Relaxation phenomena in thermal molecular plasmas

Cite as: AIP Conference Proceedings **2293**, 050003 (2020); https://doi.org/10.1063/5.0027003
Published Online: 25 November 2020

A. A. Stepanenko, and V. M. Zhdanov

Relaxation Phenomena in Thermal Molecular Plasmas

A.A. Stepanenko[1, a)] and V.M. Zhdanov[1, b)]

[1]National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 115409 Moscow, Kashirskoe highway 31, Russia

[a)] Corresponding author: aastepanenko@mephi.ru
[b)] zhdanov@plasma.mephi.ru

Abstract. We present the results of analysis of relaxation phenomena in thermal molecular plasmas. The physical assumptions and the general scalar moment equations, obtained in the 17-moment approximation of the Grad method, are given. By using these equations, we derive the expressions for the relaxation pressure and bulk viscosity coefficients associated with heavy plasma components (atoms, molecules and their ions) and electrons. To gain a deeper understanding of how the physical parameters of particles and inter-particle interactions influence on the plasma relaxation properties, we also employ the semi-qualitative model of energy relaxation for plasma components. Within this model, the expressions for the partial relaxation pressures and bulk viscosity coefficients are derived and analyzed. It is demonstrated that depending on the plasma degree of ionization and the ratio of the characteristic timescales of energy exchange between particles, the partial relaxation pressures and bulk viscosity coefficients can not only vary but also change their signs.

INTRODUCTION

Molecular plasmas are widely used in industry [1,2], in particular those fields, which employ chemical processes, as plasmas are characterized by a much higher energy content and greater selectiveness in reactions behavior compared to the conventional gas or liquid chemical systems. For this reason, understanding the physics of energy relaxation processes in molecular plasmas is vital for successful operation of industrial facilities based on this technology.

In this contribution, we analyze the relaxation phenomena, taking place in thermal molecular plasmas. We start our analysis by defining the physical assumptions on plasma parameters and present the set of scalar moment equations following from the general one [3] in the 17-moments approximation of the Grad method. We derive the expressions for the partial relaxation pressures and bulk viscosity coefficients for electrons and heavy plasma components (molecules, atoms and their ions). To gain a deeper understanding of how these relations depend on the particles physical properties, we also establish a phenomenological model of energy relaxation in plasma and use it to analyze the rigorous expressions for the partial relaxation pressure and bulk viscosity coefficients.

PHYSICAL ASSUMPTIONS AND GENERAL EQUATIONS

We will consider plasma consisting of both neutral and charged particles. The first group of particles will be represented by an arbitrary number of molecular and atomic components, whereas the second group will consist of electrons and ions, both atomic and molecular.

To analyze the relaxation processes in plasma, we have to establish the hierarchy of timescales of energy exchange between particles translational and internal degrees of freedom. For this study, we will assume that

$$\tau_E < \tau_{eh}^{int} < \tau_{eh}^{tr} << \theta \, , \tag{1}$$

where τ_E is the characteristic timescale of the energy relaxation between the translational and internal degrees of freedom of the heavy plasma particles, τ_{eh}^{int} and τ_{eh}^{tr} are the characteristic timescales of the energy exchange between electrons and internal and translational degrees of freedom of the heavy plasma particles, respectively, and

International Conference of Numerical Analysis and Applied Mathematics ICNAAM 2019
AIP Conf. Proc. 2293, 050003-1–050003-4; https://doi.org/10.1063/5.0027003
Published by AIP Publishing. 978-0-7354-4025-8/$30.00

θ is the problem timescale. Opposite cases, when $\tau_E >> \theta$ or $\tau_{eh}^{int} >> \theta$, can be reduced to situations previously considered by other authors. In the first case ($\tau_E >> \theta$), the energy exchange between the particles is fully impeded and the translational and internal particle energies are frozen at their initial values. In case $\tau_{eh}^{int} >> \theta$ (while at the same time $\tau_E << \theta$), the energy exchange between the subsystems of electrons and heavy plasma particles is absent, and the equilibrium energy distributions are established in both subsystems independently. As a result, all heavy plasma particles (no matter their charge state) can be considered as a polyatomic gas mixture, its relaxation properties having been considered previously [4].

The heavy (neutrals and ions) and light (electrons) plasma components will be characterized by separate temperatures each. For the heavy plasma particles, we will adopt that all their temperatures (both translational and internal) are equal, i.e. $T_\alpha = T_h$ ($\alpha \neq e$), whereas the electron temperature T_e can be different from T_h.

