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Dissociative attachment of an electron to a molecule: kinetic theory

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Abstract. Test particles interact with a medium by means of a bimolecular reversible chemical reaction. Two species are assumed to be much more numerous so that they are distributed according to fixed distributions: Maxwellians and Dirac's deltas. Equilibrium and its stability are investigated in the first case. For the second case, a system is constructed, in view of an approximate solution.

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1 Introduction

Among the elementary processes of collision between ions and molecules, the dissociative attachment of an electron to a molecule

$$\mathrm{P}^- + \mathrm{AB} \rightleftharpoons \mathrm{A}^- + \mathrm{PB}, \tag{1}$$

plays a role in the physics of weakly ionized gases [1,2]. However, a full kinetic study is laking. In particular, when the electric field is not vanishing, equilibrium solutions are not available for the distribution functions.

In the present paper we shall assume that particles 2 and 4 are much more numerous and can be treated as a neutral background, while particles 1 and 3 have the same (negative) charge e and are subjected to a constant electric field $\boldsymbol{E}$. (Hereinafter, particles P^-, AB, A^-, and PB will be labeled by the subscripts 1, 2, 3, 4. Each of these particles is endowed with mass m_i and internal energy of chemical bond E_i.)

First of all we recall the full Boltzmann equations for particles 1 and 3. The exact form of the collision integrals is shown. The weak form of the kinetic equations is constructed, in order to investigate conservation laws and equilibrium. Two cases are considered:

(1) particles 2 and 4 are distributed according to Maxwellians without drift velocity. Under this assumption, equilibrium and its stability are investigated when $\boldsymbol{E} = \boldsymbol{0}$. Firstly we show how to construct the equilibrium solutions. Secondly, we show the existence of a Lyapunov functional for the present problem. A physical counterpart of these mathematical results is discussed.

(2) B is heavier than P^- and A^-. In the limit $m_\mathrm{B} \to \infty$ particles 2 and 4 can be considered to be distributed according to Dirac's deltas [3]. As a consequence, the Boltzmann equations are modified. Moreover, if the electric field is small, we introduce a first order spherical harmonic expansion for the distribution functions of particles 1 and 3. The result is a system of differential-finite difference equations for the problem. By taking advantage of the smallness of $\boldsymbol{E}$, a first order solution can be constructed for the current functions.

2 Boltzmann equations for particles 1 and 3

The nonlinear integrodifferential Boltzmann equations governing the evolution of the distribution function for the reacting particles 1 and 3 reads as follows [4]:

$$\left(\frac{\partial}{\partial t} + \boldsymbol{v}\cdot\frac{\partial}{\partial \boldsymbol{x}} + e\,\frac{\boldsymbol{E}}{m_i}\cdot\frac{\partial}{\partial \boldsymbol{v}}\right) f_i = J_i[\underline{\mathrm{f}}] + Q_i[\underline{\mathrm{f}}], \tag{2}$$

where $J_i[\underline{\mathrm{f}}]$ and $Q_i[\underline{\mathrm{f}}]$ are the chemical and elastic collision integrals with $\underline{\mathrm{f}} \equiv (f_1,\, f_2,\, f_3,\, f_4)$.

The chemical collision integrals are given by

$$J_i[\underline{\mathrm{f}}] = \int \mathcal{K}_i[\underline{\mathrm{f}}]\, d\boldsymbol{w} d\boldsymbol{n}', \tag{3}$$

where, for $i = 1$, we have

$$\mathcal{K}_1[\underline{\mathrm{f}}] = \theta(g^2 - \eta_{12})\, \nu_{12}^{34}(g,\, \boldsymbol{n}\cdot\boldsymbol{n}') \times \left[\left(\frac{m_1\, m_2}{m_3\, m_4}\right)^3 f_3(\boldsymbol{v}_{12}^{34})\, f_4(\boldsymbol{w}_{12}^{34}) - f_1(\boldsymbol{v}) f_2(\boldsymbol{w})\right], \tag{4}$$

