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Account of diffusion in local thermodynamic equilibrium and two-temperature plasma models

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Abstract
A self-consistent account of the effect of diffusion on charge transport in local thermodynamic equilibrium (LTE) and two-temperature (2T) ionization-equilibrium plasmas amounts to introducing into Ohm's law, in addition to the conventional term proportional to the electric field (conduction current) and thermal-diffusion terms, also terms describing the diffusion due to plasma composition variations, which are proportional to the temperature gradient (or, in the case of 2T plasmas, to ∇T_e and ∇T_h) and to the plasma pressure gradient. These terms are calculated, with the use of the Stefan–Maxwell equations, for the particular case of 2T ionization-equilibrium atomic plasmas with singly charged ions. Also proposed is a simple way of approximate evaluation of reactive thermal conductivity in such plasmas. An online tool performing evaluation of the relevant coefficients for 2T argon, xenon, and mercury plasmas has been deployed on the internet. Representative modelling results show that the new form of Ohm's law, when introduced into standard LTE or 2T models, may describe the electric field reversal in front of arc anodes, an effect that has been simulated previously only by means of (more complex) models taking into account deviations from ionization equilibrium.

Keywords: reactive thermal conductivity, LTE and 2T modelling, diffusion currents

(Some figures may appear in colour only in the online journal)

1. Introduction

Since time scales of chemical reactions in thermal plasmas, including ionization and recombination, are usually smaller than all the other relevant time scales, including the time scale of relaxation of electron and heavy-particle temperatures T_e and T_h, there are situations where a thermal plasma is in the state of local chemical equilibrium (LCE) while thermal equilibrium holds or not. If both LCE and thermal equilibrium hold, one can speak of local thermodynamic equilibrium (LTE). Plasmas where LCE holds but thermal equilibrium does not are referred to as two-temperature (2T) plasmas.

LTE and 2T models do not involve equations of conservation of species and multicomponent diffusion (transport) equations, which are replaced by equations of chemical equilibrium. (LTE and 2T models may need to involve equations of conservation of elements, however in the case where the plasma contains atoms of only one species, which is considered in this work, such equations are not needed.) On the other hand, the diffusion of species in LCE gas mixtures, which is due to variations in the composition, affects the energy and charge transport. The former effect is well known and routinely taken into account by means of the so-called reactive thermal conductivity [1]. The latter effect, however, appears to be overlooked. In virtually all of the works dedicated to the modelling of LTE and 2T plasmas (e.g. reviews [2–5]), Ohm's law is written with account of only the conduction current. Some works take into account the thermal-diffusion current (e.g. [6]). There is also the so-called 'LTE-diffusion approximation' of Lowke and Tanaka [7]. However, there seems to be no works where Ohm's law in LCE plasmas would account for diffusion due to variations in the plasma composition.

Of course, it has been known long ago that diffusion currents in thermal plasmas are important in certain situations, for example, they are responsible for the negative potential drop and the electric field reversal in front of the arc anodes [8], and there are papers that take the diffusion current into account; e.g. [8–13]. However, all these papers use models which do not employ the assumption of LCE and instead include the electron conservation equation. Such models still remain computationally heavy and are not used very frequently; what is routinely employed in the modelling practice, including industrial modelling, are LTE and, to a lesser extent, 2T models.

It would be useful to develop a self-consistent description of diffusion currents in the framework of LTE and 2T models. This amounts to introducing into Ohm's law in LTE or 2T plasmas, in addition to the conventional term proportional to the electric field (conduction current) and thermal-diffusion terms, also terms proportional to the temperature gradient (or, in the case of 2T plasmas, terms proportional to ∇T_e and ∇T_h) and a term proportional to the plasma pressure gradient, which take into account the diffusion due to plasma composition variations. In this work, these terms are calculated, with the use of the Stefan–Maxwell equations, for the particular case of an atomic plasma with singly charged ions. A publicly available online tool for evaluation of the relevant coefficients for 2T argon, xenon, and mercury plasmas has been deployed on internet. Representative modelling results show that this form of Ohm's law, when introduced into standard LTE or 2T models, has the potential of describing the electric field reversal in front of arc anodes.

Another topic touched in this paper is as follows. A significant amount of work has been done on evaluation of transport properties of 2T plasmas, e.g. review [3] and references therein; papers [14–25] may be cited as supplementary references. In particular, ready-for-use data on transport properties of 2T argon, oxygen, and nitrogen plasmas were given in [16]. However, no data on the reactive thermal conductivity has been included since, in view of the authors [16], there still existed some difficulties in calculating this property. Similarly, no data on the reactive thermal conductivity is contained in the tables of transport properties of atmospheric-pressure 2T argon and helium plasmas given in [23] and [24]: the authors indicated that the transport of enthalpy due to diffusion can be treated directly in the governing equations, instead of defining the non-equilibrium reactive and internal thermal conductivities, and therefore did not calculate these properties [23]. In this work, a simple way of approximate evaluation of reactive thermal conductivities of 2T atomic plasmas with singly charged ions is proposed. For 2T argon, xenon, and mercury plasmas, the reactive thermal conductivities can be evaluated by means of the above-mentioned online tool.

The outline of the paper is the following. Ohm's law with account of diffusion and the reactive thermal conductivities of 2T atomic plasmas with singly charged ions are derived in section 2. Results of evaluation of the transport coefficients, introduced in section 2, for atmospheric-pressure argon plasma are shown and wherever possible compared with those from previous studies in section 3. The impact of account of diffusion currents in LTE arc modelling is illustrated in section 4. A brief summary is given in section 5.

