

# Application of Blanc's law at arbitrary electric field to gas density ratios

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**Abstract.** Application of Blanc's law for drift velocities of electrons and ions in gas mixtures at arbitrary reduced electric field strengths  $E/n_0$  was studied theoretically and by numerical examples. Corrections for Blanc's law that include effects of inelastic collisions were derived. In addition we have derived the common mean energy procedure that was proposed by Chiflikyan in a general case both for ions and electrons. Both corrected common  $E/n_0$  and common mean energy procedures provide excellent results even for electrons at moderate  $E/n_0$  where application of Blanc's law was regarded as impossible. In mixtures of two gases that have negative differential conductivity (NDC) even when neither of the two pure gases show NDC the Blanc's law procedure was able to give excellent predictions.

**PACS.** 51.10.+y Kinetic and transport theory of gases – 51.50.+v Electrical properties (ionization, breakdown, electron and ion mobility, etc.)

## 1 Introduction

Blanc's law has been developed many years ago [1] as a means to combine drift velocities or mobilities of charged particles in two gases in order to provide data for mixtures for which data were not available. In principle it is also possible to apply the law to use initial data for mixtures in order to obtain data for other mixtures or even pure gases [2]. The basic form of the Blanc's law is [1]:

$$\frac{1}{W_{\text{mix}}} = \sum_{\alpha} x_{\alpha} \frac{1}{W_{\alpha}}, \quad (1.1)$$

where  $W^{\text{mix}}$  is the drift velocity in gas mixture,  $x_{\alpha}$  the concentration of the  $\alpha$ th gas in which the drift velocity is  $W_{\alpha}$ .

However, following the development of accurate experimental techniques [3] it became obvious that, for electrons, Blanc's law is simply not useful at all. Its application for ions was, however, still pursued. The reason was that mean energies of electrons increase very quickly with the fields normalized to the gas number density ( $E/n_0$ ), while ions remain close to thermal conditions for a broad range of  $E/n_0$ . The increase occurs at quite different  $E/n_0$  for different gases, especially for mean energies between thermal and few eV. The transport properties of electrons are very strongly affected by inelastic collisions due to inefficiency of elastic collisions in energy transfer caused

by a very small electron to background gas atom mass ratio. On the other hand for ions the energy balance is determined by elastic collisions, which have efficient energy transfer in a broad  $E/n_0$  range. In other words for electrons it is likely that the distribution functions at the same  $E/n_0$  in two gases are quite different and the distribution function for the mixture is different from both. In that case application of Blanc's law is not possible. In case of ions the mean energies remain low for a broad range of reduced electric fields and therefore distribution functions are similar. However, rule of thumb was that in both cases the law is applicable close to the zero field, or to be more precise when mean energy is close to thermal.

Equation (1.1) has been tested for ions experimentally [4,5] for situation when it is not exactly applicable i.e. for  $E/n_0$  not very close to zero. Since it is practically impossible to achieve the conditions for which Blanc's law is exactly satisfied strategy was to develop a correction factor  $\delta_B$  that could give more reliable results while preserving a simple form of the law itself:

$$\frac{1}{W_{\text{mix}}} = \sum_{\alpha} x_{\alpha} \frac{1}{W_{\alpha}} + \delta_B. \quad (1.2)$$

A number of attempts to predict theoretically the deviation  $\delta_B$  at higher  $E/n_0$  values were published for ions. Mason and Hahn [6] derived an equation to calculate mobilities in gas mixtures at arbitrary reduced field strengths. There was an error in the expression for the energy partitioning. Correcting the error, Whealton et al. [7]

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obtained an equation which is successful in explaining *qualitatively* the deviations  $\delta_B$  for  $K^+$  ions [5] in mixtures of He + Ne, Ne + Ar and  $H_2 + N_2$ . This theoretical treatment applies only to situations when all the collisions between ions and gas atoms are *elastic* and the collision frequencies are slowly varying functions of  $E/n_0$ . The quantitative agreement between the equations and the experimental values was however still not satisfactory.

The situation for applying Blanc's law for electrons was regarded as hopeless for non-thermal electrons. Even for thermal electrons it was shown [2,8] that a combination of Blanc's law and Nernst-Townsend-Einstein relation needs correction if data for diffusion coefficients are to be determined [2,8]. The main reason for failure in case of non-thermal electrons was the fact that electron energy distribution functions and mean energies for pure gases and for the mixtures could be very different. However, it was suggested [2,8] that for high values of  $E/n_0$  the distribution functions may become similar and Blanc's law would work well. Under those conditions a number of inelastic processes occur, but at some energy ionization becomes dominant. Thus the overall energy controlling processes have similar energy dependences.

A strategy to use Blanc's law for electrons for moderate  $E/n_0$  with a greater accuracy was proposed by Chiflikyan [9] (which will be described in greater detail below). Basically, the idea is to use the data at the same mean energy rather than the data at the same  $E/n_0$ . Thus we shall label the standard form of Blanc's law as Common  $E/n_0$  (CEON) and Chiflikyan's approach as Common Mean Energy (CME).

At the same time Blanc's law, even in its uncorrected form, is often used in plasma modeling due to the lack of data for electron transport. In addition, one may be able to obtain data for some reactive gases or radicals only in mixtures and extrapolating such data to pure gas or to be able to derive cross-sections may employ some form of Blanc's law procedure. Thus it is of immediate importance to establish a method to obtain the data for mixtures of interest in plasma applications.

In this paper we analyze the application of Blanc's law in situations when *inelastic* collisions are present, i.e. for arbitrary  $E/n_0$  for both electrons and ions, but because electrons are a more difficult candidate for its application all examples will be for electron drift velocities. A momentum-transfer theory [10,11] is used to obtain an expression for the deviation  $\delta_B$  that is applicable in broader  $E/n_0$  range. In addition, we will derive the basic equations of the CME procedure, due to Chiflikyan, in quite a general case.

## 2 Theory

### 2.1 Common $E/n_0$ procedure

First, we shall develop the theory for the correction of the standard (CEON) procedure to employ Blanc's law. The idea is to include the effects of inelastic collisions into the correction to Blanc's law.

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  $\vec{E}$ . Let  $n(\vec{r}, t)$  be the number density of swarm particles. Suppose that there are several ( $l$ ) different species of neutral gases present with number densities  $n_\alpha$ . Let  $m_\alpha$  and  $\vec{v}_\alpha$  be mass and velocity of molecules of the  $\alpha$ th neutral gas, respectively. We introduce the standard notation [11]:  $n_0 = \sum_\alpha n_\alpha$  (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 of a colliding swarm-neutral pair), and  $\varepsilon_\alpha = \mu_\alpha v_{r\alpha}^2/2$  (kinetic energy measured in the center-of-mass reference frame).