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with $\theta(x)$ the Heaviside step function whereas, for $i = 3$, we have

$$\mathcal{K}_3[\underline{\mathrm{f}}] = \nu_{34}^{12}(g,\, \boldsymbol{n}\cdot\boldsymbol{n}') \times \left[\left(\frac{m_3\, m_4}{m_1\, m_2} \right)^3 f_1(\boldsymbol{v}_{34}^{12})\, f_2(\boldsymbol{w}_{34}^{12}) - f_3(\boldsymbol{v})\, f_4(\boldsymbol{w}) \right], \quad (5)$$

where

$$\boldsymbol{v}_{12}^{34} = \frac{1}{\mathcal{M}}\,(m_1\,\boldsymbol{v} + m_2\,\boldsymbol{w} + m_4\, g_{12}^{34}\,\boldsymbol{n}'), \quad (6)$$

$$\boldsymbol{w}_{12}^{34} = \frac{1}{\mathcal{M}}\,(m_1\,\boldsymbol{v} + m_2\,\boldsymbol{w} - m_3\, g_{12}^{34}\,\boldsymbol{n}'), \quad (7)$$

$$\boldsymbol{v}_{34}^{12} = \frac{1}{\mathcal{M}}\,(m_3\,\boldsymbol{v} + m_4\,\boldsymbol{w} + m_2\, g_{34}^{12}\,\boldsymbol{n}'), \quad (8)$$

$$\boldsymbol{w}_{34}^{12} = \frac{1}{\mathcal{M}}\,(m_3\,\boldsymbol{v} + m_4\,\boldsymbol{w} - m_1\, g_{34}^{12}\,\boldsymbol{n}'), \quad (9)$$

with $\mathcal{M} = m_1 + m_2 = m_3 + m_4$. In equations (4) and (5) we have introduced the differential collision frequencies of the forward and backward reaction $\nu_{12}^{34}(g,\, \boldsymbol{n}\cdot\boldsymbol{n}')$ and $\nu_{34}^{12}(g,\, \boldsymbol{n}\cdot\boldsymbol{n}')$, where $g = |\boldsymbol{v} - \boldsymbol{w}|$ whilst $\boldsymbol{n}$ and $\boldsymbol{n}'$ are the unit vectors of the relative velocities before and after collision, respectively. We observe that the following microreversibility condition holds

$$(m_1\, m_2)^2\, g\, \nu_{12}^{34}(g,\, \boldsymbol{n}\cdot\boldsymbol{n}') = (m_3\, m_4)^2\, g_{12}^{34}\, \nu_{34}^{12}(g,\, \boldsymbol{n}\cdot\boldsymbol{n}')\, \theta(g^2 - \eta_{34}), \quad (10)$$

where

$$g_{kl}^{ij} = \sqrt{\frac{m_k\, m_l}{m_i\, m_j}\,(g^2 - \eta_{ij})}, \quad (11)$$

with $\eta_{ij} = 2\mathcal{M}\Delta E/m_i m_j$ and $\Delta E = E_3 + E_4 - E_1 - E_2 > 0$ is the molecular heat of reaction.

Differently, the elastic collision integrals are given by

$$Q_i[\underline{\mathrm{f}}] = \int \mathcal{R}_i[\underline{\mathrm{f}}]\, d\boldsymbol{w} d\boldsymbol{n}', \quad (12)$$

where

$$\mathcal{R}_i[\underline{\mathrm{f}}] = \sum_{\ell=2,4} \nu_{i\ell}^{i\ell}(g,\, \boldsymbol{n}\cdot\boldsymbol{n}') \left[f_i(\boldsymbol{v}_{i\ell}^{i\ell})\, f_\ell(\boldsymbol{w}_{i\ell}^{i\ell}) - f_i(\boldsymbol{v})\, f_\ell(\boldsymbol{w}) \right], \quad (13)$$

and

$$\boldsymbol{v}_{i\ell}^{i\ell} = \frac{1}{m_i + m_\ell}\,(m_i\,\boldsymbol{v} + m_\ell\,\boldsymbol{w} + m_\ell\, g\,\boldsymbol{n}'), \quad (14)$$

$$\boldsymbol{w}_{i\ell}^{i\ell} = \frac{1}{m_i + m_\ell}(m_i\,\boldsymbol{v} + m_\ell\,\boldsymbol{w} - m_\ell\, g\,\boldsymbol{n}'). \quad (15)$$

