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Momentum transfer theory of nonconservative charged particle transport in mixtures of gases: General equations and negative differential conductivity

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In this paper we develop general equations for the momentum transfer theory (MTT) for swarms of particles in mixtures of gases including the effect of nonconservative (reactive) collisions. MTT equations for mean energy, drift velocity, diffusion tensor components, and rate coefficients are derived for different degrees of approximation including the hydrodynamic limit and small swarm to gas particle mass ratio. Specific formulas were developed for the criteria for negative differential conductivity (NDC) in mixtures of gases with elastic collisions only and for a single gas with reactions. The criteria and the numerical calculations are in excellent agreement, showing that NDC can be induced by light atomic constituents in purely elastic collisions and also by ionization and attachment.

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I. INTRODUCTION

A. Momentum transfer theory

Momentum transfer theory (MTT) has been developed as an approximate solution to transport equations that gives an opportunity to develop analytic forms of various transport coefficients and their relations. It consists of applying Taylor expansion to the transport coefficients at the appropriately determined value of the mean energy. Because of its simplicity, which, however, allows reasonable accuracy, it has become quite popular in discussing the basic physical explanations of transport phenomena, although it is usually not adequate for accurate transport calculations and cross section fitting.

MTT has been developed for charged particle transport in mixtures of gases having only elastic processes [1]. Results for the corrections of Blanc's law [2,3] and the relationship between diffusion coefficients and mobility [3] were obtained. Inelastic collisions have been included in the single gas MTT, and corresponding equations for energy, drift velocity and relationship between the mobility and components of the diffusion tensor were developed. Reactive collisions were included, in addition to inelastic, and the corresponding effects of attachment, annihilation [4], and ionization [5] on transport coefficients were discussed. In this paper we make a further generalization to mixtures of gases having reactive processes.

B. Negative differential conductivity

Negative differential conductivity (NDC), which should more appropriately be labeled negative differential mobility, will for the purpose of this paper and in order to follow the notation in the literature [6–10] be defined as a decrease of the drift velocity with an increasing driving field. Several explanations of the NDC effect exist in the literature [6–12] including the NDC effect in time varying fields [13–15] and applications to diffuse discharge switches [16–18]. The conditions for NDC summarized by Petrović, Crompton, and Haddad [6] (PCH), based on their model calculation and theory by Robson [7], are the following:

(i) Inelastic processes are necessary.
(ii) Increasing momentum transfer cross section favors NDC.
(iii) Decreasing inelastic cross section favors NDC.
(iv) Occurrence of NDC depends on relative magnitudes of factors (ii) and (iii).
(v) Superelastic processes will have a tendency to reduce the NDC.

Here and in the remainder of this paper, Ref. [6] will be referred to as PCH.

Conditions (ii) and (iii) have been erroneously interpreted as necessary conditions, which is clearly not so when condition (iv) is taken into account. A more justified disagreement with condition (i) was made in a paper by Shizgal [8]. This author pointed out that his calculations for the mixtures of rare gases for the conditions when inelastic processes do not make a significant contribution to the energy balance gave NDC when the most abundant constituents were heavy gases with Ramsauer-Townsend minimum (RTM), such as Xe and Kr, and the lower mass, but mostly minor, constituent was He. It was also noticed that the mass of gases plays an important role. The criterion that was also developed by Shizgal was in good qualitative but not quantitative agreement with the results of his numerical calculations. One of the basic aims of this paper is to extend the conditions given by PCH and Robson and to explain the apparent discrepancy with the results of Shizgal that makes it necessary to develop NDC criteria for the gas mixtures.

Apart from the well established occurrences of the NDC, it also became obvious to us that the phenomenon may occur under a wider range of situations. Those include the influence of the so-called "reactive" collisions [19], i.e., the processes that do not conserve the number of electrons (particles whose transport is studied). Under such conditions the NDC may be difficult to observe experimentally because they occur at high E/N, where measurements of drift velocities are fewer because of experimental problems, or under conditions of high attachment when there are few electrons.

In this paper we first develop the basic transport equations in Sec. II. Then we develop the NDC criteria in Sec. III. Discussion of the results for electron drift velocity in mixtures of atomic gases and for the case of reactive collisions is given in Sec. IV. A preliminary presentation of the results from this paper was given by Vrhovac and Petrović [20].

II. THEORETICAL EVALUATION

A. Formulation of the moment equations

Consider a swarm of particles of charge e and mass m moving with velocity $\vec{v}$ through neutral gas mixtures under the influence of an applied electrostatic field $\vec{E}$. The term "swarm" has a connotation of electron or ion swarms, but the analysis can be applied to neutral particles of positrons. Suppose that there are several (l) species of neutral gases present. Let m_α and $\vec{v}_\alpha$ be mass and velocity of molecules of the αth neutral gas, respectively. Let $n(\vec{r},t)$ be the number density of swarm particles, and let $n_\alpha(\vec{r},t)$ be the number density of the αth neutral gas. Now we introduce the standard notation:

$n_0=\sum_\alpha n_\alpha$ (number density of the gas mixture),
$\mu_\alpha=mm_\alpha/(m+m_\alpha)$ (reduced mass),
$M_\alpha=m_\alpha/(m+m_\alpha)$, $M_\alpha^0=m/(m+m_\alpha)$,
$\vec{v}_{r\alpha}=\vec{v}-\vec{v}_\alpha$ (relative velocity), and
$\varepsilon_\alpha=\frac{1}{2}\mu_\alpha\vec{v}_{r\alpha}^{\,2}$ (energy measured in the center-of-mass reference frame).

Let $f^{\text{mix}}(\vec{r},\vec{v},t)$ and $f_\alpha^{\text{mix}}(\vec{r},\vec{v},t)$ be the swarm and αth neutral gas one-particle velocity distribution function in the multicomponent mixture, respectively. By convention, all velocity distribution functions are normalized to number densities.

Averaging operators used in the development of equations are defined as

$$\langle\Phi(\vec{v},\vec{v}_\alpha)\rangle^{\text{mix}}=\frac{1}{n(\vec{r},t)}\int d^3\vec{v}f^{\text{mix}}(\vec{r},\vec{v},t)\Phi(\vec{v},\vec{v}_\alpha)\ , \qquad (1)$$

$$\langle\langle\Phi(\vec{v},\vec{v}_\alpha)\rangle\rangle_\alpha^{\text{mix}}=\frac{1}{n(\vec{r},t)n_\alpha(\vec{r},t)}\int\int d^3\vec{v}d^3\vec{v}_\alpha \times f^{\text{mix}}(\vec{r},\vec{v},t)f_\alpha^{\text{mix}}(\vec{r},\vec{v}_\alpha,t)\Phi(\vec{v},\vec{v}_\alpha)\ , \qquad (2)$$

where $\Phi(\vec{v},\vec{v}_\alpha)$ is any function of $\vec{v}$ and $\vec{v}_\alpha$. For the sake of brevity, we write $\varepsilon_\alpha^0=\langle\langle\varepsilon_\alpha\rangle\rangle_\alpha^{\text{mix}}$, $\delta\vec{v}^{\text{mix}}=\vec{v}-\langle\vec{v}\rangle^{\text{mix}}$, and $\varepsilon^0=\{\varepsilon_\alpha^0|\alpha\in I_l\}$, where $I_l=\{1,2,\ldots,l\}$ denotes an appropriate finite set of indices.

The Boltzmann equation for a swarm of particles moving through a gaseous multicomponent medium is [21]

$$\left[\frac{\partial}{\partial t}+\vec{v}\cdot\frac{\partial}{\partial\vec{r}}+\frac{e}{m}\vec{E}(\vec{r},t)\cdot\frac{\partial}{\partial\vec{v}}\right]f^{\text{mix}}(\vec{r},\vec{v},t) = \sum_{\alpha\in I_l}J_\alpha^{\text{mix}}(f^{\text{mix}},f_\alpha^{\text{mix}})\ , \qquad (3)$$

where J_α^{mix} is the collision operator, which represents the rate of change of f^{mix} due to the collisions between swarm particles and molecules of the neutral gas α. In the collision terms of the Boltzmann equation, only binary collisions are considered.

The chain of moment equations is derived by multiplying both sides of Eq. (3) by various powers of swarm particle velocity $\vec{v}$ and integrating over velocity space. The moment equations of interest correspond to those for which powers of swarm velocity are equal to 1 (equation of continuity), $m\vec{v}$ (momentum balance equation), and $\frac{1}{2}mv^2$ (energy balance equation) [22].

1. Collisions processes

To give a definite expression to the collisional terms of the moment equation we make several assumptions above collisional processes between swarm particles and gas molecules. The collision processes that we investigate are limited to elastic, inelastic, and reactive (which include attachment and ionization) collisions of individual swarm particles with normal gas molecules. We characterize all these possible processes by respective collision frequencies. A collision frequency $\nu_\alpha(\vec{r},v_{r\alpha},t)$ for collisions between the swarm particles and molecules of species α is related to the cross section $\sigma_\alpha(v_{r\alpha})$ characterizing the process by $\nu_\alpha(\vec{r},v_{r\alpha},t)=n_\alpha(\vec{r},t)v_{r\alpha}\sigma_\alpha(v_{r\alpha})$, where $\vec{v}_{r\alpha}$ is the relative velocity and $n_\alpha(\vec{r},t)$ is the number density of the αth neutral gas. We neglect the collisions of swarm particles with other swarm particles, ions, and excited molecules.

We take into account the momentum and energy loss of the swarm particle in elastic collisions arising from the finite mass of gas molecules. In the calculation of this momentum and energy loss we assume that the actual thermal energy of the molecules (each neutral gas has the same nonzero temperature T^{mix}) is not negligible compared to the mean energy of the swarm particles. The momentum transfer collision frequency for collisions between the swarm particles and molecules of species α is denoted by $\nu_\alpha^{(m)}(\vec{r},v_{r\alpha},t)$.

Let $I_\alpha^{(\text{in})}$ be a set of indices that enumerates possible inelastic collisions of a swarm particle with molecules of the gas α, while $\nu_{s\alpha}(\vec{r},v_{r\alpha},t)$, $s\in I_\alpha^{(\text{in})}$ is the corresponding collision frequency. The threshold for these inelastic collisions is denoted by ΔE_α^s, $s\in I_\alpha^{(\text{in})}$, $\alpha\in I_l$. Momentum exchange in inelastic processes is not ignored. The total momentum transfer collision frequency is given by

$$\nu_{0\alpha}^{(m)}(\vec{r},v_{r\alpha},t)=\nu_\alpha^{(m)}(\vec{r},v_{r\alpha},t)+\sum_{s\in I_\alpha^{(\text{in})}}\nu_{s\alpha}^{(m)}(\vec{r},v_{r\alpha},t)\ , \quad \alpha\in I_l\ , \qquad (4)$$

where $\nu_{s\alpha}^{(m)}(\vec{r},v_{r\alpha},t)$, $s\in I_\alpha^{(\text{in})}$ denotes momentum transfer collision frequency of collision inducing inelastic process $s\in I_\alpha^{(\mathrm{in})}$.

