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The reactive thermal conductivity for a two-temperature plasma

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Abstract

Reliable plasma thermodynamic and transport properties are required for the numerical simulation of thermal plasma systems. Although many databases for the thermal plasma properties at the local thermodynamic equilibrium (LTE) state have been compiled, the database for the two-temperature (2-T) plasma is still far from completeness. There exits considerable confusion in the literature concerning how to calculate the thermodynamic and transport properties, including the reactive thermal conductivity, for the 2-T plasma. In this paper, a detailed derivation for the reactive thermal conductivity of the 2-T argon plasma is presented using two different approaches. The present calculated results for the reactive thermal conductivity are identical to those due to Hsu [5] for the special case of LTE plasma, but are different when the electron temperature is higher than the heavy-particle temperature, the difference increases with increasing electron/heavy-particle temperature ratio, $\theta(= T_e/T_h)$, and becomes quite significant at high θ.

1. Introduction

Reliable data of plasma thermodynamic and transport properties are required for the numerical simulation of thermal plasma systems. The databases concerning the plasma properties at the local thermodynamic equilibrium (LTE) state have been compiled by different authors or research groups (e.g., [1–4]). Sometimes the thermal plasma may deviate from the LTE state, especially in the region near a cold wall (including electrodes) or near the edge of a thermal plasma jet. For such cases the plasma in the non-LTE state is often treated as a two-temperature (2-T) plasma [4], in which two different plasma temperatures, i.e., the electron temperature (T_e) and the heavy-particle temperature (T_h), are employed to characterize the plasma, whereas T_e may be equal to or higher than T_h. Hence, the calculation of 2-T plasma properties attracts attention of many researchers [5–9], but so far no commonly accepted 2-T plasma property databases have been established. There still exists considerable confusion even in the calculation method for the plasma composition, the species diffusion velocities or the reactive thermal conductivity of the 2-T plasma. Perhaps for this reason, the authors of Ref. [9] do not touch the calculation of the reactive thermal conductivity in their study of transport coefficients, and confine themselves to calculating the translational thermal conductivity components of the 2-T argon plasma in their newly published paper. Hence, it is necessary to re-examine carefully what should be modified in the calculation procedure of the properties for the 2-T plasma in comparison with the LTE plasma.

The reactive thermal conductivity is associated with the energy transport caused by the diffusion of different gas species in a gas mixture due to the existence of concentration and temperature gradients. Since the local composition of the gas mixture depends on the local gas temperature(s) for a fixed pressure and at chemical equilibrium state, the energy transport caused by the diffusive gas species can be related to the temperature gradient in the gas mixture and thus the reactive thermal conductivity can be defined and calculated [10]. The

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Nomenclature

Ar	argon atom
Ar^+	singly-ionized argon ion
Ar^{++}	doubly-ionized argon ion
D_{ij}^{a}	ambipolar diffusion coefficient concerning the ith and jth species
E_i, E_d	effective ionization energy of singly- and doubly-ionized ions with respect to the atom ground state
e	electron
h	Planck constant
h_j^*	enthalpy per particle for the jth species
Δh_r^*	enthalpy variation in the rth reaction
k_B	Boltzmann constant
$K_{p,r}$	chemical equilibrium constant for the rth reaction
m	particle mass
n; n_j	total number density; number density of the jth species
p; p_j	total pressure; partial pressure of the jth species
$\vec{q}$	energy flux vector in the gas mixture
$\vec{q}_R$	energy flux vector caused by the species diffusion in the gas mixture
T; T_e; T_h	gas temperature; electron temperature; heavy-particle temperature
x_e	mole fraction of electrons ($x_e = n_e/n$)
$z_{ex,j}^0$	partition function for the internal excitation of the jth heavy particles