We will use the set of scalar moment equations obtained in Ref. [3] and written in the 17-moments approximation of the Grad method [5]

$$\begin{aligned}
&\frac{c_V^{\text{int}}}{c_V} p_\alpha \nabla\cdot\mathbf{u} - \frac{3kp_\alpha}{2nc_V}\delta_{c0}\sum_\alpha\left(\frac{3}{2}+\langle\varepsilon_\alpha\rangle+\varepsilon_\alpha^c\right)S_\alpha - \delta_{c0}\bar{R}_{\alpha,eq.}^{r,010} = -\frac{2}{3}n\sum_\beta c_{\alpha\beta}\Delta E_\beta^{tr} + n\sum_\beta \frac{k}{c_{\beta V}^{int}} c'_{\alpha\beta}\Delta E_\beta^{\text{int}}, \\
&-\frac{p_\alpha c_{\alpha V}^{\text{int}}}{nc_V}\left[n\nabla\cdot\mathbf{u}+\delta_{c0}\sum_\alpha\left(\frac{3}{2}+\langle\varepsilon_\alpha\rangle+\varepsilon_\alpha^c\right)S_\alpha\right] - \delta_{c0}\bar{R}_{\alpha,eq.}^{r,001} = \frac{2}{3}n\sum_\beta d_{\alpha\beta}\Delta E_\beta^{tr} - n\sum_\beta \frac{k}{c_{\beta V}^{int}} d'_{\alpha\beta}\Delta E_\beta^{\text{int}}.
\end{aligned} \tag{2}$$

In this system $c_V^{int} = \sum_\alpha c_{\alpha V}^{int}$, $c_V = (3/2)k + c_V^{int}$ are, respectively, the plasma internal and total specific heats at constant pressure, $c_{\alpha V}^{int}$ is the partial (related to a single plasma component α) specific heat at constant pressure, $p_\alpha = n_\alpha kT_\alpha$ is the partial pressure for a plasma component α, $n = \sum_\alpha n_\alpha$ and $p = \sum_\alpha p_\alpha$ are, correspondingly, the total plasma concentration and pressure, $\langle\varepsilon_\alpha\rangle$ is the mean internal energy of particles of species α, ε_α^c is the reduced dissociation (for molecules) / ionization (for atoms) energy, S_α is the production rate for particles of species α, $\bar{R}_{\alpha,eq}^{r,0nq}$ are the moments of the reactive collision integral, and **u** is the mass-averaged plasma velocity. The Kronecker delta δ_{c0} is introduced to distinguish the cases of weak (c = 1) and strong (c = 0) deviation of plasma from chemical equilibrium. The quantities $\Delta E_\alpha^{tr} = E_\alpha^{tr} - (3/2)kT_\alpha$ and $\Delta E_\alpha^{int} = E_\alpha^{int} - c_{\alpha V}^{int} T_\alpha$ are the deviations of the mean translational and internal energies of particles of species α from their equilibrium values.

The matrix elements $c_{\alpha\beta}$, $c'_{\alpha\beta}$, $d_{\alpha\beta}$ and $d'_{\alpha\beta}$ describe the rates of the energy relaxation between the particles degrees of freedom. In general case, these expressions are rather cumbersome [5]. For this reason, below we present the expression for only one coefficient $c_{\alpha\beta}$, which can be represented as ($y_\alpha = n_\alpha / n$)

$$\begin{aligned}
c_{\alpha\beta} = {} & \delta_{\alpha\beta} y_\alpha \sum_\gamma \frac{2m_\gamma^2}{\left(m_\alpha + m_\gamma\right)^2}\left[\frac{c_{\alpha V}^{int}}{k}\tau_{E\alpha\gamma}^{-1}\left(1+\delta_{\alpha\gamma}\right) + \frac{3}{2}\frac{m_\alpha}{m_\gamma}\tau_{\alpha\gamma}^{-1}\left(1-\delta_{\alpha\gamma}\right)\right] + \\
& + \left(1-\delta_{\alpha\beta}\right) y_\alpha \frac{2m_\alpha m_\beta}{\left(m_\alpha + m_\beta\right)^2}\left(\frac{c_{\alpha V}^{int}}{k}\tau_{E\alpha\beta}^{-1} - \frac{3}{2}\tau_{\alpha\beta}^{-1}\right),
\end{aligned} \tag{3}$$