Reactive collisions for electron swarms include creation (ionization by electron impact) or loss (electron attachment to electronegative gas molecules or positron annihilation) of a swarm particle. Let $\nu_{s\alpha}^{(A)}(\vec{r},v_{r\alpha},t)$ be the rate at which swarm particles are lost in collisions through the attachment channel $s\in I_\alpha^{(A)}$. In the case of electron ionization the incident electron collides with a molecule and two electrons emerge after the collision, one being the scattered incident electron and the other being the ejected electron; it is a three body problem. In approximation of a mass ratio of $m/m_\alpha \ll 1$, we can ignore the motion of the molecule, so that the available kinetic energy and momentum after the ionization are divided between the two electrons. We consider only single ionization with ionization energy $\varepsilon_\alpha^{(I)}$, but the resulting ion can be left in any one of its internal excited states, characterized by excitation energy $\Delta\varepsilon_{s\alpha}^{(I)}$, $s\in I_\alpha^{(I)}$. Let $\nu_{s\alpha}^{(I)}(\vec{r},v_{r\alpha},t)$ be the ionization frequency for sth ionization channel $s\in I_\alpha^{(I)}$. The total rates for attachment (A) and ionization (I) are defined by formulas:

$$\nu_\alpha^{(A)}(\vec{r},v_{r\alpha},t)=\sum_{s\in I_\alpha^{(A)}}\nu_{s\alpha}^{(A)}(\vec{r},v_{r\alpha},t)\ ,$$

$$\nu_\alpha^{(I)}(\vec{r},v_{r\alpha},t)=\sum_{s\in I_\alpha^{(I)}}\nu_{s\alpha}^{(I)}(\vec{r},v_{r\alpha},t),\quad \alpha\in I_l\ . \tag{5}$$

2. *Moment equations*

We extend the moment equations derived by Robson [4] and Robson and Ness [5] to include gas mixtures by taking appropriately weighted sums of collision terms in momentum equations. Using arguments similar to Robson's we find

Equation of continuity:

$$\frac{\partial}{\partial t}n(\vec{r},t)+\frac{\partial}{\partial\vec{r}}\cdot[n(\vec{r},t)\langle\vec{v}\rangle^{\mathrm{mix}}]$$
$$=-n(\vec{r},t)\sum_{\alpha\in I_l}\langle\langle\nu_\alpha^{(A)}(\vec{r},v_{r\alpha},t)\rangle\rangle_\alpha^{\mathrm{mix}}$$
$$+n(\vec{r},t)\sum_{\alpha\in I_l}\langle\langle\nu_\alpha^{(I)}(\vec{r},v_{r\alpha},t)\rangle\rangle_\alpha^{\mathrm{mix}}\ . \tag{6}$$

Momentum balance equation:

$$\frac{\partial}{\partial t}[mn(\vec{r},t)\langle\vec{v}\rangle^{\mathrm{mix}}]+\frac{\partial}{\partial\vec{r}}[mn(\vec{r},t)\langle\{\vec{v},\vec{v}\}\rangle^{\mathrm{mix}}]$$
$$-n(\vec{r},t)e\vec{E}(\vec{r},t)$$
$$=-n(\vec{r},t)\sum_{\alpha\in I_l}\mu_\alpha\langle\langle\vec{v}_{r\alpha}\nu_{0\alpha}^{(m)}(\vec{r},v_{r\alpha},t)\rangle\rangle_\alpha^{\mathrm{mix}}$$
$$-n(\vec{r},t)m\sum_{\alpha\in I_l}\langle\langle\vec{v}\nu_\alpha^{(A)}(\vec{r},v_{r\alpha},t)\rangle\rangle_\alpha^{\mathrm{mix}}\ . \tag{7}$$

Energy balance equation:

$$\frac{\partial}{\partial t}\left[\tfrac{1}{2}mn(\vec{r},t)\langle v^2\rangle^{\mathrm{mix}}\right]+\frac{\partial}{\partial\vec{r}}\cdot\left[\tfrac{1}{2}mn(\vec{r},t)\langle v^2\vec{v}\rangle^{\mathrm{mix}}\right]-n(\vec{r},t)e\vec{E}(\vec{r},t)\langle\vec{v}\rangle^{\mathrm{mix}}$$
$$=-n(\vec{r},t)\sum_{\alpha\in I_l}\frac{\mu_\alpha}{m+m_\alpha}\langle\langle[mv^2-m_\alpha v_\alpha^2-(m-m_\alpha)\vec{v}\cdot\vec{v}_\alpha]\nu_{0\alpha}^{(m)}(\vec{r},v_{r\alpha},t)\rangle\rangle_\alpha^{\mathrm{mix}}$$
$$-n(\vec{r},t)\sum_{\alpha\in I_l}\sum_{s\in I_\alpha^{(\mathrm{in})}}\langle\langle\nu_{s\alpha}(\vec{r},v_{r\alpha},t)\rangle\rangle_\alpha^{\mathrm{mix}}\Delta E_\alpha^s-n(\vec{r},t)\tfrac{1}{2}m\sum_{\alpha\in I_l}\langle\langle v^2\nu_\alpha^{(A)}(\vec{r},v_{r\alpha},t)\rangle\rangle_\alpha^{\mathrm{mix}}$$
$$-n(\vec{r},t)\sum_{\alpha\in I_l}\langle\langle\nu_\alpha^{(I)}(\vec{r},v_{r\alpha},t)\rangle\rangle_\alpha^{\mathrm{mix}}\varepsilon_\alpha^{(I)}-n(\vec{r},t)\sum_{\alpha\in I_l}\sum_{s\in I_\alpha^{(I)}}\langle\langle\nu_{s\alpha}^{(I)}(\vec{r},v_{r\alpha},t)\rangle\rangle_\alpha^{\mathrm{mix}}\Delta\varepsilon_{s\alpha}^{(I)}\ . \tag{8}$$

In the momentum balance equation [Eq. (13)], the tensor $\{\cdot,\cdot\}$ is a dyadic product of vectors, defined by

$$\{\vec{A},\vec{B}\}\vec{C}=\vec{A}(\vec{B}\odot\vec{C}),\quad \vec{C}\{\vec{A},\vec{B}\}=(\vec{C}\odot\vec{A})\vec{B}\ , \tag{9}$$

where $\odot$ is the scalar product.

B. Momentum transfer approximation

Now let us replace the variables

$$v_{r\alpha}\rightarrow\varepsilon_\alpha=\tfrac{1}{2}\mu_\alpha v_{r\alpha}^2,\quad \alpha\in I_l \tag{10}$$

in expressions for collisional frequencies,

$$\nu_\alpha=\nu_\alpha(\vec{r},v_{r\alpha},t)\rightarrow\tilde{\nu}_\alpha=\tilde{\nu}_\alpha(\vec{r},\varepsilon_\alpha,t),\quad \alpha\in I_l\ . \tag{11}$$

When we expand $\tilde{\nu}_\alpha(\vec{r},\varepsilon_\alpha,t)$ in the Taylor series in the vicinity of ε_α^0, we obtain

$$\tilde{\nu}_\alpha(\vec{r},\varepsilon_\alpha,t)=\tilde{\nu}_\alpha(\vec{r},\varepsilon_\alpha^0,t)+\left[\frac{d\tilde{\nu}_\alpha(\vec{r},\varepsilon_\alpha,t)}{d\varepsilon_\alpha}\right]_{\varepsilon_\alpha=\varepsilon_\alpha^0}$$
$$\times(\varepsilon_\alpha-\varepsilon_\alpha^0)+o(\varepsilon_\alpha-\varepsilon_\alpha^0)\ , \tag{12}$$

where the remainder consists of terms of higher-order derivates of $\tilde{\nu}_\alpha(\vec{r},\varepsilon_\alpha,t)$. We assume that the Taylor expansion [Eq. (12)] converges rapidly in the neighborhood of ε_α^0, with a provision for special modifications required to make this approximation satisfactory for inelastic collisions with a high threshold [5,7]. The extended momentum transfer approximation consists of retention of several terms in the Taylor expansion [4]. Momentum and energy loss rates for attachment are calculated using the first two terms on the right-hand side of Eq. (12) and the assumption that the distribution function of swarm particles is a shifted Maxwellian. We also assume that the background gas is in the thermal equilibrium (characterized by Maxwellian distribution and temperature T^{mix}).

Using the momentum transfer approximation, we find from Eq. (6) the equation of continuity,

$$\frac{\partial}{\partial t}n(\vec{r},t)+\frac{\partial}{\partial\vec{r}}\cdot[n(\vec{r},t)\langle\vec{v}\rangle^{\mathrm{mix}}] =-n(\vec{r},t)\tilde{\nu}^{(A)}(\vec{r},\varepsilon^0,t)+n(\vec{r},t)\tilde{\nu}^{(I)}(\vec{r},\varepsilon^0,t)\ , \tag{13}$$

where we introduced the notation

$$\begin{aligned}\tilde{\nu}^{(A)}(\vec{r},\varepsilon^0,t)&=\sum_{\alpha\in I_l}\tilde{\nu}_\alpha^{(A)}(\vec{r},\varepsilon_\alpha^0,t)\ ,\\ \tilde{\nu}^{(I)}(\vec{r},\varepsilon^0,t)&=\sum_{\alpha\in I_l}\tilde{\nu}_\alpha^{(I)}(\vec{r},\varepsilon_\alpha^0,t)\ .\end{aligned} \tag{14}$$

By substracting the products of $m\langle\vec{v}\rangle^{\mathrm{mix}}$ and $\frac{1}{2}m\langle v^2\rangle^{\mathrm{mix}}$ with the equation of continuity [Eq. (6)] from Eqs. (7) and (8) and by using momentum transfer approximation, one obtains a more useful form of the momentum and energy balance equations:

$$\begin{aligned}&mn(\vec{r},t)\left[\frac{\partial}{\partial t}+\langle\vec{v}\rangle^{\mathrm{mix}}\cdot\frac{\partial}{\partial\vec{r}}\right]\langle\vec{v}\rangle^{\mathrm{mix}}-n(\vec{r},t)e\vec{E}(\vec{r},t)+\mathrm{div}\hat{P}^{\mathrm{mix}}\\ &\qquad=-n(\vec{r},t)m\langle\vec{v}\rangle^{\mathrm{mix}}\tilde{\nu}_0^{(m)}(\vec{r},\varepsilon^0,t)-n(\vec{r},t)m\langle\vec{v}\rangle^{\mathrm{mix}}[\xi^{\mathrm{mix}}\tilde{\nu}_1^{(A)}(\vec{r},\varepsilon^0,t)+\tilde{\nu}^{(I)}(\vec{r},\varepsilon^0,t)]\ ,\end{aligned} \tag{15}$$

$$\begin{aligned}&n(\vec{r},t)\left[\frac{\partial}{\partial t}+\langle\vec{v}\rangle^{\mathrm{mix}}\cdot\frac{\partial}{\partial\vec{r}}\right]\left[\frac{1}{2}m\langle v^2\rangle^{\mathrm{mix}}\right]+\frac{\partial}{\partial\vec{r}}\cdot\left[\hat{P}^{\mathrm{mix}}\langle\vec{v}\rangle^{\mathrm{mix}}+\frac{3}{2}\vec{Q}^{\mathrm{mix}}\right]-n(\vec{r},t)e\vec{E}(\vec{r},t)\langle\vec{v}\rangle^{\mathrm{mix}}\\ &\quad=-n(\vec{r},t)[m\langle v^2\rangle^{\mathrm{mix}}-3kT^{\mathrm{mix}}]\tilde{\nu}_{00}^{(m)}(\vec{r},\varepsilon^0,t)-n(\vec{r},t)\sum_{\alpha\in I_l}\sum_{s\in I_\alpha^{(\mathrm{in})}}\tilde{\nu}_{s\alpha}(\vec{r},\varepsilon_\alpha^0,t)\Delta E_\alpha^s\\ &\quad\quad-n(\vec{r},t)\tfrac{1}{2}m[\langle v^2\rangle^{\mathrm{mix}}-(\langle\vec{v}\rangle^{\mathrm{mix}})^2]\xi^{mix}\tilde{\nu}_1^{(A)}(\vec{r},\varepsilon^0,t)-n(\vec{r},t)\sum_{\alpha\in I_l}\tilde{\nu}_\alpha^{(I)}(\vec{r},\varepsilon_\alpha^0,t)\varepsilon_\alpha^{(I)}\\ &\quad\quad-n(\vec{r},t)\sum_{\alpha\in I_l}\sum_{s\in I_\alpha^{(I)}}\tilde{\nu}_{s\alpha}^{(I)}(\vec{r},\varepsilon_\alpha^0,t)\Delta\varepsilon_{s\alpha}^{(I)}-n(\vec{r},t)\tfrac{1}{2}m\langle v^2\rangle^{\mathrm{mix}}\tilde{\nu}^{(I)}(\vec{r},\varepsilon^0,t)\ .\end{aligned} \tag{16}$$