Greek symbols

θ	electron/heavy-particle temperature ratio ($\theta = T_e/T_h$)
$\lambda_{re}, \lambda_{rh}$	reactive thermal conductivity components related to ∇T_e and ∇T_h
λ_R	total reactive thermal conductivity defined with respect to ∇T_h
$\lambda_{tr,j}$	translational thermal conductivity due to the jth species
ν_{rj}	stoichiometric coefficient of the jth species in the rth reaction.
ρ	gas density
$\vec{\psi}_j$	particle flux vector of the jth species in the gas mixture

Subscripts

1 or a	atom
2 or d	doubly-ionized ion
3 or i	singly-ionized ion
4 or e	electron
h	heavy-particle (atom, ion)
r	the rth reaction, reactive
R	reactive

calculation method of the reactive thermal conductivity for a non-ionized reacting gas mixture in local chemical equilibrium state was proposed in Ref. [10]. This approach was successfully extended to LTE plasmas in Refs. [1–3], and was also employed in Refs. [5–8] to calculate the reactive thermal conductivity of the 2-T argon plasma. However, there still exist at least two problems which are not well resolved in available studies concerning the calculation of the reactive thermal conductivity for the 2-T plasma. The first is associated with the employment of the Saha equation modified to the 2-T plasma and the second is related with the employment of the expressions for the diffusion velocities of different species under 2-T plasma conditions. The correct form of the 2-T plasma Saha equation for the composition calculation and the correct expressions for the species diffusion velocities under 2-T plasma conditions were discussed in some details, respectively, in our previous papers [11,12]. Having had the results obtained in Refs. [11,12], the present paper will focus to the calculation of reactive thermal conductivity of the 2-T argon plasma.

So far two different approaches were used to calculate the reactive thermal conductivity for the 2-T plasma. The first one was proposed in Ref. [6], in which the expressions of the reactive thermal conductivity were derived for the 2-T plasma by using its relationship to the species number densities and their derivatives with respect to plasma temperature(s). The second one [5,7] was based on the employment of the modified form of the Van't Hoff's equation (or chemical equilibrium constant) as used in [1,10]. Although these two approaches seem to be equally feasible, their final expressions for the reactive thermal conductivity of 2-T plasma are different from each other, in their formulations. Hence, it is interesting to know whether the calculated results are identical for the reactive thermal conductivity obtained using the two different approaches.

In this paper, detailed derivations are presented concerning the reactive thermal conductivity for the 2-T plasma using the two different approaches mentioned above, and typical calculated results will be presented for the reactive thermal conductivity of the 2-T argon plasma and compared with those obtained in previous studies.

2. Definition of the reactive thermal conductivity

Suppose a stationary plasma consisting of N species and carrying temperature and concentration gradients, the energy flux from the region with higher temperatures to the region with lower temperatures can be calculated by

$$\vec{q} = -\sum_s \lambda_{\mathrm{tr},s} \nabla T_s + \sum_s h_s^* \vec{\psi}_s \tag{1}$$

where $\lambda_{\mathrm{tr},s}$ is the translational thermal conductivity component associated with the kinetic energy transport of the sth species, T_s is the characteristic temperature of the sth species. h_s^* is the enthalpy per particle, and $\vec{\psi}_s$ is the particle flux vector due to the diffusion of the sth species [1/(m^2 s)]. Similarly to the case studied in [10] for the non-ionized gas mixture, the reactive thermal conductivity for a plasma can be defined by

$$\vec{q}_\mathrm{R} = \sum_s h_s^* \vec{\psi}_s = -\lambda_{\mathrm{R},j} \nabla T_j \tag{2}$$