Let  $f^{\text{mix}}(\vec{r}, \vec{v}, t)$  and  $f_\alpha^{\text{mix}}(v_\alpha)$  be the swarm and  $\alpha$ th neutral gas one-particle velocity distribution function in the multicomponent mixture, respectively. If only one of the neutral species (say  $\alpha$ ) is present,  $f^\alpha(\vec{r}, \vec{v}, t)$  and  $f_\alpha(v_\alpha)$  denote the corresponding velocity distribution functions. We assume that each neutral gas in the multicomponent mixture has Maxwellian distribution with the same nonzero temperature  $T_\alpha^{\text{mix}} = T^{\text{mix}}$ ,  $\alpha \in I_l$ . With  $T^\alpha$  we denote the temperature of one-component mixture (pure  $\alpha$ th gas) and assume that  $T^{\text{mix}} = T^\alpha$ .

Averaging operators used in the development of equations are defined as:

$$\langle \Phi(\vec{v}, \vec{v}_\alpha) \rangle^{\text{mix}} = \frac{1}{n(\vec{r}, t)} \int d^3\vec{v} f^{\text{mix}}(\vec{r}, \vec{v}, t) \Phi(\vec{v}, \vec{v}_\alpha), \quad (2.1)$$

$$\begin{aligned} \langle\langle \Phi(\vec{v}, \vec{v}_\alpha) \rangle\rangle_\alpha^{\text{mix}} &= \frac{1}{n(\vec{r}, t)n_\alpha} \iint d^3\vec{v} d^3\vec{v}_\alpha f^{\text{mix}}(\vec{r}, \vec{v}, t) \\ &\times f_\alpha^{\text{mix}}(v_\alpha) \Phi(\vec{v}, \vec{v}_\alpha), \end{aligned} \quad (2.2)$$

$$\langle \Phi(\vec{v}, \vec{v}_\alpha) \rangle^\alpha = \frac{1}{n(\vec{r}, t)} \int d^3\vec{v} f^\alpha(\vec{r}, \vec{v}, t) \Phi(\vec{v}, \vec{v}_\alpha), \quad (2.3)$$

$$\begin{aligned} \langle\langle \Phi(\vec{v}, \vec{v}_\alpha) \rangle\rangle_\alpha &= \frac{1}{n(\vec{r}, t)n_0} \iint d^3\vec{v} d^3\vec{v}_\alpha \\ &\times f^\alpha(\vec{r}, \vec{v}, t) f_\alpha(v_\alpha) \Phi(\vec{v}, \vec{v}_\alpha), \end{aligned} \quad (2.4)$$

where  $\Phi(\vec{v}, \vec{v}_\alpha)$  is any function of  $\vec{v}$  and  $\vec{v}_\alpha$ . For the sake of brevity, we write  $\varepsilon_\alpha^0 = \langle\langle \varepsilon_\alpha \rangle\rangle_\alpha^{\text{mix}}$  and  $\varepsilon'_\alpha = \langle\langle \varepsilon_\alpha \rangle\rangle_\alpha$ .

At this point we should discuss the definition of the mean energies  $\varepsilon_\alpha^0$  and  $\varepsilon'_\alpha$ . With  $\varepsilon_\alpha$  we denote the mean kinetic energy of the swarm-neutral pair in the center-of-mass reference frame. In that case  $\varepsilon_\alpha^0$  represents the mean energy in case of the gas mixture. At the same time  $\varepsilon'_\alpha$  is the mean kinetic energy when swarm of particles moves through a pure gas  $\alpha$ . Evidently  $\varepsilon_\alpha^0$  and  $\varepsilon'_\alpha$  are not equal for the same value of the reduced electric field  $E/n_0$ . It is easy to show that

$$\varepsilon_\alpha^0 = \langle\langle \varepsilon_\alpha \rangle\rangle_\alpha^{\text{mix}} = \frac{1}{2} \mu_\alpha \left[ \langle v^2 \rangle^{\text{mix}} + \frac{3kT_\alpha^{\text{mix}}}{m_\alpha} \right], \quad \alpha \in I_l, \quad (2.5)$$

$$\varepsilon'_\alpha = \langle\langle \varepsilon_\alpha \rangle\rangle_\alpha = \frac{1}{2} \mu_\alpha \left[ \langle v^2 \rangle^\alpha + \frac{3kT^\alpha}{m_\alpha} \right], \quad \alpha \in I_l. \quad (2.6)$$

The collisional processes that we include in the theory are limited to elastic and inelastic collisions of

individual swarm particles with normal gas molecules. A collision frequency  $\nu_\alpha(v_{r\alpha})$  for collisions between the swarm particles and molecules of species  $\alpha$  is related to the cross-section  $\sigma_\alpha(v_{r\alpha})$  characterizing the collision process by  $\nu_\alpha(v_{r\alpha}) = n_\alpha v_{r\alpha} \sigma_\alpha(v_{r\alpha})$ . The momentum transfer collision frequency for elastic collisions between the swarm particles and molecules of species  $\alpha$  is denoted by  $\nu_\alpha^{(m)}(v_{r\alpha})$ .

Let  $I_\alpha^{(\text{in})}$  be a set of indices that enumerates all possible inelastic collisions of swarm particle with molecules of the gas  $\alpha$ , while  $\nu_{s\alpha}(v_{r\alpha})$ ,  $s \in I_\alpha^{(\text{in})}$  is the corresponding collision frequency. The threshold for these inelastic collisions is denoted by  $\Delta E_\alpha^s$ ,  $s \in I_\alpha^{(\text{in})}$ ,  $\alpha \in I_l$ . The total momentum transfer collision frequency is given by

$$\nu_{0\alpha}^{(m)}(v_{r\alpha}) = \nu_\alpha^{(m)}(v_{r\alpha}) + \sum_{s \in I_\alpha^{(\text{in})}} \nu_{s\alpha}^{(m)}(v_{r\alpha}), \quad \alpha \in I_l, \quad (2.7)$$

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

For convenience we shall take collision frequencies  $\nu_\alpha(v_{r\alpha})$  as a function of energies  $\varepsilon_\alpha$ :

$$v_{r\alpha} \rightarrow \varepsilon_\alpha = \frac{1}{2} \mu_\alpha v_{r\alpha}^2 \Rightarrow \nu_\alpha(v_{r\alpha}) \rightarrow \tilde{\nu}_\alpha(\varepsilon_\alpha) = n_\alpha \sqrt{2\varepsilon_\alpha / \mu_\alpha} \tilde{\sigma}_\alpha(\varepsilon_\alpha), \quad \alpha \in I_l. \quad (2.8)$$

It is convenient to introduce collision frequencies  $\tilde{\eta}_\alpha(\varepsilon_\alpha)$  normalized to unit number density, i.e.  $\tilde{\eta}_\alpha(\varepsilon_\alpha) = n_\alpha^{-1} \tilde{\nu}_\alpha(\varepsilon_\alpha)$ .