In Eqs. (15) and (16) the pressure tensor $\hat{P}^{\mathrm{mix}}$ and vector heat conductivity $\vec{Q}^{\mathrm{mix}}$ are defined as follows:

$$\begin{aligned}\hat{P}^{\mathrm{mix}}&=mn(\vec{r},t)\langle\{\delta\vec{v}^{\mathrm{mix}},\delta\vec{v}^{\mathrm{mix}}\}\rangle^{\mathrm{mix}}\\ \vec{Q}^{\mathrm{mix}}&=\tfrac{1}{3}mn(\vec{r},t)\langle\delta\vec{v}^{\mathrm{mix}}(\delta\vec{v}^{\mathrm{mix}})^2\rangle^{\mathrm{mix}}\ .\end{aligned} \tag{17}$$

We introduced the notation

$$\begin{aligned}\tilde{\nu}_0^{(m)}(\vec{r},\varepsilon^0,t)&=\sum_{\alpha\in I_l}M_\alpha\tilde{\nu}_{0\alpha}^{(m)}(\vec{r},\varepsilon_\alpha^0,t)\ ,\\ \tilde{\nu}_{00}^{(m)}&=\sum_{\alpha\in I_l}M_\alpha M_\alpha^0\tilde{\nu}_{0\alpha}^{(m)}(\vec{r},\varepsilon_a^0,t)\ ,\end{aligned} \tag{18}$$

$$\begin{aligned}\tilde{\nu}_1^{(A)}(\vec{r},\varepsilon^0,t)&=\sum_{\alpha\in I_l}M_\alpha\tilde{\nu}_{\alpha 1}^{(A)}(\vec{r},\varepsilon_\alpha^0,t)\ ,\\ \tilde{\nu}_{\alpha 1}^{(A)}(\vec{r},\varepsilon_\alpha^0,t)&=\left[\frac{d\nu_\alpha^{(A)}(\vec{r},\varepsilon_\alpha,t)}{d\varepsilon_\alpha}\right]_{\varepsilon_\alpha=\varepsilon_\alpha^0}\ ,\quad\alpha\in I_l\end{aligned} \tag{19}$$

$$\xi^{\mathrm{mix}}=\tfrac{2}{3}\tfrac{1}{2}m[\langle v^2\rangle^{\mathrm{mix}}-(\langle\vec{v}\rangle^{\mathrm{mix}})^2]\ . \tag{20}$$

C. Hydrodynamic limit and transport coefficients

1. Hydrodynamic regime

We assume that the stage of evolution of the swarm is the hydrodynamic limit (HDL). In the HDL, the space-time dependence of all properties is carried by the number density $n(\vec{r},t)$ and the swarm can be characterized by time-independent transport coefficients.

The starting point of the hydrodynamic description is the continuity equation for the number density,

$$\frac{\partial}{\partial t}n(\vec{r},t)+\frac{\partial}{\partial\vec{r}}\cdot[n(\vec{r},t)\langle\vec{v}\rangle^{\mathrm{mix}}]=\left[\frac{\partial n(\vec{r},t)}{\partial t}\right]_{\mathrm{coll}}\ , \tag{21}$$

which describes the change in $n(\vec{r},t)$ due to a particle flux $n(\vec{r},t)\vec{v}(\vec{r},t)$ and the production term $[\partial n(\vec{r},t)/\partial t]_{\mathrm{coll}}$. The assumption is made that both of these quantities can be expressed as power series in the gradient operator ∇ with constant coefficients. Equation (21) is expressed as [23]

$$\left[\frac{\partial}{\partial t}+\sum_{k=0}^{\infty}\omega^{(k)}\odot(-\nabla)^k\right]n(\vec{r},t)=0\ . \tag{22}$$

The constants $\omega^{(k)}$ are tensorial transport coefficients of the order k, and $\odot$ indicates a k-fold scalar product. By truncating Eq. (22) at $k=2$, we obtain the familiar diffusion equation

$$\left[\frac{\partial}{\partial t}+\vec{W}^{\mathrm{mix}}\cdot\frac{\partial}{\partial\vec{r}}-\left[\hat{D}^{\mathrm{mix}}\frac{\partial}{\partial\vec{r}}\right]\cdot\frac{\partial}{\partial\vec{r}}\right]n(\vec{r},t)=-\alpha^*n(\vec{r},t)\ , \tag{23}$$

where we identify $\alpha^{*}=-\omega^{(0)}$ as the reaction rate, $\vec{W}^{\mathrm{mix}}=(\omega_i^{(1)})_{i=1}^{3}$ as the drift velocity, and $\hat{D}^{\mathrm{mix}}=(\omega_{ij}^{(2)})_{i,j=1,1}^{3,3}$ as the diffusion tensor.

In the HDL, the momentum and energy balance equations [Eqs. (15) and (16)] become

$$-e\vec{E}+k\hat{T}^{\mathrm{mix}}\vec{G}(\vec{r},t)=-m\langle\vec{v}\rangle^{\mathrm{mix}}\bar{\nu}_{(m)}^{\mathrm{mix}}, \tag{24}$$

$$\begin{aligned}\langle\vec{v}\rangle^{\mathrm{mix}}k\hat{T}^{\mathrm{mix}}\vec{G}(\vec{r},t)+\tfrac{3}{2}\vec{q}^{\,\mathrm{mix}}\vec{G}(\vec{r},t)-e\vec{E}\langle\vec{v}\rangle^{\mathrm{mix}}\\ =-\left[m\langle v^2\rangle^{\mathrm{mix}}-3kT^{\mathrm{mix}}\right]\tilde{\nu}_{00}^{(m)}-\sum_{\alpha\in I_l}\sum_{s\in I_\alpha^{(\mathrm{in})}}\tilde{\nu}_{s\alpha}\Delta E_\alpha^{s}\\ -\tfrac{1}{2}m[\langle v^2\rangle^{\mathrm{mix}}+(\langle\vec{v}\rangle^{\mathrm{mix}})^2]\xi^{\mathrm{mix}}\tilde{\nu}_1^{(A)}-\sum_{\alpha\in I_l}\tilde{\nu}_\alpha^{(I)}\varepsilon_\alpha^{(I)}\\ -\sum_{\alpha\in I_l}\sum_{s\in I_\alpha^{(I)}}\tilde{\nu}_{s\alpha}^{(I)}\Delta\varepsilon_{s\alpha}^{(I)}-\tfrac{1}{2}m\langle v^2\rangle^{\mathrm{mix}}\tilde{\nu}^{(I)},\end{aligned} \tag{25}$$

where $\hat{T}^{\mathrm{mix}}$ is the temperature tensor defined by

$$k\hat{T}^{\mathrm{mix}}=\frac{1}{n(\vec{r},t)}\hat{P}^{\mathrm{mix}}, \tag{26}$$

while

$$\vec{q}^{\,\mathrm{mix}}=\frac{1}{n(\vec{r},t)}\vec{Q}^{\mathrm{mix}}, \tag{27}$$

$$\vec{G}(\vec{r},t)=\frac{1}{n(\vec{r},t)}\frac{\partial}{\partial\vec{r}}n(\vec{r},t), \tag{28}$$

and

$$\bar{\nu}_{(m)}^{\mathrm{mix}}=\tilde{\nu}_0^{(m)}+\xi^{\mathrm{mix}}\tilde{\nu}_1^{(A)}+\tilde{\nu}^{(I)}. \tag{29}$$

If we take the product of $\langle\vec{v}\rangle^{\mathrm{mix}}$ with the momentum balance equation [Eq. (24)] and subtract from the energy balance equation [Eq. (25)], it can be written in an equivalent form

$$\begin{aligned}\tfrac{3}{2}\vec{q}_{\mathrm{mix}}\vec{G}(\vec{r},t)=-(m\langle v^2\rangle^{\mathrm{mix}}-3kT^{\mathrm{mix}})\tilde{\nu}_{00}^{(m)}+m(\langle\vec{v}\rangle^{\mathrm{mix}})^2\tilde{\nu}_0^{(m)}-\sum_{\alpha\in I_l}\sum_{s\in I_\alpha^{(\mathrm{in})}}\tilde{\nu}_{s\alpha}\Delta E_\alpha^{s}\\ -\sum_{\alpha\in I_l}\tilde{\nu}_\alpha^{(I)}\varepsilon_\alpha^{(I)}-\sum_{\alpha\in I_l}\sum_{s\in I_\alpha^{(I)}}\tilde{\nu}_{s\alpha}^{(I)}\Delta\varepsilon_{s\alpha}^{(I)}-\tfrac{1}{2}m\langle v^2\rangle^{\mathrm{mix}}(\xi^{\mathrm{mix}}\tilde{\nu}_1^{(A)}+\tilde{\nu}^{(I)})+\tfrac{1}{2}m(\langle\vec{v}\rangle^{\mathrm{mix}})^2(\xi^{\mathrm{mix}}\nu_1^{(A)}+2\tilde{\nu}^{(I)}).\end{aligned} \tag{30}$$

We can rewrite Eq. (30) in terms of the average energies in the center-of-mass frame:

$$\langle\langle\varepsilon_\alpha\rangle\rangle_\alpha^{\mathrm{mix}}=M_\alpha\tfrac{1}{2}m\langle v^2\rangle^{\mathrm{mix}}+M_\alpha^{0}\tfrac{3}{2}kT^{\mathrm{mix}},\quad \alpha\in I_l. \tag{31}$$

When we substitute Eq. (31) into Eq. (30), we obtain the following set of equations:

$$\langle\langle\varepsilon_\alpha\rangle\rangle_\alpha^{\mathrm{mix}}=\tfrac{1}{2}m(\langle\vec{v}\rangle^{\mathrm{mix}})^2M_\alpha r^{\mathrm{mix}}+\tfrac{3}{2}kT^{\mathrm{mix}}M_\alpha\left[\frac{M_c^{0}}{M_\alpha}+s^{\mathrm{mix}}\right]-M_\alpha\bar{\Omega}^{\mathrm{mix}}-M_\alpha\tfrac{3}{2}\vec{q}^{\,\mathrm{mix}}\vec{G}(\vec{r},t)\frac{1}{\bar{\nu}_{(e)}^{\mathrm{mix}}},\quad \alpha\in I_l, \tag{32}$$

where we use the notations

$$\bar{\nu}_{(e)}^{\mathrm{mix}}=2\tilde{\nu}_{00}^{(m)}+\xi^{\mathrm{mix}}\tilde{\nu}_1^{(A)}+\tilde{\nu}^{(I)}, \tag{33}$$

$$r^{\mathrm{mix}}=\frac{2\tilde{\nu}_0^{(m)}+\xi^{\mathrm{mix}}\tilde{\nu}_1^{(A)}+2\tilde{\nu}^{(I)}}{\bar{\nu}_{(e)}^{\mathrm{mix}}},\quad s^{\mathrm{mix}}=\frac{2\tilde{\nu}_{00}^{(m)}}{\bar{\nu}_{(e)}^{\mathrm{mix}}}, \tag{34}$$

$$\bar{\Omega}^{\mathrm{mix}}=\frac{\bar{\Lambda}^{\mathrm{mix}}}{\bar{\nu}_{(e)}^{\mathrm{mix}}},\quad \bar{\Lambda}^{\mathrm{mix}}=\sum_{\alpha\in I_l}\bar{\Lambda}_\alpha^{\mathrm{mix}}, \tag{35}$$

and

$$\bar{\Lambda}_\alpha^{\mathrm{mix}}=\sum_{s\in I_\alpha^{(\mathrm{in})}}\tilde{\nu}_{s\alpha}\Delta E_\alpha^{s}+\tilde{\nu}_\alpha^{(I)}\varepsilon_\alpha^{(I)}+\sum_{s\in I_\alpha^{(I)}}\tilde{\nu}_{s\alpha}^{(I)}\Delta\varepsilon_{s\alpha}^{(I)},\quad \alpha\in I_l. \tag{36}$$