where $\vec{q}_\mathrm{R}$ is the additional energy flux caused by the diffusive transport due to various gas species, T_j is of the jth characteristic temperature, and $\lambda_{\mathrm{R},j}$ is the reactive thermal conductivity defined with respect to the temperature gradient ∇T_j. For the 2-T plasma studied here, there exist generally two different characteristic temperatures, i.e. the electron temperature T_e and the heavy-particle (atom, ion, etc.) temperature T_h. Hence, the choice of the temperature gradient ∇T_j in Eq. (2) should be clearly indicated when the calculated values of the reactive thermal conductivity are presented, although the calculated results with respect to ∇T_h can be easily converted to those with respect to ∇T_e for a fixed electron/heavy-particle temperature ratio. In this paper, the heavy-particle temperature gradient ∇T_h is chosen to define the reactive thermal conductivity of the 2-T plasma, and this reactive thermal conductivity will be denoted by λ_R. Eq. (2) can thus be rewritten as

$$\vec{q}_\mathrm{R} = \sum_s h_s^* \vec{\psi}_s = -\lambda_\mathrm{R} \nabla T_\mathrm{h} \tag{3}$$

In order to calculate the reactive thermal conductivity as the quotient of $-\sum_s h_s^* \vec{\psi}_s$ divided by ∇T_h, one needs obviously to calculate the particle flux vectors $\vec{\psi}_s$ for each species. It is expected that the calculation of the reactive thermal conductivity will involve the gas pressure, the plasma composition, the electron temperature and heavy-particle temperature, the reaction heats of the ionization-recombination reactions, and the multi-component diffusion coefficients.

3. Theoretical derivation with the first approach

3.1. Description of the 2-T argon plasma system

For simplicity, let us consider a 2-T argon plasma system consisting of four components, i.e. argon atoms, singly-ionized ions, doubly-ionized ions and electrons. The singly- and doubly-ionized reactions taking place simultaneously in such a plasma system can be expressed as follows:

$$\mathrm{Ar} = \mathrm{Ar}^+ + \mathrm{e} \tag{4a}$$

$$\mathrm{Ar}^{++} = \mathrm{Ar}^+ - \mathrm{e} \tag{4b}$$

where Ar, Ar^{++}, Ar^+ and e represent argon atoms, doubly-ionized ions, singly-ionized ions and electrons, and will be denoted with subscripts 1, 2, 3 and 4 or a, d, i and e, respectively. It is noted that the species Ar only appears in Eq. (4a), whereas the species Ar^{++} only appears in Eq. (4b).

3.2. The modified Saha equations for the 2-T argon plasma

Using correct 2-T plasma Saha equations is the prerequisite for the calculation of the number densities of the gas species, and the employment of the Saha equations will affect the calculated results of the thermodynamic and transport properties of the plasma. In the literature, two different forms of Saha equation were employed for the 2-T plasma. This subject was discussed in some detail in out previous paper [11], with a rigorous thermodynamic derivation of the Saha equations modified to a 2-T plasma system. The correct expressions of the Saha equation (or mass action law) for the 2-T argon plasma system with ionization reactions described by Eqs. (4a) and (4b) can be expressed as

$$\frac{n_\mathrm{e} n_\mathrm{i}}{n_\mathrm{a}} = \frac{2 z_{\mathrm{ex},i}^0}{z_{\mathrm{ex},a}^0} \left(\frac{2\pi m_\mathrm{e} k_\mathrm{B} T_\mathrm{e}}{h^2} \right)^{3/2} \exp\left(-\frac{E_\mathrm{i}}{k_\mathrm{B} T_\mathrm{e}} \right) \tag{5a}$$

$$\frac{n_\mathrm{e} n_\mathrm{d}}{n_\mathrm{i}} = \frac{2 z_{\mathrm{ex},d}^0}{z_{\mathrm{ex},i}^0} \left(\frac{2\pi m_\mathrm{e} k_\mathrm{B} T_\mathrm{e}}{h^2} \right)^{3/2} \exp\left(-\frac{E_\mathrm{d} - E_\mathrm{i}}{k_\mathrm{B} T_\mathrm{e}} \right) \tag{5b}$$