The weak form of the kinetic equations for $i = 1$ and 3 is obtained by multiplication times a pair of sufficiently smooth functions $\phi_1(\boldsymbol{v})$ and $\phi_3(\boldsymbol{v})$, respectively, integration over $\boldsymbol{v}$, and by summing [5]:

$$\int \frac{\partial f_1}{\partial t}\phi_1(\boldsymbol{v})\, d\boldsymbol{v} + \int \frac{\partial f_3}{\partial t}\, \phi_3(\boldsymbol{v})\, d\boldsymbol{v} = \int \mathcal{K}_1[\underline{\mathrm{f}}] \left[\phi_1(\boldsymbol{v}) - \phi_3(\boldsymbol{v}_{12}^{34}) \right] d\boldsymbol{v}\, d\boldsymbol{w}\, d\boldsymbol{n}' + \frac{1}{2} \int \mathcal{R}_1[\underline{\mathrm{f}}] \left[\phi_1(\boldsymbol{v}) - \phi_1(\boldsymbol{v}_{12}^{12}) \right] d\boldsymbol{v}\, d\boldsymbol{w}\, d\boldsymbol{n}' + \frac{1}{2} \int \mathcal{R}_3[\underline{\mathrm{f}}] \left[\phi_3(\boldsymbol{v}) - \phi_3(\boldsymbol{v}_{34}^{34}) \right] d\boldsymbol{v}\, d\boldsymbol{w}\, d\boldsymbol{n}'. \quad (16)$$

Observe that for $\phi_1(\boldsymbol{v}) = \phi_3(\boldsymbol{v}) = 1$ we get $dn_1/dt + dn_3/dt = 0$, with $n_i = \int f_i\, d\boldsymbol{v}$, that is the total number of test particles is conserved.

3 Case (1)

We assume particles 2 and 4 much more numerous, so that they can be treated as an equilibrium background at a fixed temperature T [6]:

$$f_\ell = m_\ell^3 \exp\left[\beta\left(\mu_\ell - E_\ell - \frac{1}{2}\, m_\ell v^2 \right) \right], \quad (17)$$

with $\ell = 2,\, 4$ and μ_ℓ fixed.

From the weak form of the Boltzmann equation, by setting

$$\phi_1 = \ln\left\{ \tilde{f}_1\, \exp\left[\beta\left(\mu_2 - E_2 - \frac{1}{2}\, m_2\, v^2 \right) \right] \right\}, \quad (18)$$

$$\phi_3 = \ln\left\{ \tilde{f}_3\, \exp\left[\beta\left(\mu_4 - E_4 - \frac{1}{2}\, m_4\, v^2 \right) \right] \right\}, \quad (19)$$

where $\tilde{f}_i = f_i/m_i^3$, we obtain

$$\mathcal{D} = \int \nu_{12}^{34}(g,\, \boldsymbol{n}\cdot\boldsymbol{n}')\, (m_1\, m_2)^3\, \ln \frac{\tilde{f}_3(\boldsymbol{v}_{12}^{34})\, \tilde{f}_4(\boldsymbol{w}_{12}^{34})}{\tilde{f}_1(\boldsymbol{v})\, \tilde{f}_2(\boldsymbol{w})} \times [\tilde{f}_1(\boldsymbol{v})\, \tilde{f}_2(\boldsymbol{w}) - \tilde{f}_3(\boldsymbol{v}_{12}^{34})\, \tilde{f}_4(\boldsymbol{w}_{12}^{34})]\, d\boldsymbol{v}\, d\boldsymbol{w}\, d\boldsymbol{n}' + \frac{1}{2} \sum_{i,\ell} (m_i\, m_\ell)^3 \int \nu_{i\ell}^{i\ell}(g,\, \boldsymbol{n}\cdot\boldsymbol{n}')\, \ln \frac{\tilde{f}_i(\boldsymbol{v}_{i\ell}^{i\ell}) \tilde{f}_\ell(\boldsymbol{w}_{i\ell}^{i\ell})}{\tilde{f}_i(\boldsymbol{v})\, \tilde{f}_\ell(\boldsymbol{w})} \times [\tilde{f}_i(\boldsymbol{v})\, \tilde{f}_\ell(\boldsymbol{w}) - \tilde{f}_i(\boldsymbol{v}_{i\ell}^{i\ell})\, \tilde{f}_\ell(\boldsymbol{w}_{i\ell}^{i\ell})]\, d\boldsymbol{v}\, d\boldsymbol{w}\, d\boldsymbol{n}' \le 0, \quad (20)$$

($i = 1$ and 3; $\ell = 2$ and 4), where $\mathcal{D}$ is the left hand side of equation (16). Based on these results, by standard methods of kinetic theory [4], we have