The systems (2) are written for all plasma components, herein equations for the heavy plasma components cannot be separated from those for electrons (as it is usually done, e.g., when analyzing transport processes in plasma [5]), as this step would violate the condition of energy conservation in plasma. For this reason, the systems (2) are linearly dependent and have to be supplied with the additional physical condition following from the definition of the moments ΔE_α^{tr} and ΔE_α^{int}

$$\sum_{\alpha\neq e} n_\alpha \left(\Delta E_\alpha^{tr} + \Delta E_\alpha^{int}\right) + n_e \Delta E_e = 0\,. \tag{4}$$

Combined together, the relations (1)-(4) form the basis for the further analysis of relaxation processes in plasma.

PLASMA RELAXATION PROPERTIES

The physical parameters describing the energy content in plasma and its distribution over the particles degrees of freedom are the partial pressures of the plasma components. The presence of volumetric sources of chemical energy (due to reactions) and plasma compressibility push the particles distribution function away from equilibrium. As a result, in the expression for p_α we can anticipate the presence of additional components [5], driven by the above physical mechanisms. Below we will consider the electron pressure and the pressure of the heavy plasma particles

$$p_e = \frac{2}{3} n_e E_e = n_e k T_e + \frac{2}{3} n_e \Delta E_e \,, \tag{5}$$

$$p_h = \sum_{\alpha \neq e} p_\alpha = \frac{2}{3} \sum_{\alpha \neq e} n_\alpha E_\alpha^{tr} = \sum_{\alpha \neq e} n_\alpha k T_\alpha + \frac{2}{3} \sum_{\alpha \neq e} n_\alpha \Delta E_\alpha^{tr} = n_h k T_h + \frac{2}{3} n_h \Delta E_h^{tr} \,. \tag{6}$$

Here $n_h = \sum_{\alpha \neq e} n_\alpha$ is the total concentration of the heavy plasma particles and $\Delta E_h^{tr} = \sum_{\alpha \neq e} \left(n_\alpha / n_h \right) \Delta E_\alpha^{tr}$. As seen, along equilibrium components $n_\alpha k T_\alpha$, Eqs. (5), (6) contain non-equilibrium contributions, which can be re-cast as

$$\frac{2}{3} n_e \Delta E_e = p_e^{rel} - \zeta_e \nabla \cdot \mathbf{u} \,, \qquad \frac{2}{3} n_h \Delta E_h^{tr} = p_h^{rel} - \zeta_h \nabla \cdot \mathbf{u} \,, \tag{7}$$

where p_e^{rel} and ζ_e are, respectively, the partial relaxation pressure and bulk viscosity coefficient for electrons, p_h^{rel} and ζ_h are the partial relaxation pressure and bulk viscosity coefficient for the heavy plasma particles.

To find the relaxation pressures and bulk viscosity coefficients, we have to solve Eqs. (3) and (4). Excluding [with the use of the identity (4)] the electron equation and terms with ΔE_e from the system (3), and solving the resulting equations, after some algebra we can arrive at the following expressions for p_e^{rel} , p_h^{rel} , ζ_e and ζ_h

$$p_h^{rel} = \delta_{c0} \begin{vmatrix} \bar{c}_{\alpha\beta} & \bar{c}'_{\alpha\beta} & a_\beta \\ \bar{d}_{\alpha\beta} & \bar{d}'_{\alpha\beta} & b_\beta \\ y_\beta & 0 & 0 \end{vmatrix} \begin{vmatrix} \bar{c}_{\alpha\beta} & \bar{c}'_{\alpha\beta} \\ \bar{d}_{\alpha\beta} & \bar{d}'_{\alpha\beta} \end{vmatrix}^{-1} , \qquad \zeta_h = -\frac{1}{c_V} \begin{vmatrix} \bar{c}_{\alpha\beta} & \bar{c}'_{\alpha\beta} & c_V^{int} p_\beta \\ \bar{d}_{\alpha\beta} & \bar{d}'_{\alpha\beta} & c_{\beta V}^{int} p_\beta \\ y_\beta & 0 & 0 \end{vmatrix} \begin{vmatrix} \bar{c}_{\alpha\beta} & \bar{c}'_{\alpha\beta} \\ \bar{d}_{\alpha\beta} & \bar{d}'_{\alpha\beta} \end{vmatrix}^{-1} , \tag{8}$$