where $z_{\mathrm{ex},a}^0$, $z_{\mathrm{ex},i}^0$ and $z_{\mathrm{ex},d}^0$ are the partition functions for the internal excitation of atoms, singly-ionized ions and doubly-ionized ions, while E_i and E_d are the effective ionization energy (including the lowering of the ionization energy [4]) of singly-ionized ions and doubly-ionized ions with respect to the atom ground state. Eqs. (5a) and (5b) are so-called 2-T Saha equations. On the other hand, the following Saha equations have been employed for the calculation of 2-T plasma properties in Refs. [5,6,8]:

$$n_\mathrm{e} \left(\frac{n_\mathrm{i}}{n_\mathrm{a}} \right)^{1/\theta} = \frac{2 z_{\mathrm{ex},i}^0}{z_{\mathrm{ex},a}^0} \left(\frac{2\pi m_\mathrm{e} k_\mathrm{B} T_\mathrm{e}}{h^2} \right)^{3/2} \exp\left(-\frac{E_\mathrm{i}}{k_\mathrm{B} T_\mathrm{e}} \right) \tag{6a}$$

$$n_\mathrm{e} \left(\frac{n_\mathrm{d}}{n_\mathrm{i}} \right)^{1/\theta} = \frac{2 z_{\mathrm{ex},d}^0}{z_{\mathrm{ex},i}^0} \left(\frac{2\pi m_\mathrm{e} k_\mathrm{B} T_\mathrm{e}}{h^2} \right)^{3/2} \exp\left(-\frac{E_\mathrm{d} - E_\mathrm{i}}{k_\mathrm{B} T_\mathrm{e}} \right) \tag{6b}$$

where θ is the electron/heavy-particle temperature ratio, i.e. $\theta = T_e/T_h$. However, the thermodynamic derivation in [13] for Eqs. (6a) and (6b) has been proved to be incorrect [11]. As a result, the 2-T plasma composition and properties based on employing Eqs. (6a) and (6b) are questionable.

3.3. Expressions for the diffusion velocities

The expressions for the diffusion velocities or particle fluxes under 2-T plasma conditions are also required for the calculation the reactive thermal conductivity. In Ref. [5], the expression of the diffusion driving force for the LTE plasmas was employed without modification for calculating the diffusion velocities of the different gas species in the 2-T argon plasma. Consequently, the correctness of the calculated results of the diffusion velocities or particle fluxes and thus the reactive thermal conductivity for the 2-T argon plasma presented in Ref. [5] is questionable. In Ref. [12], the expressions for the diffusion driving force, ambipolar diffusion coefficients, ambipolar thermal diffusion coefficients, diffusion velocities and the electric conductivity of the 2-T plasma were presented. The research results presented in Ref. [12] can be summarized as follows: (i) The expression for the diffusion driving force under 2-T plasma conditions is different from that for the LTE plasmas [1,5] or for the non-ionized reacting gas mixtures [10]. (ii) The newly derived expressions for the diffusion driving force, the ambipolar diffusion coefficients, the ambipolar thermal diffusion coefficients, the diffusion velocities and the electric conductivity for the 2-T plasma can be reduced to their counterparts for the LTE plasma or for the single-temperature gas mixture, as expected.

Based on the derivation presented in Ref. [12], if we neglect the influence due to the thermal diffusion and external force (except for internal electric field), the number flux vector of the sth species for a fixed total pressure can be written as

$$\vec{\psi}_s = \frac{n}{\rho k_B T_s} \sum_j \frac{T_s}{T_j} m_j D^a_{sj} \nabla p_j \tag{7}$$

where D^a_{sj} is the ambipolar diffusion coefficient [12].