Proposition 1. The equilibrium condition

$$\frac{\partial f_1}{\partial t} = \frac{\partial f_3}{\partial t} = 0, \quad (21)$$

is equivalent to

$$\tilde{f}_i(\boldsymbol{v}_{i\ell}^{i\ell})\, \tilde{f}_\ell(\boldsymbol{w}_{i\ell}^{i\ell}) = \tilde{f}_i(\boldsymbol{v})\, \tilde{f}_\ell(\boldsymbol{w}), \quad (22)$$

$$\tilde{f}_3(\boldsymbol{v}_{12}^{34})\, \tilde{f}_4(\boldsymbol{w}_{12}^{34}) = \tilde{f}_1(\boldsymbol{v})\, \tilde{f}_2(\boldsymbol{w}), \quad (23)$$

with $i = 1,\, 3$ and $\ell = 2,\, 4$ •

From the first equation we get

$$\tilde{f}_i = \exp\left[\beta\left(\mu_i - E_i - \frac{1}{2}\,m_i\,v^2\right)\right], \tag{24}$$

while the second one gives $\mu_1 + \mu_2 = \mu_3 + \mu_4$.

In order to investigate the stability of such equilibrium solution, we introduce the following functional:

$$\begin{aligned}\mathcal{L} = H - \beta \int f_1\left(\mu_1 - E_1 - \frac{1}{2}\,m_1\,v^2\right)\,d\boldsymbol{v}\\ -\beta \int f_3\left(\mu_3 - E_3 - \frac{1}{2}\,m_3\,v^2\right)\,d\boldsymbol{v},\end{aligned} \tag{25}$$

where $H = \int \mathcal{H}\,d\boldsymbol{v}$, $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_3$ and $\partial\mathcal{H}_i/\partial f_i = \ln \tilde{f}_i$.

Proposition 2. $\mathcal{L}$ is a Lyapunov functional for the present problem •

Proof. First of all, from equations (16) and (20) we verify that

$$\frac{d\mathcal{L}}{dt} = \mathcal{D} \,\le\, 0. \tag{26}$$

Moreover, by introducing the first Taylor expansion of H around the equilibrium

$$\begin{aligned}\int \hat{\mathcal{H}}\,d\boldsymbol{v} &= \int\left[\mathcal{H}^* + \left(\frac{\partial\mathcal{H}}{\partial f_1}\right)^*(f_1 - f_1^*) + \left(\frac{\partial\mathcal{H}}{\partial f_3}\right)^*(f_3 - f_3^*)\right]d\boldsymbol{v}\\ &= \int\left[\mathcal{H}^* + \beta\left(\mu_1 - E_1 - \frac{1}{2}\,m_1\,v^2\right)\,(f_1 - f_1^*)\right.\\ &\quad\left. + \,\beta\left(\mu_3 - E_3 - \frac{1}{2}\,m_3\,v^2\right)\,(f_3 - f_3^*)\right]d\boldsymbol{v},\end{aligned} \tag{27}$$

where $*$ means "at equilibrium", from equations (25) and (27) we obtain

$$\begin{aligned}\mathcal{L} - \mathcal{L}^* &= \int \left(\mathcal{H} - \mathcal{H}^*\right)d\boldsymbol{v}\\ &\quad+\beta \int\left(\mu_1 - E_1 - \frac{1}{2}\,m_1\,v^2\right)\,(f_1 - f_1^*)\,d\boldsymbol{v}\\ &\quad+\beta \int\left(\mu_3 - E_3 - \frac{1}{2}\,m_3\,v^2\right)\,(f_3 - f_3^*)\,d\boldsymbol{v}\\ &= \int (\mathcal{H} - \hat{\mathcal{H}})\,d\boldsymbol{v}.\end{aligned} \tag{28}$$

Due to the convexity of $\mathcal{H}$ we can conclude that $\mathcal{L} \ge \mathcal{L}^*$.

The inequality

$$\frac{d\mathcal{L}}{dt} \le 0, \tag{29}$$

can be interpreted on a physical ground. In fact, by introducing the entropy $S = -H$, we get the following thermodynamic inequality:

$$dS \ge \frac{1}{T}\,\left(d\mathcal{E} - \mu_1^*\,dn_1 - \mu_3^*\,dn_3\right), \tag{30}$$

where $\mathcal{E} = \int f_1\,(E_1 + m_1\,v^2/2)\,d\boldsymbol{v} + \int f_3\,(E_3 + m_3\,v^2/2)\,d\boldsymbol{v}$ is the total energy density of test particles. With respect to Clausius inequality, we observe an additional term due to the fact that the medium of field particles 2 and 4 not only provides heat to the gas of test particles 1 and 3 but also modifies its composition.