2. Ohm's law and reactive thermal conductivity in 2T ionization-equilibrium atomic plasmas with singly charged ions

2.1. The Stefan–Maxwell equations

Let us consider a plasma of an atomic gas. For simplicity, the treatment is restricted to the case where the plasma temperature is not very high and multiple ionization is insignificant, so the plasma comprises atoms, singly charged ions, and electrons. (For example, for an argon arc at atmospheric pressure, which is a kind of a standard high-pressure arc, and a mercury arc at the pressure of 100, which is typical for high-intensity discharge lamps, this is the case if the plasma temperature does not exceed approximately 20 000.) The ions and the atoms have the same temperature, which will be designated T_h: $T_i = T_a = T_h$. Thermal equilibrium between the heavy particles and the electrons may or may not hold, so $T_e \neq T_h$ in the general case.

Equations describing the multicomponent diffusion in gas mixtures are derived in the kinetic theory of gases, e.g. [26–30]. These equations are written in two forms: equations resolved with respect to diffusion fluxes, which involve the multicomponent diffusion coefficients, and equations resolved with respect to diffusion forces, which are usually called the Stefan–Maxwell equations and in the first approximation involve binary diffusion coefficients. The derivation of this section would be more straightforward if the equations resolved with respect to diffusion fluxes were used. However, we will use the Stefan–Maxwell equations since they are easier for practical evaluation.

Following [31], we write the Stefan–Maxwell equations [29, 30] as

$$-\nabla p_\alpha + n_\alpha q_\alpha \mathbf{E} + \frac{\rho_\alpha}{\rho}\left[\nabla p - e\left(n_i - n_e\right)\mathbf{E}\right] - \sum_\beta \frac{n_\alpha n_\beta k T_{\alpha\beta} C_{\alpha\beta}}{n D_{\alpha\beta}}\left(\mathbf{V}_\alpha - \mathbf{V}_\beta\right) - \mathbf{R}_\alpha^T = 0, \quad (1)$$

where

$$\mathbf{R}_\alpha^T = C_\alpha^{(h)} n_\alpha k \nabla T_h + C_\alpha^{(e)} n_\alpha k \nabla T_e. \quad (2)$$

Here $\alpha, \beta = i, e, a$; the indices i, e, and a are attributed to the ions, electrons, and neutral atoms, respectively; m_α and q_α are mass and charge of a particle of species α; T_α, $\rho_\alpha = n_\alpha m_\alpha$, $p_\alpha = n_\alpha k T_\alpha$, and $\mathbf{V}_\alpha$ are the temperature, mass density, partial pressure, and diffusion velocity of the species α; $n = \sum_\beta n_\beta$, $\rho = \sum_\beta \rho_\beta$, and $p = \sum_\beta p_\beta$ are the total number and mass densities and pressure of the plasma; $T_{ia} = T_h$, $T_{ea} = T_{ei} = T_e$; $D_{\alpha\beta}$ are binary diffusion coefficients evaluated in the first approximation in expansion in the Sonine polynomials in the method of Chapman–Enskog and $C_{\alpha\beta}$ are coefficients of the order unity introducing corrections arising in higher approximations (note that $D_{\beta\alpha} = D_{\alpha\beta}, C_{\beta\alpha} = C_{\alpha\beta}$); terms $\mathbf{R}_\alpha^T$ account for thermal diffusion (note that $\mathbf{R}_e^T$ does not contain a term proportional to ∇T_h, which is small due to the smallness of the electron-to-ion mass ratio m_e/m_i) and $C_\alpha^{(h)}$, $C_\alpha^{(e)}$, and $C_e^{(e)}$ are coefficients describing thermal diffusion; and $\mathbf{E}$ is the electric field.

It follows from the definitions of the diffusion velocities and the current density $\mathbf{j}$ that

$$\rho_i \mathbf{V}_i + \rho_e \mathbf{V}_e + \rho_a \mathbf{V}_a = 0, \tag{3}$$

$$\mathbf{j} = e(n_i \mathbf{V}_i - n_e \mathbf{V}_e). \tag{4}$$

In the following, the ion and electron number densities n_i and n_e will be set equal because of quasi-neutrality.

It is natural to simplify the subsequent derivation by dropping terms of the order of $\sqrt{m_e/m_i}$ and higher, which is consistent with attributing different temperatures to the electrons and the heavy particles. In this spirit, we will set $C_e^{(h)} = 0$ in equation (2) with $\alpha = e$. Further simplifications along the same line will be made below.

In this work, the use will be made of explicit approximate analytical formulas for the coefficients appearing in equations (1) and (2) and the relevant material constants for argon plasmas given in [31]. Note that the material constants for xenon and mercury plasmas are given in [33] and [31], respectively; a free online tool realizing the evaluation by means of these formulas (and also of the formulas for the translational thermal conductivities of the electron and heavy-particle gases, which are also given in [31]) is available on the internet [34].

In order to give an idea of the accuracy of the approach [31], in figure 1 the electrical and thermal conductivities of 1 bar 2T argon plasma, evaluated with the use of results [31] for three values of the ratio $\theta = T_e/T_h$, are compared with the computed values [23] and (in the case of LTE, $\theta = 1$) computed values [32]. The data on electrical conductivity, shown in figure 1(a) by the solid lines, have been obtained from the data [31] by means of an equation equivalent to equation (7) below. The data on translational thermal conductivity of electrons, shown in figure 1(b) by the solid lines, have been obtained by means of equation (50) of [31]. The data on translational thermal conductivity of heavy particles, shown in figure 1(c) by the solid line, have been obtained by means of adding quantities given by equations (55) and (56) of [31]. One can see that the data on the electrical conductivity and the electron translational thermal conductivity obtained with the use of results [31] are reasonably close to the values [23, 32]. As far as the translational thermal conductivity of the heavy particles is concerned, there is an appreciable difference in the range $T_e \gtrsim 12\,000$ K. The analysis has shown that this difference stems not from different sets of collision integrals (the collision integrals for Ar used in [31] are close to those from [32]) but rather from the approximate nature of evaluation employed in [31]. On the other hand, this difference is likely to produce little effect in practice: the high-pressure arc plasma is close to LTE at T_e that high; what matters in the LTE case is the sum $\kappa_{hp} + \kappa_e$ rather than these quantities separately, and one can see from figures 1(b) and (c) that κ_{hp} is significantly smaller than κ_e in this T_e range.