When the plasma system is in a quasi-steady state, the following relations will be applicable to the reactions described by Eqs. (4a) and (4b):

$$\vec{\psi}_3 = -(\vec{\psi}_1 + \vec{\psi}_2) \tag{8a}$$

$$\vec{\psi}_4 = 2\vec{\psi}_2 + \vec{\psi}_3 = -\vec{\psi}_1 + \vec{\psi}_2 \tag{8b}$$

Substituting Eqs. (8a) and (8b) into Eq. (3), one can obtain the following expression:

$$\vec{q}_R = \sum_{s=1}^{4} h^*_s \vec{\psi}_s = -\sum_{r=1}^{2} \Delta h^*_r \vec{\psi}_r = -\lambda_R \nabla T_h \tag{9}$$

where Δh^*_r is the enthalpy variation of the rth reaction described by Eq. (4a) ($r = 1$) or Eq. (4b) ($r = 2$), and can be expressed as

$$\Delta h^*_1 = h^*_i + h^*_e - h^*_a = \frac{5}{2} k_B T_e + k_B T_e^2 \left(\frac{\partial \ln z^0_{ex,i}}{\partial T_e} - \frac{\partial \ln z^0_{ex,a}}{\partial T_e} \right) + E_i \tag{10a}$$

$$\Delta h^*_2 = h^*_i - h^*_e - h^*_d = -\left[\frac{5}{2} k_B T_e + k_B T_e^2 \left(\frac{\partial \ln z^0_{ex,d}}{\partial T_e} - \frac{\partial \ln z^0_{ex,i}}{\partial T_e} \right) + E_d - E_i \right] \tag{10b}$$

in which

$$h^*_a = \frac{5}{2} k_B T_h + k_B T_e^2 \frac{\partial \ln z^0_{ex,a}}{\partial T_e} \tag{11a}$$

$$h^*_i = \frac{5}{2} k_B T_h + k_B T_e^2 \frac{\partial \ln z^0_{ex,i}}{\partial T_e} + E_i \tag{11b}$$

$$h^*_d = \frac{5}{2} k_B T_h + k_B T_e^2 \frac{\partial \ln z^0_{ex,d}}{\partial T_e} + E_d \tag{11c}$$

$$h^*_e = \frac{5}{2} k_B T_e \tag{11d}$$

denote the enthalpies per particle for atoms, singly-ionized ions, doubly-ionized ions and electrons, respectively.

3.4. Derivation of the reactive thermal conductivity (approach 1)

Now, a detailed derivation will be given for the reactive thermal conductivity of the 2-T argon plasma using the approach similar to that presented in Ref. [6]. It should be pointed out that a three-component gas was assumed in Ref. [6], i.e. doubly-ionized ionization is completely neglected. Although this assumption is valid at lower plasma temperatures where only single ionization is important, it is not applicable to higher plasma temperatures where both single ionization and double ionization cannot be ignored. Here, the plasma system is assumed to be composed of four components and thus the two ionization–recombination reactions described by Eqs. (4a) and (4b) are involved.

Substituting Eq. (7) into Eq. (9), we have

$$\vec{q}_R = -\sum_{r=1}^{2} \Delta h^*_r \vec{\psi}_r = -\sum_{r=1}^{2} \frac{n}{\rho k_B T_h} \Delta h^*_r \sum_{j=1}^{4} \frac{T_h}{T_j} m_j D^a_{rj} \nabla p_j \tag{12}$$

As the partial pressure of the jth species, p_j, is the function of the electron temperature and the heavy particle temperature for a fixed total pressure, ∇p_j can be expressed as

$$\nabla p_j = \frac{\partial p_j}{\partial T_\mathrm{e}}\nabla T_\mathrm{e} + \frac{\partial p_j}{\partial T_\mathrm{h}}\nabla T_\mathrm{h} \quad (j = 1,2,3,4) \tag{13}$$