4 Case (2)

In the limit $m_B \to \infty$ we have

$$\frac{m_1\,m_2}{m_3\,m_4} \to \frac{m_1}{m_3}, \tag{31}$$

and the following relations hold

$$\begin{aligned}g_{12}^{34} &\to v^- = \sqrt{\frac{m_1}{m_3}\,v^2 - \eta_3},\\ g_{34}^{12} &\to v^+ = \sqrt{\frac{m_3}{m_1}\,v^2 + \eta_1},\end{aligned} \tag{32}$$

$$\begin{aligned}&\boldsymbol{v}_{12}^{34} \to \boldsymbol{w} + v^-\boldsymbol{n}', &&\boldsymbol{v}_{34}^{12} \to \boldsymbol{w} + v^+\boldsymbol{n}',\\ &\boldsymbol{w}_{12}^{34} \to \boldsymbol{w}, &&\boldsymbol{w}_{34}^{12} \to \boldsymbol{w},\\ &\boldsymbol{v}_{i\ell}^{i\ell} \to \boldsymbol{w} + v\,\boldsymbol{n}', &&\boldsymbol{w}_{i\ell}^{i\ell} \to \boldsymbol{w} - v\,\boldsymbol{n}',\end{aligned} \tag{33}$$

where $\eta_i = 2\,\Delta E/m_i$. Moreover we can pose $\boldsymbol{n} \to \boldsymbol{\Omega}$, $\boldsymbol{n}' \to \boldsymbol{\Omega}'$ and $g \to v$.

By taking into account that $f_\ell(\boldsymbol{w}) = \mathcal{N}_\ell\,\delta(\boldsymbol{w})$ for $\ell = 2$ and 4, the integrals $J_i[\underline{f}]$ and $Q_i[\underline{f}]$ read now

$$\begin{aligned}J_1[\underline{f}] = \int \theta(v^2 - \eta_1)\,\nu_{12}^{34}(v,\,\boldsymbol{\Omega}\cdot\boldsymbol{\Omega}')\\ \times\left[\left(\frac{m_1}{m_3}\right)^3 \mathcal{N}_4\,f_3(v^-\,\boldsymbol{\Omega}') - \mathcal{N}_2\,f_1(\boldsymbol{v})\right]d\boldsymbol{\Omega},\end{aligned} \tag{34}$$

$$\begin{aligned}J_3[\underline{f}] = \int \left(\frac{m_1}{m_3}\right)^2 \frac{v^+}{v}\,\nu_{12}^{34}(v^+,\,\boldsymbol{\Omega}\cdot\boldsymbol{\Omega}')\\ \times\left[\left(\frac{m_3}{m_1}\right)^2 \mathcal{N}_2\,f_1(v^+\,\boldsymbol{\Omega}') - \mathcal{N}_4\,f_3(\boldsymbol{v})\right]d\boldsymbol{\Omega},\end{aligned} \tag{35}$$

$$\begin{aligned}Q_1[\underline{f}] = \int \left[\mathcal{N}_2\,\nu_{12}^{12}(v,\,\boldsymbol{\Omega}\cdot\boldsymbol{\Omega}') + \mathcal{N}_4\,\nu_{14}^{14}(v,\,\boldsymbol{\Omega}\cdot\boldsymbol{\Omega}')\right]\\ \times\left[f_1(v\,\boldsymbol{\Omega}') - f_1(\boldsymbol{v})\right]d\boldsymbol{\Omega},\end{aligned} \tag{36}$$

$$\begin{aligned}Q_3[\underline{f}] = \int \left[\mathcal{N}_2\,\nu_{32}^{32}(v,\,\boldsymbol{\Omega}\cdot\boldsymbol{\Omega}') + \mathcal{N}_4\,\nu_{34}^{34}(v,\,\boldsymbol{\Omega}\cdot\boldsymbol{\Omega}')\right]\\ \times\left[f_3(v\,\boldsymbol{\Omega}') - f_3(\boldsymbol{v})\right]d\boldsymbol{\Omega}.\end{aligned} \tag{37}$$

Equilibrium and its stability for the present problem are investigated in [5]. Our purpose here is to construct model equations suitable for an approximate solution.