Data on the electron thermal-diffusion coefficient, depicted by the solid lines in figure 2, have been computed by means of the formula

$$D_e^T = \frac{k m_e \sigma T_h C_e^{(e)}}{e^2 \theta} \tag{5}$$

with the use of the results [31]. Again, these data are reasonably close to the values [23, 32].

2.2. Ohm's law with account of diffusion in 2T ionization-equilibrium atomic plasmas

Let us solve the Stefan–Maxwell equations (1) for the ions and electrons, $\alpha = i, e$, for $\mathbf{V}_i - \mathbf{V}_a$ and $\mathbf{V}_e - \mathbf{V}_a$. With the use the expressions obtained, equation (4) may be written as

$$\mathbf{j} = \sigma \mathbf{E} - nF_1 \left[C_{ea} D_{ia} \left(\nabla p_i + \mathbf{R}_i^T \right) - C_{ia} D_{ea} \frac{T_h}{T_e} \left(\nabla p_e + \mathbf{R}_e^T \right) + \frac{n_e}{\rho} \left(m_e C_{ia} D_{ea} \frac{T_h}{T_e} - m_i C_{ea} D_{ia} \right) \nabla p \right] \tag{6}$$

where

$$\sigma = n_e n F_1 e \left(C_{ia} D_{ea} \frac{T_h}{T_e} + C_{ea} D_{ia} \right), \tag{7}$$

$$F_1 = \frac{e}{kT_h} \left[C_{ea} C_{ia} n_a + \frac{C_{ei} n_e}{D_{ei}} \left(C_{ia} D_{ea} + C_{ea} D_{ia} \frac{T_e}{T_h} \right) \right]^{-1}. \tag{8}$$

The first term on the right-hand side (rhs) of equation (6) represents the conduction current and σ is the electrical conductivity of the plasma. The other terms on the rhs of equation (6) describe the diffusion component of the electric current, originating in the species diffusion caused by partial pressures gradients and thermal diffusion.

Let us assume now that the plasma is in ionization equilibrium, so the particle densities are related by the Saha equation. The latter is written as

$$\frac{n_e^2}{n_a} = \Omega, \quad \Omega = \frac{2Z_i}{Z_a} \left(\frac{2\pi m_e k}{h^2} \right)^{3/2} T_e^{3/2} \exp\left(-\frac{A_a}{kT_e} \right). \tag{9}$$

Here Z_a and Z_i are the partition functions of the atom and the ion, h is the Planck's constant, and A_a is the energy of ionization of an atom. Using equation (9) and Dalton's law, one can express the gradients of the electron and ion partial pressures, ∇p_e and ∇p_i, in terms of ∇T_e, ∇T_h, and ∇p. Substituting these expressions into equation (6), one can write

$$\mathbf{j} = \sigma \left(\mathbf{E} + \chi_e \nabla \frac{kT_e}{e} + \chi_h \nabla \frac{kT_h}{e} + F_p \nabla \frac{p}{e} \right), \tag{10}$$

where

$$\chi_e = \chi_{e1} + \chi_{e2}, \quad \chi_h = \chi_{h1} + \chi_{h2}, \tag{11}$$