Under spatially uniform, steady state conditions the momentum and energy balance equations may be written in the following forms [11]:

$$e\vec{E} = m \langle \vec{v} \rangle^{\text{mix}} \sum_\alpha M_\alpha n_\alpha \tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon_\alpha^0), \quad (2.9)$$

$$e\vec{E} \cdot \langle \vec{v} \rangle^{\text{mix}} = \left[ m \langle v^2 \rangle^{\text{mix}} - 3kT^{\text{mix}} \right] \sum_\alpha M_\alpha M_\alpha^0 n_\alpha \tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon_\alpha^0) + \sum_\alpha n_\alpha \tilde{\Lambda}_\alpha(\varepsilon_\alpha^0). \quad (2.10)$$

The quantity  $\tilde{\Lambda}_\alpha(\varepsilon_\alpha)$  is

$$\tilde{\Lambda}_\alpha = \sum_{s \in I_\alpha^{(\text{in})}} \Delta E_\alpha^s \tilde{\eta}_{s\alpha}(\varepsilon_\alpha), \quad \alpha \in I_l. \quad (2.11)$$

Here the normalized collision frequency for inelastic process ( $s$ ) is  $\tilde{\eta}_{s\alpha}$ ,  $s \in I_\alpha^{(\text{in})}$ .

In pure gases consisting of one of the mixture components ( $\alpha$ ) we can simplify equations (2.9) and (2.10):

$$e\vec{E} = m \langle \vec{v} \rangle^\alpha M_\alpha n_0 \tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon'_\alpha), \quad \alpha \in I_l, \quad (2.12)$$

$$e\vec{E} \cdot \langle \vec{v} \rangle^\alpha = \left[ m \langle v^2 \rangle^\alpha - 3kT^\alpha \right] M_\alpha M_\alpha^0 n_0 \tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon'_\alpha) + n_0 \tilde{\Lambda}_\alpha(\varepsilon'_\alpha), \quad \alpha \in I_l, \quad (2.13)$$

where  $T^\alpha$  is the gas temperature of the pure  $\alpha$ th gas. We assume that the temperatures  $T^{\text{mix}}$  and  $T^\alpha$ ,  $\alpha \in I_l$  are the same.

If vector  $\vec{E}$  is aligned with  $z$ -axis of the reference frame, elimination of electric field  $\vec{E}$  between equations (2.9), (2.10) and (2.12) gives

$$\frac{1}{\langle \vec{v} \rangle_z^{\text{mix}}} = \sum_\alpha x_\alpha \frac{1}{\langle \vec{v} \rangle_z^\alpha} + \delta_B, \quad (2.14)$$

where

$$\delta_B = \sum_\alpha \frac{\tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon_\alpha^0) - \tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon'_\alpha)}{\tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon'_\alpha)} x_\alpha \frac{1}{\langle \vec{v} \rangle_z^\alpha}. \quad (2.15)$$

Equation (2.14) is of the same form as equation (1.2). Note that, in the absence of reactive collisions mean velocities  $\langle \vec{v} \rangle_z^{\text{mix}}$  and  $\langle \vec{v} \rangle_z^\alpha$  are equal to the corresponding drift velocities.

When we expand collision frequencies in Taylor series in the vicinity of the mean energy  $\varepsilon'_\alpha$  we obtain

$$\tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon_\alpha^0) = \tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon'_\alpha) + \frac{d\tilde{\eta}_{\alpha 0}^{(m)}}{d\varepsilon'_\alpha} \delta\varepsilon'_\alpha + o(\delta\varepsilon'_\alpha), \quad \alpha \in I_l, \quad (2.16)$$

where  $\delta\varepsilon'_\alpha = \varepsilon_\alpha^0 - \varepsilon'_\alpha$ ,  $\alpha \in I_l$ . We assume that the Taylor expansions (2.16) converge rapidly in the neighborhood of mean energies  $\varepsilon'_\alpha$ . Substituting these expansions into equation (2.15) leads after some algebra to the following expression:

$$\delta_B = \sum_\alpha x_\alpha \frac{\frac{1}{E_z} - \frac{1}{\langle \vec{v} \rangle_z^\alpha} \frac{d\langle \vec{v} \rangle_z^\alpha}{dE_z}}{\langle \vec{v} \rangle_z^\alpha} \frac{\delta\varepsilon'_\alpha}{\frac{d\varepsilon'_\alpha}{dE_z}}. \quad (2.17)$$

The details of this calculation are given in Appendix A. This result indicates that the correction  $\delta_B$  is determined by deviation of mean energies  $\varepsilon'_\alpha$ ,  $\alpha \in I_l$ , in pure gases from the mean energies  $\varepsilon_\alpha^0$ ,  $\alpha \in I_l$ , of swarm particles in the gas mixture at the same value of reduced electric field  $E/n_0$ .

We can express the deviation from Blanc's law entirely in terms of the properties of the swarm particles in pure components:

$$\delta_B = \sum_\alpha \frac{1 + \frac{m_\alpha}{2e} \frac{\langle \vec{v} \rangle_z^\alpha}{E_z/n_0} \frac{d\tilde{\Lambda}_\alpha}{d\varepsilon'_\alpha}}{\frac{m_\alpha}{2e} \frac{\langle \vec{v} \rangle_z^\alpha}{E_z/n_0} \tilde{\Lambda}_\alpha(\varepsilon'_\alpha) + m_\alpha (\langle \vec{v} \rangle_z^\alpha)^2 \frac{d \ln \langle \vec{v} \rangle_z^\alpha}{d \ln E_z} \left( 1 - \frac{d \ln \langle \vec{v} \rangle_z^\alpha}{d \ln E_z} \right)^{-1}} \times \frac{1}{2} \mu_\alpha \left\{ \frac{1 - \sum_\alpha x_\alpha \frac{1}{\langle \vec{v} \rangle_z^\alpha} \sum_\alpha x_\alpha \frac{\tilde{\Lambda}_\alpha(\varepsilon'_\alpha)}{e(E_z/n_0)}}{\sum_\alpha x_\alpha \frac{1}{\langle \vec{v} \rangle_z^\alpha} \sum_\alpha x_\alpha M_\alpha^0 \frac{1}{\langle \vec{v} \rangle_z^\alpha}} - \frac{1}{M_\alpha^0} \left[ (\langle \vec{v} \rangle_z^\alpha)^2 + \frac{\tilde{\Lambda}_\alpha(\varepsilon'_\alpha)}{e(E_z/n_0)} \langle \vec{v} \rangle_z^\alpha \right] \right\} x_\alpha \frac{1}{\langle \vec{v} \rangle_z^\alpha}. \quad (2.18)$$