2. *Transport coefficients*

Following a procedure similar to Robson's [4], Eqs. (24) and (32) can be written as

$$\langle\vec{v}\rangle^{\mathrm{mix}}=\psi_1(\varepsilon^{0},(\langle\vec{v}\rangle^{\mathrm{mix}})^2)\left[\vec{E}-\frac{k}{e}\hat{T}^{\mathrm{mix}}\vec{G}\right], \tag{37}$$

$$\langle\langle\varepsilon_\alpha\rangle\rangle_\alpha^{\mathrm{mix}}=\psi_2^{\alpha}(\varepsilon^{0},(\langle\vec{v}\rangle^{\mathrm{mix}})^2)-M_\alpha\tfrac{3}{2}\vec{q}^{\,\mathrm{mix}}\vec{G}\frac{1}{\tilde{\nu}_{(e)}^{\mathrm{mix}}},\quad \alpha\in I_l. \tag{38}$$

The functions ψ_1 and ψ_2^{α}, $\alpha\in I_l$, of Eqs. (37) and (38), respectively, are defined as follows:

$$\psi_1(\varepsilon^{0},(\langle\vec{v}\rangle^{\mathrm{mix}})^2)=\frac{e}{m\bar{\nu}_{(m)}^{\mathrm{mix}}}, \tag{39}$$

$$\begin{aligned}\psi_2^{\alpha}(\varepsilon^{0},(\langle\vec{v}\rangle^{\mathrm{mix}})^2)=\tfrac{1}{2}m(\langle\vec{v}\rangle^{\mathrm{mix}})^2M_\alpha r^{\mathrm{mix}}\\ +\frac{3}{2}kT^{\mathrm{mix}}M_\alpha\left[\frac{M_\alpha^{0}}{M_\alpha}+s^{\mathrm{mix}}\right]-M_\alpha\bar{\Omega}^{\mathrm{mix}},\\ \alpha\in I_l.\end{aligned} \tag{40}$$

If the heat flux on the right-hand side of Eq. (38) is neglected, then both $\langle \vec{v} \rangle^{\mathrm{mix}}$ and $\langle\langle \varepsilon_\alpha \rangle\rangle_\alpha^{\mathrm{mix}}$, $\alpha \in I_l$ depend on $\vec{E}$ and $\vec{G}$ through the combination $\vec{E}-(k/e)\hat{T}^{\mathrm{mix}}\vec{G}$. If functions $\vec{\omega}^{\mathrm{mix}}=\vec{\omega}^{\mathrm{mix}}(\vec{E})$ and $\varepsilon_\alpha^{\mathrm{mix}}=\varepsilon_\alpha^{\mathrm{mix}}(\vec{E})$, $\alpha \in I_l$, satisfy the following system of equations:

$$\vec{\omega}^{\mathrm{mix}}(\vec{E})=\psi_1((\varepsilon_\alpha^{\mathrm{mix}})_{\alpha\in I_l},(\omega^{\mathrm{mix}})^2)\vec{E} \ , \tag{41}$$

$$\varepsilon_\alpha^{\mathrm{mix}}(\vec{E})=\psi_2^\alpha((\varepsilon_\alpha^{\mathrm{mix}})_{\alpha\in I_l},(\omega^{\mathrm{mix}})^2), \quad \alpha\in I_l \ , \tag{42}$$

we can write

$$\langle \vec{v} \rangle^{\mathrm{mix}}=\vec{\omega}^{\mathrm{mix}}\left[\vec{E}-\frac{k}{e}\hat{T}^{\mathrm{mix}}\vec{G}\right] , \tag{43}$$

$$\langle\langle \varepsilon_\alpha \rangle\rangle_\alpha^{\mathrm{mix}}=\varepsilon_\alpha^{\mathrm{mix}}\left[\vec{E}-\frac{k}{e}\hat{T}^{\mathrm{mix}}\vec{G}\right], \quad \alpha\in I_l \ . \tag{44}$$

Functions $\vec{\omega}^{\mathrm{mix}}$ and $\varepsilon_\alpha^{\mathrm{mix}}$, $\alpha\in I_l$, are, respectively, average velocity and energy in spatially uniform conditions and are found from the solution of Eqs. (41) and (42). The reaction rate $\tilde{\nu}^*=\tilde{\nu}^{(A)}-\tilde{\nu}^{(I)}$ is also a function of $\vec{E}-(k/e)\hat{T}^{\mathrm{mix}}\vec{G}$:

$$\tilde{\nu}^*=\alpha^*\left[\vec{E}-\frac{k}{e}\hat{T}^{\mathrm{mix}}\vec{G}\right] . \tag{45}$$

The calculation of transport coefficients of swarm particles in gas mixtures proceeds in a similar manner as in Robson [4]. In the hydrodynamic regime $|\vec{G}|$ is small. We expand functions $\vec{\omega}^{\mathrm{mix}}$ [Eq. (43)] and α^* [Eq. (45)] to first and second order in $\vec{G}$, respectively. Substituting these expansions into the equation of continuity [Eq. (21)] leads after some algebra to the diffusion equation [Eq. (23)], where

$$\vec{W}^{\mathrm{mix}}(\vec{E})=\vec{\omega}^{\mathrm{mix}}(\vec{E})-\frac{k}{e}\hat{T}^{\mathrm{mix}}\frac{\partial\alpha^*(\vec{E})}{\partial\vec{E}} \tag{46}$$

is the drift velocity and

$$D_{ij}^{\mathrm{mix}}=\frac{k}{e}\sum_{k=1}^{3}t_{ik}^{\mathrm{mix}}\left[\frac{\partial}{\partial E_k}W_j^{\mathrm{mix}}+\frac{1}{2}\frac{k}{e}\sum_{l=1}^{3}t_{jl}^{\mathrm{mix}}\frac{\partial}{\partial E_l}\right. \\ \left.\times\left[\frac{\partial\alpha^*}{\partial E_k}\right]\right] , \\ i,j=1,2,3 \tag{47}$$

is the diffusion tensor. Net average reaction rate is evaluated from

$$\alpha^*(\vec{E})=\tilde{\nu}^*[\varepsilon^0(\vec{E})]=\tilde{\nu}^{(A)}[\varepsilon^0(\vec{E})]-\tilde{\nu}^{(I)}[\varepsilon^0(\vec{E})] \ . \tag{48}$$

The temperature tensor $\hat{T}^{\mathrm{mix}}=(t_{ij}^{\mathrm{mix}})_{i,j=1,1}^{3,3}$ must be evaluated from higher-order moment equations. Equation (47) shows that the generalized Einstein relation [4] is satisfied for reacting swarm particles if the reaction rate $\tilde{\nu}^*$ is independent of energy. As the diffusion tensor $\hat{D}^{\mathrm{mix}}$ is symmetric, the coordinate axes can be chosen to lie along its principal axis. Thus diffusion tensor $\hat{D}^{\mathrm{mix}}$ is diagonal, and Eq. (47) reduces to the equation for transverse diffusion coefficient,

$$D_\perp^{\mathrm{mix}}=\frac{kT_\perp^{\mathrm{mix}}}{e}\left[K^{\mathrm{mix}}+\frac{1}{2}\frac{kT_\perp^{\mathrm{mix}}}{e}\frac{1}{E}\frac{d\alpha^*}{dE}\right] , \tag{49}$$

and the equation for longitudinal diffusion coefficients,

$$D_\parallel^{\mathrm{mix}}=\frac{kT_\parallel^{\mathrm{mix}}}{e}\left[K^{\mathrm{mix}}\left[1+\frac{d\ln K^{\mathrm{mix}}}{d\ln E}\right]+\frac{1}{2}\frac{kT_\parallel^{\mathrm{mix}}}{e}\frac{d^2\alpha^*}{dE^2}\right] . \tag{50}$$

In these expressions $T_\perp^{\mathrm{mix}}$ and $T_\parallel^{\mathrm{mix}}$ are transverse and longitudinal components, respectively, of temperature tensor $\hat{T}^{\mathrm{mix}}$. Mobility K^{mix} is defined by $\vec{W}^{\mathrm{mix}}(\vec{E})=K^{\mathrm{mix}}(E)\vec{E}$.

The procedure for finding transport coefficients for reacting swarm particles in gas mixtures is as follows:

(i) Find $1+3$ functions ω_q^{mix}, $q=x,y,z$, $\varepsilon_\alpha^{\mathrm{mix}}$, $\alpha\in I_l$ by solving the system of nonlinear equations [Eqs. (41) and (42)] for the given value of the electric field.

(ii) Find the reaction rate α^* from Eq. (48).

(iii) Find $T_\perp^{\mathrm{mix}}$ and $T_\parallel^{\mathrm{mix}}$ from higher-order moment equations.

(iv) Find W^{mix}, $D_\perp^{\mathrm{mix}}$, and $D_\parallel^{\mathrm{mix}}$ from Eqs. (46), and (49), and (50).

3. *Light, charged swarm particles*

We now consider light, charged ($q=e$) swarm particles so that $m/m_\alpha \ll 1$, $\alpha=1,\ldots,l$. The small mass ratio enables certain simplifying assumptions to be made in the above expressions. It is clear that $M_\alpha\approx 1$, $M_\alpha^0\ll 1$, and $\varepsilon^{\mathrm{mix}}\equiv\varepsilon_\alpha^0\approx(1/2)m\langle v^2\rangle^{\mathrm{mix}}$, $\alpha=1,\ldots,l$. We can also assume that $\langle v^2\rangle \gg (\langle\vec{v}\rangle^{\mathrm{mix}})^2$ (random motion dominates directed motion along the applied electric field if E/n_0 is not too large) and hence

$$\xi^{\mathrm{mix}}\approx\tfrac{2}{3}\tfrac{1}{2}m\langle v^2\rangle^{\mathrm{mix}}\approx\frac{2}{3}\varepsilon^{\mathrm{mix}} \ . \tag{51}$$

Our approximations are the following:

(i)

$$\begin{aligned}&\tilde{\nu}_0^{(m)}(\varepsilon^{\mathrm{mix}})\gg\tilde{\nu}^{(A)}(\varepsilon^{\mathrm{mix}}), \quad \tilde{\nu}_0^{(m)}(\varepsilon^{\mathrm{mix}})\gg\tilde{\nu}^{(I)}(\varepsilon^{\mathrm{mix}}) \ , \\ &\tilde{\nu}_0^{(m)}(\varepsilon^{\mathrm{mix}})\gg\xi^{\mathrm{mix}}\tilde{\nu}_1^{(A)}(\varepsilon^{\mathrm{mix}})\approx\tfrac{2}{3}\varepsilon^{\mathrm{mix}}\tilde{\nu}_1^{(A)}(\varepsilon^{\mathrm{mix}}) \ .\end{aligned} \tag{52}$$

(ii) Distribution of electron velocities is very nearly isotropic for small enough E/n_0.