Substituting Eq. (13) into Eq. (12) results in

$$\begin{aligned}\vec{q}_\mathrm{R} &= -\sum_{r=1}^{2}\frac{n}{\rho k_\mathrm{B}T_\mathrm{h}}\Delta h_r^*\left(\sum_{j=1}^{3} m_j D_{rj}^\mathrm{a}\frac{\partial p_j}{\partial T_\mathrm{e}} + \frac{T_\mathrm{h}}{T_\mathrm{e}} m_\mathrm{e} D_{re}^\mathrm{a}\frac{\partial p_\mathrm{e}}{\partial T_\mathrm{e}}\right)\nabla T_\mathrm{e} \\ &\quad -\sum_{r=1}^{2}\frac{n}{\rho k_\mathrm{B}T_\mathrm{h}}\Delta h_r^*\left(\sum_{j=1}^{3} m_j D_{rj}^\mathrm{a}\frac{\partial p_j}{\partial T_\mathrm{h}} + \frac{T_\mathrm{h}}{T_\mathrm{e}} m_\mathrm{e} D_{re}^\mathrm{a}\frac{\partial p_\mathrm{e}}{\partial T_\mathrm{h}}\right)\nabla T_\mathrm{h} \\ &= -k_{r\mathrm{e}}\nabla T_\mathrm{e} - k_{r\mathrm{h}}\nabla T_\mathrm{h}\end{aligned} \tag{14}$$

where

$$k_{r\mathrm{e}} = \sum_{r=1}^{2}\frac{n}{\rho k_\mathrm{B}T_\mathrm{h}}\Delta h_r^*\left(\sum_{j=1}^{3} m_j D_{rj}^\mathrm{a}\frac{\partial p_j}{\partial T_\mathrm{e}} + \frac{T_\mathrm{h}}{T_\mathrm{e}} m_\mathrm{e} D_{re}^\mathrm{a}\frac{\partial p_\mathrm{e}}{\partial T_\mathrm{e}}\right) \tag{15a}$$

$$k_{r\mathrm{h}} = \sum_{r=1}^{2}\frac{n}{\rho k_\mathrm{B}T_\mathrm{h}}\Delta h_r^*\left(\sum_{j=1}^{3} m_j D_{rj}^\mathrm{a}\frac{\partial p_j}{\partial T_\mathrm{h}} + \frac{T_\mathrm{h}}{T_\mathrm{e}} m_\mathrm{e} D_{re}^\mathrm{a}\frac{\partial p_\mathrm{e}}{\partial T_\mathrm{h}}\right) \tag{15b}$$

can be treated as the reactive thermal conductivity components related to ∇T_e and ∇T_h, respectively.

Having Eqs. (15a) and (15b), the subsequent task is to derive the expressions for $\partial p_j/\partial T_\mathrm{e}$ $(j = 1,2,3)$, $\partial p_\mathrm{e}/\partial T_\mathrm{e}$, $\partial p_j/\partial T_\mathrm{h}$ $(j = 1,2,3)$ and $\partial p_\mathrm{e}/\partial T_\mathrm{h}$. The plasma composition can be determined by the set of equations including the Saha equations (5a) and (5b), the Dalton's law and the quasi-neutrality condition of the plasma.

The Dalton's law gives

$$p = \sum_{s=1}^{4} p_s = \sum_{s=1}^{3} p_s + p_\mathrm{e} \tag{16}$$

For a fixed total pressure, the partial derivatives of the partial pressures with respect to T_e or T_h can be obtained from Eq. (16) as:

$$\sum_{s=1}^{3}\frac{\partial p_s}{\partial T_\mathrm{e}} + \frac{\partial p_\mathrm{e}}{\partial T_\mathrm{e}} = 0 \tag{17a}$$

$$\sum_{s=1}^{3}\frac{\partial p_s}{\partial T_\mathrm{h}} + \frac{\partial p_\mathrm{e}}{\partial T_\mathrm{h}} = 0 \tag{17b}$$