The calculation of  $\delta_B$  proceeds in a similar manner as in [7]. The details of this calculation are given in Appendix B. Equation (2.18) can be recommended as an expression for finding deviation  $\delta_B$  from Blanc's law in the presence of inelastic collisions. When inelastic collisions are not present, equation (2.18) is identical to the deviation from Blanc's law proposed by Whealton et al. [7]:

$$\delta_B = \sum_{\alpha} \left( 1 - \frac{d \ln \langle \vec{v} \rangle_z^{\alpha}}{d \ln E_z} \right) \left[ m_{\alpha} (\langle \vec{v} \rangle_z^{\alpha})^2 \frac{d \ln \langle \vec{v} \rangle_z^{\alpha}}{d \ln E_z} \right]^{-1} \\ \times \frac{1}{2} \mu_{\alpha} \left[ \left( \sum_{\alpha} x_{\alpha} \frac{1}{\langle \vec{v} \rangle_z^{\alpha}} \sum_{\alpha} x_{\alpha} M_{\alpha}^0 \frac{1}{\langle \vec{v} \rangle_z^{\alpha}} \right)^{-1} \right. \\ \left. - \frac{1}{M_{\alpha}^0} (\langle \vec{v} \rangle_z^{\alpha})^2 \right] x_{\alpha} \frac{1}{\langle \vec{v} \rangle_z^{\alpha}}. \quad (2.19)$$

## 2.2 Common mean energy procedure for Blanc's law

Chiffikyan was the first to take advantage of a possibility to compensate the very different electron energy distribution functions in application of Blanc's law for electrons. The common mean energy approach (CME) [9] as an analog of the Blanc's law was developed under following assumptions:

1. the basis of Chiffikyan's theory is the two-term theory as developed for electron transport and therefore the applications are limited to the electron mobilities;
2. swarm is stationary and spatially homogeneous;
3. a basic requirement (and limitation) of the theory is that the average energy of electrons is *well* below the lowest excitation threshold of electronic levels. This condition enables one to neglect the dissociation, excitation, and ionization of electronic states;
4. for convenience it should be possible to represent the cross-sections for the relevant collision processes by the power functions.

The CME Blanc's law for drift velocities of electrons in homogeneous steady-state low-temperature weakly-ionized highly non-equilibrium multicomponent gaseous plasmas has the form [9]:

$$1 = \sum_{\alpha} x_{\alpha} \frac{E'_{\alpha}/n_0}{E/n_0} \left[ \frac{W^{\text{mix}}(E/n_0)}{W_{\alpha}(E'_{\alpha}/n_0)} \right]^{\pm 1}, \quad (2.20)$$

where  $E'_{\alpha}/n_0$  and  $W_{\alpha}$  are the reduced electric field and drift velocity of electrons in the  $\alpha$ th component,  $E/n_0$  and  $W^{\text{mix}}$  are the analogous parameters in a mixture and  $x_{\alpha}$  is the fractional concentration of the  $\alpha$ th gas component. It is required that  $E'_{\alpha}/n_0$ ,  $W_{\alpha}$ ,  $E/n_0$  and  $W^{\text{mix}}$  are to be taken at the *same* value of average electron energy. It may be difficult to accept that both signs in the exponent are acceptable and lead to reasonable results.

The theory proposed to support the form of the law [9] is actually based on integral definition of the drift velocity developed within the two term theory of electron transport. Such form necessitated the assumptions given above

including the power dependence of the cross-section on the energy. The results were questioned in the literature on two grounds [12], the presented data were in disagreement with the data that could be calculated on the basis of available cross-sections and because of the special assumptions that were part of the theory. However, the most striking result that was presented by Chiffikyan was that the proposed procedure was able to predict the negative differential conductivity even in mixtures of gases that did not show NDC on their own.

The NDC was studied by a number of authors but it appeared that a combination of a simple theory and model calculations of Petrović et al. [13] and a more elaborate theory based on MTT of Robson [14] provided a complete explanation. However, Shizgal has questioned these explanations by pointing out the NDC in rare gas mixtures [15]. It is interesting to note that in the papers discussing the Blanc's law, Chiffikyan also, and independently of Vrhovac and Petrović [11], gave an explanation of the NDC in mixtures of rare gases and suggested that it is in accordance with the existing explanations of NDC [13,14]. Unfortunately Chiffikyan did not show both the calculated data for the pure gases and for the mixture, only the data for the mixture. This made it difficult for his procedure to be widely accepted and the ability of Blanc's law to predict NDC was not appreciated. On the other hand NDC was show to be a very characteristic kinetic phenomenon that may be used as test of kinetic theories and that may occur in a wide range of situations. Any implementation of Blanc's law that sought acceptance in plasma modeling should be able to give predictions of NDC even if constituent gases do not show it.

### 2.2.1 Theoretical basis for CME procedure

We shall show that the final result of Chiffikyan (see Eq. (2.20)), which he labels as analogous of the Blanc's law may be developed on the basis of the MTT. The assumptions in our development are:

1. we will not limit ourselves to the transport of *electrons*. We are able to show that the final result of Chiffikyan is valid for the *ions* as well;
2. swarm is also assumed to be stationary and spatially homogeneous;
3. we are not limited to elastic collisions only. *Inelastic* collisions are included in the general theory.

We shall consider momentum and energy balance separately. First, the momentum balance will be used to derive the mixture law for mobility. The basic idea of the further development is strictly formal. We want to eliminate in equation (2.9) the momentum transfer frequency  $\tilde{\eta}_{\alpha 0}^{(m)}$ . In order to achieve that, equation (2.12) will be employed. The energies, which are used in equations (2.9) and (2.12) to calculate the momentum transfer frequency  $\tilde{\eta}_{\alpha 0}^{(m)}$  are not the same. We assume that there is unique correspondence between  $E/n_0$  and mean energies  $\varepsilon'_{\alpha}$ . In that case we may choose the  $E'_{\alpha}$  in equation (2.12) that would correspond to  $\varepsilon'_{\alpha}$  which is equal to the mean energy  $\varepsilon_{\alpha}^0$  of the

swarm particles in the gas mixture and which corresponds to the value of electric field of  $E$  (see Eq. (2.9)). We then arrive at

$$eE'_\alpha = mW_\alpha(E'_\alpha)M_\alpha n_0 \tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon_\alpha^0), \quad \alpha \in I_l. \quad (2.21)$$

If we use equation (2.21) to eliminate the momentum transfer collision frequency  $\tilde{\eta}_{\alpha 0}^{(m)}$  in equation (2.9) and after some simple algebra one obtains:

$$1 = \sum_\alpha x_\alpha \frac{E'_\alpha/n_0}{E/n_0} \frac{W_\alpha^{\text{mix}}(E/n_0)}{W_\alpha(E'_\alpha/n_0)}. \quad (2.22)$$

So to summarize, in this equation the drift velocity for the mixture at a given  $E/n_0$  may be obtained from the drift velocities  $W_\alpha$  for the components  $\alpha$  obtained at  $E'_\alpha/n_0$  which correspond to the same mean energy as in the mixture.

