Dissociative attachment of an electron to a molecule: kinetic theory

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I. INTRODUCTION

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

\[ P^- + AB \rightleftharpoons A^- + PB \]  

(1)

plays a role in the physics of weakly ionized gases [1, 2]. However, a full kinetic study is lacking. 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 3 are 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.

II. 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 [3]:

\[
\left( \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) J_i[f] = \int \mathcal{K}_i[f] \, d\mathbf{w} \, d\mathbf{n}', \tag{3}
\]

where, for \( i = 1 \), we have

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

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

\[
\mathcal{K}_3[f] = \nu_{34}^3(g, \mathbf{n} \cdot \mathbf{n}') \times \left[ \left( \frac{m_3 m_4}{m_1 m_2} \right)^3 f_1(v_{34}^{12}) f_2(w_{34}^{12}) - f_3(v)f_4(w) \right], \tag{5}
\]

where

\[
v_{12}^{34} = \frac{1}{M} \left( m_1 v + m_2 w + m_4 g_{12} g_{34} n' n \right), \tag{6}
\]

\[
w_{12}^{34} = \frac{1}{M} \left( m_1 v + m_2 w - m_3 g_{12} g_{34} n' n \right), \tag{7}
\]

\[
v_{34}^{12} = \frac{1}{M} \left( m_3 v + m_4 w + m_2 g_{34} g_{12} n' n \right), \tag{8}
\]

\[
w_{34}^{12} = \frac{1}{M} \left( m_3 v + m_4 w - m_1 g_{34} g_{12} n' n \right). \tag{9}
\]
with \( M = m_1 + m_2 = m_3 + m_4 \). In Eqs. (4) and (5) we have introduced the differential collision frequencies of the forward and backward reaction \( \nu_{ij}^{\pm}(g, n \cdot n') \) and \( \nu_{ij}^{\pm}(g, n \cdot n') \), where \( g = |v - w| \) whilst \( n \) and \( n' \) are the unit vectors of the relative velocities before and after collision, respectively. We observe that the following holds

\[
\begin{align*}
(12) & \quad m_1 m_2 g \nu_{ij}^{\pm}(g, n \cdot n') = \\
(13) & \quad m_3 m_4 g \nu_{ij}^{\pm}(g, n \cdot n') \theta(g^2 - \eta_{ij}) ,
\end{align*}
\]

where

\[
\eta_{ij} = 2 M \Delta E/m_i \mu_j \text{ and } \Delta E = E_2 - E_1 - E_2 > 0 \text{ is the molecular heat of reaction.}
\]

Differently, the elastic collision integrals are given by

\[
Q_i[f] = \int \mathcal{R}_i[f] d\nu d\nu' ,
\]

where

\[
\mathcal{R}_i[f] = \sum_{\ell=2,4} \nu_{ij}^{\pm}(g, n \cdot n') \left[ f_i(v_{ij}^{\pm}) f_{\ell}(w_{ij}^{\pm}) - f_i(v) f_{\ell}(w) \right] ,
\]

and

\[
\begin{align*}
\nu_{ij}^{\pm} & = \frac{1}{m_i + m_\ell} (m_i v + m_\ell w + m_\ell g n') , \quad \ell = 2, 4 \quad \text{(14)} \\
w_{ij}^{\pm} & = \frac{1}{m_i + m_\ell} (m_i v + m_\ell w - m_\ell g n') . \quad \text{(15)}
\end{align*}
\]

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

\[
\int \frac{\partial f_1}{\partial t} \phi_1(v) dv + \int \frac{\partial f_3}{\partial t} \phi_3(v) dv = \int \mathcal{R}_1[f] \left[ \phi_1(v) - \phi_3(v_{12}^{34}) \right] d\nu d\nu' + \frac{1}{2} \int \left( \mathcal{R}_1[f] \left[ \phi_1(v) - \phi_1(v_{12}^{13}) \right] + \mathcal{R}_3[f] \left[ \phi_3(v) - \phi_3(v_{34}^{12}) \right] \right) d\nu d\nu' . \quad \text{(16)}
\]

Observe that for \( \phi_1(v) = \phi_3(v) = 1 \) we get \( d\nu_i / dt + d\nu_3 / dt = 0 \), with \( n_i = \int f_i dv \), that is the total number of test particles is conserved.

### III. 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 \( T \) [3]:

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

with \( \ell = 2, 4 \) and \( \mu_\ell \) fixed.