$$p_e^{rel} = -\delta_{c0} \begin{vmatrix} \bar{c}_{\alpha\beta} & \bar{c}'_{\alpha\beta} & a_\beta \\ \bar{d}_{\alpha\beta} & \bar{d}'_{\alpha\beta} & b_\beta \\ y_\beta & \left(2 c_{\beta V}^{int} / 3k \right) y_\beta & 0 \end{vmatrix} \begin{vmatrix} \bar{c}_{\alpha\beta} & \bar{c}'_{\alpha\beta} \\ \bar{d}_{\alpha\beta} & \bar{d}'_{\alpha\beta} \end{vmatrix}^{-1} , \quad \zeta_e = \frac{1}{c_V} \begin{vmatrix} \bar{c}_{\alpha\beta} & \bar{c}'_{\alpha\beta} & c_V^{int} p_\beta \\ \bar{d}_{\alpha\beta} & \bar{d}'_{\alpha\beta} & c_{\beta V}^{int} p_\beta \\ y_\beta & \left(2 c_{\beta V}^{int} / 3k \right) y_\beta & 0 \end{vmatrix} \begin{vmatrix} \bar{c}_{\alpha\beta} & \bar{c}'_{\alpha\beta} \\ \bar{d}_{\alpha\beta} & \bar{d}'_{\alpha\beta} \end{vmatrix}^{-1} . \tag{9}$$

In these expressions the indices $\alpha, \beta \neq e$, the elements a_α and b_α are expressed as

$$a_\beta = \frac{3 k p_\beta}{2 n c_V} \sum_\alpha \left(\frac{3}{2} + \langle \varepsilon_\alpha \rangle + \varepsilon_\alpha^c \right) S_\alpha + \bar{R}_{\beta,eq.}^{r,010} \,, \qquad b_\beta = \frac{p_\beta c_{\beta V}^{int}}{n c_V} \sum_\alpha \left(\frac{3}{2} + \langle \varepsilon_\alpha \rangle + \varepsilon_\alpha^c \right) S_\alpha + \bar{R}_{\beta,eq.}^{r,001} \,, \tag{10}$$

and the matrix elements $\bar{c}_{\alpha\beta}$, $\bar{c}'_{\alpha\beta}$, $\bar{d}_{\alpha\beta}$, $\bar{d}'_{\alpha\beta}$ are defined as

$$\begin{aligned} \bar{c}_{\alpha\beta} &= c_{\alpha\beta} - \left(n_\beta / n_e \right) c_{\alpha e}, & \bar{c}'_{\alpha\beta} &= c'_{\alpha\beta} + \left(2 c_{\beta V}^{int} / 3k \right) \left(n_\beta / n_e \right) c_{\alpha e}, \\ \bar{d}_{\alpha\beta} &= d_{\alpha\beta} - \left(n_\beta / n_e \right) d_{\alpha e}, & \bar{d}'_{\alpha\beta} &= d'_{\alpha\beta} + \left(2 c_{\beta V}^{int} / 3k \right) \left(n_\beta / n_e \right) d_{\alpha e}. \end{aligned} \tag{11}$$

The total relaxation pressure and bulk viscosity coefficient for plasma as a whole are related to the partial quantities as

$$p_{tot}^{rel} = p_h^{rel} + p_e^{rel} \,, \qquad \zeta_{tot} = \zeta_h + \zeta_e \,. \tag{12}$$

It is worth noting that the relations (9) for the electron relaxation pressure and bulk viscosity coefficient generalize those derived in Ref. [6] to the case of the hierarchy of energy relaxation timescales (1).

PHENOMENOLOGICAL ANALYSIS OF RESULTS

The rigorous analysis of the derived expressions (8), (9) is mathematically complicated. For this reason, to get a deeper understanding of how the relaxation properties depend on the parameters of particles and inter-particle interactions, we introduce the semi-qualitative model of energy relaxation in plasma. We consider three-component plasma consisting of molecules and molecular ions of the same species (denoted as "*h*") and electrons (denoted as "*e*"). The system of the phenomenological energy relaxation equations for plasma components can be written as