In further development we follow the same procedure as in the previous considerations. Equation (2.13) may be written for the energy balance of the swarm in gas  $\alpha$ , with electric field  $E'_\alpha$  chosen so that the mean energy  $\varepsilon'_\alpha$  of swarm in gas  $\alpha$ , is the same as the mean energy  $\varepsilon_\alpha^0$  in the gas mixture which corresponds to the electric field of  $E$  in equation (2.10):

$$eE'_\alpha W_\alpha(E'_\alpha) = [m\langle v^2 \rangle^\alpha(E'_\alpha) - 3kT^\alpha] \times M_\alpha M_\alpha^0 n_0 \tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon_\alpha^0) + n_0 \tilde{\Lambda}_\alpha(\varepsilon_\alpha^0), \quad \alpha \in I_l. \quad (2.23)$$

Using equation (2.23) we eliminate the momentum transfer collision frequency  $\tilde{\eta}_{\alpha 0}^{(m)}$  in equation (2.10).

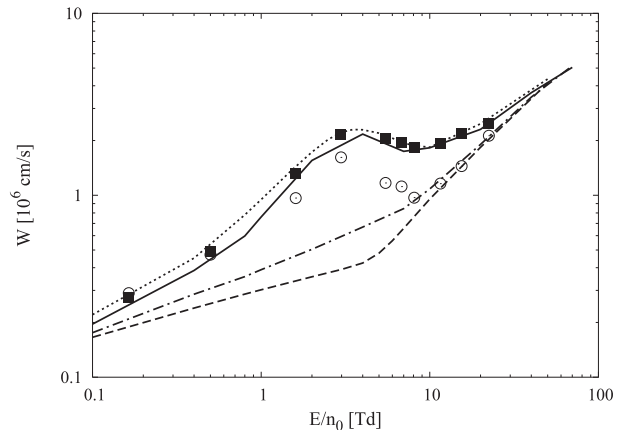
From (2.5) and (2.6) it follows that

$$m\langle v^2 \rangle^{\text{mix}} - 3kT^{\text{mix}} = m\langle v^2 \rangle^\alpha(E'_\alpha) - 3kT^\alpha = \frac{2}{M_\alpha} \left[ \varepsilon_\alpha^0 - \frac{3}{2}kT^{\text{mix}} \right], \quad \alpha \in I_l. \quad (2.24)$$

And after some simple algebra from (2.10), (2.23) and (2.24) we obtain:

$$1 = \sum_\alpha x_\alpha \frac{E'_\alpha/n_0}{E/n_0} \frac{W_\alpha(E'_\alpha/n_0)}{W_\alpha^{\text{mix}}(E/n_0)}. \quad (2.25)$$

The procedure of applying and testing this mixture law would consist of preparing correspondence between  $E/n_0$  and mean energy for all constituents and for the mixture and choosing the corresponding drift velocities to enter into the mixture law. This is certainly more complex than the standard form of Blanc's law and may not be applicable in case when one has only the data for drift velocities for pure component gases and not the data required to estimate the mean energies. Nevertheless it is worth checking whether this procedure would be useful in fluid modeling of plasmas where one may be able to prepare the tables ahead of simulation and also to use some other transport coefficient such as  $D/\mu$  as an equivalent of mean energy.



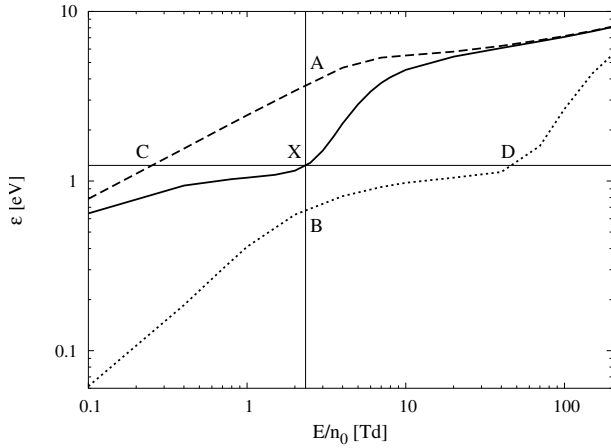
**Fig. 1.** Calculated drift velocities for electrons in 1% N<sub>2</sub> + 99% Ar mixture versus  $E/n_0$ . Symbols show values calculated from equation (2.25) (■) and equation (2.22) (○) (CME). The dotted curve was calculated using the two-term Boltzmann equation; the dashed curve is from standard Blanc's law calculations (Eq. (1.1)); the solid line is from equations (1.2) and (2.18) (CEON); and the dot-dashed line is from equations (1.2) and (2.19) (elastic collisions used in the correction).

### 3 Calculations and discussion

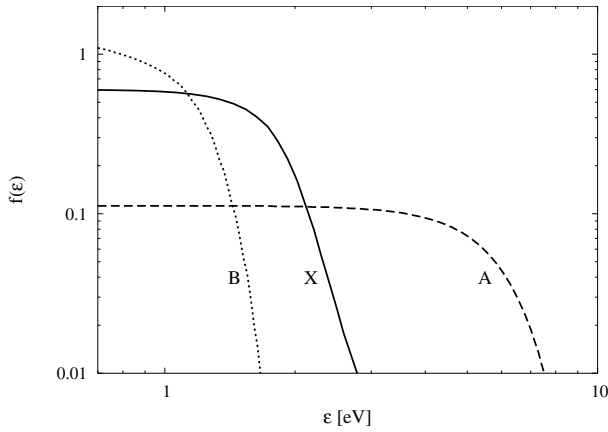
We have made a number of calculations for binary mixtures of real gases in order to verify the application of different forms of Blanc's law. Calculations of drift velocities have been performed by a standard two-term theory (2TT) [8, 16, 17] with the cross-sections for gases from the recommendations of the JILA Data Center [18]. The calculated data were used with one of the versions of Blanc's law by using different combinations of gases and mixture compositions. We have performed calculations for electrons in He + Kr, Ar + N<sub>2</sub>, CH<sub>4</sub> + Ar and O<sub>2</sub> + N<sub>2</sub> gas mixtures.

The most difficult case for application of Blanc's law in general is the combination of atomic gas where inelastic collisions have high threshold (11 eV in case of Ar) and some molecular gas where vibrational and rotational excitation control electron energy at much lower energies. First, we consider what happens when a small amount of molecular gas is added to argon. The drift velocities of electrons in 1% N<sub>2</sub> + 99% Ar gas mixture are shown in Figure 1. Solid squares are the results obtained by solving energy balance equation (2.25), and open circles are the results obtained by solving momentum balance equation (2.22). Results obtained when equations (1.2) is corrected by (2.18) are in excellent agreement with two-term solution of the Boltzmann transport equation and calculations based on Chiflikyan's CME approach (Eq. (2.25)). All the corrected methods could predict the NDC in gas mixtures, even though NDC is not present in pure gases. Results obtained by using the term (2.19), including elastic collisions only, are in poor agreement with the calculated data for mixtures which shows that in Ar + N<sub>2</sub> mixture, inelastic collisions are a necessary condition for NDC to occur.