$$F_p = F_{p1} + F_{p2}, \tag{12}$$

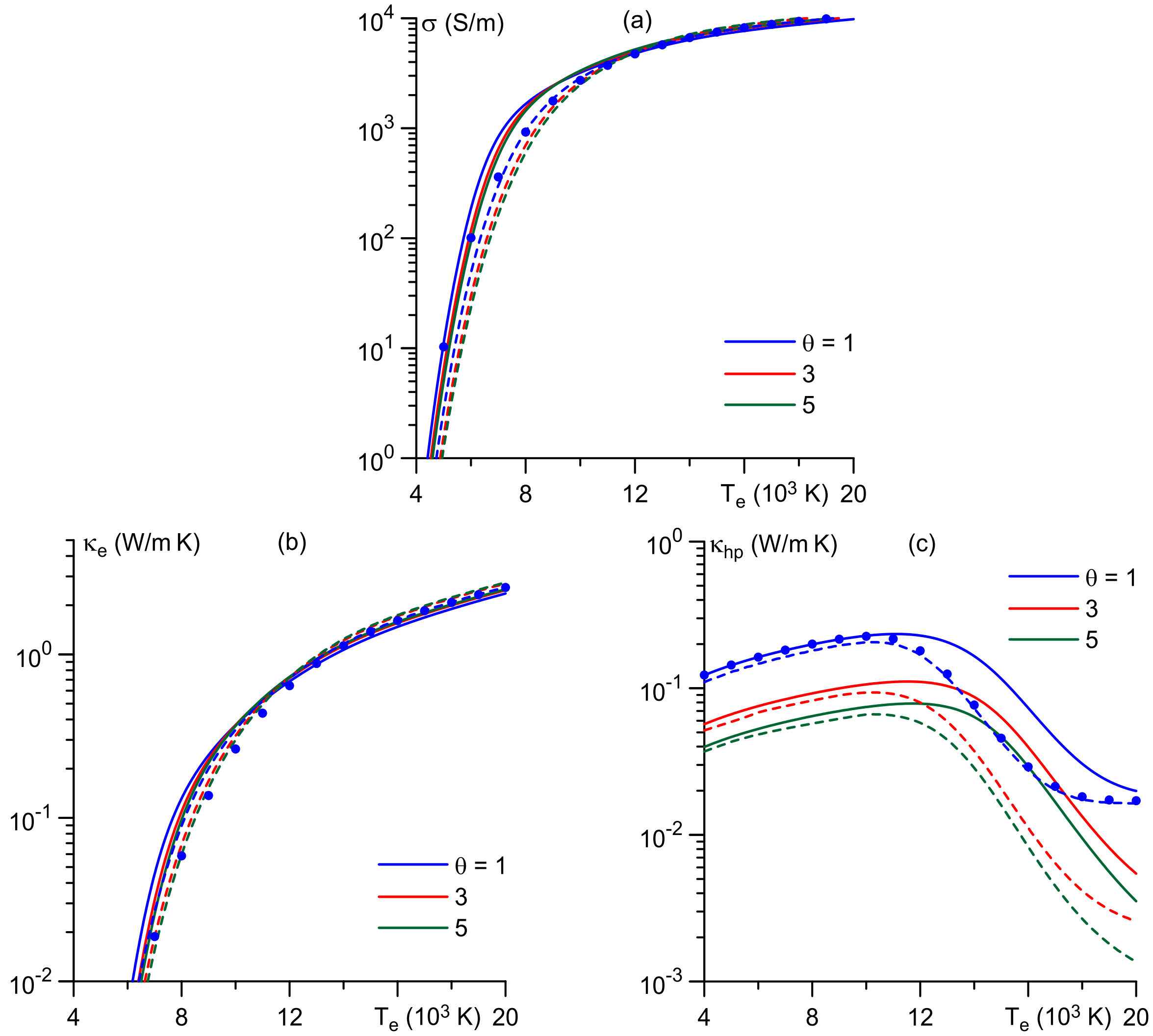

Figure 1. Electrical conductivity (a) and translational thermal conductivity of the electrons (b) and heavy particles (c). 2T argon plasma. $p = 1$ bar, different values of the ratio $\theta = T_e/T_h$. Solid: evaluation with the use of data [31]. Dashed: computed values [23]. Circles: computed values [32] ($\theta = 1$).

$$\chi_{e1} = \frac{F_2 T_h^2}{2T_e}\left\{C_{ia}D_{ea}\left[2\frac{A_a}{T_e}n_a + k\left(7n_a + 2n_e\right)\right] - C_{ea}D_{ia}\left[2n_a\frac{A_a}{T_e} - k\left(2n_e\frac{T_e}{T_h} - 3n_a\right)\right]\right\}, \quad (13)$$

$$\chi_{e2} = F_3\left[C_e^{(e)}C_{ia}D_{ea}\frac{T_e}{T_h} - C_i^{(e)}C_{ea}D_{ia}\right], \quad (14)$$

$$\chi_{h1} = -kF_2T_h\left(n_a + n_e\right)\left(C_{ia}D_{ea} + C_{ea}D_{ia}\right), \quad (15)$$

$$\chi_{h2} = -C_i^{(h)}C_{ea}D_{ia}F_3, \quad F_2 = \frac{F_3}{p + n_a k T_h}, \quad (16)$$

$$F_3 = \left(C_{ia}D_{ea}\frac{T_h}{T_e} + C_{ea}D_{ia}\right)^{-1}, \quad (17)$$

$$F_{p1} = F_2 k T_h\left(C_{ia}D_{ea} - C_{ea}D_{ia}\right), \quad (18)$$

$$F_{p2} = \frac{F_3}{\rho}\left(m_i C_{ea}D_{ia} - m_e C_{ia}D_{ea}\frac{T_h}{T_e}\right). \quad (19)$$

Equation (10) represents Ohm's law in 2T ionization-equilibrium atomic plasmas written with account of the diffusion currents. χ_{e1} and χ_{h1} describe the diffusion currents caused by gradients of partial pressures of the charged particles, and χ_{e2} and χ_{h2} describe the thermal-diffusion currents. All the coefficients χ_e, χ_h, χ_{e1}, χ_{e2}, χ_{h1}, and χ_{h2} are dimensionless. In the following, χ_{e1} and χ_{h1} will be referred to as diffusion–current ratios; χ_{e2} and χ_{h2} will be referred to as thermal diffusion–current ratios; and χ_e and χ_h will be referred to as net diffusion–current ratios.

In the LTE case, where $T_e = T_h$, equation (15) assumes the simple form $\chi_{h1} = -1/2$.

In the limiting case of fully ionized plasma, equations (13) and (15) assume the form

$$\chi_{e1} = \frac{T_h}{T_e + T_h}, \quad (20)$$

$$\chi_{h1} = -\frac{T_e}{T_e + T_h}\frac{C_{ia}D_{ea} + C_{ea}D_{ia}}{C_{ia}D_{ea} + C_{ea}D_{ia}T_e/T_h}. \quad (21)$$

Since the cross section of the electron–atom collisions is usually smaller or much smaller than that of the ion–atom collisions, D_{ia} is of the order of $\sqrt{m_e/m_i}$ or smaller compared to D_{ea}. Therefore, the terms involving D_{ia} in equations (7), (8), (13)–(15), (17), (18) and (21) may be dropped.

In particular, equation (21) assumes the form

$$\chi_{h1} = -\frac{T_e}{T_e + T_h}. \quad (22)$$

Using formulas (20) and (22), one can check readily that the terms of Ohm's law (10) in the fully ionized plasma, involving the diffusion-current ratios χ_{e1} and χ_{h1}, cancel in the LTE case and may be combined to give $\frac{1}{en_e}\nabla p_e$ (setting aside a term proportional to ∇p) in the case $T_e \neq T_h$, as they should.

2.3. Reactive thermal conductivity in 2T ionization-equilibrium atomic plasmas

The equation of conservation of ions reads

$$\frac{\partial n_e}{\partial t} + \nabla \cdot [n_e(\mathbf{V}_i + \mathbf{u})] = \omega_e, \quad (23)$$

where $\mathbf{u}$ is the mean mass velocity of the mixture and ω_e is the net rate of production of the ion-electron pairs in volume reactions (ionization and recombination).