Hence, $T_\perp^{\mathrm{mix}}\approx T_\parallel^{\mathrm{mix}}\approx(\tfrac{2}{3})k^{-1}\varepsilon^{\mathrm{mix}}$, where $T_\perp^{\mathrm{mix}}$ and $T_\parallel^{\mathrm{mix}}$ denote diagonal components of the temperature tensor.

Using the above assumptions, we can simplify Eqs. (41) and (42),

$$\vec{\omega}^{\mathrm{mix}}(\vec{E})=\psi_1(\varepsilon^{\mathrm{mix}},(\omega^{\mathrm{mix}})^2)\vec{E} \ , \tag{53}$$

$$\varepsilon^{\mathrm{mix}}(\vec{E})=\psi_2(\varepsilon^{\mathrm{mix}},(\omega^{\mathrm{mix}})^2) \ , \tag{54}$$

where

$$\psi_1(\varepsilon^{\mathrm{mix}})=\frac{e}{m\sum_{\alpha\in I_l}\tilde{\nu}_{0\alpha}^{(m)}} \ , \tag{55}$$

$$\psi_2(\varepsilon^{\mathrm{mix}},(\omega^{\mathrm{mix}})^2)=\frac{\frac{1}{2}m(\omega^{\mathrm{mix}})^2 2\sum_{\alpha\in I_l}\tilde{\nu}_{0\alpha}^{(m)}+\frac{3}{2}kT^{\mathrm{mix}}\tilde{\nu}_e^{\mathrm{mix}}-\sum_{\alpha\in I_l}\overline{\Lambda}_\alpha^{\mathrm{mix}}}{\tilde{\nu}_e^{\mathrm{mix}}+\frac{2}{3}\varepsilon^{\mathrm{mix}}\sum_{\alpha\in I_l}\tilde{\nu}_{\alpha 1}^{(A)}+\sum_{\alpha\in I_l}\tilde{\nu}_\alpha^{(I)}}\,, \tag{56}$$

and

$$\tilde{\nu}_e^{\mathrm{mix}}=2\sum_{\alpha\in I_l}M_\alpha M_\alpha^0\tilde{\nu}_{0\alpha}^{(m)}\approx 2\sum_{\alpha\in I_l}\frac{m}{m_\alpha}\tilde{\nu}_{0\alpha}^{(m)}\,. \tag{57}$$

Equations (53) and (54) are to be solved for $\vec{\omega}^{\mathrm{mix}}$ and $\varepsilon^{\mathrm{mix}}$ for a given value of the field $\vec{E}$.

Drift velocity $\vec{W}^{\mathrm{mix}}$ and transverse and longitudinal diffusion coefficients $D_\perp^{\mathrm{mix}}$ and $D_\parallel^{\mathrm{mix}}$, respectively, can be calculated from [see Eqs. (46)–(50)]

$$W^{\mathrm{mix}}=\omega^{\mathrm{mix}}(E)+\Delta W^{\mathrm{mix}}\,, \tag{58}$$

$$D_\perp^{\mathrm{mix}}=\frac{1}{e}\frac{2}{3}\varepsilon^{\mathrm{mix}}\left[K^{\mathrm{mix}}-\frac{1}{2E}\Delta W^{\mathrm{mix}}\right], \tag{59}$$

$$D_\parallel^{\mathrm{mix}}=\frac{1}{e}\frac{2}{3}\varepsilon^{\mathrm{mix}}\left[K^{\mathrm{mix}}\left[1+\frac{d\ln K^{\mathrm{mix}}}{d\ln E}\right]-\frac{1}{2}\varepsilon^{\mathrm{mix}}\frac{d}{dE}\left[\frac{\Delta W^{\mathrm{mix}}}{\varepsilon^{\mathrm{mix}}}\right]\right], \tag{60}$$

where

$$\Delta W^{\mathrm{mix}}=-\frac{1}{e}\frac{2}{3}\varepsilon^{\mathrm{mix}}\frac{d\alpha^*(E)}{dE}\,. \tag{61}$$

III. NDC CRITERION

Several criteria for NDC can be obtained by differentiation of Eq. (54) [7], depending on the chosen simplifying assumptions. In all cases, however, mean energy monotonically increases with the increasing field. A general complete solution can be obtained numerically but not in an elegant analytical form. Thus we choose two cases relevant to our further discussion and examples, one dealing with mixtures of gases that have only elastic processes and the other for a single reactive gas.

A. Gas mixtures: Elastic collisions only

Here we assume no inelastic or reactive (ionization and attachment) collisions. Equations (53) and (54) can thus be simplified:

$$\omega^{\mathrm{mix}}=\frac{eE}{m\sum_{\alpha\in I_l}\tilde{\nu}_{0\alpha}^{(m)}}\,, \tag{62}$$

$$\varepsilon^{\mathrm{mix}}=\frac{1}{2}m(\omega^{\mathrm{mix}})^2\frac{\sum_{\alpha\in I_l}\tilde{\nu}_{0\alpha}^{(m)}}{\sum_{\alpha\in I_l}\frac{m}{m_\alpha}\tilde{\nu}_{0\alpha}^{(m)}}+3kT^{\mathrm{mix}}\,. \tag{63}$$

By differentiation of Eq. (63) with respect to E, we obtain the criterion for NDC under the specified circumstances:

$$1-\left[1-\frac{\frac{3}{2}kT^{\mathrm{mix}}}{\varepsilon^{\mathrm{mix}}}\right]\frac{d\ln}{d\ln\varepsilon^{\mathrm{mix}}}\left[\frac{\sum_{\alpha\in I_l}\tilde{\nu}_{0\alpha}^{(m)}}{\sum_{\alpha\in I_l}\frac{m}{m_\alpha}\tilde{\nu}_{0\alpha}^{(m)}}\right]<0\,. \tag{64}$$

For binary gas mixtures, this criterion [Eq. (64)] becomes

$$1-\frac{1}{2}\left[\frac{eE}{m}\right]^2\frac{m_1}{(\tilde{\nu}_{01}^{(m)}+\tilde{\nu}_{02}^{(m)})^2}\frac{d}{d\varepsilon}\left[\frac{\tilde{\nu}_{01}^{(m)}+\tilde{\nu}_{02}^{(m)}}{\tilde{\nu}_{01}^{(m)}+\frac{m_1}{m_2}\tilde{\nu}_{02}^{(m)}}\right]<0\,. \tag{65}$$

From Eq. (64) one can find the conditions for the left-hand side (lhs) of the equation to be negative. The derivate with respect to the energy has the collision frequencies in the numerator and the mass normalized collision frequencies in the denominator. The different energy dependencies of collision frequencies are required with quite different masses as well, which would reduce or amplify the difference in the denominator. The NDC will not occur for low mean energies close to the thermal equilibrium because of the first bracket in the second term of Eq. (64).

For binary mixtures with $m_1 \ll m_2$ and $\tilde{\nu}_{01}^{(m)}\approx\mathrm{const}$, a rapid increase of $\tilde{\nu}_{02}^{(m)}$ with E will tend to induce a negative slope of W versus E, i.e., an NDC, if n_{01}/n_{02} is sufficiently small. In the case that collisional frequencies for both gases have the same energy dependence, $\tilde{\nu}_{01}^{(m)}\approx\mathrm{const}\times\tilde{\nu}_{02}^{(m)}$, or that $m_1\approx m_2$, the derivate with respect to energy will be zero. In addition the NDC will not occur for a single gas with elastic scattering only because of cancellation of collision frequencies, which are the only source of energy dependence required to make the lhs of Eq. (64) negative. This case is covered by Robson's criterion, but a relatively straightforward extension of Robson's theory with a limited expansion of the physical interpretation is required to explain the NDC in mixtures of rare gases.

B. Single gas: Elastic, inelastic, and reactive collisions

Equations (53) and (54) written for a single pure component are

$$\omega=\frac{eE}{m\tilde{\nu}_0^{(m)}}\,, \tag{66}$$

$$\varepsilon=\frac{(\frac{1}{2}m_0\omega^2+\frac{3}{2}kT)\tilde{\nu}_e-\overline{\Lambda}}{\tilde{\nu}_e+\tilde{\nu}^{(I)}+\frac{2}{3}\varepsilon\tilde{\nu}_1^{(A)}}\,, \tag{67}$$

where $\tilde{\nu}_e$ and $\overline{\Lambda}$ are given by Eqs. (57) and (36). By differentiation of Eq. (67) with respect to E, we obtain the criterion for the negative slope of the average velocity ω versus E/N as

$$\frac{d}{d\varepsilon}\left[\varepsilon\mathfrak{T}_e^{(*)}\right]+\frac{d\overline{\Omega}_e^{(*)}}{d\varepsilon}<0\ , \tag{68}$$

where

$$\mathfrak{T}_e^{(*)}=1+\frac{\tilde{\nu}^{(I)}+\frac{2}{3}\varepsilon\tilde{\nu}_1^{(A)}}{\tilde{\nu}_e} \tag{69}$$

and

$$\overline{\Omega}_e^{(*)}=\frac{\overline{\Lambda}}{\tilde{\nu}_e}\ . \tag{70}$$

In previous calculations we assumed that [see Eq. (52)]

$$|\tilde{\nu}^{(I)}+\tfrac{2}{3}\varepsilon\tilde{\nu}_1^{(A)}|<\tilde{\nu}_e\ . \tag{71}$$

Finally, from Eqs. (58) and (61) we see that the criterion for NDC, i.e., for dW/dE, is

$$\frac{dW}{dE}=\frac{d\omega}{dE}-\frac{1}{e}\frac{2}{3}\left[\frac{d\varepsilon}{dE}\frac{d\alpha}{dE}+\varepsilon\frac{d^2\alpha}{dE^2}\right]<0\ . \tag{72}$$

In Eq. (68), we would designate $\varepsilon\mathfrak{T}_e^{(*)}$ as the "reactive term" and $\overline{\Omega}_e^{(*)}$ as the "inelastic term." The derivate of the "reactive term" is equal to 1 in the absence of nonconservative collisions. The "inelastic term" appears to be identical to that of Robson [7] in his Eq. (19). There is nevertheless a difference in the presence of the additional ionization term in $\overline{\Omega}_e^{(*)}$ and a different meaning of collisional frequencies calculated from the MTT that includes a more complete energy and momentum balance. If, however, one uses separately calculated or measured collision rates, Eq. (68) with its "reactive term" set to 1, the criterion is identical to that of Robson both in form and in final results. The "inelastic term" in Eq. (68) does not contain attachment. The "reactive term" contains attachment as the first derivate of the collisional frequency, so ionization and attachment are not equivalent in inducing NDC [see Eq. (19)].

The most important difference between the NDC criterion of Robson and the one presented here for reactive gases is in the presence of the first term on the l.h.s. of Eq. (68). The first term of Eq. (68) can be written as

$$\frac{d}{d\varepsilon}(\varepsilon\mathfrak{T}_e^{(*)})=1+\frac{\tilde{\nu}^{(I)}+\frac{2}{3}\varepsilon\tilde{\nu}_1^{(A)}}{\tilde{\nu}_e}+\varepsilon\frac{d}{d\varepsilon}\left[\frac{\tilde{\nu}^{(I)}+\frac{2}{3}\varepsilon\tilde{\nu}_1^{(A)}}{\tilde{\nu}_e}\right]\ . \tag{73}$$

A sufficient condition for decreasing the "reactive term" with E/n_0 is a decrease of ionization and decrease of the slope of attachment collisional frequency with mean energy. Decreasing ionization frequency is not likely to occur for the relevant mean energies, so the issue of the shape of the ionization cross section is purely academic. However, the attachment rate may have the appropriate shape that would induce the negative slope of average velocity ω versus E/N. Observation of such an effect may not be easy because of a larger effect of attachment on the number density in swarm experiments, but this effect is in principle possible. The NDC effect may also affect measurement of attachment rates in mixtures of attaching and nonattaching gases when the assumption that the drift velocity is not affected by the momentum transfer of the attaching gas is made [16–18,24,25].