Two approaches in applying Blanc's law are illustrated in Figure 2, which shows mean electron energies in pure



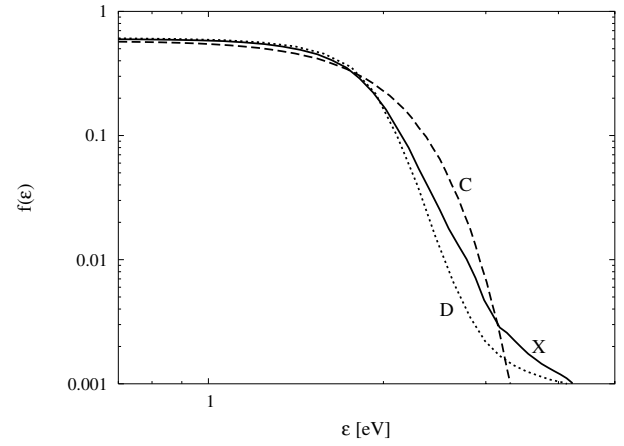
**Fig. 2.** Comparison of calculated electron mean energies versus  $E/n_0$  in Ar (dashed curve),  $N_2$  (dotted curve) and 1%  $N_2$  + 99% Ar mixture (solid line).



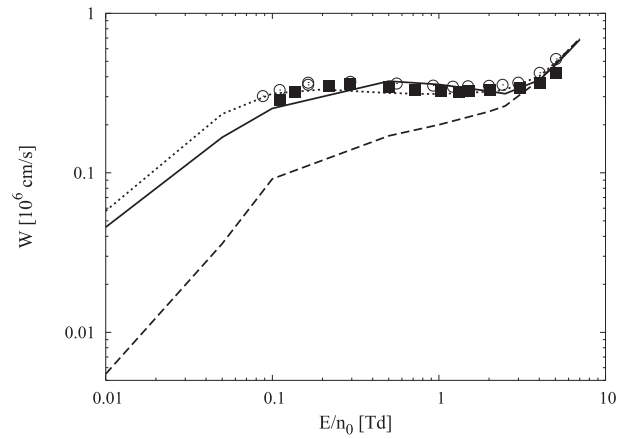
**Fig. 3.** Comparison of EEDF at  $E/n_0 = 2.2$  Td in Ar (dashed curve),  $N_2$  (dotted curve) and 1%  $N_2$  + 99% Ar mixture (solid line).

gases and in gas mixture. The standard procedure of Blanc's law (Eq. (1.2)) involves combination of drift velocities at the same value of  $E/n_0$  (point A for Ar and point B for  $N_2$ ) to get data for the gas mixture (point X). The values of mean energies (points A and B) are about 3.7 and 0.7 eV (respectively) at 2.2 Td and the electron energy distribution functions (EEDF) are quite different (Fig. 3). But if we consider the same value of mean energy, at the point X which is 1.2 eV, the corresponding value of  $E/n_0$  in Ar is 0.25 Td (point C), while in  $N_2$  the corresponding value is as high as 45 Td (point D). EEDF for these very different values of  $E/n_0$  show similar behavior for both pure gases and for the mixture (Fig. 4). This leads to correct predictions of drift velocities in the gas mixtures calculated by using CME procedure as employed in formula (2.20).

As shown in Figure 5, for noble gases (such as He and Kr) which have high excitation thresholds, correction of Blanc's law that neglects inelastic collisions is reasonable at  $E/n_0$  values considered here. The results presented here show that electron drift velocities calculated by us-



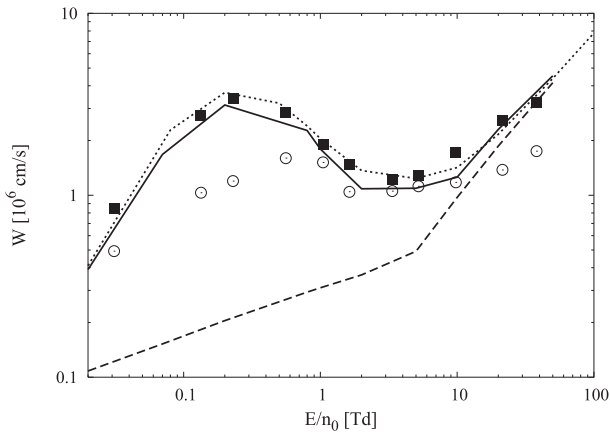
**Fig. 4.** Comparison of EEDF in Ar at  $E/n_0 = 0.25$  Td (dashed curve),  $N_2$  at  $E/n_0 = 45$  Td (dotted curve) and 1%  $N_2$  + 99% Ar mixture at  $E/n_0 = 2.2$  Td (solid line).



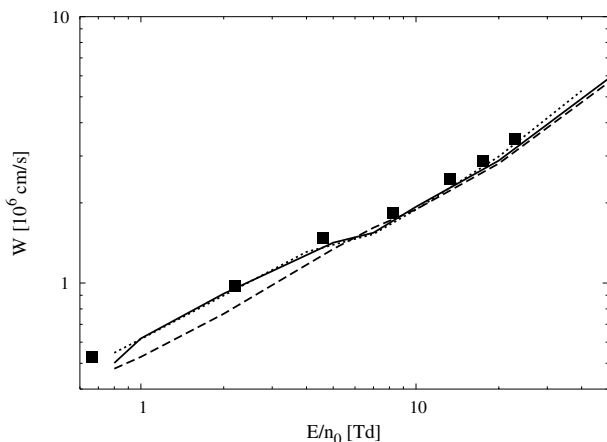
**Fig. 5.** Comparison of calculated and measured electron drift velocities for 7% He + 93% Kr mixture versus  $E/n_0$ . The open circles are experimental results from [12]; the solid squares are from present calculations by using the Chiflikyan's CME procedure (Eq. (2.25)); the dotted curve was calculated using the two-term theory; the dashed curve is from standard Blanc's law (Eq. (1.1)); the solid line is obtained in CEON approach by using equations (1.2) and (2.19).

ing (2.19), which are in excellent agreement with measured drift velocities, drift velocities by two-term theory, and the method proposed by Chiflikyan (Eq. (2.25)). The present results also show, that there is a very small effect of NDC, and that some inelastic process is not always required for NDC [11,15,19]. Helium, which is the gas with a lower abundance in the mixtures with krypton or xenon, controls the mean energy by elastic collisions. 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 [11].

Figure 6 shows calculated drift velocities of electrons for 97% Ar + 3%  $CH_4$  gas mixtures using the same methods mentioned above. Methane has a strong NDC in a wide range of  $E/n_0$ . It is evident that at lower  $E/n_0$



**Fig. 6.** Comparison of calculated electron drift velocities versus  $E/n_0$  for 97% Ar + 3% CH<sub>4</sub> mixture. Symbols show values calculated in CME approach from equation (2.25) (■) and equation (2.22) (○). The dotted curve was calculated by using the two-term approximation; the dashed curve is from standard Blanc's law calculations (Eq. (1.1)); the solid line is obtained by using equations (1.2) and (2.18) in CEON approach.



