.46)$$

Note that c^{rap} may be evaluated at \bar{T} since T^{tr} and T^{rap} are deviations from \bar{T} in the Navier-Stokes regime. We also know that $\psi^{\text{tr}} + \psi^{\text{rap}}$ is a collisional invariant so that $\langle\langle f^{(0)} \phi, \psi^{\text{tr}} + \psi^{\text{rap}} \rangle\rangle = 0$ and

$$(c^{\text{tr}} + c^{\text{rap}})\bar{T} = c^{\text{tr}}T_1^{\text{tr}} + c^{\text{rap}}T_1^{\text{rap}}. \quad (3.47)$$

In the next section, we evaluate the first order perturbations $T_1^{\text{tr}} - \bar{T}$ and $T_1^{\text{rap}} - \bar{T}$ in terms of the divergence of the velocity field and the relaxation pressure.

Note that relations similar to (3.46) may be obtained for one-temperature polyatomic gas models. In a one-temperature kinetic framework, starting from the thermodynamic equilibrium temperature T , one may *reconstruct* approximations T_1^{int} and T_1^{tr} of the internal and translational temperatures in the Navier-Stokes regime as in (3.46).

3.7 The rapid mode volume viscosity and the relaxation pressure

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

$$nc^{\text{tr}}(T_1^{\text{tr}} - \bar{T}) = -\frac{1}{3} \langle\langle f^{(0)} \phi^{\kappa}, \psi^{\text{tr}} \rangle\rangle \nabla \cdot \mathbf{v} + \langle\langle f^{(0)} \phi^{\omega}, \psi^{\text{tr}} \rangle\rangle \omega_0^{\text{sl}}, \quad (3.48)$$

$$nc^{\text{rap}}(T_1^{\text{rap}} - \bar{T}) = -\frac{1}{3} \langle\langle f^{(0)} \phi^{\kappa}, \psi^{\text{rap}} \rangle\rangle \nabla \cdot \mathbf{v} + \langle\langle f^{(0)} \phi^{\omega}, \psi^{\text{rap}} \rangle\rangle \omega_0^{\text{sl}}. \quad (3.49)$$

Since $\psi^{\text{tr}} + \psi^{\text{rap}}$ is a collisional invariant, the scalar products $\langle\langle f^{(0)}\phi^\kappa, \psi^{\text{tr}} \rangle\rangle$ and $\langle\langle f^{(0)}\phi^\kappa, \psi^{\text{rap}} \rangle\rangle$ are such that $\langle\langle f^{(0)}\phi^\kappa, \psi^{\text{tr}} \rangle\rangle + \langle\langle f^{(0)}\phi^\kappa, \psi^{\text{rap}} \rangle\rangle = 0$. Similarly, the scalar products $\langle\langle f^{(0)}\phi^\omega, \psi^{\text{tr}} \rangle\rangle$ and $\langle\langle f^{(0)}\phi^\omega, \psi^{\text{rap}} \rangle\rangle$ are such that $\langle\langle f^{(0)}\phi^\omega, \psi^{\text{tr}} \rangle\rangle + \langle\langle f^{(0)}\phi^\omega, \psi^{\text{rap}} \rangle\rangle = 0$. On the other hand, we have the expression of the volume viscosity κ^{rap}

$$\kappa^{\text{rap}} = \frac{1}{9}k_{\text{B}}\bar{T}\langle\langle f^{(0)}\phi^\kappa, \psi^\kappa \rangle\rangle = \frac{1}{9}k_{\text{B}}\bar{T}[\phi^\kappa, \phi^\kappa].$$

Noting that $\psi^\kappa - \frac{2c^{\text{rap}}}{(c^{\text{tr}}+c^{\text{rap}})k_{\text{B}}\bar{T}}\psi^{\text{tr}} + \frac{2c^{\text{tr}}}{(c^{\text{tr}}+c^{\text{rap}})k_{\text{B}}\bar{T}}\psi^{\text{rap}}$ is a collisional invariant, we obtain upon taking the scalar product with $f^{(0)}\phi^\kappa$ a second relation between $\langle\langle f^{(0)}\phi^\kappa, \psi^{\text{tr}} \rangle\rangle$ and $\langle\langle f^{(0)}\phi^\kappa, \psi^{\text{rap}} \rangle\rangle$ which are thus expressed in terms of κ^{rap} after some algebra. Similarly, we know that

$$\tilde{p}^{\text{rel}} = \frac{1}{3}k_{\text{B}}\bar{T}\langle\langle f^{(0)}\phi^\omega, \psi^\kappa \rangle\rangle,$$

and upon expressing ψ^κ in terms of ψ^{tr} , ψ^{rap} and a collisional invariant, and taking the scalar product with $f^{(0)}\phi^\omega$, we obtain a second relation between $\langle\langle f^{(0)}\phi^\omega, \psi^{\text{tr}} \rangle\rangle$ and $\langle\langle f^{(0)}\phi^\omega, \psi^{\text{rap}} \rangle\rangle$ which are then evaluated in terms of \tilde{p}^{rel} . After some algebra, it is obtained that

$$nk_{\text{B}}T_1^{\text{tr}} = nk_{\text{B}}\bar{T} - \kappa^{\text{rap}}\nabla\cdot\mathbf{v} + \tilde{p}^{\text{rel}}\omega_0^{\text{sl}}, \quad (3.50)$$

$$nk_{\text{B}}T_1^{\text{rap}} = nk_{\text{B}}\bar{T} - \frac{c^{\text{tr}}}{c^{\text{rap}}}(-\kappa^{\text{rap}}\nabla\cdot\mathbf{v} + \tilde{p}^{\text{rel}}\omega_0^{\text{sl}}). \quad (3.51)$$

We notably deduce that the expression $nk_{\text{B}}\bar{T} - \kappa^{\text{rap}}\nabla\cdot\mathbf{v} + \tilde{p}^{\text{rel}}$ appearing in the pressure tensor may be written $nk_{\text{B}}T_1^{\text{tr}}$ in the Navier-Stokes regime. The volume viscosity term $-\kappa^{\text{rap}}\nabla\cdot\mathbf{v}$ and the relaxation pressure $p^{\text{rel}} = \tilde{p}^{\text{rel}}\omega_0^{\text{sl}}$ modify the partial equilibrium temperature pressure term $nk_{\text{B}}\bar{T}$ into a translational temperature pressure term $nk_{\text{B}}T_1^{\text{tr}}$.

The fast mode volume viscosity is obtained as in classical one-temperature models [45, 46] and found to be

$$\kappa^{\text{rap}} = \left(\frac{c^{\text{rap}}}{c^{\text{tr}} + c^{\text{rap}}}\right)^2 \frac{(k_{\text{B}}\bar{T})^3}{2[(\Delta E^{\text{rap}})^2]}. \quad (3.52)$$

Note that in principle, we should write the bracket in the form $[(\Delta E^{\text{rap}})^2]^{\text{rap}}$ since we have to evaluate the average as in the definition (2.29) but summing only over the fast reactions. However, thanks to the scaling in the Boltzmann equations, the relative difference between $[(\Delta E^{\text{rap}})^2]^{\text{rap}}$ and the complete bracket $[(\Delta E^{\text{rap}})^2]$ obtained by summing over the fast and the slow collisions is $\mathcal{O}(\epsilon)$ and thus may be neglected.

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

$$\tilde{p}^{\text{rel}} = \frac{1}{3}k_{\text{B}}\bar{T}\langle\langle f^{(0)}\phi^\kappa, \psi^\omega \rangle\rangle = \frac{1}{3}k_{\text{B}}\bar{T}\langle\langle \phi^\kappa, \tilde{\mathcal{J}}^{\text{sl},(0)} \rangle\rangle,$$

and we have first to evaluate the perturbed function ϕ^κ . The corresponding standard Galerkin variational approximation space is the space spanned by $\phi^{0010} = \frac{3}{2} - \frac{1}{2}\frac{m}{k_{\text{B}}\bar{T}}(\mathbf{c} - \mathbf{v})\cdot(\mathbf{c} - \mathbf{v})$ and $\phi^{0001\text{rap}} = (\bar{E}^{\text{rap}} - E_1^{\text{rap}})/k_{\text{B}}\bar{T}$. The function $\phi^{0001\text{sl}} = (\bar{E}^{\text{sl}} - E_1^{\text{sl}})/k_{\text{B}}T^{\text{sl}}$ is indeed a collisional invariant of the rapid collision operator and must be discarded. We also discard higher degree polynomials in a first approximation. The transport linear system associated with this Galerkin variational approximation space is similar to the system investigated in References [45, 46] and, after some lengthy algebra, it is found that

$$\phi^\kappa = -\frac{3}{p} \frac{c^{\text{rap}}}{(c^{\text{tr}} + c^{\text{rap}})^2} \frac{(k_{\text{B}}\bar{T})^3}{2[(\Delta E^{\text{rap}})^2]} (c^{\text{rap}}\phi^{0010} - c^{\text{tr}}\phi^{0001\text{rap}}). \quad (3.53)$$