From the weak form of the Boltzmann equation, by setting

\[
\begin{align*}
\phi_1 & = \ln \left( \tilde{f}_1 \exp \left[ \beta \left( \mu_2 - E_2 - \frac{1}{2} m_2 v^2 \right) \right] \right) , \quad \text{(18)} \\
\phi_3 & = \ln \left( \tilde{f}_3 \exp \left[ \beta \left( \mu_4 - E_4 - \frac{1}{2} m_4 v^2 \right) \right] \right) , \quad \text{(19)}
\end{align*}
\]

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

\[
D = \int \nu_{ij}^{34}(g, n \cdot n') (m_1 m_2)^3 \ln \frac{\tilde{f}_{ij}(v_{12}^{34}) \tilde{f}_{ij}(w_{12}^{34})}{\tilde{f}_i(v) \tilde{f}_i(w)} \tilde{f}_1(v) \tilde{f}_2(w) - \tilde{f}_3(v_{12}^{34}) \tilde{f}_4(w_{12}^{34})] d\nu d\nu'
\]

\[
+ \frac{1}{2} \sum_{i, \ell} (m_i m_\ell)^3 \int \nu_{ij}^{\pm}(g, n \cdot n') \ln \frac{\tilde{f}_i(v_{ij}^{\pm}) \tilde{f}_i(v) \tilde{f}_i(w)}{\tilde{f}_i(v_{ij}^{\pm}) \tilde{f}_i(v)} [\tilde{f}_i(v) \tilde{f}_\ell(w) - \tilde{f}_i(v_{ij}^{\pm}) \tilde{f}_\ell(w_{ij}^{\pm})] d\nu d\nu' \leq 0 , \quad \text{(20)}
\]

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

\[ \frac{\partial f_1}{\partial t} = \frac{\partial f_3}{\partial t} = 0, \]

is equivalent to

\[ \tilde{f}_1(v_1^{\ell}) \tilde{f}_1(w_1^{\ell}) = \tilde{f}_2(v) \tilde{f}_3(w), \]
\[ \tilde{f}_3(v_3^{\ell}) \tilde{f}_4(w_1^{\ell}) = \tilde{f}_1(v) \tilde{f}_2(w), \]

with \( i = 1, 3 \) and \( \ell = 2, 4 \).

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

\[ \tilde{f}_1(v_1^{\ell}) \tilde{f}_1(w_1^{\ell}) = \tilde{f}_2(v) \tilde{f}_3(w), \]
\[ \tilde{f}_3(v_3^{\ell}) \tilde{f}_4(w_1^{\ell}) = \tilde{f}_1(v) \tilde{f}_2(w), \]

where \( \tilde{f}_1 \) 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.

IV. CASE (2)

In the limit \( m_B \to \infty \) we have

\[ \frac{m_1 m_2}{m_3 m_4} \to \frac{m_1}{m_3}, \]

and the following relations hold

\[ g_{12}^{34} \to v'^- = \sqrt{\frac{m_1}{m_3} v^2 - \eta}; \quad g_{34}^{12} \to v'^+ = \sqrt{\frac{m_3}{m_1} v^2 + \eta}, \]
\[ v_{12}^{34} \to w + v' n', \quad v_{12}^{34} \to w + v' n', \quad v_{12}^{34} \to w + v' n', \quad w_{12}^{34} \to w, \]

where \( \eta = 2 \Delta E/m_i \). Moreover we can pose \( n \to \Omega \), \( n' \to \Omega' \) and \( g \to v \).
By taking into account that $f_\ell(w) = N_\ell \delta(w)$ for $\ell = 2$ and 4, the integrals $J_i[f]$ and $Q_i[f]$ read now

\[ J_i[f] = \int \theta(v^2 - \eta_1) \nu_{i2}^{34}(v, \Omega, \Omega') \left[ \left( \frac{m_1}{m_3} \right)^3 N_4 f_3(v^+ \Omega') - N_2 f_1(v) \right] d\Omega, \quad (33) \]

\[ J_3[f] = \int \left( \frac{m_1}{m_3} \right)^2 v_1^+ \nu_{i2}^{34}(v^+, \Omega, \Omega') \left[ \left( \frac{m_3}{m_1} \right) N_2 f_1(v^+ \Omega') - N_4 f_3(v) \right] d\Omega, \quad (34) \]

\[ Q_1[f] = \int [N_2 \nu_{i2}^{12}(v, \Omega, \Omega') + N_4 \nu_{i4}^{14}(v, \Omega, \Omega')] [f_1(v \Omega') - f_1(v)] d\Omega, \quad (35) \]

\[ Q_3[f] = \int [N_2 \nu_{i2}^{32}(v, \Omega, \Omega') + N_4 \nu_{i4}^{34}(v, \Omega, \Omega')] [f_3(v \Omega') - f_3(v)] d\Omega. \quad (36) \]

Equilibrium and its stability for the present problem are investigated in [3]. 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 $f_i(v \Omega)$:

\[ f_i(v \Omega) = N_i(v) + \Omega \cdot J_i(v), \quad (37) \]

where

\[ N_i(v) = \frac{1}{4\pi} \int f_i(v \Omega) d\Omega, \quad (38) \]