The heat of the ionization/recombination is

$$Q_r = \omega_e \left(\frac{5}{2}kT_e + A_a\right). \quad (24)$$

Using equation (23), one can rewrite equation (24) as

$$Q_r = \nabla \cdot \left[\mathbf{q}_r + \left(\frac{5}{2}kT_e + A_a\right) n_e\mathbf{u}\right] + \left(\frac{5}{2}kT_e + A_a\right)\frac{\partial n_e}{\partial t} - n_e\frac{5}{2}k(\mathbf{V}_i + \mathbf{u}) \cdot \nabla T_e, \quad (25)$$

where the density of the reactive heat flux is defined as

$$\mathbf{q}_r = \left(\frac{5}{2}kT_e + A_a\right) n_e\mathbf{V}_i. \quad (26)$$

The Stefan–Maxwell equation (1) for the atoms, $\alpha = a$, does not involve the electric field and may be used, jointly with equations (3) and (4), in order to express $\mathbf{V}_i$, $\mathbf{V}_e$, and $\mathbf{V}_a$ in terms of ∇p_a, $\mathbf{R}_a^T$, and $\mathbf{j}$. In particular,

$$n_e\mathbf{V}_i = F_4\left[\nabla p_a + \mathbf{R}_a^T + \left(\frac{(m_an_a + m_en_e)\, T_eC_{ea}}{m_anD_{ea}} + \frac{m_en_eT_hC_{ia}}{m_anD_{ia}}\right)\frac{k}{e}\mathbf{j} - \frac{m_an_a}{\rho}\nabla p\right], \quad (27)$$

where

$$F_4 = \frac{m_anD_{ea}D_{ia}F_3}{kT_en_e\left(m_an_a + (m_e + m_i)\, n_e\right)}. \quad (28)$$

Substituting equation (27) into equation (26), one can write

$$\mathbf{q}_r = F_4\left(\frac{5}{2}kT_e + A_a\right)\left(\nabla p_a + \mathbf{R}_a^T - \frac{m_an_a}{\rho}\nabla p\right) + G_j\left(\frac{5}{2}kT_e + A_a\right)\mathbf{j}, \quad (29)$$

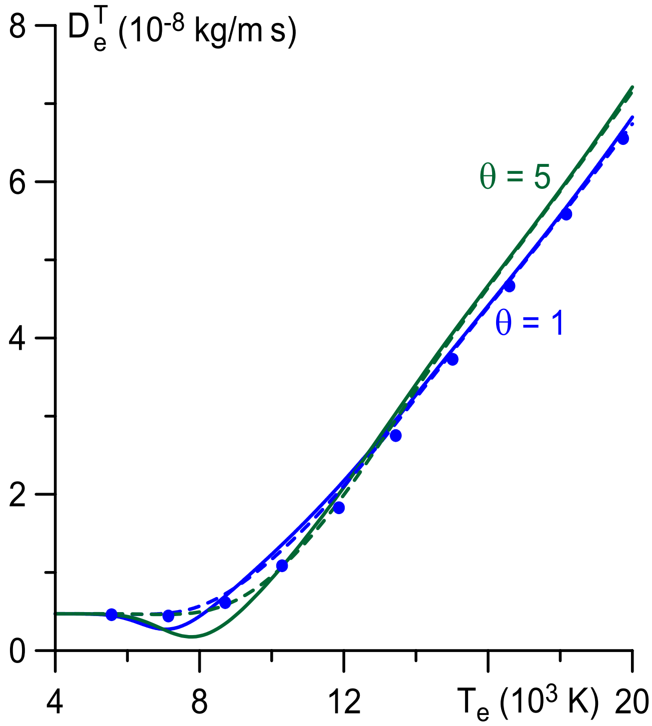

Figure 2. Electron thermal-diffusion coefficient in 2T argon plasma. $p = 1$ bar. Solid: evaluation with the use of data [31]. Dashed: computed values [23]. Circles: computed values [32] ($\theta = 1$).

where

$$G_j = F_4\frac{k}{e}\left(\frac{(m_an_a + m_en_e)\, T_eC_{ea}}{m_anD_{ea}} + \frac{m_en_eT_hC_{ia}}{m_anD_{ia}}\right). \quad (30)$$

Let us now assume that the plasma is in ionization equilibrium and the particle densities are related by the Saha equation (9). Using this equation and Dalton's law, one can express ∇p_a in terms of ∇T_e, ∇T_h, and ∇p, similarly as in section 2.2. Substituting this expression into equation (29), one can express the reactive heat flux as

$$\mathbf{q}_r = -\kappa_{re}\nabla T_e - \kappa_{rh}\nabla T_h + G_j\left(\frac{5}{2}kT_e + A_a\right)\mathbf{j} + G_p\nabla p, \quad (31)$$

where

$$\kappa_{re} = \frac{n_aT_hF_5}{T_e^2}\left[2A_a\left(T_e + T_h\right) + kT_e\left(7T_e + 3T_h\right)\right] - C_a^{(e)}n_akF_6, \quad (32)$$

$$\kappa_{rh} = 2n_akF_5\left(T_e - T_h\right), \quad (33)$$

$$G_p = -2F_5\left(T_h + T_e\right) - \frac{m_an_a}{\rho}F_6, \quad (34)$$

$$F_5 = \frac{kn_eF_6}{p + n_akT_h}, \quad F_6 = F_4\left(\frac{5}{2}kT_e + A_a\right). \quad (35)$$

The coefficients κ_{re} and κ_{rh} may be termed reactive thermal conductivities.