The scalar products $\langle\langle \phi^{0010}, \tilde{\mathcal{J}}^{\text{sl},(0)} \rangle\rangle$ and $\langle\langle \phi^{0001\text{rap}}, \tilde{\mathcal{J}}^{\text{sl},(0)} \rangle\rangle$ are next evaluated in the form

$$\langle\langle \phi^{0010}, \tilde{\mathcal{J}}^{\text{sl},(0)} \rangle\rangle = \frac{[(\Delta E^{\text{rap}} + \Delta E^{\text{sl}})(\Delta E^{\text{sl}})\zeta^{\text{sl}}]}{[(\Delta E^{\text{sl}})^2\zeta^{\text{sl}}]k_{\text{B}}\bar{T}}, \quad (3.54)$$

$$\langle\langle \phi^{0001\text{rap}}, \tilde{\mathcal{J}}^{\text{sl},(0)} \rangle\rangle = -\frac{[(\Delta E^{\text{rap}})(\Delta E^{\text{sl}})\zeta^{\text{sl}}]}{[(\Delta E^{\text{sl}})^2\zeta^{\text{sl}}]k_{\text{B}}\bar{T}}. \quad (3.55)$$

The resulting rescaled relaxation pressure \tilde{p}^{rel} is then given by

$$\tilde{p}^{\text{rel}} = -\frac{(k_{\text{B}}\bar{T})^3 c^{\text{rap}}}{2p(c^{\text{tr}} + c^{\text{rap}})^2} \frac{c^{\text{rap}}[(\Delta E^{\text{sl}})^2\zeta^{\text{sl}}] + (c^{\text{tr}} + c^{\text{rap}})[(\Delta E^{\text{rap}})(\Delta E^{\text{sl}})\zeta^{\text{sl}}]}{2[(\Delta E^{\text{rap}})^2\zeta^{\text{sl}}][(\Delta E^{\text{sl}})^2\zeta^{\text{sl}}]}. \quad (3.56)$$

Furthermore, in the relaxation regime, we may express the zeroth order source term ω_0^{sl} in term of $\nabla \cdot \mathbf{v}$ in the expression of $p^{\text{rel}} = \omega_0^{\text{sl}} \hat{p}^{\text{rel}}$ and we finally obtain that

$$p^{\text{rel}} = \hat{p}^{\text{rel}} \nabla \cdot \mathbf{v}, \quad (3.57)$$

where

$$\hat{p}^{\text{rel}} = \frac{(k_{\text{B}} \bar{T})^3 c^{\text{sl}} c^{\text{rap}}}{(c^{\text{tr}} + c^{\text{rap}})^2 c_{\text{v}}} \frac{c^{\text{rap}} [(\Delta E^{\text{sl}})^2 \zeta^{\text{sl}}] + (c^{\text{tr}} + c^{\text{rap}}) [(\Delta E^{\text{rap}})(\Delta E^{\text{sl}}) \zeta^{\text{sl}}]}{2 [(\Delta E^{\text{rap}})^2 \zeta^{\text{sl}}] [(\Delta E^{\text{sl}})^2 \zeta^{\text{sl}}]}, \quad (3.58)$$

and the relaxation pressure finally adds a contribution to the effective volume viscosity.

3.8 The perturbed source term

We further have to evaluate the perturbed source term $\delta \omega_1^{\text{sl}}$ or equivalently the scalar products $w_1^{\kappa} = -\frac{1}{3} \langle \langle f^{(0)} \phi^{\kappa}, \mathcal{W}^{\text{sl}} \rangle \rangle$ and $w_1^{\text{sl}} = \langle \langle f^{(0)} \phi^{\omega}, \mathcal{W}^{\text{sl}} \rangle \rangle$, and next $\delta \omega_1^{\text{sl}} = w_1^{\kappa} \nabla \cdot \mathbf{v} + w_1^{\text{sl}} \omega_0^{\text{sl}}$. We first investigate the product w_1^{κ} and then the product w_1^{sl} .

The perturbed distribution function ϕ^{κ} has already been evaluated in terms of ϕ^{0010} and $\phi^{0001\text{rap}}$ and we are left with the calculation of $\langle \langle f^{(0)} \phi^{0010}, \mathcal{W}^{\text{sl}} \rangle \rangle$ and $\langle \langle f^{(0)} \phi^{0001\text{rap}}, \mathcal{W}^{\text{sl}} \rangle \rangle$ in order to evaluate w_1^{κ} . After lengthy calculations, these scalar products may be expressed in the form

$$\langle \langle f^{(0)} \phi^{0010}, \mathcal{W}^{\text{sl}} \rangle \rangle = -\frac{2n^2}{k_{\text{B}} \bar{T}} \left([(\Delta E^{\text{sl}})(\Delta E^{\text{sl}} + \Delta E^{\text{rap}})] + 2 [(\Delta E^{\text{sl}})^2 \phi^{0010} \zeta^{\text{sl}}] \frac{\bar{T} - T^{\text{sl}}}{T^{\text{sl}}} \right), \quad (3.59)$$

$$\langle \langle f^{(0)} \phi^{0001\text{rap}}, \mathcal{W}^{\text{sl}} \rangle \rangle = \frac{2n^2}{k_{\text{B}} \bar{T}} \left([(\Delta E^{\text{sl}})(\Delta E^{\text{rap}})] - 2 [(\Delta E^{\text{sl}})^2 \phi^{0001\text{rap}} \zeta^{\text{sl}}] \frac{\bar{T} - T^{\text{sl}}}{T^{\text{sl}}} \right). \quad (3.60)$$

On the other hand, we may also evaluate the difference between $[(\Delta E^{\text{sl}})(\Delta E^{\text{sl}} + \Delta E^{\text{rap}})]$ and $[(\Delta E^{\text{sl}})(\Delta E^{\text{sl}} + \Delta E^{\text{rap}}) \zeta^{\text{sl}}]$ and the difference between $[(\Delta E^{\text{sl}})^2]$ and $[(\Delta E^{\text{sl}})^2 \zeta^{\text{sl}}]$ in the form

$$[(\Delta E^{\text{sl}})(\Delta E^{\text{rap}})] = [(\Delta E^{\text{sl}})(\Delta E^{\text{rap}}) \zeta^{\text{sl}}] + [(\Delta E^{\text{sl}})^2 (\Delta E^{\text{rap}}) \hat{\zeta}^{\text{sl}}] \frac{\bar{T} - T^{\text{sl}}}{k_{\text{B}} \bar{T} T^{\text{sl}}},$$

$$[(\Delta E^{\text{sl}})^2] = [(\Delta E^{\text{sl}})^2 \zeta^{\text{sl}}] + [(\Delta E^{\text{sl}})^3 \hat{\zeta}^{\text{sl}}] \frac{\bar{T} - T^{\text{sl}}}{k_{\text{B}} \bar{T} T^{\text{sl}}}$$

where

$$\hat{\zeta}^{\text{sl}} = \int_0^1 \int_0^s \exp\left(\left(\frac{\Delta E^{\text{sl}}}{k_{\text{B}} \bar{T}} - \frac{\Delta E^{\text{sl}}}{k_{\text{B}} T^{\text{sl}}}\right) r\right) dr ds. \quad (3.61)$$

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

$$\langle \langle f^{(0)} \phi^{0010}, \mathcal{W}^{\text{sl}} \rangle \rangle \approx -\frac{2n^2}{k_{\text{B}} \bar{T}} [(\Delta E^{\text{sl}})(\Delta E^{\text{sl}} + \Delta E^{\text{rap}}) \zeta^{\text{sl}}], \quad (3.62)$$

$$\langle \langle f^{(0)} \phi^{0001\text{rap}}, \mathcal{W}^{\text{sl}} \rangle \rangle \approx \frac{2n^2}{k_{\text{B}} \bar{T}} [(\Delta E^{\text{sl}})(\Delta E^{\text{rap}}) \zeta^{\text{sl}}]. \quad (3.63)$$

The resulting perturbed source term is then in the form

$$w_1^{\kappa} = -\left(\frac{c^{\text{rap}}}{c^{\text{tr}} + c^{\text{rap}}}\right)^2 p \frac{[(\Delta E^{\text{sl}})^2 \zeta^{\text{sl}}]}{[(\Delta E^{\text{rap}})^2]} - \frac{p c^{\text{rap}}}{c^{\text{tr}} + c^{\text{rap}}} \frac{[(\Delta E^{\text{sl}})(\Delta E^{\text{rap}}) \zeta^{\text{sl}}]}{[(\Delta E^{\text{rap}})^2]} \quad (3.64)$$