If we assume no ionization and inelastic collisions, the criterion for $d\omega/dE<0$ becomes $d(\varepsilon\mathfrak{T}_e^{(*)})/d\varepsilon<0$, i.e.,

$$1+\frac{\frac{2}{3}\varepsilon\tilde{\nu}_1^{(A)}}{\tilde{\nu}_e}+\varepsilon\frac{d}{d\varepsilon}\left[\frac{\frac{2}{3}\varepsilon\tilde{\nu}_1^{(A)}}{\tilde{\nu}_e}\right]<0\ . \tag{74}$$

We can see that NDC can also occur in the absence of inelastic collisions. It is clear that if the reaction $\tilde{\nu}^{(A)}$ is independent of energy, then $\tilde{\nu}_1^{(A)}$ is equal to zero in Eq. (74) and attachment has no influence on the NDC.

The criterion has been developed for the average velocity in Eq. (68). When reactive collisions are present and their rate is dependent on the energy (i.e., $d\alpha/dE\neq 0$), the actual drift velocity W is not equal to the average velocity ω. In this case, the decrease of the ionization collision frequency will again favor the NDC, amplified by the usually rapidly increasing mean energy as a function of E/N. As for the attachment, the opposite is true. However, in this case the overall criterion [Eq. (72)] also has a term dependent on the second derivate of the effective average loss rate α. The occurrence of NDC will be decided between the effect of the average velocity and the effect related to the first and the second derivate of the net average reaction rate. The NDC due to these effects, even due to ionization only, may become realizable in practical situations.

One should bear in mind that the definition of the collisional frequencies for the inelastic processes in Eq. (36) also includes the superelastic collisions. The superelastic processes will reduce the likelihood of NDC when they significantly affect the energy balance, but depending on the shape they will be able to contribute positively also toward NDC under appropriate circumstances, depending on the shape of the cross sections. The influence of superelastic processes on the NDC has been discussed as a part of a wider range of effects of excited states on electron transport in a separate paper [13] (see also PCH).

IV. MODEL CALCULATION AND DISCUSSION

A. On the NDC in mixtures of atomic gases

As mentioned in the Introduction the calculations of Shizgal [8] have yielded the NDC effect in the mixtures of atomic gases, which under the conditions of calculation have only elastic processes that affect the electron transport. In the paper by PCH, a simple criterion has been developed for gases that have inelastic processes, and thereby the energy loss in the elastic collisions has been neglected. This term has been originally included [12], and a more general but complex formula for the NDC criterion has been derived [7,12] but has been applied to single gas situations only. When such a theory is applied to situations described by Shizgal, NDC is predicted in good agreement with calculations [8].

In this paper, however, we develop a similar criterion on the basis of a more complete MTT developed quite generally for the mixtures of gases. A simple physical explanation can be developed on the basis of both approaches. Helium, which is the gas with a lower abundance in the mixtures with krypton or xenon, controls the mean energy by elastic collisions, as mentioned by Shizgal. Thus the electron to helium mass ratio, which is much more favorable for the energy transfer than that of heavier gases, acts in such a way that the elastic collisions with helium play the role of inelastic collisions in the theory of PCH and Robson. This fact has been considered independently of our work [20] by Garscadden and co-workers [26], who have taken advantage of this effect to measure drift velocities in helium—heavier rare gas mixtures—and thus obtain data for determination of the accurate cross sections for heavier gases based on the accurate cross sections for helium. In these mixtures, helium effectively replaces hydrogen or nitrogen, often used to moderate electrons.

We have made a number of model calculations for the pairs of gases chosen by Shizgal [8] in order to verify the simple explanation given above and to test the MTT theory and the corresponding criterion given in the present paper. Calculations have been performed with a standard two-term-theory-based numerical solution [12,27,28] and with the cross sections for rare gases from the recommendations of the JILA Data Center [29].

In addition to the Boltzmann equation (BE) solutions described in the previous paragraph, we have performed a numerical solution to the MTT equations [Eqs. (53) and (54)] and also of the l.h.s. of the NDC criterion. While developed on the basis of the same theory, thus having the same built-in assumptions and approximations, the criterion and the solution based on MTT equations should be viewed as separate entities that can be used to check each other. The criterion is an analytical tool for understanding the physics behind the NDC. In principle, experimental data or BE-solution-based rate coefficients, which are more accurate than the MTT-based coefficients, can be used as an input into the criterion. In principle it is best to compare the applicability of the criterion against a single complete set of results, drift velocities and the rate coefficients coming from the same source.

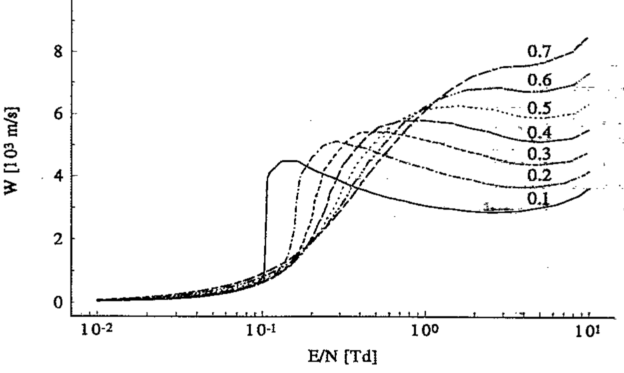

FIG. 1. Drift velocities in He-Xe mixture for the abundance of He equal to 10–70 %.

In Fig. 1 we show the drift velocities, calculated by using MTT, for different abundances of He in He-Xe mixtures. The NDC is observed for a wide range of abundances of He less than 60%, similar to the results of Shizgal.

The importance of the mass of helium being different from that of the other atomic gas in the mixture is shown in Fig. 2(a), where we vary the mass of the lighter atom, and in Fig. 2(b), where we vary the mass of the heavier atom. In both cases, the effect of NDC disappears when masses of the two atoms move closer together. The observation is in agreement with both the analytical form of the NDC criterion and the general qualitative explanation offered in this paper.

Finally, we vary the cross section (Fig. 3). Atoms can have either their original cross sections or that of the other atom. When both atoms have the cross sections of helium, the effect of Xe on overall transport becomes very small because of its larger mass and small energy exchange. Thus one essentially obtains behavior characteristic of pure helium, the gradually increasing drift velocity. When both gases have the cross section of the xenon, there is a strong effect of helium's energy exchange in the region of the Ramsauer-Townsend minimum, whereby the drift velocity increases very rapidly and then levels off without the NDC. This is, of course, in agree-

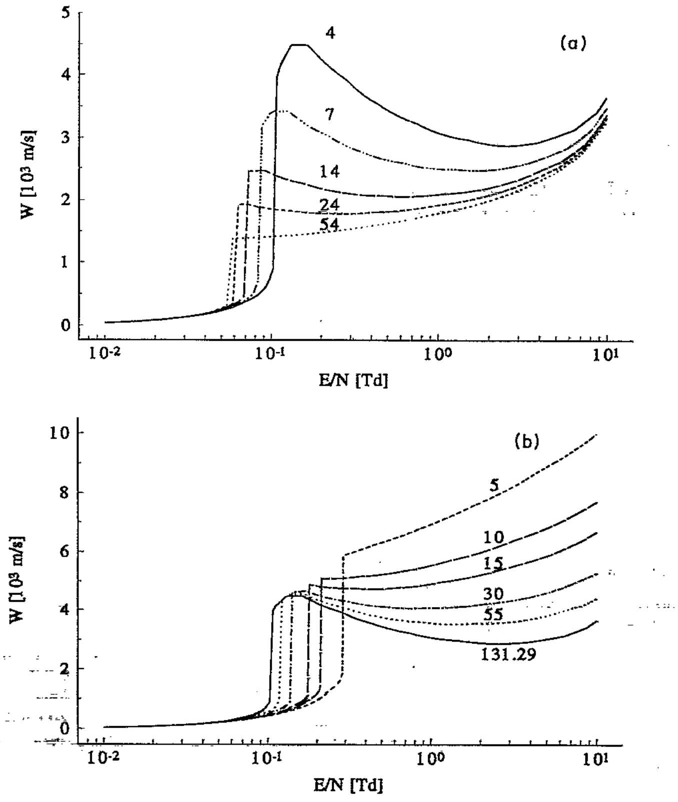

FIG. 2. (a) Drift velocities for the He-Xe mixture (abundance of He equal to 10%) with variation of the mass of the lighter gas: $m_{\mathrm{He}}=4$, 7, 14, 24, and 54 amu. (b) Drift velocities for the He-Xe mixture (abundance of He equal to 10%) with variation of the mass of the heavier gas: $m_{\mathrm{Xe}}=131.29$, 55, 30, 15, 10, and 5 amu.

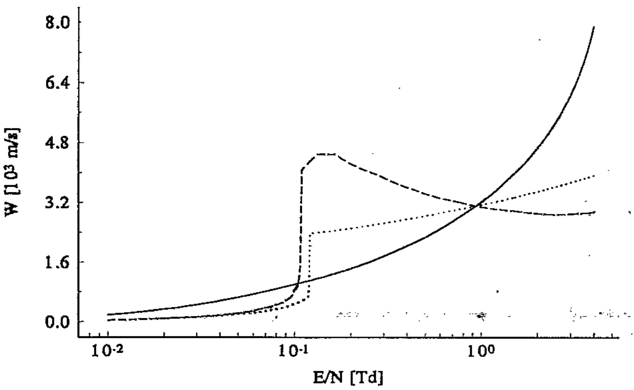

FIG. 3. Drift velocities for different cross sections assigned to constituents; solid line: σ(He), σ(Xe)=σ(He); dotted line: σ(He)=σ(Xe), σ(Xe); dashed line: σ(He), σ(Xe).

ment with the predictions of the criterion [Eq. (65)], whereby the two collisional frequencies cancel each other, and even through the drift velocity suddenly increases no NDC will occur.

When the NDC criterion of the Eq. (65) is calculated, there is an excellent agreement between the NDC range obtained in numerical calculations of drift velocities and region when the NDC condition becomes negative. For example, we found from solution of Boltzmann's equation, using the ELENDIF code [29], that the NDC effect in He-Xe mixture (0.1% He) occurs for E/n_0 in the range $\approx 0.17-2.4$ Td. The NDC interval obtained using the criterion [Eq. (65)] is $\approx 0.15-0.25$ Td. The agreement ($\approx 5\%$) exceeds the accuracy of obtaining the drift velocities by MTT ($\approx 10-20\,\%$), which indicates that the criterion is more general than the application of MTT itself in obtaining the transport data. An even better agreement is obtained if the Boltzmann equation collision frequencies are applied in the criterion.

Similar behavior of the calculated data has been observed for He-Kr mixtures, and no effect has been observed for other studied combinations of rare gas atoms. As we have not used identical sets of cross sections and as there is an additional inaccuracy induced by the application of the MTT, the results presented here are not in agreement in all details with those of Shizgal [8] concerning the magnitude of the drift velocities and the NDC range. However, a good qualitative agreement exists. An even better agreement exists for the drift velocities when a two-term Boltzmann equation is used to calculate collision frequencies. It should also be noted that when the Boltzmann code used by PCH is applied, the same NDC effect in the similar mixtures is observed. Thus it appears unlikely that the explanation offered by Shizgal, that PCH failed to predict the NDC because they used a basis but incomplete two-term formula for the drift velocity, is correct. In fact the "Condition 1" of PCH was based on the criterion developed by Robson, and both criteria did not depend on the form of the formula used to calculate the drift velocity from the energy distribution function. In this paper we have shown that the theory of Robson as applied to gas mixtures, and the simple theory of PCH if extended to include energy exchange in elastic collisions [12], would both predict the effects observed by Shizgal.