In the LTE case, where $T_e = T_h$, equation (33) assumes the form $\kappa_{rh} = 0$ and the second term on the rhs of equation (31) vanishes. κ_{re} becomes equal to the reactive thermal

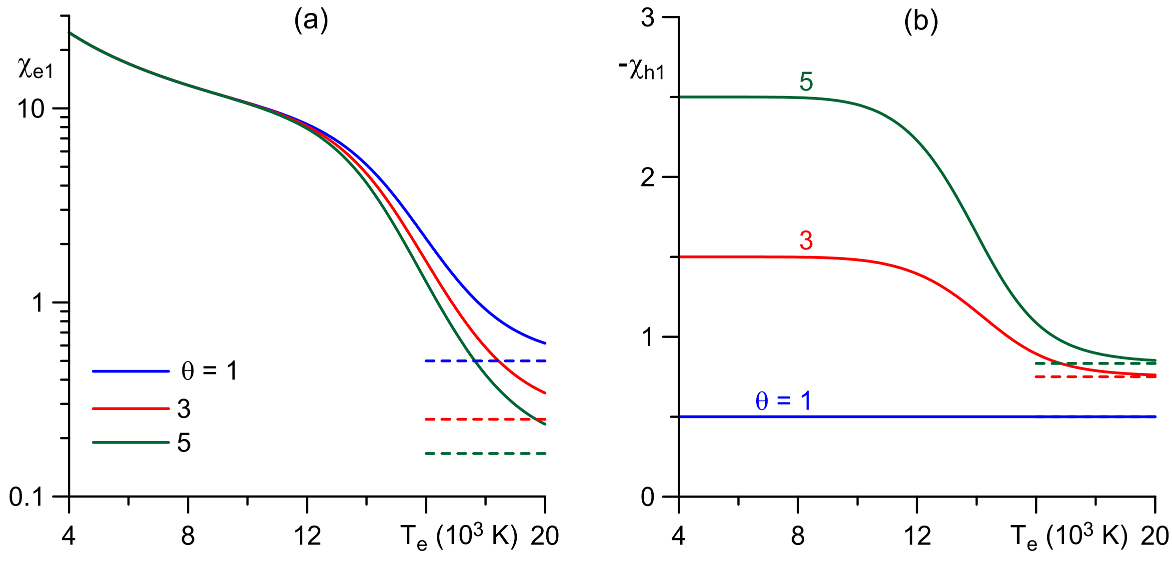

Figure 3. Diffusion–current ratios in 2T argon plasma. $p = 1$ bar. Dashed: asymptotic values in the fully ionized plasma.

conductivity of LTE atomic plasmas, which is well known; e.g. [32]. On the other hand, the above formulas for κ_{re} and κ_{rh}, while not being new from the theoretical point of view, may be useful for rapid evaluation of reactive thermal conductivities in 2T atomic plasmas with singly charged ions under conditions where no calculation results have been published.

There is a question to be addressed before the above results can be applied to 2T plasmas. LTE plasmas models include the energy equation for the plasma on the whole and this equation includes the reactive heat term, in our case, the term $-Q_R$, where Q_R is given by equation (25) supplemented with equation (31). The situation is less certain in 2T plasma models: there are separate energy equations for the electrons and the heavy particles and the term Q_R may, in principle, be included in either equation or split between the two. The authors [3] believe that, as far as atomic plasma is concerned, this term has to be included into the electron energy equation, however this opinion still has not been universally accepted.

The dominating ionization mechanism in atomic plasmas is ionization by electron impact $\mathrm{A} + e \longrightarrow \mathrm{A}^+ + 2e$. It follows from the momentum conservation that velocity of a heavy particle does not change appreciably during such collisions. Hence, the ionization energy can come only from the translational energy of the electron gas. Similarly, velocity of a heavy particle does not change appreciably during recombination $\mathrm{A}^+ + 2e \longrightarrow \mathrm{A} + e$ and the ionization energy released in this reaction is converted into the translational energy of the electron gas. For this reason, the term accounting for ionization/recombination heat in ionization-equilibrium atomic 2T plasmas should appear in the electron energy equation, as proposed in [3]. It should be stressed that this choice is is consistent with standard practice in the modelling of cold plasmas.

Note that this question is indirectly related to the question of Saha equation in 2T plasmas, which was debated some time ago (e.g. discussion in [3, 23, 35, 36]): some authors wrote it in a form that is different from equation (9) and involves the heavy-particle temperature T_h (e.g. [37]). However, since the average relative speed of a collision between an electron and a heavy particle is governed by T_e and is virtually independent of T_h, the reactive rate constants and, consequently, the equilibrium constant, which appears on the rhs of the 2T Saha equation, can hardly depend on T_h. Therefore, there are no reasons to doubt equation (9). Again, this is consistent with standard practice in the modelling of cold plasmas: the rate coefficient of ionization by electron impact is considered to depend on the local reduced electric field or, equivalently, local mean electron energy, but not on the heavy-particle temperature.

3. Evaluation of the transport coefficients

In order to compute the transport coefficients introduced in sections 2.2 and 2.3, in particular, the diffusion–current ratios χ_{e1}, χ_{h1} and the reactive thermal conductivities κ_{re}, κ_{rh}, information on the coefficients appearing in the Stefan–Maxwell equations (1) and (2) is needed. In particular, one can employ approximate formulas for the latter coefficients and relevant material constants for argon, xenon, and mercury plasmas given in [31, 33]. A publicly available online tool computing the transport coefficients in this way has been deployed on internet [34] for convenience. As an example, results of evaluation for 2T atmospheric-pressure argon plasma are shown below and compared, wherever possible, with those from previous studies.

Figure 3 shows the diffusion-current ratios. The dashed lines depict asymptotic values in the limiting case of the fully ionized plasma, given by equations (20) and (22). Since $\chi_{h1} = -1/2$ in the LTE case as indicated in section 2.2, the solid and dashed lines for $\theta = 1$ in figure 3(b) coincide.