On the other hand, in order to evaluate the scalar perturbed distribution function ϕ^{ω} , we may use the same orthogonal polynomials as for the scalar function ϕ^{κ} . The transport linear system is easily evaluated following the Galerkin variational approximation procedure and the classical formulas associated with the transport linear systems [45]. Upon expanding ϕ^{ω} in the form

$$\phi^{\omega} = -\frac{3}{p} (\alpha^{10} \phi^{0010} + \alpha^{01\text{rap}} \phi^{0001\text{rap}}), \quad (3.65)$$

we obtain a linear system $K\alpha = \beta$ where K is similar to the matrix presented in References [45, 46] but now at temperature \bar{T} . The nullspace of K is the vector $(1, 1)^t$ and we have the constraint $c^{\text{tr}} \alpha^{10} + c^{\text{rap}} \alpha^{01\text{rap}} = 0$. The right hand side is evaluated from [45]

$$\beta^{10} = -\frac{1}{3n} \langle \langle f^{(0)} \phi^{0010}, \psi^{\omega} \rangle \rangle, \quad \beta^{01\text{rap}} = -\frac{1}{3n} \langle \langle f^{(0)} \phi^{0001\text{rap}}, \psi^{\omega} \rangle \rangle, \quad (3.66)$$

and after some algebra, it is found that

$$\beta^{10} = \frac{1}{3p} \left(-\frac{[(\Delta E^{\text{sl}})(\Delta E^{\text{sl}} + \Delta E^{\text{rap}})\zeta^{\text{sl}}]}{[(\Delta E^{\text{sl}})^2\zeta^{\text{sl}}]} + \frac{c^{\text{tr}}}{c^{\text{tr}} + c^{\text{rap}}} \right), \quad (3.67)$$

$$\beta^{01\text{rap}} = \frac{1}{3p} \left(\frac{[(\Delta E^{\text{sl}})(\Delta E^{\text{rap}})\zeta^{\text{sl}}]}{[(\Delta E^{\text{sl}})^2\zeta^{\text{sl}}]} + \frac{c^{\text{rap}}}{c^{\text{tr}} + c^{\text{rap}}} \right). \quad (3.68)$$

The linear system is easily solved and it is found that

$$\phi^\omega = -\frac{1}{p^2} \frac{1}{c^{\text{tr}} + c^{\text{rap}}} \frac{(k_{\text{B}}\bar{T})^3}{2[(\Delta E^{\text{rap}})^2]} \left(\frac{[(\Delta E^{\text{sl}})(\Delta E^{\text{rap}})\zeta^{\text{sl}}]}{[(\Delta E^{\text{sl}})^2\zeta^{\text{sl}}]} + \frac{c^{\text{rap}}}{c^{\text{tr}} + c^{\text{rap}}} \right) (c^{\text{rap}} \phi^{0010} - c^{\text{tr}} \phi^{0001\text{rap}}). \quad (3.69)$$

Using the expressions (3.62) and (3.63) the perturbed source term w_1^{sl} is first obtained in the form

$$w_1^{\text{sl}} = -\frac{1}{(c^{\text{tr}} + c^{\text{rap}})^2} \frac{((c^{\text{tr}} + c^{\text{rap}})[(\Delta E^{\text{sl}})(\Delta E^{\text{rap}})\zeta^{\text{sl}}] + c^{\text{rap}}[(\Delta E^{\text{sl}})^2\zeta^{\text{sl}}])^2}{[(\Delta E^{\text{rap}})^2][(\Delta E^{\text{sl}})^2\zeta^{\text{sl}}]}. \quad (3.70)$$

However, we have already assumed that the coupling between the modes is weak in such a way that the square $[(\Delta E^{\text{sl}})(\Delta E^{\text{rap}})\zeta^{\text{sl}}]^2$ may be neglected and this yields

$$w_1^{\text{sl}} = -\left(\frac{c^{\text{rap}}}{c^{\text{tr}} + c^{\text{rap}}} \right)^2 \frac{[(\Delta E^{\text{sl}})^2\zeta^{\text{sl}}]}{[(\Delta E^{\text{rap}})^2]} - \frac{1}{c^{\text{tr}} + c^{\text{rap}}} \frac{[(\Delta E^{\text{sl}})(\Delta E^{\text{rap}})\zeta^{\text{sl}}]}{[(\Delta E^{\text{rap}})^2][(\Delta E^{\text{sl}})^2\zeta^{\text{sl}}]}. \quad (3.71)$$

Note that the approximate expressions (3.62) and (3.63), as well as the relaxation approximation are used since we are interested in volume viscosity effects and in recovering the equilibrium volume viscosity. However, the full nonequilibrium model may still be evaluated from the expressions (3.59) and (3.60).

3.9 The effective volume viscosity

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

$$\kappa = \kappa^{\text{rap}} - \hat{p}^{\text{rel}} + \kappa^{\text{sl}} - \kappa^{\text{sl}} w_1^{\text{sl}} + \kappa^{\text{sl}} c_{\text{v}} w_1^{\kappa} / c^{\text{sl}} p, \quad (3.72)$$

where we have written for convenience $p^{\text{rel}} = \hat{p}^{\text{rel}} \nabla \cdot \mathbf{v}$. Collecting from the previous sections the expressions of κ^{rap} , \hat{p}^{rel} , κ^{sl} and of the perturbed source terms, w_1^{κ} and w_1^{sl} , it is found that

$$\begin{aligned} \kappa = & \left(\frac{c^{\text{rap}}}{c^{\text{tr}} + c^{\text{rap}}} \right)^2 \frac{(k_{\text{B}}\bar{T})^3}{2[(\Delta E^{\text{rap}})^2]} \\ & - \frac{c^{\text{sl}}}{c_{\text{v}}} \left(\frac{c^{\text{rap}}}{c^{\text{tr}} + c^{\text{rap}}} \right)^2 \frac{(k_{\text{B}}\bar{T})^3 c^{\text{sl}} c^{\text{rap}}}{2[(\Delta E^{\text{rap}})^2]} - \frac{c^{\text{rap}} c^{\text{sl}}}{(c^{\text{tr}} + c^{\text{rap}}) c_{\text{v}}} \frac{(k_{\text{B}}\bar{T})^3 [(\Delta E^{\text{rap}})(\Delta E^{\text{sl}})\zeta^{\text{sl}}]}{2[(\Delta E^{\text{rap}})^2\zeta^{\text{sl}}][(\Delta E^{\text{sl}})^2\zeta^{\text{sl}}]} \\ & + \frac{c^{\text{sl}} \tilde{c}^{\text{sl}}}{c_{\text{v}} \tilde{c}_{\text{v}}} \frac{k_{\text{B}}^3 (\bar{T})^2 T^{\text{sl}}}{2[(\Delta E^{\text{sl}})^2\zeta^{\text{sl}}]} \\ & - \frac{\tilde{c}^{\text{sl}}}{\tilde{c}_{\text{v}}} \left(\frac{c^{\text{rap}}}{c^{\text{tr}} + c^{\text{rap}}} \right)^2 \frac{k_{\text{B}}^3 \bar{T}^2 T^{\text{sl}}}{2[(\Delta E^{\text{rap}})^2]} - \frac{c^{\text{rap}} \tilde{c}^{\text{sl}}}{(c^{\text{tr}} + c^{\text{rap}}) \tilde{c}_{\text{v}}} \frac{k_{\text{B}}^3 \bar{T}^2 T^{\text{sl}} [(\Delta E^{\text{sl}})(\Delta E^{\text{rap}})]}{2[(\Delta E^{\text{rap}})^2][(\Delta E^{\text{sl}})^2\zeta^{\text{sl}}]} \\ & + \frac{c^{\text{sl}} \tilde{c}^{\text{sl}}}{c_{\text{v}} \tilde{c}_{\text{v}}} \left(\frac{c^{\text{rap}}}{c^{\text{tr}} + c^{\text{rap}}} \right)^2 \frac{k_{\text{B}}^3 \bar{T}^2 T^{\text{sl}}}{2[(\Delta E^{\text{rap}})^2]} + 2 \frac{c^{\text{rap}} c^{\text{sl}} \tilde{c}^{\text{sl}}}{(c^{\text{tr}} + c^{\text{rap}}) c_{\text{v}} \tilde{c}_{\text{v}}} \frac{k_{\text{B}}^3 \bar{T}^2 T^{\text{sl}} [(\Delta E^{\text{sl}})(\Delta E^{\text{rap}})]}{2[(\Delta E^{\text{rap}})^2][(\Delta E^{\text{sl}})^2\zeta^{\text{sl}}]}. \end{aligned} \quad (3.73)$$

Now a close examination of the nonequilibrium effective volume viscosity (3.73) reveals that its asymptotic limit at thermodynamic equilibrium is *exactly* the one-temperature two-mode volume viscosity derived from the Chapman-Enskog method in the Appendix and given by

$$\kappa = \left(\frac{c^{\text{rap}}}{c_{\text{v}}} \right)^2 \frac{(k_{\text{B}}T)^3}{2[(\Delta E^{\text{rap}})^2]} - \frac{c^{\text{rap}} c^{\text{sl}}}{c_{\text{v}}^2} \frac{(k_{\text{B}}T)^3 [(\Delta E^{\text{rap}})(\Delta E^{\text{sl}})]}{[(\Delta E^{\text{rap}})^2][(\Delta E^{\text{sl}})^2]} + \left(\frac{c^{\text{sl}}}{c_{\text{v}}} \right)^2 \frac{(k_{\text{B}}T)^3}{2[(\Delta E^{\text{sl}})^2]}. \quad (3.74)$$

More specifically, the first, second, fifth and seventh terms of (3.73) converge toward the first term of (3.74), the third, sixth and eighth terms of (3.73) converge toward the second term of (3.74), and the fourth terms of (3.73) converge toward the third term of (3.74).

4 Numerical experiments

The results derived in the preceding sections are assessed against numerical experiments for a polyatomic gas with a single internal mode. Results are obtained by solving the appropriate Boltzmann transport equation via a Monte Carlo method. The transport properties of the model system are investigated by looking at the spontaneous fluctuations at thermal equilibrium [54, 22, 55, 56].