Then, the Saha equations (5a) and (5b) for the 2-T argon plasma can be rewritten as

$$\frac{p_\mathrm{e}p_\mathrm{i}}{p_\mathrm{a}} = \frac{(2k_\mathrm{B}T_\mathrm{e})z_{\mathrm{ex},i}^0}{z_{\mathrm{ex},a}^0}\left(\frac{2\pi m_\mathrm{e}k_\mathrm{B}T_\mathrm{e}}{h^2}\right)^{\frac{3}{2}}\exp\left(-\frac{E_\mathrm{i}}{k_\mathrm{B}T_\mathrm{e}}\right) \tag{18a}$$

$$\frac{p_\mathrm{e}p_\mathrm{d}}{p_\mathrm{i}} = \frac{(2k_\mathrm{B}T_\mathrm{e})z_{\mathrm{ex},d}^0}{z_{\mathrm{ex},i}^0}\left(\frac{2\pi m_\mathrm{e}k_\mathrm{B}T_\mathrm{e}}{h^2}\right)^{\frac{3}{2}}\exp\left(-\frac{E_\mathrm{d}-E_\mathrm{i}}{k_\mathrm{B}T_\mathrm{e}}\right) \tag{18b}$$

Taking logarithms of both sides of Eqs. (18a) and (18a), and calculating their partial differentiation with respect to T_e or T_h, we get

$$\frac{1}{p_4}\frac{\partial p_4}{\partial T_\mathrm{e}} + \frac{1}{p_3}\frac{\partial p_3}{\partial T_\mathrm{e}} - \frac{1}{p_1}\frac{\partial p_1}{\partial T_\mathrm{e}} = \frac{5}{2}\frac{1}{T_\mathrm{e}} + \frac{\partial \ln z_{\mathrm{ex},i}^0}{\partial T_\mathrm{e}} - \frac{\partial \ln z_{\mathrm{ex},a}^0}{\partial T_\mathrm{e}} + \frac{E_\mathrm{i}}{k_\mathrm{B}T_\mathrm{e}^2} \tag{19a}$$

$$\frac{1}{p_4}\frac{\partial p_4}{\partial T_\mathrm{e}} + \frac{1}{p_2}\frac{\partial p_2}{\partial T_\mathrm{e}} - \frac{1}{p_3}\frac{\partial p_3}{\partial T_\mathrm{e}} = \frac{5}{2}\frac{1}{T_\mathrm{e}} + \frac{\partial \ln z_{\mathrm{ex},d}^0}{\partial T_\mathrm{e}} - \frac{\partial \ln z_{\mathrm{ex},i}^0}{\partial T_\mathrm{e}} + \frac{E_\mathrm{d}-E_\mathrm{i}}{k_\mathrm{B}T_\mathrm{e}^2} \tag{19b}$$

$$\frac{1}{p_4}\frac{\partial p_4}{\partial T_\mathrm{h}} + \frac{1}{p_3}\frac{\partial p_3}{\partial T_\mathrm{h}} - \frac{1}{p_1}\frac{\partial p_1}{\partial T_\mathrm{h}} = 0 \tag{19c}$$

$$\frac{1}{p_4}\frac{\partial p_4}{\partial T_\mathrm{h}} + \frac{1}{p_2}\frac{\partial p_2}{\partial T_\mathrm{h}} - \frac{1}{p_3}\frac{\partial p_3}{\partial T_\mathrm{h}} = 0 \tag{19d}$$

Eqs. (17a), (19a) and (19b) and Eqs. (17b), (19c) and (19d) constitute two sets of linear equations as follows:

$$AX_1 = b_1\frac{\partial p_\mathrm{e}}{\partial T_\mathrm{e}} + b_2 \tag{20a}$$

$$AX_2 = b_1\frac{\partial p_\mathrm{e}}{\partial T_\mathrm{h}} \tag{20b}$$

where

$$A = \begin{bmatrix} 1 & 1 & 1 \\ 1/p_1 & 0 & -1/p_3 \\ 0 & -1/p_2 & 1/p_3 \end{bmatrix},$$

$$X_1 = \begin{bmatrix} \partial p_1/\partial T_\mathrm{e} \\ \partial p_2/\partial T_\mathrm{e} \\ \partial p_3/\partial T_\mathrm{e} \end{bmatrix}, \quad X_2 = \begin{bmatrix} \partial p_1/\partial T_\mathrm{h} \\ \partial p_2/\partial T_\mathrm{h} \\ \partial p_3/\partial T_\mathrm{h} \end{bmatrix} \tag{21a}$$