Figure 4 shows reactive thermal conductivities κ_{re} and κ_{rh}. Also shown in figure 4(a) are data [32], referring to the case of LTE. The agreement is quite good. Note that the reactive thermal conductivity κ_{rh} for $T_e = T_h$ vanishes, as seen from equation (33), and is not shown in figure 4(b).

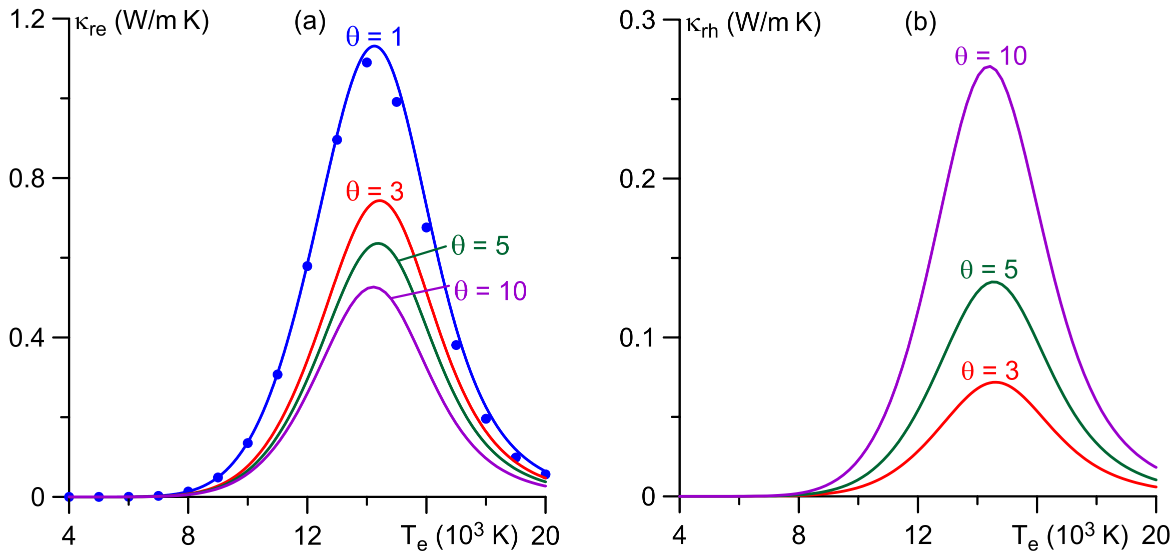

Figure 4. Reactive thermal conductivities in 2T argon plasma. $p = 1$ bar. Solid: this work. Circles: computed values [32] ($\theta = 1$).

A combination of reactive thermal conductivities defined as $\lambda_R = \kappa_{rh} + \theta\kappa_{re}$ is shown in figure 5. There is a good agreement with the computed values from [36]. (The dotted line for the particular case $\theta = 1$ coincides with the solid and is not seen on the graph.) Note that λ_R is considered here for the purposes of comparison and not as a single effective coefficient, which would characterize both electron and heavy-particle heat fluxes; of course, no one single thermal conductivity coefficient would be sufficient to describe the electron and heavy-particle heat fluxes in 2T plasmas.

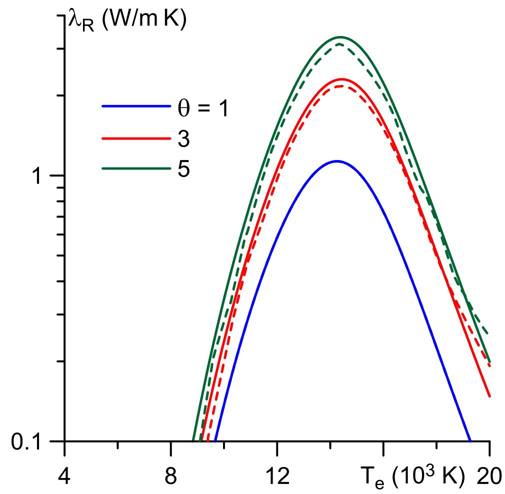

Figure 5. Comparison with results [36]. Argon plasma, $p = 1$ bar. Solid: this work. Dashed: computed data from [36].

4. Describing the negative anode voltage in the framework of LTE modelling

One can hope that the account of diffusion current will allow one to self-consistently describe, in the framework of LTE and 2T models, the negative potential drop and the electric field reversal in front of arc anodes. An illustrative example is shown in figure 6, where computed distributions of the axial current density and its components and of the axial electric field on the axis of a 1 cm long free-burning atmospheric-pressure argon arc under conditions of the experiment [38] are given for two values of arc current $I = 20, 200$ A. Here z is the axial coordinate with the origin at the anode surface, so $z = 0$ is the anode and $z = 10$ mm the cathode.

The solid lines depict distributions of the current density j_z (figure 6(a)) and electric field E_z (figure 6(b)) from [39]. The modelling [39] was performed in the LTE approximation without account of diffusion current caused by partial pressures gradients; in terms of this work, it was set $\chi_{e1} = \chi_{h1} = 0$. Thermal diffusion was taken into account, however its effect was small, hence the axial current density and axial electric field as computed in [39] satisfy the equality $j_z \approx \sigma E_z$. In the coordinate system chosen, j_z is positive (directed from the anode to the cathode) and, consequently, E_z is positive at all points for both currents $I = 20$ A and 200 A.

The dotted lines in figure 6(a) depict the diffusion current caused by partial pressures gradients, $j_z^{(d)} = (\chi_e + \chi_h)\,\frac{\partial}{\partial z}\frac{kT_h}{e}$, evaluated using the temperature gradient from [39]. The dashed lines represent the conduction current evaluated as $j_z^{(E)} = j_z - j_z^{(d)}$ in figure 6(a) and the corresponding electric field $E_z' = j_z^{(E)}/\sigma$ in figure 6(b).