We first establish that the two temperature model of Section 2.2 gives an accurate description of the system transport properties as compared to direct solutions of the Boltzmann equation, in particular when the relaxation time is large as compared to the characteristic flow timescale. The one temperature model, instead, fails to describe the system behavior even in conditions of thermal equilibrium. The reason is that the one temperature model is the limit of the two temperature model when T^{tr} and T^{int} are equal (or close) *and* a relaxation approximation is valid, as discussed in Section 2.7.

We next verify that, when the relaxation time is small enough as compared to the characteristic flow timescale, both the two temperature model—with no volume viscosity—and the one temperature model—which includes a volume viscosity—are adequate to describe the properties of the system. In this limit, the two temperature model thus reduces to the one temperature model.

Interestingly, the dynamics of spontaneous fluctuations can actually be probed by light scattering experiments [56, 57, 58].

Before showing the results, we introduce the quantities used to describe the thermal fluctuations (Section 4.1) and the theoretical fluctuation spectra predicted by the one temperature (Section 4.2) and two temperature (Section 4.3) models, respectively. We then describe the Monte Carlo method used to solve the Boltzmann transport equation (Section 4.4). In Section 4.5 the physical model used for the calculations is described and, finally, Section 4.6 presents the results.

4.1 Kinetic theory of spontaneous fluctuations

The dynamics of the fluctuations of a variable $A(\mathbf{r}, t)$ is discussed by introducing the space-time correlation function

$$\delta A^2(\mathbf{r}, t; \mathbf{r}', t') = \langle \delta A(\mathbf{r}, t) \delta A(\mathbf{r}', t') \rangle, \quad (4.1)$$

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

$$\delta A^2(\mathbf{r}, t; \mathbf{r}', t') = \delta A^2(|\mathbf{r} - \mathbf{r}'|, t - t'). \quad (4.2)$$

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 [56]

$$\delta n^2(k, \omega) = \int e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \delta n^2(\mathbf{r}, t) d\mathbf{r} dt. \quad (4.3)$$

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 $\langle \delta \rho_k^*(0) \widetilde{\delta \rho_k}(s) \rangle$.

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

$$\frac{S(k, \omega)}{S(k)} = 2Re \lim_{\epsilon \rightarrow 0} \frac{\langle \delta \rho_k^*(0) \widetilde{\delta \rho_k}(s) \rangle}{\langle \delta \rho_k^*(0) \delta \rho_k(0) \rangle}. \quad (4.4)$$

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 following parameter

$$y = \frac{8}{3\sqrt{2}\pi} \frac{\rho_0 \sqrt{k_B T / m}}{\eta k}, \quad (4.5)$$

where ρ_0 is the equilibrium density, η is the shear viscosity and k is the fluctuation wavenumber. The collisionless limit corresponds to $y \rightarrow 0$, whereas the hydrodynamic limit ($k \rightarrow 0$) is approached for $y \geq 5$. In the following we derive the thermal fluctuation power spectra in the hydrodynamic regime as obtained by the one temperature model (eqs. (2.5), (2.6), (2.48)) and the two temperature model (eqs. (2.5), (2.6), (2.7), (2.8)) fluid equations.

4.2 Fluctuation power spectrum from the one-temperature model

The fluctuation power spectrum for a fluid described by the (1T) Navier Stokes equations is reported in the book by J.P. Boon and S. Yip [54]

$$\begin{aligned} \delta\rho^2(k, \omega) = & \frac{\gamma - 1}{\gamma} \frac{2\chi k^2}{\omega^2 + (\chi k^2)^2} + \frac{1}{\gamma} \left[\frac{\Gamma k^2}{(\omega + c_0 k)^2 + (\Gamma k^2)^2} + \frac{\Gamma k^2}{(\omega - c_0 k)^2 + (\Gamma k^2)^2} \right] \\ & + \frac{1}{\gamma} [\Gamma + (\gamma - 1)\chi] \frac{k}{c_0} \left[\frac{\omega + c_0 k}{(\omega + c_0 k)^2 + (\Gamma k^2)^2} - \frac{\omega - c_0 k}{(\omega - c_0 k)^2 + (\Gamma k^2)^2} \right], \end{aligned} \quad (4.6)$$

where γ is the specific heat ratio, c_0 the speed of sound, χ the thermal diffusivity and

$$\Gamma = \frac{1}{2} \left(\frac{\frac{4}{3}\eta + \kappa}{\rho_0} + (\gamma - 1)\chi \right),$$

is the sound absorption coefficient.

The spectrum of the density autocorrelation function gives information on thermodynamic and transport properties of the fluid. The position of the Brillouin peaks is a measure of the speed of sound. The width of the Rayleigh peak is a measure of the thermal diffusivity, the width of the Brillouin peaks a measure of the sound absorption coefficient, the Rayleigh-to-Brillouin peak area ratio a measure of the specific heat ratio (Landau-Placzek ratio).

4.3 Fluctuation power spectrum from the two-temperature model

Since the fluctuation power spectrum has not been explicitly reported in the literature we sketch here the main steps required for its calculation. We start from the fluid equations (eqs. (2.5), (2.6), (2.7), (2.8)) that we rewrite here for convenience

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (4.7)$$

$$\partial_t (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v} + p \mathbf{I}) + \nabla \cdot \mathbf{II} = 0, \quad (4.8)$$

$$\partial_t \mathcal{E}^{\text{tr}} + \nabla \cdot (\mathbf{v} \mathcal{E}^{\text{tr}}) + \nabla \cdot \mathbf{Q}^{\text{tr}} = -p \nabla \cdot \mathbf{v} - \mathbf{II} : \nabla \mathbf{v} - \omega_1^{\text{int}}, \quad (4.9)$$

$$\partial_t \mathcal{E}^{\text{int}} + \nabla \cdot (\mathbf{v} \mathcal{E}^{\text{int}}) + \nabla \cdot \mathbf{Q}^{\text{int}} = \omega_1^{\text{int}}. \quad (4.10)$$

Taking into account the Navier-Stokes expression for the pressure tensor, eq. (2.11), we rewrite eq. (4.8) as

$$\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v} + \frac{k_{\text{B}} T^{\text{tr}}}{m} \frac{\nabla \rho}{\rho} + \frac{k_{\text{B}}}{m} \nabla T^{\text{tr}} - \frac{\eta}{\rho} \left[\nabla^2 \mathbf{v} + \frac{1}{3} \nabla (\nabla \cdot \mathbf{v}) \right] = 0. \quad (4.11)$$

Analogously, making use of expressions (2.12), (2.13), we rewrite eqs. (4.9), (4.10) as

$$\begin{aligned} \partial_t T^{\text{tr}} + \mathbf{v} \cdot \nabla T^{\text{tr}} + \frac{p}{nc^{\text{tr}}} \nabla \cdot \mathbf{v} - \frac{\lambda^{\text{tr, tr}}}{nc^{\text{tr}}} \nabla^2 T^{\text{tr}} \\ - \frac{\lambda^{\text{tr, int}}}{nc^{\text{tr}}} \nabla^2 T^{\text{int}} - 2 \frac{\eta}{nc^{\text{tr}}} (\nabla \mathbf{v})_0^s : \nabla \mathbf{v} + \frac{1}{nc^{\text{tr}}} \omega_1^{\text{int}} = 0, \end{aligned} \quad (4.12)$$

$$\partial_t T^{\text{int}} + \mathbf{v} \cdot \nabla T^{\text{int}} - \frac{\lambda^{\text{int, int}}}{nc^{\text{int}}} \nabla^2 T^{\text{int}} - \frac{\lambda^{\text{int, tr}}}{nc^{\text{int}}} \nabla^2 T^{\text{tr}} - \frac{1}{nc^{\text{int}}} \omega_1^{\text{int}} = 0, \quad (4.13)$$

where $(\nabla \mathbf{v})_0^s = \frac{1}{2} [\nabla \mathbf{v} + (\nabla \mathbf{v})^t] - \frac{2}{3} (\nabla \cdot \mathbf{v}) \mathbf{I}$. Note that the transport coefficients are considered as fixed parameters.