As usual in the physics of weakly ionized gases [1], if both the spatial gradients and the electric field are small we may resort to a first order spherical harmonic expansion of $f_i(v\,\boldsymbol{\Omega})$:

$$f_i(v\,\boldsymbol{\Omega}) = N_i(v) + \boldsymbol{\Omega}\cdot\boldsymbol{J}_i(v), \tag{38}$$

where

$$N_i(v) = \frac{1}{4\,\pi}\int f_i(v\,\boldsymbol{\Omega})\,d\boldsymbol{\Omega}, \tag{39}$$

and

$$\boldsymbol{J}_i(v) = \frac{3}{4\,\pi}\int \boldsymbol{\Omega}\,f_i(v\,\boldsymbol{\Omega})\,d\boldsymbol{\Omega}. \tag{40}$$

By projecting over $\mathbf{1}$ and $\boldsymbol{\Omega}$ we get, after some manipulations, the following system for the new unknown functions $F_i(\xi) = N_i(v)$ and $\boldsymbol{G}_i(\xi) = \boldsymbol{J}_i(v)$:

$$\frac{\partial F_1(\xi)}{\partial t} + \frac{\sqrt{\xi}}{3}\,\boldsymbol{\nabla}\cdot\boldsymbol{G}_1(\xi) - \frac{e\,\boldsymbol{E}}{m_1}\cdot\frac{2}{3\sqrt{\xi}}\frac{\partial}{\partial\xi}[\xi\,\boldsymbol{G}_1(\xi)] = \theta(\xi-\eta_1)\,\nu^{34}_{12(0)}(\xi)\left[\left(\frac{m_1}{m_3}\right)^3\mathcal{N}_4\,F_3\left(\xi^-\right) - \mathcal{N}_2\,F_1(\xi)\right], \tag{41}$$

$$\frac{\partial F_3(\xi)}{\partial t} + \frac{\sqrt{\xi}}{3}\,\boldsymbol{\nabla}\cdot\boldsymbol{G}_3(\xi) - \frac{e\,\boldsymbol{E}}{m_3}\cdot\frac{2}{3\sqrt{\xi}}\frac{\partial}{\partial\,\xi}[\xi\,\boldsymbol{G}_3(\xi)] = \left(\frac{m_1}{m_3}\right)^2\nu^{34}_{12(0)}\left(\xi^+\right)\sqrt{\frac{\xi^+}{\xi}} \times\left[\left(\frac{m_3}{m_1}\right)^3\mathcal{N}_2\,F_1\left(\xi^+\right) - \mathcal{N}_4\,F_3(\xi)\right], \tag{42}$$

$$\frac{\partial \boldsymbol{G}_1(\xi)}{\partial t} + \sqrt{\xi}\boldsymbol{\nabla}F_1(\xi) - \frac{2\,e\,\boldsymbol{E}}{m_1}\sqrt{\xi}\frac{\partial F_1(\xi)}{\partial\xi} = \theta(\xi-\eta_1)\left[\nu^{34}_{12(1)}(\xi)\left(\frac{m_1}{m_3}\right)^3\mathcal{N}_4\,\boldsymbol{G}_3\left(\xi^-\right) - \mathcal{N}_2\,\boldsymbol{G}_1(\xi)\,\nu^{34}_{12(0)}(\xi)\right] - \gamma_1(\xi)\,\mathbf{G}_1(\xi), \tag{43}$$

$$\frac{\partial \boldsymbol{G}_3(\xi)}{\partial t} + \sqrt{\xi}\,\boldsymbol{\nabla}F_3(\xi) - \frac{2\,e\,\boldsymbol{E}}{m_3}\sqrt{\xi}\frac{\partial F_3(\xi)}{\partial\xi} = \left(\frac{m_1}{m_3}\right)^2\sqrt{\frac{\xi^+}{\xi}}\left[\nu^{34}_{12(1)}\left(\xi^+\right)\left(\frac{m_3}{m_1}\right)^3\mathcal{N}_2\,\boldsymbol{G}_1\left(\xi^+\right) - \mathcal{N}_4\,\boldsymbol{G}_3(\xi)\,\nu^{34}_{12(0)}\left(\xi^+\right)\right] - \gamma_3(\xi)\,\boldsymbol{G}_3(\xi), \tag{44}$$

where we have posed $\xi^\pm = (v^\pm)^2$ and

$$\gamma_i(\xi) = \mathcal{N}_2\,\nu^{i2}_{i2(t)}(\xi) + \mathcal{N}_4\,\nu^{i4}_{i4(t)}(\xi), \tag{45}$$

being $\nu^{lm}_{ij(t)}(\xi) = \nu^{lm}_{ij(0)}(\xi) - \nu^{lm}_{ij(1)}(\xi)$ and

$$\nu^{lm}_{ij(k)}(\xi) = 2\,\pi\int_{-1}^{+1}\mu^k\,\nu^{lm}_{ij}(\xi,\mu)\,d\mu, \tag{46}$$

with $k = 1$ and 2.