By projecting over $\Omega$ we get, after some manipulations, the following system for the new unknowns functions $F_i(\xi) = N_i(v)$ and $G_i(\xi) = J_i(v)$:

\[ \frac{\partial F_1(\xi)}{\partial t} + \frac{\sqrt{\xi}}{3} \nabla \cdot G_1(\xi) - \frac{eE}{m_1} \frac{2}{3\sqrt{\xi}} \frac{\partial}{\partial \xi} [\xi G_1(\xi)] = \theta(\xi - \eta_1) \nu_{12(0)}^{34}(\xi) \left[ \left( \frac{m_1}{m_3} \right)^3 N_4 F_3(\xi^-) - N_2 F_1(\xi) \right], \quad (40) \]

\[ \frac{\partial F_3(\xi)}{\partial t} + \frac{\sqrt{\xi}}{3} \nabla \cdot G_3(\xi) - \frac{eE}{m_1} \frac{2}{3\sqrt{\xi}} \frac{\partial}{\partial \xi} [\xi G_3(\xi)] = \left( \frac{m_1}{m_3} \right)^2 \nu_{12(0)}^{34}(\xi^+) \sqrt{\xi^+} \left[ \left( \frac{m_3}{m_1} \right)^3 N_2 F_1(\xi^+) - N_4 F_3(\xi) \right], \quad (41) \]

\[ \frac{\partial G_1(\xi)}{\partial t} + \sqrt{\xi} \nabla F_1(\xi) - \frac{2eE}{m_1} \sqrt{\xi} \frac{\partial F_1(\xi)}{\partial \xi} = \theta(\xi - \eta_1) \left[ \nu_{12(1)}^{34}(\xi) \left( \frac{m_1}{m_3} \right)^3 N_4 G_3(\xi^-) - N_2 G_1(\xi) \nu_{12(0)}^{34}(\xi^-) \right] - \gamma_1(\xi) G_1(\xi), \quad (42) \]

\[ \frac{\partial G_3(\xi)}{\partial t} + \sqrt{\xi} \nabla F_3(\xi) - \frac{2eE}{m_1} \sqrt{\xi} \frac{\partial F_3(\xi)}{\partial \xi} = \left( \frac{m_1}{m_3} \right)^2 \sqrt{\xi^+} \left[ \nu_{12(1)}^{34}(\xi^+) \left( \frac{m_3}{m_1} \right)^3 N_2 G_1(\xi^+) - N_4 G_3(\xi) \nu_{12(0)}^{34}(\xi^+) \right] - \gamma_3(\xi) G_3(\xi), \quad (43) \]

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

\[ \gamma_i(\xi) = N_2 \nu_{i2(1)}^{34}(\xi) + N_4 \nu_{i4(1)}^{34}(\xi), \quad (44) \]

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

\[ \nu_{ij(k)}^{lm}(\xi) = 2 \pi \int_{-1}^{+1} \mu^k \nu_{ij}^{lm}(\xi, \mu) d\mu, \quad (45) \]

with $k = 1$ and 2.

Consider now the stationary space-homogeneous equa-
tions We observe that for $E = 0$ the following equilibrium solutions hold:

$$F_i = C_i \exp\left(-\frac{m_i \xi}{2 \kappa T}\right),$$

(46)

where

$$C_3 N_4 = \left(\frac{m_3}{m_1}\right)^3 \exp\left(-\frac{\Delta E}{\kappa T}\right),$$

(47)

(mass action law). Finally, we observe that the electric field must be a small quantity, $|E| = \epsilon$, so that we can expand $F_i$ and $G_i$ as follows

$$F_i = F_i^{(0)} + \epsilon F_i^{(1)} + \ldots,$$

$$G_i = \epsilon G_i^{(1)} + \ldots.$$  (48)

Since $F_i^{(0)}$ are already known, by solving equations (40) and (41), we can obtain the expression of $G_i^{(1)}$, in the case of isotropic reaction collision frequency $\nu_{12}^{(0)}$:

$$G_1^{(1)} = -\frac{e E C_1}{\kappa T} \sqrt{\xi} \exp\left(-\frac{m_1 \xi}{2 \kappa T}\right) \cdot \frac{\theta(\xi - \eta_1)}{N_2 \nu_{12}^{(0)}(\xi)} + \gamma_1(\xi),$$

(49)

$$G_3^{(1)} = -\frac{e E C_3}{\kappa T} \xi \exp\left(-\frac{m_3 \xi}{2 \kappa T}\right) N_4 \left(\frac{m_3}{m_1}\right)^2 \nu_{12}^{(0)}(\nu^+ \nu^+ + \sqrt{\xi} \gamma_3(\xi)),$$

(50)

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

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.

V. 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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