We now linearize eqs. (4.7), (4.11), (4.12), (4.13) around the equilibrium solution. Introducing the fluctuations

$$\delta\rho = \rho - \rho_0, \quad \delta\mathbf{v} = \mathbf{v}, \quad \delta T^{\text{tr}} = T^{\text{tr}} - T_0, \quad \delta T^{\text{int}} = T^{\text{int}} - T_0. \quad (4.14)$$

where the subscript denotes the equilibrium average value, into the equations, one obtains, to the first order in the fluctuations, the following set of linearized equations

$$\partial_t \delta \rho + \rho_0 \nabla \cdot \mathbf{v} = 0, \quad (4.15)$$

$$\left[\partial_t - \frac{\eta}{\rho_0} (\nabla^2 + \frac{1}{3} \nabla \nabla \cdot) \right] \mathbf{v} + \frac{k_B T_0}{m} \frac{1}{\rho_0} \nabla \delta \rho + \frac{k_B}{m} \nabla \delta T^{\text{tr}} = 0, \quad (4.16)$$

$$\left[\partial_t - \frac{\lambda^{\text{tr, tr}}}{n c^{\text{tr}}} \nabla^2 + \frac{c^{\text{int}}}{c^{\text{tr}}} \frac{1}{\tau_1} \right] \delta T^{\text{tr}} + \frac{p}{n c^{\text{tr}}} \nabla \cdot \mathbf{v} - \left[\frac{\lambda^{\text{tr, int}}}{n c^{\text{tr}}} \nabla^2 + \frac{c^{\text{int}}}{c^{\text{tr}}} \frac{1}{\tau_1} \right] \delta T^{\text{int}} = 0, \quad (4.17)$$

$$\left[\partial_t - \frac{\lambda^{\text{int, int}}}{n c^{\text{int}}} \nabla^2 + \frac{1}{\tau_1} \right] \delta T^{\text{int}} - \left[\frac{\lambda^{\text{int, tr}}}{n c^{\text{int}}} \nabla^2 + \frac{1}{\tau_1} \right] \delta T^{\text{tr}} = 0, \quad (4.18)$$

where we have formally introduced the internal energy relaxation time as

$$\omega_1^{\text{int}} = \frac{n c^{\text{int}}}{\tau_1} (T^{\text{tr}} - T^{\text{int}}). \quad (4.19)$$

Denoting the spatial Fourier transform by

$$\delta A_k(t) = \int d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} \delta A(\mathbf{r}, t), \quad (4.20)$$

and the Laplace transform by

$$\widetilde{\delta A}_k(s = \epsilon + i\omega) = \int dt e^{-st} \delta A_k(t), \quad (4.21)$$

where $i^2 = -1$ and $k^2 = \mathbf{k} \cdot \mathbf{k}$, we now perform a double Laplace-Fourier transformation of the linearized equations

$$s \widetilde{\delta \rho}_k(s) + i\mathbf{k} \cdot \widetilde{\mathbf{j}}_k(s) = \delta \rho_k(0), \quad (4.22)$$

$$\left(s + \frac{4}{3} \frac{\eta}{\rho_0} k^2 \right) \widetilde{\mathbf{j}}_k(s) + \frac{k_B}{m} i\mathbf{k} (T_0 \widetilde{\delta \rho}_k(s) + \widetilde{g}_k(s)) = \mathbf{j}_k(0), \quad (4.23)$$

$$\left(s + \frac{\lambda^{\text{tr, tr}}}{n c^{\text{tr}}} k^2 + \frac{c^{\text{int}}}{c^{\text{tr}}} \frac{1}{\tau_1} \right) \widetilde{g}_k(s) + \frac{k_B T_0}{c^{\text{tr}}} i\mathbf{k} \cdot \widetilde{\mathbf{j}}_k(s) + \left(\frac{\lambda^{\text{tr, int}}}{n c^{\text{tr}}} k^2 - \frac{c^{\text{int}}}{c^{\text{tr}}} \frac{1}{\tau_1} \right) \widetilde{h}_k(s) = g_k(0), \quad (4.24)$$

$$\left(s + \frac{\lambda^{\text{int, int}}}{n c^{\text{int}}} k^2 + \frac{1}{\tau_1} \right) \widetilde{h}_k(s) + \left(\frac{\lambda^{\text{int, tr}}}{n c^{\text{int}}} k^2 - \frac{1}{\tau_1} \right) \widetilde{g}_k(s) = h_k(0), \quad (4.25)$$

where $\widetilde{\mathbf{j}}_k(s)$, $\widetilde{g}_k(s)$, $\widetilde{h}_k(s)$ are the Fourier transforms of $\rho_0 \mathbf{v}$, $\rho_0 \delta T^{\text{tr}}$, $\rho_0 \delta T^{\text{int}}$, respectively.

We now solve this linear system for $\widetilde{\delta \rho}_k(s)$ with the Kramer rule and then construct the correlation function $\langle \delta \rho_k^*(0) \widetilde{\delta \rho}_k(s) \rangle$

$$\langle \delta \rho_k^*(0) \widetilde{\delta \rho}_k(s) \rangle = \frac{N(k, s)}{M(k, s)} \langle \delta \rho_k^*(0) \delta \rho_k(0) \rangle. \quad (4.26)$$

where $M(k, s)$ is the determinant of the coefficient matrix for the linear system and $N(k, s)$ is obtained from $M(k, s)$ by deleting the first row and the first column, keeping in mind that the macroscopic variables are statistically independent variables so that cross-correlation terms vanish. The functions $M(k, s)$ and $N(k, s)$ are therefore polynomials in s of degree 4 and 3, respectively, and, by taking the limit $\epsilon \rightarrow 0$, we can then write

$$N(k, \omega) = -i\omega^3 - b_1(k)\omega^2 + ib_2(k)\omega + b_3(k), \quad (4.27)$$

$$M(k, \omega) = \omega^4 - ib_1(k)\omega^3 - b_4(k)\omega^2 + ib_5(k)\omega + b_6(k), \quad (4.28)$$

where the expressions for the polynomials $b_j(k)$, $1 \leq j \leq 6$, are easily evaluated. We have now all ingredients to compute the fluctuation power spectrum from eq. (4.4).

4.4 Simulation of spontaneous fluctuations in a dilute gas

Thermodynamic fluctuations in gases, provided the density is low enough that only bimolecular collisions are effective, are described by the Boltzmann equation. We then aim to compare the theoretical results derived in Sections 4.2, 4.3 with those of a numerical experiment where a Monte Carlo method is applied to the solution of the Boltzmann transport 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 an integro-differential equation for the space-time correlator of the fluctuations of the distribution function is obtained [59]. 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 (DSMC)[23]. 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 [27]. The principle of the method is the decoupling, over a small timestep, 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[60].

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[61], 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.

When setting up a simulation, appropriate simulation and sampling requirements have to be specified. Provided the typical requirements of DSMC simulations are met (timestep, cell size, number of simulated particles per cell) results are not very sensitive to the particular values chosen for the simulation parameters. In this study the following values have been employed throughout

- Cell width to mean free path ratio: 0.3
- Timestep to mean free time ratio: 0.05
- Average number of simulated particles per cell: 20

Also, we mention that implementing periodic boundary conditions can introduce spurious correlations due to the finite size of the simulation sample. Therefore the simulation domain is kept in contact with an infinite reservoir of the gas at the specified equilibrium conditions. Care must be taken, in this case, to sample accurately the statistics of the incoming particles[62].

The details on how the data are sampled, instead, have a big impact on the simulated spectra. First, given a minimum wavelength to be sampled, fluctuation data are averaged over the appropriate number of cells so that shorter wavelengths do not contribute. The same is done in the time domain.

The maximum sampled frequency should be chosen carefully so that all significant frequencies are sampled correctly. Neglected frequencies spuriously contribute to the sampled spectrum with a

phenomenon known as *aliasing*. We choose to sample up to the 16th harmonic, both in the space and time domains.

A number of wavelengths must be simulated in order to increase the signal-to-noise ratio. A compromise must be sought, obviously, between quality of the results and computational cost. For each spectrum we sample 4096 time points and 64 wavelengths (corresponding to 2048 spatial points). With these parameters we obtain a signal-to-noise ratio of 10^{-3} , i.e., the high frequency background noise lies 3 orders of magnitude below the maximum value.

The use of Monte Carlo particle methods for the study of hydrodynamic fluctuations in gases has been demonstrated many years ago by M. Mansour and coworkers [21] who studied with DSMC a nonequilibrium gas subject to a fixed heat flux; also, one of the authors has applied DSMC to the simulation of the fluctuation power spectra in a monoatomic gas (Argon) showing that DSMC gives correct results both in hydrodynamic and rarefied regimes [22].

In the present case we apply the method to the simulation of the spontaneous fluctuations of a model gas with internal degrees of freedom. We then turn to a discussion of the properties of the model system under study.

4.5 Physical system

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

$$a_0 = 1, \quad E_0 = 0 \text{ J}, \quad (4.29)$$

$$a_1 = 9, \quad E_1 = k_B \cdot 1000 \text{ J}. \quad (4.30)$$

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

$$p(0 \leftarrow 1) = p_0, \quad (4.31)$$

$$p(1 \leftarrow 0) = \begin{cases} 0 & \epsilon_k < E_1 \\ a_1 p_0 (1 - \frac{E_1}{\epsilon_k}) & \epsilon_k \geq E_1 \end{cases} \quad (4.32)$$

where $\epsilon_k = \frac{1}{2}\mu g^2$ is the kinetic energy in collision.

For this simple model all thermodynamic and transport properties can be calculated explicitly. In particular, in thermal equilibrium ($T^{\text{tr}} \approx T^{\text{int}} \approx T_0$)

$$\tau_c = \frac{1}{\sqrt{2}} \frac{1}{\sigma n} \frac{1}{\sqrt{k_B T_0/m}}, \quad (4.33)$$

$$c^{\text{int}} = k_B \left(\frac{E_1}{k_B T_0}\right)^2 \frac{n_1}{n} \frac{n_0}{n}, \quad (4.34)$$

$$\tau_0^{-1} = n K_1^0 (1 + a_1 e^{-\frac{E_1}{k_B T_0}}), \quad (4.35)$$

$$K_1^0 = 4 p_0 \sigma \sqrt{\frac{k_B T_0}{\pi m}} \quad (4.36)$$

where τ_c denotes the mean collision time. Note that in the calculation of the fluctuation power spectrum for the two temperature model the zero-order approximation, τ_0 has been used in place of τ_1 since we have seen in Section 2.6 that the term w_1^{int} is small.