For $I = 200$ A, the diffusion current is small in the arc bulk and appreciable in the vicinity of the electrodes. Near the cathode, $j_z^{(d)}$ is negative and much smaller than the net current density j_z; thus, the effect of diffusion current is not dramatic. In contrast, near the anode $j_z^{(d)}$ is positive and exceeds j_z, so that the conduction current $j_z^{(E)}$ undergoes a reversal. The electric field evaluated with account of the diffusion current, E_z', changes sign in front of the anode as well; the well-known phenomenon of negative potential drop and the electric field reversal in front of high-current arc anodes [8].

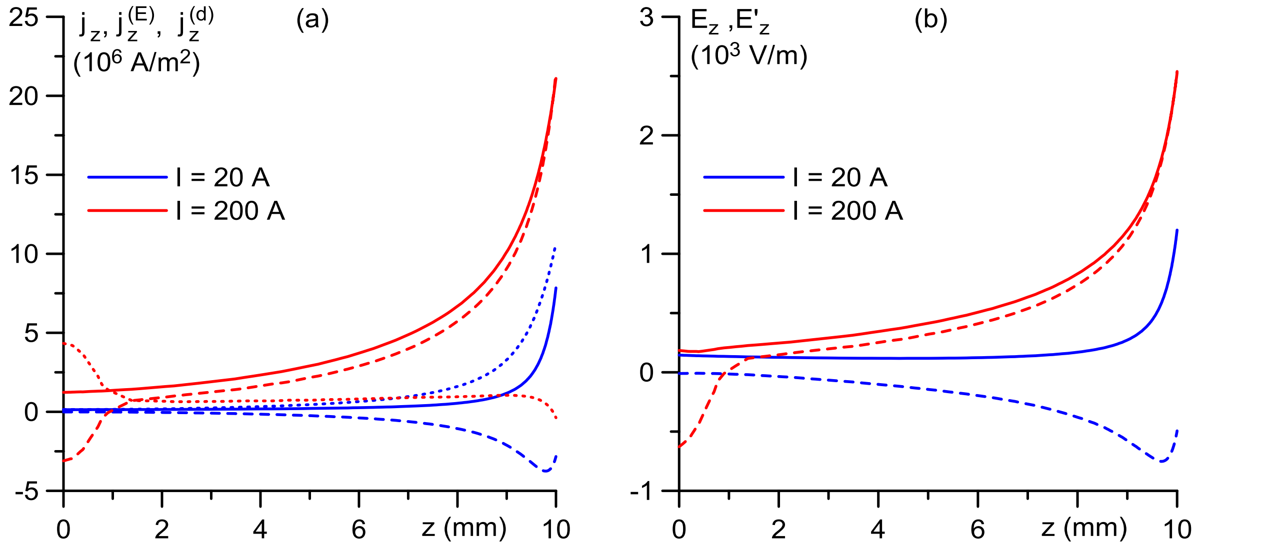

Figure 6. Distributions of the axial current density and electric field on the axis of argon arc under conditions of the experiment [38]. Solid: modelling [39]. Dotted: the diffusion current (a). Dashed: the conduction current (a) and electric field evaluated with account of diffusion current (b).

Previously, this phenomenon was described by means of (more complex) models which do not employ the assumption of LCE and instead include the electron conservation equation; e.g. [13]. The above shows that the self-consistent description of diffusion currents in the framework of the LTE approximation has the potential of adequately describing this phenomenon as well. Note that the above-described distributions of the diffusion current $j_z^{(d)}$ and the electric field E_z' conform to those shown in figure 9 of [13].

For $I = 20$ A, the diffusion current $j_z^{(d)}$ is positive at all points (the electrons diffuse from the cathode to the anode) and slightly exceeds the net current j_z in the arc bulk and near the anode and significantly exceeds j_z near the cathode. Accordingly, the conduction current $j_z^{(E)}$ and the electric field evaluated with account of the diffusion current, E_z', are negative at all points, being small in the arc bulk and near the anode and appreciable near the cathode. Again, these results conform to those given by the non-equilibrium model [13].

5. Conclusions

The diffusion of species in chemical-equilibrium gas mixtures, which is due to variations in the composition of the mixture, affects the energy and charge transport. The former effect is well known and routinely taken into account in terms of the reactive thermal conductivity. The latter effect results in the appearance in Ohm's law in LTE or 2T plasmas, in addition to the conventional term proportional to the electric field (conduction current) and thermal-diffusion terms, of new terms proportional to the temperature gradient (or, in the case of 2T plasmas, proportional to ∇T_e and ∇T_h) and to the plasma pressure gradient. In this work, expressions for these terms are derived, with the use of the Stefan–Maxwell equations, for the particular case of atomic plasmas with singly charged ions. Also proposed is a simple way of approximate evaluation of reactive thermal conductivity in such plasmas. A publicly available online tool, computing the coefficients appearing in the new form of Ohm's law and the reactive thermal conductivities for argon, xenon, and mercury plasmas, has been deployed on internet [34].

As an example, the new form of Ohm's law is used for estimation of the diffusion current in terms of the results of previous LTE modelling of a free-burning atmospheric-pressure argon arc [39]. The results obtained conform to those given by the non-equilibrium model [13] and, in particular, describe the well-known phenomenon of negative potential drop and the electric field reversal in front of anodes of high-current arcs.

The derived formulas refer to the particular case where the plasma temperature is not very high so that multiple ionization is insignificant. This is the case in many applications; for example, in [5], 15 000 K and 1 bar are mentioned as typical thermal plasma conditions. On the other hand, there are situations where the plasma contains a significant amount of multiply charged ions, e.g. in non-transferred arcs, where the temperature can be well over 20 000 K. The formula (10) remains valid in such cases, however formulas for the net diffusion-current ratios χ_e and χ_h have to be re-derived.

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