$$\begin{aligned} &n_h \frac{d}{dt}\Delta E_h^{tr} + Q_h^{tr} = -n_h \nu_E \left(\Delta E_h^{tr} - \zeta \Delta E_h^{int}\right) - n_e \nu_{eh}^{tr}\left(\Delta E_h^{tr} - \Delta E_e\right), \\ &n_h \frac{d}{dt}\Delta E_h^{int} + Q_h^{int} = n_h \nu_E \left(\Delta E_h^{tr} - \zeta \Delta E_h^{int}\right) - n_e \nu_{eh}^{int}\left(\zeta \Delta E_h^{int} - \Delta E_e\right), \\ &n_e \frac{d}{dt}\Delta E_e + Q_e = -n_e \nu_{eh}^{tr}\left(\Delta E_e - \Delta E_h^{tr}\right) - n_e \nu_{eh}^{int}\left(\Delta E_e - \zeta \Delta E_h^{int}\right), \end{aligned} \tag{13}$$

where $\zeta = 3k/\left(2c_{hV}^{int}\right)$, c_{hV}^{int} is the specific heat for the heavy plasma particles, S_h^{tr}, S_h^{int} and S_e are, correspondingly, the general expressions for the external energy sources in plasma [4]. As was mentioned above, Eqs. (13) are linearly dependent and have to be provided with an additional physical condition, following from the definition of the moments ΔE_e, ΔE_h^{tr} and ΔE_h^{int}

$$n_h\left(\Delta E_h^{tr} + \Delta E_h^{int}\right) + n_e \Delta E_e = 0 \,. \tag{14}$$

Solving Eqs. (13) and (14) for partially ionized plasma, $n_e / n_h = \alpha \sim 1$, in case, when $\nu_{eh}^{int} / \nu_{eh}^{tr} >> 1$ and $\nu_E / \nu_{eh}^{tr} \sim \left(m_h / m_e\right)^{1/2} >> 1$, and taking into account the form of the sources Q_α [4], it can be demonstrated that

$$p_h^{rel} \propto \left(1 - \frac{\zeta\alpha}{1+\zeta\alpha}\frac{\nu_E}{\nu_{eh}^{int}}\right), \quad \zeta_h \propto \left(1 - \frac{\zeta\alpha}{1+\zeta\alpha}\frac{\nu_E}{\nu_{eh}^{int}}\right), \quad p_e^{rel} \propto \left(1 - \frac{\zeta}{1+\zeta}\frac{\nu_{eh}^{int}}{\nu_E}\right), \quad \zeta_e \propto \left(1 - \frac{\alpha\zeta}{1+\zeta}\frac{\nu_{eh}^{int}}{\nu_E}\right). \tag{15}$$

As one can see, the partial relaxation coefficients can change their signs depending on the plasma degree of ionization and the ratios of the characteristic timescales of energy exchange between particles. This feature is in contrast to the case of polyatomic gas mixtures, where the relaxation properties are strictly positive [4].

CONCLUSIONS

We have analyzed the relaxation properties for electrons and heavy particles in thermal molecular plasmas, characterized by an arbitrary degree of deviation from chemical equilibrium. For the analysis, we have employed the general system of moment equations for partially ionized reactive plasma, simplified within the 17-moments approximation of the Grad method accounting for only those moments in the expansion of the heavy particles distribution functions, which have explicit physical meaning. Within this approximation, we have derived the expressions for the partial and total relaxation pressures and bulk viscosity coefficients. Phenomenological analysis of the derived relations has revealed that depending on the parameters of plasma particles and inter-particle interactions, the partial relaxation properties of the plasma components can change their sign. This feature is in contrast to the case of polyatomic gas mixtures, where the relaxation properties are strictly positive.

ACKNOWLEDGMENTS

This work has been financially supported by the Grant No. 14.Y26.31.0008 of the Ministry of Education and Science of the Russian Federation government and by National Research Nuclear University MEPhI in the framework of the Russian Academic Excellence Project (Contract No. 02.a03.21.0005 on 27.08.2013).

REFERENCES

1. D. L. Flamm, O. Auciello, *Plasma deposition, treatment, and etching of polymers: the treatment and etching of polymers* (Academic press, San Diego, 2012).
2. E. Gomez, D. A. Rani, C. R. Cheeseman, et al., J. Haz. Mat. **161**, 614-626 (2008).
3. V. M. Zhdanov, A. A. Stepanenko, Physica A **446**, 35-53 (2016).
4. V. M. Zhdanov, M. Y. Alievskii, *Processes of transfer and relaxation in molecular gases* (Nauka, Moscow, 1989).
5. V. M. Zhdanov, *Transport Processes in Multicomponent Plasma* (Taylor&Francis, London, 2002).
6. V. M. Zhdanov, A. A. Stepanenko, Physica A **461**, 310-324 (2016).