**Fig. 7.** Comparison of calculated electron drift velocities versus  $E/n_0$  for 40% O<sub>2</sub> + 60% N<sub>2</sub> mixture. Solid squares (■) show values calculated from equation (2.25) in CME approach. The dotted curve was calculated by using the two-term theory; the dashed curve is from standard Blanc's law (Eq. (1.1)); the solid line is obtained by using equations (1.2) and (2.18) in CEON approach.

Blanc's law without correction (Eq. (1.1)) disagrees significantly, while at higher  $E/n_0$  agreements between all methods is excellent.

Our final example is 40% O<sub>2</sub> + 60% N<sub>2</sub> gas mixtures and results are shown in Figure 7. Because of similar energy dependence of collision frequencies there is little difference between drift velocities for the two pure gases so all forms of Blanc's law provide good results.

In all cases it is evident that the pure Blanc's law (Eq. (1.1)) at low  $E/n_0$  is not valid. All methods, except the basic Blanc's law and the Blanc's law with correction that includes only elastic collisions, predict the NDC. Because of the first derivative, application of Eq. (2.18) is not always simple but it is possible. At lower values of  $E/n_0$

we suggest equations (1.2) and (2.18). At higher values of  $E/n_0$  pure Blanc's law (Eq. (1.1)) is a good approximation.

## 4 Conclusion

In this paper we have analyzed two strategies to correct Blanc's law in order to determine the drift velocities of charged particles in mixtures of gases. The need for simple while sufficiently accurate technique is certainly high due to the requirements for modeling of a broad range of plasma technological devices. We have derived the correction to standard common  $E/n_0$  version of the law that includes inelastic processes and we have also given a broader theoretical basis for the common mean energy technique of Chiflikyan. Numerical examples were made for several gases that show or do not show NDC and in all cases the best results were obtained by CME procedure with negative exponent, i.e. from the energy balance equation and also by CEON procedure with correction for inelastic collisions.

The CME procedure requires the knowledge of mean energy while CEON procedure requires application of the inelastic terms (rate coefficients). The numerical procedure involved in CEON is much more complex and may lead to some ambiguities especially if fitting of experimental data in order to perform smoothing is involved. Thus we would recommend the CME procedure developed by Chiflikyan as the best choice. Neither of the two techniques is as simple as the basic Blanc's law procedure but CME comes close.

The uncorrected Blanc's law cannot be used with any degree of reliability for electrons at moderate (and even small) values of  $E/n_0$ . In no cases it was able to predict the NDC unless it existed in at least one of the constituent gases. However, for high  $E/n_0$  even the basic Blanc's law becomes as good as any technique since the differences between mean energies for different gases at the same  $E/n_0$  are small. This is certainly important as it may not be expected that a broad range of experimental data will be available for those conditions.

The second CME procedure, with positive sign in the exponent, which was obtained from the momentum balance was somewhat inferior to two other, corrected, techniques. However qualitatively it was able to predict NDC in difficult cases when basic Blanc's law failed.

Our results indicate that the objections to the first paper presenting CME procedure were mainly result of poor cross-sections used by Chiflikyan in the original paper [9,20]. Even with a rather complicated theory that gave results only for special forms of cross-sections it was obvious that the procedure itself has a much broader scope than that defined by the assumptions of the theory. Our theory gives a firmer ground and broadens the scope covered by the assumptions of the theory. Yet even in that case it is obvious that the CME procedure has applicability that is much broader. The same may be said of the corrected CEON procedure.

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## Appendix A: Derivation of equation (2.17)

When we substitute equation (2.16) into equation (2.15), we obtain

$$\delta_B \approx \sum_{\alpha} \frac{1}{\tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon'_{\alpha})} \frac{d\tilde{\eta}_{\alpha 0}^{(m)}}{d\varepsilon'_{\alpha}} \delta\varepsilon'_{\alpha} x_{\alpha} \frac{1}{\langle \vec{v} \rangle_z^{\alpha}}. \quad (\text{A.1})$$

Differentiation of equation (2.12) with respect to electric field  $E_z$  gives

$$\frac{e}{mn_0 M_{\alpha}} = \langle \vec{v} \rangle_z^{\alpha} \frac{d\tilde{\eta}_{\alpha 0}^{(m)}}{d\varepsilon'_{\alpha}} \frac{d\varepsilon'_{\alpha}}{dE_z} + \tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon'_{\alpha}) \frac{d\langle \vec{v} \rangle_z^{\alpha}}{dE_z}, \quad \alpha \in I_l. \quad (\text{A.2})$$

Using equations (2.12) and (A.2) we obtain

$$\frac{1}{\tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon'_{\alpha})} \frac{d\tilde{\eta}_{\alpha 0}^{(m)}}{d\varepsilon'_{\alpha}} = \frac{\frac{1}{E_z} - \frac{1}{\langle \vec{v} \rangle_z^{\alpha}} \frac{d\langle \vec{v} \rangle_z^{\alpha}}{dE_z}}{\frac{d\varepsilon'_{\alpha}}{dE_z}}, \quad \alpha \in I_l. \quad (\text{A.3})$$

This leads immediately to equation (2.17).

## Appendix B: Derivation of equation (2.18)

Except for minor technical difficulties, our strategy is the same as the one Robson and coworkers followed in reference [7] to establish the correction  $\delta_B$  in the presence of elastic collisions. The starting point of our derivation is equation (A.1). We first write the expression for the energy partitioning in the presence of inelastic collisions [11]:

$$\varepsilon'_{\alpha} = \langle \langle \varepsilon_{\alpha} \rangle \rangle_{\alpha} = \frac{1}{2} m_{\alpha} (\langle \vec{v} \rangle_z^{\alpha})^2 + \frac{3}{2} kT^{\alpha} - \frac{1}{2M_{\alpha}^0} \frac{\tilde{\Lambda}_{\alpha}(\varepsilon'_{\alpha})}{\tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon'_{\alpha})}, \quad \alpha \in I_l. \quad (\text{B.1})$$

By differentiation of equation (B.1) with respect to  $E_z$ , we obtain

$$\frac{d\varepsilon'_{\alpha}}{dE_z} = \frac{m_{\alpha} \langle \vec{v} \rangle_z^{\alpha} \frac{d\langle \vec{v} \rangle_z^{\alpha}}{dE_z}}{1 + \frac{1}{2M_{\alpha}^0} \frac{\frac{d\tilde{\Lambda}_{\alpha}}{d\varepsilon'_{\alpha}} \tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon'_{\alpha}) - \tilde{\Lambda}_{\alpha}(\varepsilon'_{\alpha}) \frac{d\tilde{\eta}_{\alpha 0}^{(m)}}{d\varepsilon'_{\alpha}}}{\left(\tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon'_{\alpha})\right)^2}}, \quad \alpha \in I_l. \quad (\text{B.2})$$