As for the transport coefficients, the contribution of inelastic processes to the collision integrals cannot be neglected in the case of fast relaxation.

The shear and volume viscosities have been evaluated from the following expressions

$$\eta = \frac{5}{16} \frac{\sqrt{\pi m k_B T_0}}{\sigma}, \quad (4.37)$$

$$\kappa = \frac{k_B p}{c_v^2} c^{\text{int}} \tau_0^{\text{int}}. \quad (4.38)$$

The thermal conductivities have been evaluated from [45]

$$\lambda^{\text{tr, tr}} = \frac{m}{6T} \langle a^{\text{tr}}, b^{\text{tr}} \rangle, \quad \lambda^{\text{tr, int}} = \frac{m}{6T} \langle a^{\text{tr}}, b^{\text{int}} \rangle, \quad (4.39)$$

$$\lambda^{\text{int, tr}} = \frac{m}{6T} \langle a^{\text{int}}, b^{\text{tr}} \rangle, \quad \lambda^{\text{int, int}} = \frac{m}{6T} \langle a^{\text{int}}, b^{\text{int}} \rangle. \quad (4.40)$$

where a^{tr} and a^{int} are solutions of the linear systems $A \cdot a^{\text{tr}} = b^{\text{tr}}$ and $A \cdot a^{\text{int}} = b^{\text{int}}$, where

$$b^{\text{tr}} = \begin{pmatrix} 3\frac{5}{2} \frac{k_B}{m} T_0 \\ 0 \end{pmatrix}, \quad b^{\text{int}} = \begin{pmatrix} 0 \\ 3\frac{c^{\text{int}}}{m} T_0 \end{pmatrix}. \quad (4.41)$$

The matrix elements are those described in Ferziger's book [5], eqs. (11.3-57); for the present model they read

$$A_{11} = 4\Omega^{(2,2)} + \frac{c^{\text{int}}}{k_B} \frac{1}{n\tau_0^{\text{int}}} \frac{8 + \frac{8}{3}x + \frac{11}{4}x^2}{x^2}, \quad (4.42)$$

$$A_{12} = A_{21} = -\frac{5}{4} \frac{c^{\text{int}}}{k_B} \frac{1}{n\tau_0^{\text{int}}}, \quad (4.43)$$

$$A_{22} = 4\sqrt{\frac{k_B T_0}{\pi m}} \frac{c^{\text{int}}}{k_B} \Omega^{(1,1)} + \frac{c^{\text{int}}}{k_B} \frac{1}{n\tau_0^{\text{int}}} \left(\frac{7}{4} + \frac{n_1}{n} \frac{x}{2} \right). \quad (4.44)$$

where $x = \frac{E_1}{k_B T_0}$.

The resulting expressions for the thermal conductivity coefficients reduce to the eqs. (11.3-60) of Ferziger's book [5] only in the limit $\frac{A_{12}}{A_{11}} \ll 1$ and $\frac{A_{12}}{A_{22}} \ll 1$. When the relaxation is slow, the cross terms $\lambda^{\text{tr, int}}$ and $\lambda^{\text{int, tr}}$ are not very important. For $p_0 = 0.01$ for instance, we have $\lambda^{\text{tr, tr}} = 1.08 \cdot 10^{-2}$, $\lambda^{\text{tr, int}} = 1.36 \cdot 10^{-4}$, $\lambda^{\text{int, tr}} = 1.36 \cdot 10^{-4}$, and $\lambda^{\text{int, int}} = 7.22 \cdot 10^{-3}$.

On the other hand, these cross contributions are important when relaxation is fast. For $p_0 = 0.1$, for instance, we have $\lambda^{\text{tr, tr}} = 7.46 \cdot 10^{-3}$, $\lambda^{\text{tr, int}} = 7.07 \cdot 10^{-4}$, $\lambda^{\text{int, tr}} = 7.07 \cdot 10^{-4}$, and $\lambda^{\text{int, int}} = 5.49 \cdot 10^{-3}$. In this situation, the differences are noticeable, and comparison with the DSMC results shows that inclusion of the cross contributions are important.

4.6 Results and discussion

Simulations are conducted for the model gas described in the preceding section, in the following conditions

Temperature $T = 285.71 \text{ K}$

Density $n = 2.4 \cdot 10^{21} \text{ m}^{-3}$

The fluctuation spectra are sampled at the wavelength $2\pi/k = 0.02 \text{ m}$ 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 $\tau_0 \approx 7.0 \cdot 10^{-5} \text{ s}$ ($Z \equiv \frac{\tau_0}{\tau_c} = 49$). 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 $\tau_0 = 7.0 \cdot 10^{-6} \text{ s}$ ($Z \equiv \frac{\tau_0}{\tau_c} = 4.9$).

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 not trivial since there is an important contribution of the bulk viscosity to

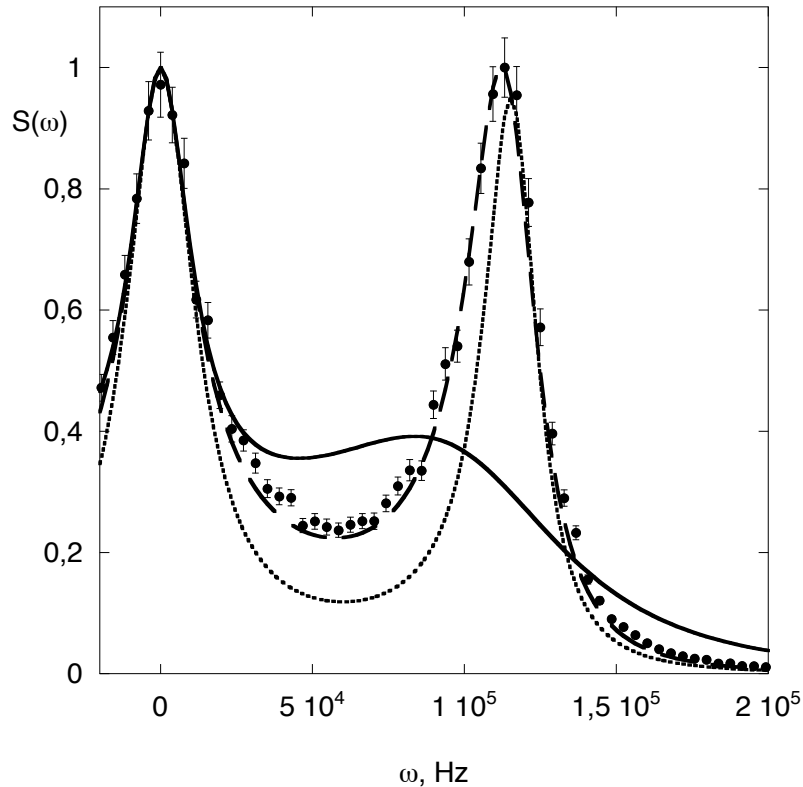


Figure 1: Fluctuation power spectra for the slow relaxation case ($p_0 = 0.01$). The spectra are normalized to unit maximum value. Full line: 1T model; dotted line: frozen; dashed line: 2T model; symbols: DSMC.

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.

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[63]. 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.

5 Conclusions

We have investigated the relaxation of internal temperature and the concept of volume viscosity in nonequilibrium gas models derived from the kinetic theory. When the rate for internal energy exchange is slow, the relaxation approximation leads to the definition of a multitemperature volume viscosity coefficient. In the near thermodynamic equilibrium limit, the full classical one-temperature polyatomic gas model including the volume viscosity is recovered.

The Monte Carlo simulations of spontaneous fluctuations near thermal equilibrium obtained by solving the Boltzmann equation fully agree with these theoretical results. When the characteristic time of internal energy relaxation is larger than the flow characteristic time, the two temperature model gives an accurate description of the system and the one temperature model fails. On the other

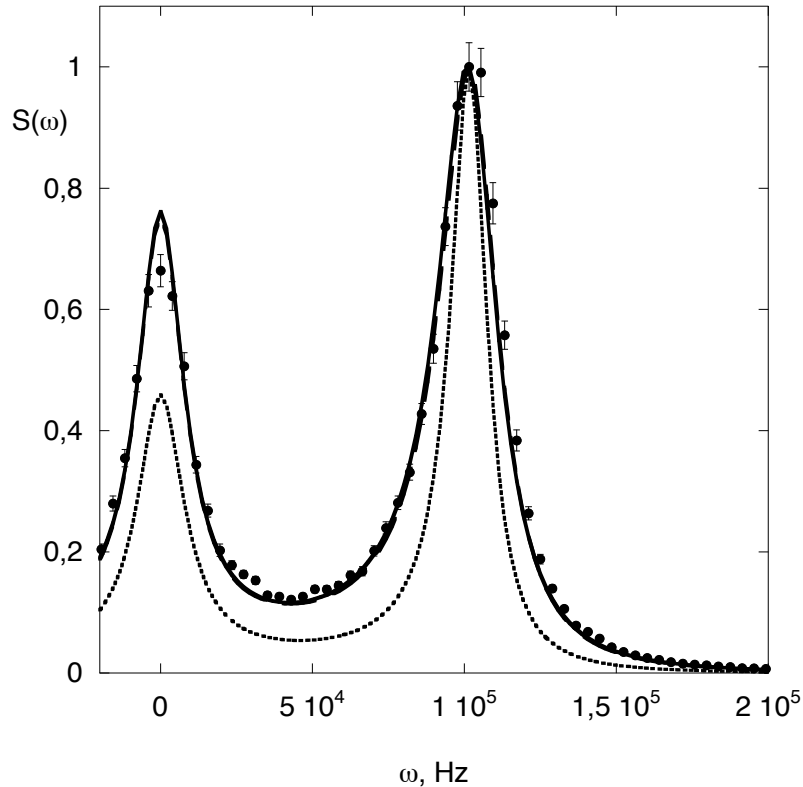


Figure 2: Fluctuation power spectra for the fast relaxation case ($p_0 = 0.1$). The spectra are normalized to unit maximum value. Full line: 1T model; dotted line: 1T model without bulk viscosity; dashed line: 2T model; symbols: DSMC.

hand, when the characteristic time of internal energy relaxation is smaller than the flow time, both the two temperature model and the one temperature model *including the volume viscosity* are adequate to describe the fluid.