Consider now the stationary space-homogeneous equations We observe that for $\boldsymbol{E} = \mathbf{0}$ the following equilibrium solutions hold:

$$F_i = C_i\,\exp\left(-\frac{m_i\,\xi}{2\,k_{\rm B}\,T}\right), \tag{47}$$

where

$$\frac{C_3\,\mathcal{N}_4}{C_1\,\mathcal{N}_2} = \left(\frac{m_3}{m_1}\right)^3\exp\left(-\frac{\Delta E}{k_{\rm B}\,T}\right), \tag{48}$$

(mass action law).

Finally, we observe that the electric field must be a small quantity, $|\boldsymbol{E}| = \epsilon$, so that we can expand F_i and $\boldsymbol{G}_i$ as follows

$$F_i = F_i^{(0)} + \epsilon F_i^{(1)} + \ldots, \qquad \boldsymbol{G}_i = \epsilon\,\boldsymbol{G}_i^{(1)} + \ldots. \tag{49}$$

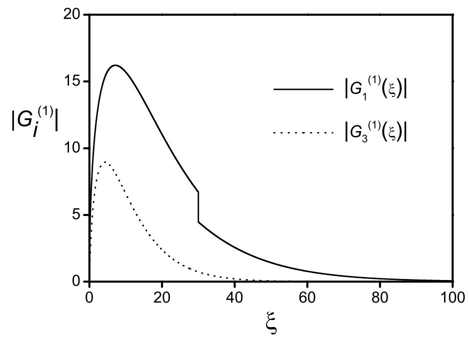

Fig. 1. Plot of the current function $|G_1^{(1)}(\xi)|$ (full line) for the charge particles P^- and $|G_3^{(1)}(\xi)|$ (dotted line) for the charge particles A^-, in arbitrary units.

Since $F_i^{(0)}$ are already known, by solving equations (41) and (42), we can obtain the expression of $G_i^{(1)}$, in the case of isotropic reaction collision frequency $\nu^{34}_{12(0)}$:

$$G_1^{(1)} = -\frac{eEC_1}{k_{\rm B}T}\,\frac{\sqrt{\xi}\exp(-m_1\xi/2k_{\rm B}T)}{\theta(\xi-\eta_1)\mathcal{N}_2\nu^{34}_{12(0)}(\xi)+\gamma_1(\xi)}, \tag{50}$$

$$G_3^{(1)} = -\frac{eEC_3}{k_{\rm B}\,T}\,\frac{\xi\exp(-m_3\xi/2k_{\rm B}T)}{\mathcal{N}_4(m_1/m_3)^2\nu^{34}_{12(0)}\left(\xi^+\right)\sqrt{\xi^+}+\sqrt{\xi}\gamma_3(\xi)}, \tag{51}$$

where $G_i^{(1)} = \boldsymbol{G}_i^{(1)}\cdot\boldsymbol{e}$, with $\boldsymbol{e}$ the unit vector of $\boldsymbol{E}$.

In Figure 1 we depict, in arbitrary unity, the plots of $|G_1^{(1)}(\xi)|$ (full line) and $|G_3^{(1)}(\xi)|$ (dotted line). Since the forward equation has a threshold for $\xi = \eta_1$, the collision frequency of particles 1 suddenly increases, and a discontinuity in the relevant plot of $|G_1^{(1)}(\xi)|$ occurs.

5 Conclusions

Two linear Boltzmann models have been constructed for test particles reacting with a medium of numerous field particles. In the first case the field particles are distributed according Maxwellians with vanishing drift velocity. Theorems on equilibrium and its stability are given, as well as their connection with thermodynamics. In the second case we consider particles B heavier than particles P^- and A^-. By means of first order spherical harmonic expansion, four equations can be constructed, suitable for an approximate solution.

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