The NDC criterion developed by Shizgal did not give quantitative agreement with the calculations by the same author [8]. The criterion indicated the importance of different masses on the slope of the cross section but not as directly as our formula [Eq. (65)]. The presently derived theory produces a criterion together with a simple physical explanation and with direct numerical applicability leading to good quantitative comparisons.

B. NDC induced by reactive collisions

In this section we discuss the possibility that the NDC may be induced by the reactive collisions by showing examples based on model cross sections. It is clear that the best choice of the examples are those starting from the cross sections that satisfy the basic NDC conditions of PCH, yet in such a degree that the plateau in drift velocity dependence on E/N is produced, not the negative slope. Under such conditions, however, including attachment or changing the character of one of the inelastic processes into nonconservative ionizing collisions leading to production of new electrons may induce the NDC.

As the initial set of cross sections we choose one of the models of PCH, which is on the verge of allowing NDC and is shown in Fig. 4. We incorporate a "smoothing factor" [7,30] in the expression for average collision frequency if the cross section varies rapidly near its threshold. First, we study the effect of ionization. In Fig. 5(a) we show the calculated drift velocities for the model gas when both inelastic processes are conservative. Under those circumstances the average velocity ω is equal to the drift velocity W [see Eqs. (58) and (61)]. When, however, one of the processes is allowed to produce new electrons, then both the average velocity of the swarm and the effective drift velocity W show NDC, though at quite different values of E/N [Fig. 5(a)]. The effect for ω is more interesting as its mechanism is similar to that of the conservative case; i.e., the NDC is not induced because of

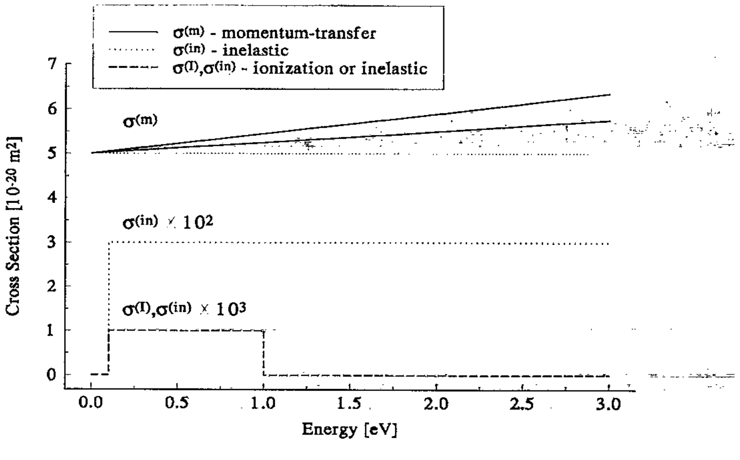

FIG. 4. Model cross sections with ionization.

the effects of transition from the average velocity to the drift velocity. The condition for NDC developed with the MTT and given in Eq. (68) describes the effect on ω, and in Fig. 5(b) we show the calculation of the criterion in Eq. (68) for nonconservative and for conservative cases. In the latter there is no NDC, while in the former the NDC occurs between 1.8 and 4.6 Td, in excellent agreement with the MTT calculations of the drift velocity. The extension of the criterion to the calculation of W is straightforward, and the effect described in the criterion [Eq. (72)] is bigger but more directly predictable from the knowledge of the shape of the cross sections.

In a similar model (the slope of the momentum transfer cross section has the value 0.45) we further show the influence of the magnitude of the cross section by varying the cross section for the nonconservative process [Fig. 6(a)]. When its magnitude is decreased tenfold, there is a minute effect on the drift velocity and the introduction of the nonconservative character of the process does not affect the drift velocity [see Figs. 5(a) and 6(a)]. When, however, the magnitude is increased ten times, even in the conservative case the NDC is induced, which can be expected, but the effect is considerably higher in the nonconservative case [Fig. 6(b)]. When the NDC criterion [Eq. (68)] is applied to all these cases, the agreement among the calculated NDC region, the degree of NDC, and the predictions of the condition in Eq. 68 is excellant, much better than the accuracy of drift velocities calculated by MTT. The NDC induced in the drift velocity [Fig. 6(c)] is larger still, and the NDC range and magnitude are in accordance with those calculated from the criterion in Eq. (72).

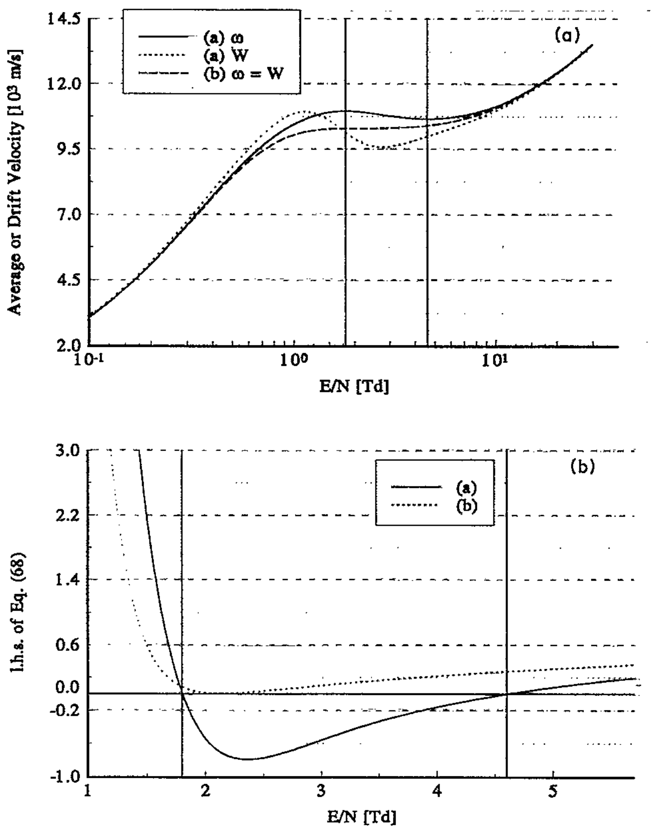

FIG. 5. (a) Calculated average and drift velocities: (a) ionization is present; (b) two inelastic processes. (b) The criterion for NDC [see Eq. (68)]. The region between vertical lines corresponds to the negative slope of average velocity versus E/N, where the inequality (68) holds: (*a*) ionization is present; (*b*) two inelastic processes.

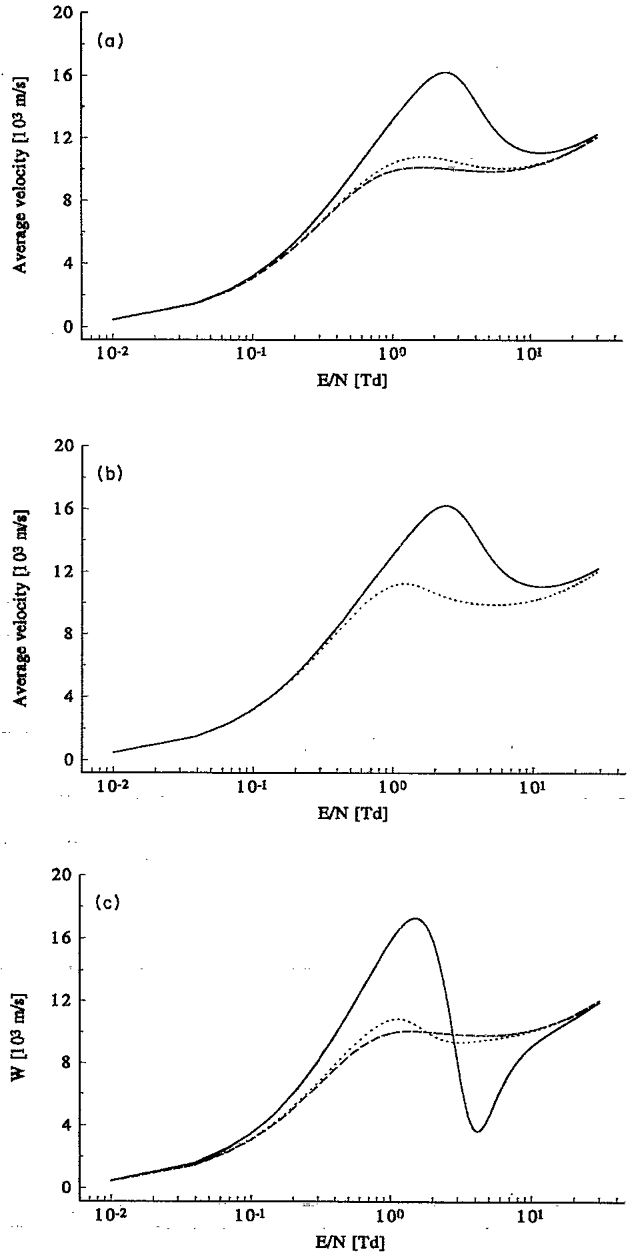

FIG. 6. (a) Average velocities with variation of the magnitude of ionization cross section: solid curve, $\sigma^{(I)}=0.01$ Å^2; dotted curve, $\sigma^{(I)}=0.001$ Å^2; dashed curve, $\sigma^{(I)}=0.0001$ Å^2. (b) The influence of ionization collisions on the average velocity: solid curve, ionization is present, $\sigma^{(I)}=0.01$ Å^2; dotted curve, two inelastic processes, $\sigma^{(\mathrm{in})}=0.01$ Å^2. (c) Drift velocities with variation of the magnitude of ionization cross section: solid curve, $\sigma^{(I)}=0.01$ Å^2; dotted curve, $\sigma^{(I)}=0.001$ Å^2; dashed curve, $\sigma^{(I)}=0.0001$ Å^2.

The same model (Fig. 4) is taken as the basis for the study of the influence of attachment except that this time we have only one inelastic process. The model does not predict the NDC, though it is on the verge, and we introduce the attachment cross section identical in shape to the second cross section of the ionization model but with different cross section amplitudes. The results of calculations based on the MTT equations and on the MTT criterion are shown in Figs. 7(a) and 7(b). We must stress that the influence of the attachment is not merely affecting the number density and thus the overall mobility, which will occur separately. The influence also affects the average and the drift velocities, and the effect is significant. Again, in this range of examples, the NDC prediction of the criterion agrees extremely well with the calculated drift velocities [Fig. 7(c)].