Finally, when there is a fast and a slow internal energy mode, there are four contributions to the volume viscosity in the relaxation regime and, in the thermodynamic equilibrium limit, the sum of these four terms converge towards the one-temperature two-mode volume viscosity obtained independently from the Chapman-Enskog method. Future work should consider numerical simulations with multiple internal energy modes and more generally states far from thermodynamic equilibrium.

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A The one-temperature two-mode volume viscosity

We investigate in this section the volume viscosity associated with a one-temperature two-mode polyatomic gas. The standard linear system associated with the evaluation of the two-mode volume viscosity is obtained with the Galerkin variational approximation space spanned by the orthogonal polynomials $\phi^{0010} = \frac{3}{2} - \frac{1}{2} \frac{m}{k_B T} (\mathbf{c} - \mathbf{v}) \cdot (\mathbf{c} - \mathbf{v})$, $\phi^{0001\text{rap}} = (\bar{E}^{\text{rap}} - E_i^{\text{rap}})/k_B T$, and $\phi^{0001\text{sl}} = (\bar{E}^{\text{sl}} - E_i^{\text{sl}})/k_B T$. Note that the general solution of the Transport Linear Systems as well as their mathematical structure has been investigated [45, 46, 64, 65, 66, 67]. Of course, the modes are termed ‘rapid’ and ‘slow’ for notational consistency with the nonequilibrium framework, but in the thermodynamic equilibrium framework they are all fast. The corresponding linear system of size 3 is in the form [46]

$$\begin{cases} K\alpha = \beta, \\ \langle \mathcal{K}, \alpha \rangle = 0, \end{cases} \quad (\text{A.1})$$

where K denotes the system matrix, \mathcal{K} the constraint vector, $\alpha = (\alpha^{10}, \alpha^{01\text{rap}}, \alpha^{01\text{sl}})^t$ the unknown vector, $\beta = (\beta^{10}, \beta^{01\text{rap}}, \beta^{01\text{sl}})^t$ the right hand side vector, and the volume viscosity is finally given by $\kappa = \alpha^{10}\beta^{10} + \alpha^{01\text{rap}}\beta^{01\text{rap}} + \alpha^{01\text{sl}}\beta^{01\text{sl}}$. 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 $\mathcal{K} = (c^{\text{tr}}, c^{\text{rap}}, c^{\text{sl}})^t$, and the right hand side vector by $\beta = (c^{\text{rap}} + c^{\text{sl}}, -c^{\text{rap}}, -c^{\text{sl}})^t/c_v$.

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

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

$$\kappa = \frac{1}{c_v^2} \frac{(c^{\text{rap}})^2 K^{\text{sl,sl}} - 2c^{\text{rap}}c^{\text{sl}}K^{\text{rap,sl}} + (c^{\text{sl}})^2 K^{\text{rap,rap}}}{K^{\text{rap,rap}}K^{\text{sl,sl}} - K^{\text{rap,sl}}K^{\text{rap,sl}}}. \quad (\text{A.2})$$

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 $K^{\text{rap,rap}}$ is large and that the cross terms $K^{\text{rap,sl}} = K^{\text{sl,rap}}$ are also small. We therefore neglect the square term $K^{\text{sl,rap}}K^{\text{rap,sl}}$ in the previous expression and the limiting value of the effective nonequilibrium volume viscosity should thus be

$$\kappa = \left(\frac{c^{\text{rap}}}{c_v}\right)^2 \frac{(k_{\text{B}}T)^3}{2\langle (\Delta E^{\text{rap}})^2 \rangle} - \frac{c^{\text{rap}}c^{\text{sl}}}{c_v^2} \frac{(k_{\text{B}}T)^3 \langle (\Delta E^{\text{rap}})(\Delta E^{\text{sl}}) \rangle}{\langle (\Delta E^{\text{rap}})^2 \rangle \langle (\Delta E^{\text{sl}})^2 \rangle} + \left(\frac{c^{\text{sl}}}{c_v}\right)^2 \frac{(k_{\text{B}}T)^3}{2\langle (\Delta E^{\text{sl}})^2 \rangle}. \quad (\text{A.3})$$

References

- [1] M. Kohler, Reibung in mäßig verdünnten gasen als folge verzögerter einstellung der energie, *Zeitschr. Phys.*, 125, (1949), pp 715-732.
- [2] J.O. Hirschfelder, C.F. Curtiss, R.B. Bird, 'Molecular theory of gases and liquids', New-York, Wiley, (1954).
- [3] L. Waldmann, E. Trübenbacher, Formale kinetische Theorie von Gasgemischen aus anregbaren molekülen, *Zeitschr. Naturforsch.*, 17a, (1962), pp 363-376.
- [4] S. Chapman and T.G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, Cambridge University Press, (1970).
- [5] J.H. Ferziger, H.G. Kaper, *Mathematical theory of transport processes in gases*, North Holland, Amsterdam, (1972).
- [6] F.R. McCourt, J.J. Beenakker, W.E. Köhler, I. Kuscer, *Non equilibrium phenomena in polyatomic gases*, Volume I: Dilute gases, Volume II: Cross sections, scattering and rarefied gases, Clarendon Press, Oxford, (1990).
- [7] V. Giovangigli, *Multicomponent flow modeling*, Birkhäuser, Boston, (1999).
- [8] A. Ern and V. Giovangigli, *The Kinetic equilibrium regime*, *Physica-A*, 260 (1998), pp. 49–72.
- [9] S.R. de Groot and P. Mazur, *Non-equilibrium thermodynamics* Dover publications, Inc. New York, 1984.
- [10] J. Keizer *Statistical Thermodynamics of Nonequilibrium Processes*, Springer-Verlag, New York, (1987).
- [11] P.W. Hermans, L.F.J. Hermans, and J.J.M. Beenakker, A survey of experimental data related to the non-spherical interaction for the hydrogen isotopes and their mixture with noble gases, *Physica A*, 122, (1983), pp 173–211.
- [12] G.J. Prangma, L.J.M. Borsboom, H.F.P. Knaap, C.J.N. Van den Meijdenberg, and J.J.M. Beenakker, Rotational relaxation in ortho Hydrogen between 170 and 300 K, *Physica*, 61, (1972), pp 527–538.