Inserting equation (B.2) into equation (A.2), we get with the help of equation (2.12)

$$\frac{1}{\tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon'_{\alpha})} \frac{d\tilde{\eta}_{\alpha 0}^{(m)}}{d\varepsilon'_{\alpha}} = \frac{1 + \frac{mn_0 M_{\alpha}}{2eM_{\alpha}^0} \frac{\langle \vec{v} \rangle_z^{\alpha}}{E_z} \frac{d\tilde{\Lambda}_{\alpha}}{d\varepsilon'_{\alpha}}}{\frac{mn_0 M_{\alpha}}{2eM_{\alpha}^0} \frac{\langle \vec{v} \rangle_z^{\alpha}}{E_z} \tilde{\Lambda}_{\alpha}(\varepsilon'_{\alpha}) + m_{\alpha} (\langle \vec{v} \rangle_z^{\alpha})^2 \frac{\frac{d \ln \langle \vec{v} \rangle_z^{\alpha}}{d \ln E_z}}{1 - \frac{d \ln \langle \vec{v} \rangle_z^{\alpha}}{d \ln E_z}}}, \quad \alpha \in I_l. \quad (\text{B.3})$$

From equations (2.5) and (2.6) we get immediately

$$\delta\varepsilon'_{\alpha} = \frac{1}{2} \mu_{\alpha} \left( \langle v^2 \rangle^{\text{mix}} - \langle v^2 \rangle^{\alpha} \right), \quad \alpha \in I_l. \quad (\text{B.4})$$

From equations (2.10) and (2.12), the mean-square velocity  $\langle v^2 \rangle^{\text{mix}}$  can be evaluated:

$$\langle v^2 \rangle^{\text{mix}} = \frac{\langle \vec{v} \rangle_z^{\text{mix}} - \sum_{\alpha} x_{\alpha} \frac{\tilde{\Lambda}_{\alpha}(\varepsilon_{\alpha}^0)}{M_{\alpha} m \tilde{\nu}_{\alpha 0}^{(m)}(\varepsilon'_{\alpha})} \frac{1}{\langle \vec{v} \rangle_z^{\alpha}}}{\sum_{\alpha} x_{\alpha} \frac{M_{\alpha}^0 \tilde{\nu}_{\alpha 0}^{(m)}(\varepsilon_{\alpha}^0)}{\tilde{\nu}_{\alpha 0}^{(m)}(\varepsilon'_{\alpha})} \frac{1}{\langle \vec{v} \rangle_z^{\alpha}}} + \frac{1}{m} 3kT^{\text{mix}}. \quad (\text{B.5})$$

Elimination of electric field  $E_z$  between equations (2.12) and (2.13) gives

$$\langle v^2 \rangle^{\alpha} = \frac{1}{M_{\alpha}^0} (\langle \vec{v} \rangle_z^{\alpha})^2 + \frac{1}{m} 3kT^{\alpha} - \frac{\tilde{\Lambda}_{\alpha}(\varepsilon'_{\alpha})}{m M_{\alpha} M_{\alpha}^0 \tilde{\nu}_{\alpha 0}^{(m)}(\varepsilon'_{\alpha})}, \quad \alpha \in I_l. \quad (\text{B.6})$$

Substituting expressions (B.5) and (B.6) into the equations (B.4) leads after some algebra to the following formula:

$$\delta\varepsilon'_{\alpha} = \frac{1}{2} \mu_{\alpha} \times \left[ \left( 1 - \sum_{\alpha} x_{\alpha} \frac{\tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon_{\alpha}^0)}{\tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon'_{\alpha})} \frac{1}{\langle \vec{v} \rangle_z^{\alpha}} \sum_{\alpha} x_{\alpha} \frac{\tilde{\Lambda}_{\alpha}(\varepsilon_{\alpha}^0)}{m M_{\alpha} \tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon'_{\alpha})} \frac{1}{\langle \vec{v} \rangle_z^{\alpha}} \right) \times \left( \sum_{\alpha} x_{\alpha} \frac{\tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon_{\alpha}^0)}{\tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon'_{\alpha})} \frac{1}{\langle \vec{v} \rangle_z^{\alpha}} \sum_{\alpha} x_{\alpha} \frac{M_{\alpha}^0 \tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon_{\alpha}^0)}{\tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon'_{\alpha})} \frac{1}{\langle \vec{v} \rangle_z^{\alpha}} \right)^{-1} - \frac{1}{M_{\alpha}^0} (\langle \vec{v} \rangle_z^{\alpha})^2 + \frac{\tilde{\Lambda}_{\alpha}(\varepsilon'_{\alpha})}{m M_{\alpha} M_{\alpha}^0 \tilde{\eta}_{\alpha 0}^{(m)}(\varepsilon'_{\alpha})} \right], \quad \alpha \in I_l. \quad (\text{B.7})$$

We can simplify equation (B.7) by expanding the collision frequencies  $\tilde{\Lambda}_{\alpha}$  in Taylor series of  $\delta\varepsilon'_{\alpha}$  similar to equation (2.16)

$$\tilde{\Lambda}_{\alpha}(\varepsilon_{\alpha}^0) = \tilde{\Lambda}_{\alpha}(\varepsilon'_{\alpha}) + \frac{d\tilde{\Lambda}_{\alpha}}{d\varepsilon'_{\alpha}} \delta\varepsilon'_{\alpha} + o(\delta\varepsilon'_{\alpha}), \quad \alpha \in I_l. \quad (\text{B.8})$$



Substituting equations (2.16) and (B.8) into equation (B.7), we obtain

$$\delta\varepsilon'_\alpha = \frac{1}{2}\mu_\alpha \left[ \left( 1 - \sum_\alpha x_\alpha \frac{1}{\langle \vec{v} \rangle_z^\alpha} \sum_\alpha x_\alpha \frac{\tilde{\Lambda}_\alpha(\varepsilon'_\alpha)}{e(E_z/n_0)} \right) \times \left( \sum_\alpha x_\alpha \frac{1}{\langle \vec{v} \rangle_z^\alpha} \sum_\alpha x_\alpha M_\alpha^0 \frac{1}{\langle \vec{v} \rangle_z^\alpha} \right)^{-1} - \frac{1}{M_\alpha^0} \left( (\langle \vec{v} \rangle_z^\alpha)^2 + \frac{\tilde{\Lambda}_\alpha(\varepsilon'_\alpha)}{e(E_z/n_0)} \langle \vec{v} \rangle_z^\alpha \right) \right] + R_\alpha, \quad \alpha \in I_l. \quad (\text{B.9})$$

Quantity  $R_\alpha$  denotes all other terms which include derivatives of collisional frequencies  $\tilde{\eta}_{\alpha 0}^{(m)}$  and  $\tilde{\Lambda}_\alpha$ . Since these terms provide higher order corrections to Blanc's law, we neglect them. Finally, using equations (A.1), (B.3) and (B.9) we readily obtain expression (2.18).

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