When the attachment cross section is extended between the threshold at 0.1 eV to the higher energies, the

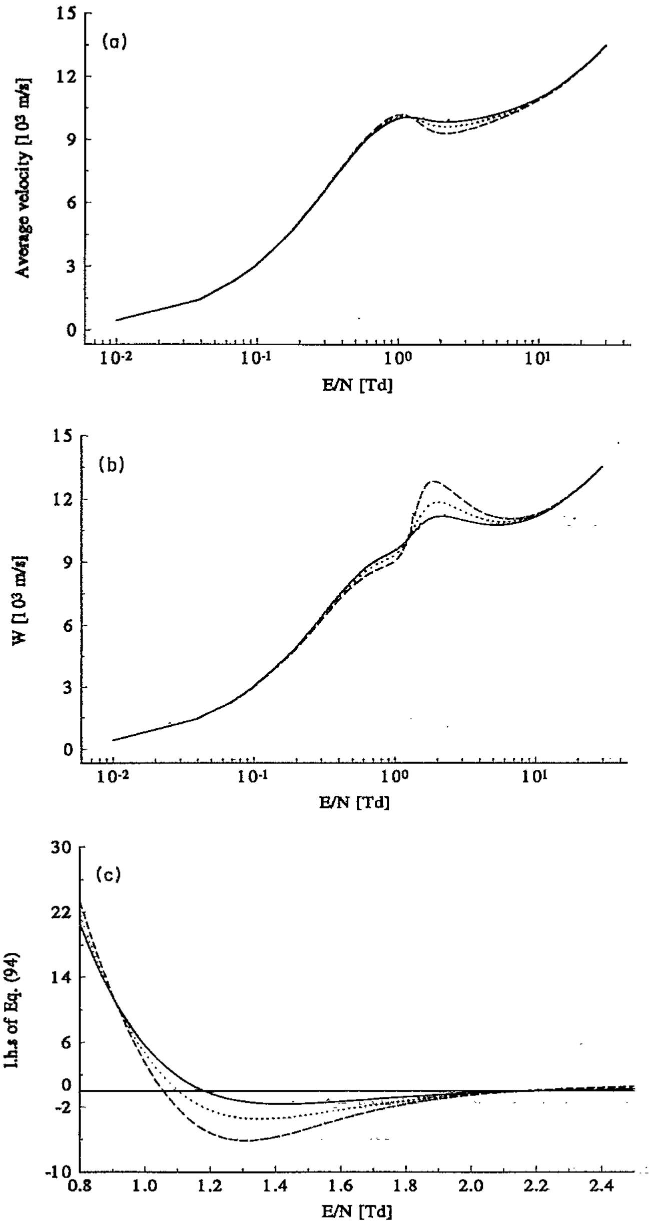

FIG. 7. (a) Average velocities with variation of the magnitude of attachment cross section: solid curve, $\sigma^{(A)}=0.001$ Å^2; dotted curve, $\sigma^{(A)}=0.0016$ Å^2; dashed curve, $\sigma^{(A)}=0.0024$ Å^2. (b) Drift velocities with variation of the magnitude of attachment cross section: solid curve, $\sigma^{(A)}=0.001$ Å^2; dotted curve, $\sigma^{(A)}=0.0016$ Å^2; dashed curve, $\sigma^{(A)}=0.0024$ Å^2. (c) Criterion for negative slope of average velocity including the influence of magnitude of attachment cross section: solid curve, $\sigma^{(A)}=0.001$ Å^2; dotted curve, $\sigma^{(A)}=0.0016$ Å^2; dashed curve $\sigma^{(A)}=0.0024$ Å^2.

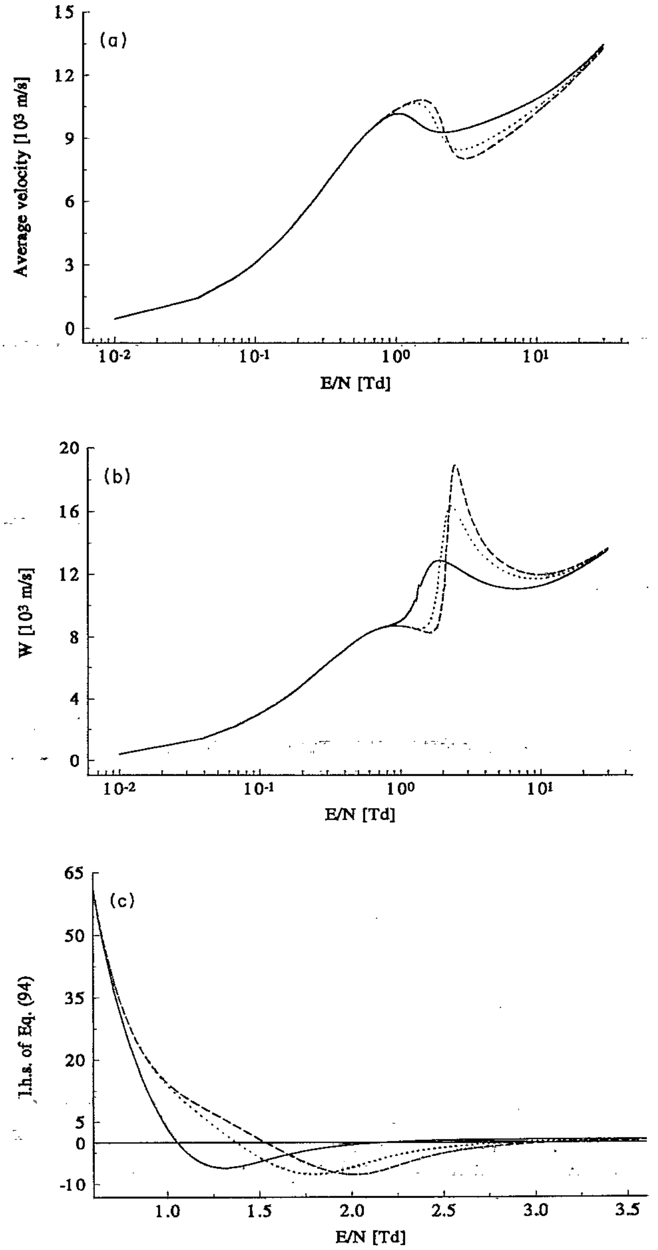

FIG. 8. (a) Average velocities where the attachment cross sections ($\sigma^{(A)}=0.0024$ Å^2) cutoffs have these values: solid curve, 1 eV; dotted curve, 2 eV; dashed curve, 2.5 eV. (b) Drift velocities where the attachment cross section ($\sigma^{(A)}=0.0024$ Å^2) cutoffs have these values: solid curve, 1 eV; dotted curve, 2 eV; dashed curve, 2.5 eV. (c) Criterion for negative slope of average velocity where the attachment cross section ($\sigma^{(A)}=0.0024$ Å^2) cutoffs have these values: solid curve, 1 eV; dotted curve, 2 eV; dashed curve, 2.5 eV.

effect of attachment on average and drift velocity increases significantly [Figs. 8(a) and (b)]. The shape of the average velocity under those circumstances is shown in Fig. 8(a). The predictions of the criterion [Eq. (68)] agree very well Fig. 8(c) with the calculated average velocity. The effect of attachment is sufficiently large to produce a local minimum even in the drift velocity dependence on the E/N with a second NDC due to the additional terms in the criterion for drift velocity [Eq. (72)].

V. CONCLUSION

In this paper we have developed MTT for electron transport in mixtures of reactive gases. The previous work of Robson [4] has been limited to the transport in a single reactive gas, and some extensions to mixtures are not trivial. The theory takes a more complete inclusion of momentum transfer in inelastic collisions as well. Equations have been developed that upon solution yield MTT values of drift velocity and mean energy, which can be further used to obtain rate coefficients and diffusion coefficients or characteristic energies. Finally, on the basis of the developed equations, we have derived the criteria for the NDC in two cases, but further derivations are possible depending on specific simplifying assumptions.

In the case of gas mixtures the criterion does not include the reactive collisions, as it has been derived for the specific case of inelastic processes only. However, an extension to include the inelastic processes is relatively simple. The criterion predicts the occurrence of NDC in mixtures of gases even when only elastic processes occur. In this case NDC is the result of the fact that light atomic gas controls the energy. The elastic collisions of light atoms act as a substitute for inelastic process in Robson's theory. With this provision, the basic conclusions of the criterion are the same as those of PCH and Robson. The mixture situation adds to the requirements that the masses and the cross sections of the atoms controlling the momentum transfer and energy transfer be considerably different; the preference for the former is that they have increasing cross section, with the energy in the relevant E/N range. The criterion that was developed here agrees well with the calculations of Shizgal and shows that the simple physical explanation developed by PCH and Robson, with the extension to mixtures of atomic gases, is correct.

However, the criteria developed by PCH and Robson do not predict the NDC induced by reactive collisions, and we show this process in the case of a single reactive gas. Development of a general criterium for arbitrary mixtures in a simple analytical form appears to be impossible, but the basis for numerical predictions in a form simpler than calculating the drift velocities as a function of E/N exists.

The influence of reactive collisions (in the case of electrons), of the ionization, and of the attachment is twofold: on the mean energy and on the effective drift velocity. There is a definite influence on the mean electron energy, which can be described by a simple NDC criterion. It is a generalized form of the criterion of Robson and reduces to it under the identical conditions. Thus all the conclusions of PCH and Robson are included in that criterion. The reactive extension is given by the term shown in Eq. (68), which in case of Robson's theory is equal to 1.

The drift velocity, however, under the influence of reactive collisions, is different from the average electron velocity [4]. The simple form of the drift velocity W is given by Eq. (58). Thus the criterion for the NDC for W will have an extension to that for the average velocity because of E/N dependence of the ionization and attachment rates. The effect of those two is larger in general than that for the average velocity, yet under some conditions the NDC in the average velocity may be directly visible in the drift velocity versus E/N dependence, as has been shown. The conditions under which ionization affects the average velocity to produce the NDC may appear to be unphysical since ionization cross sections usually do not decrease rapidly or decrease for sufficiently high energies so that the redistribution of energy in elastic collisions may be the dominant energy loss process. Yet under those conditions the elastic scattering cross section may become quite small, and further study is needed to check how drift velocities behave at very high E/N if such knowledge is required. Under those conditions it is more likely that nonequilibrium transport will develop with its own, quite different physical basis [31,32]. In any case NDC induced by nonconservative nature of ionization in drift velocity is possible in realistic situations, even when such an effect in the average velocity is not likely.

The question of the influence of the attachment is, however, less academic; it is directly relevant to such studies in which very strong NDC has been observed in otherwise very difficult experiments wherein attachment reduces the number of electrons significantly and makes it difficult to determine the drift velocity [25,33]. A relatively large effect of attachment on inducing the NDC has been noticed and described for the model cross sections, which are not too different from the realistic cross sections.

The measurements of drift velocity at moderate and high values of E/N, where reactive effects may be expected to be important, are scarce. This is due to difficulties in determining the transient time of electrons with high mean energies and in achieving a system without significant influence of the boundaries over a large volume. The data are, however, needed in many aspects of discharge modeling and used on the basis of calculations that usually do not take reactive collisions into account. With a large number of devices whose mere application depends on a good knowledge of the drift velocity or even on the occurrence of NDC, it appears justified, beyond the academic interest, to invest further effort into understanding the transport of electrons (and other types of swarms) under high driving field conditions in the presence of reactive collisions.

Finally, having failed once before to make a complete set of requirements for the NDC, we only state that a more complete set of requirements for the NDC has been described, which in conjunction with the work of PCH and Robson describes all the known cases of NDC, and the criteria as analytical forms that give a better physical insight can be used quite generally outside the realms of the MTT. The quantitative agreement of the NDC ranges and relative importance of the effect obtained from the criteria are excellent in all cases. It is, however, still possible that a new mechanism driving the NDC may exist. The present theory, while describing all the known cases of NDC, may not be able to describe the NDC that may arise in circumstances in which a complex structure of the electron energy distribution functions (EEDF) develops and changes in such way as to promote NDC (as has been suggested by Garscadden and Nagpal [26]). However, we are yet to find a good example that would not meet the description based on the MTT. In addition, none of the conditions that favor NDC as listed by PCH and discussed by Robson and the present paper should be taken as necessary. Those are just separate driving mechanisms that favor the NDC, and whether it will occur or not depends on the absolute magnitudes of those mechanisms and of the mechanisms working against the NDC. The presently developed criteria, as well as those of Robson, give a more direct description of the balance of the mechanisms and give good quantitative predictions and physical insight into the effect of NDC.

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