- [13] G.J. Prangma, A.H. Alberga, and J.J.M. Beenakker, Ultrasonic determination of the volume viscosity of N_2 , CO , CH_4 , and CD_4 between 77 and 300K, *Physica*, 64, (1973), pp 278–288.
- [14] L. Tisza, Supersonic absorption and Stokes viscosity relation, *Physical Review*, 61, (1941), pp 531–536.
- [15] A.F. Turfa, H.F.P. Knaap, B.J. Thijsse, and J.J.M. Beenakker, A classical dynamics study of rotational relaxation in nitrogen gases, *Physical A*, 112, (1982), pp 19–28.
- [16] S.M. Karim and L. Rosenhead, The second coefficient of viscosity of Liquids and gases, *Reviews of Modern Physics*, 24, (1952), pp 108–116.
- [17] G. Emanuel, Bulk viscosity of a dilute polyatomic gas, *Phys. Fluids, A*, 2, (1990), pp 2252–2254.
- [18] G. Emanuel, Effect of bulk viscosity on a hypersonic boundary layer *Phys. Fluids, A*, 4, (1992), pp 491–495.
- [19] R. E. Graves and B. Argrow, Bulk viscosity : past to present, *Journal of Thermophysics and Heat Transfer*, 13, (1999), pp 337–342.
- [20] G. Billet, V. Giovangigli, and G. de Gassowski, Impact of Volume Viscosity on a Shock/Hydrogen Bubble Interaction, *Comb. Theory Mod.*, 12, (2008), pp. 221–248.
- [21] M. Malek Mansour, A.L. Garcia, G.C. Lie, E. Clementi, Fluctuating Hydrodynamics in a Dilute Gas, *Phys. Rev. Lett.*, 58, (1987), pp 874–877.
- [22] D. Bruno, M. Capitelli, S. Longo, P. Minelli, Monte Carlo simulation of light scattering spectra in atomic gases, *Chem. Phys. Lett.*, 422, (2006), pp 571–574.
- [23] M.S. Ivanov, S.F. Gimelshein, Computational hypersonic rarefied flows, *Annu. Rev. Fluid Mech.*, 30, (1998), pp 469–505.
- [24] E. Oran, C. Oh, and B. Cybyk. Direct simulation Monte Carlo: Recent advances and applications, *Ann. Rev. Fluid Mech.*, 30, 1998, pp. 403–441.
- [25] G. Bird. Recent advances and current challenges for DSMC, *Comp. Math. App.*, 35, (1998), 1-2:1–14.
- [26] A. Frezzotti. A particle scheme for the numerical solution of the Enskog equation, *Phys. Fluids*, 9, (1997), pp. 1329–1335.
- [27] D. Bruno, M. Capitelli, S. Longo, Direct Simulation of non-equilibrium kinetics under shock conditions in nitrogen, *Chem. Phys. Lett.*, 360, (2002), pp 31–37.
- [28] M. Capitelli, I. Armenise, D. Bruno, M. Cacciatore, R. Celiberto, G. Colonna, O. de Pascale, P. Diomede, F. Esposito, C. Gorse, K. Hassouni, A. Laricchiuta, S. Longo, D. Pagano, D. Pietanza, and M. Rutigliano, Non-equilibrium Plasma Kinetics: A state-to-state approach, *Plasma Sourc. Sci. Tech.*, 16, (2007), pp S30–S44.
- [29] G. Colonna, I. Armenise, D. Bruno, and M. Capitelli, Reduction of state-to-state kinetics to macroscopic models in hypersonic flows, *J. Thermophys. Heat Transf.*, 20, (2006), pp 477–486.
- [30] A. Chikhaoui, J. P. Dudon, E. V. Kustova, E. A. Nagnibeda, Transport properties in reacting mixture of polyatomic gases, *Physica A*, 247, (1997), pp 526–552.
- [31] E. V. Kustova, On the simplified state-to-state transport coefficients, *Chem. Phys.*, 270, (2001), pp 177–195.
- [32] E.V. Kustova, E.A. Nagnibada, and A. Chikhaoui, On the accuracy of nonequilibrium transport coefficients calculation, *Chem. Phys.*, 270, (2001), pp. 459–469.
- [33] V. M. Zhdanov, *Transport processes in multicomponent plasmas*, Taylor and Francis, London, (2002).
- [34] E.A. Nagnibeda and E.A. Kustova, *Kinetic Theory of Transport and Relaxation Processes in Non-Equilibrium Reacting Flows*, Saint-Petersburg University press (in russian) (2003).

- [35] E. Nagnibeda and E. Kustova, *Non-equilibrium reacting gas flow*, Springer Verlag, Berlin, (2009).
- [36] R. Brun, *Introduction to Reactive Gas Dynamics*, Oxford University press, Oxford, (2009).
- [37] E. G. Kolesnichenko and Y. E. Gorbachev, Gas-dynamic equations for spatially inhomogeneous gas mixtures with internal degrees of freedom. I. General theory, *Appl. Math. Mod.*, 34, (2010), pp 3778–3790.
- [38] S.I. Braginskii, Transport processes in a plasma, M.A. Leontovich editor, *Rev. of plasma phys.*, 1, (1965), pp 205–311.
- [39] S.I. Braginskii, Transport phenomena in a completely ionized two-temperature plasma *Soviet physics JETP*, 6(33), (1958), pp 358–369.
- [40] D. Bruno, M. Capitelli, and A. Dangola, Transport coefficients of partially ionized gases: A revisitiation, *AIAA Paper*, AIAA-2003-4039, (2003).
- [41] D. Bruno, A. Laricchiuta, M. Capitelli, C. Catalfamo, A. Chikhaoui, E. V. Kustova, and D. Giordano, Transport properties of equilibrium Argon plasma in a magnetic field, *AIAA Paper*, AIAA-2004-2161, (2004).
- [42] D. Bruno, C. Catalfamo, A. Laricchiuta, D. Giordano, and M. Capitelli, Convergence of Chapman-Enskog calculation of transport coefficients of magnetized Argon plasma, *Phys. Plasmas*, 13, (2006), 72307.
- [43] B. Graille, T. Magin and M. Massot, Kinetic Theory of Plasmas: Translational Energy, *Math. Mod. Meth. App. Sci.*, 10, (2009), pp. 1–2.
- [44] V. Giovangigli, B. Graille, T. Magin, and M. Massot, Multicomponent Transport in Weakly Ionized Mixtures, *Plasma Sources Sci. Tech.*, 19, (2010), 034002.
- [45] A. Ern and V. Giovangigli, Multicomponent Transport Algorithms, *Lecture Notes in Physics*, New series Monographs m24, (1994).
- [46] A. Ern and V. Giovangigli, Volume viscosity of dilute polyatomic gas mixtures, *Eur. J. Mech., B/Fluids*, 14, (1995), pp 653–669.
- [47] P. Garcia-Ybara, C. Nicoli, and P. Clavin, Soret and dilution effects on premixed flames, *Comb. Sci. Tech.*, 42, (1984), pp 87–109.
- [48] D.E. Rosner, Thermal (Soret) diffusion effects on interfacial mass transport rates, *PhysicoChemical Hydrodynamics*, 1, (1996), pp 159–185.
- [49] R.D. Hancock, F.R. Schauer, R.P. Lucht, V.R. Katta, and K.Y. Hsu, Thermal diffusion effects and vortex-flame interactions in hydrogen jet diffusion flames, *Proc. Combust. Inst.*, 26, (1996), pp 1087–1093.
- [50] A. Ern and V. Giovangigli, Thermal Diffusion Effects in Hydrogen-Air and Methane-Air Flames, *Comb. Theory Mod.*, 2, (1998), pp 349–372.
- [51] A. Ern and V. Giovangigli, Impact of multicomponent transport on planar and counterflow hydrogen/air and methane/air flames, *Comb. Sci. Tech.*, 149, (1999), pp 157–181.
- [52] R. Bendahkha, V. Giovangigli, and D. Rosner, Soret effects in laminar counterflow spray diffusion flames, *Comb. Theory Mod.*, 6, (2002), pp 1–17.
- [53] R. Hilbert, F. Tap, H. El-Rabii, and D. Thevenin, Impact of Detailed Chemistry and Transport Models on Turbulent Combustion Simulations, *Prog. Ener. Comb. Science*, 30, (2004), pp 61–117.
- [54] J. P. Boon, S. Yip, Hydrodynamic fluctuations, in *Molecular Hydrodynamics*, Dover, New York, (1991), pp 237-278.
- [55] R. Kubo, M. Toda, N. Hashitsume, Fluctuation and dissipation theorem, in *Statistical Physics II*, Springer, Berlin, (1978), pp 167-170.
- [56] B.J. Berne, R. Pecora, Light scattering from hydrodynamic modes, in *Dynamic Light Scattering*, Dover, New York, (2000), pp 223-246.

- [57] A. Einstein, Theorie der Opaleszenz von homogenen Flüssigkeiten und Flüssigkeitsgemischen in der Nähe des kritischen Zustandes, *Ann. Physik*, 33, (1910), pp 1275-1298.
- [58] R.D. Mountain, Spectral Distribution of Scattered Light in a Simple Fluid, *Rev. Mod. Phys.*, 38, (1966), pp 205-214.
- [59] E.M. Lifshitz, L.P. Pitaevskii, Fluctuations of the distribution function in an equilibrium gas, in *Physical Kinetics*, Butterworth-Heinemann, Oxford, (1995), pp 79-84.
- [60] K. Koura, H. Matsumoto, Variable Soft Sphere Molecular Model for Inverse-Power-Law or Lennard-Jones Potential, *Physics of Fluids A*, 3, (1991), pp 2459-2465.
- [61] L.D. Landau, E.M. Lifshitz, Spatial correlation of density fluctuations, in *Statistical Physics (Part 1)*, Butterworth-Heinemann, Oxford, (1980), pp 350-353.
- [62] M.W. Tysanner, A.L. Garcia, Non-equilibrium behaviour of equilibrium reservoirs in molecular simulations, *Int. J. Numer. Meth. Fluids*, 48, (2005), pp 1337-1349.
- [63] X. Pan, M.N. Shneider, R.B. Miles, Coherent Rayleigh-Brillouin scattering in molecular gases, *Phys. Rev. A*, 69, (2004), 033814.
- [64] A. Ern and V. Giovangigli, Fast and accurate multicomponent transport property evaluation, *J. Comp. Phys.*, 120, (1995), pp 105-116.
- [65] A. Ern and V. Giovangigli, Optimized transport algorithms for flame codes, *Comb. Sci. Tech.*, 118, (1995), pp 387-395.
- [66] A. Ern, V. Giovangigli, The structure of transport linear systems in dilute isotropic gas mixtures, *Phys. Rev. E*, 53, (1996), pp 485-492.
- [67] A. Ern, V. Giovangigli, Thermal conduction and thermal diffusion in dilute polyatomic gas mixtures, *Physica A*, 214, (1995), pp 526-546.