$$b_1 = \begin{bmatrix} -1 \\ 1/p_\mathrm{e} \\ 1/p_\mathrm{e} \end{bmatrix}, \quad b_2 = \begin{bmatrix} 0 \\ -C_1 \\ -C_2 \end{bmatrix} \tag{21b}$$

and

$$C_1 = \frac{5}{2}\frac{1}{T_\mathrm{e}} + \frac{\partial \ln z_{\mathrm{ex},i}^0}{\partial T_\mathrm{e}} - \frac{\partial \ln z_{\mathrm{ex},a}^0}{\partial T_\mathrm{e}} + \frac{E_\mathrm{i}}{k_\mathrm{B}T_\mathrm{e}^2} \tag{22a}$$

$$C_2 = \frac{5}{2}\frac{1}{T_\mathrm{e}} + \frac{\partial \ln z_{\mathrm{ex},d}^0}{\partial T_\mathrm{e}} - \frac{\partial \ln z_{\mathrm{ex},i}^0}{\partial T_\mathrm{e}} + \frac{E_\mathrm{d}-E_\mathrm{i}}{k_\mathrm{B}T_\mathrm{e}^2} \tag{22b}$$

According to Cramer's rule, the solution of Eq. (20a) can be expressed as

$$\frac{\partial p_1}{\partial T_\mathrm{e}} = \frac{|A_1^1|}{|A|} + \frac{|A_1^2|}{|A|} \tag{23a}$$

$$\frac{\partial p_2}{\partial T_e} = \frac{|A_2^1|}{|A|} + \frac{|A_2^2|}{|A|} \tag{23b}$$

$$\frac{\partial p_3}{\partial T_e} = \frac{|A_3^1|}{|A|} + \frac{|A_3^2|}{|A|} \tag{23c}$$

where

$$|A_1^1| = \left(\frac{1}{p_2p_3} - \frac{2}{p_3p_4} - \frac{1}{p_2p_4}\right)\frac{\partial p_e}{\partial T_e} \tag{24a}$$

$$|A_1^2| = \left(\frac{1}{p_2} + \frac{1}{p_3}\right)C_1 + \frac{C_2}{p_3} \tag{24b}$$

$$|A_2^1| = \left(\frac{1}{p_1p_3} + \frac{2}{p_3p_4} + \frac{1}{p_1p_4}\right)\frac{\partial p_e}{\partial T_e} \tag{24c}$$

$$|A_2^2| = -\frac{C_1}{p_3} - \left(\frac{1}{p_1} + \frac{1}{p_3}\right)C_2 \tag{24d}$$

$$|A_3^1| = \left(\frac{1}{p_2p_4} - \frac{1}{p_1p_4} + \frac{1}{p_1p_2}\right)\frac{\partial p_e}{\partial T_e} \tag{24e}$$

$$|A_3^2| = -\frac{C_1}{p_2} + \frac{C_2}{p_1} \tag{24f}$$

Similarly, the solution of Eq. (20b) is:

$$\frac{\partial p_1}{\partial T_h} = \frac{\left(\frac{1}{p_2p_3} - \frac{2}{p_3p_4} - \frac{1}{p_2p_4}\right)}{|A|}\frac{\partial p_e}{\partial T_h} \tag{25a}$$

$$\frac{\partial p_2}{\partial T_h} = \frac{\left(\frac{1}{p_1p_3} + \frac{2}{p_3p_4} + \frac{1}{p_1p_4}\right)}{|A|}\frac{\partial p_e}{\partial T_h} \tag{25b}$$

$$\frac{\partial p_3}{\partial T_h} = \frac{\left(\frac{1}{p_2p_4} - \frac{1}{p_1p_4} + \frac{1}{p_1p_2}\right)}{|A|}\frac{\partial p_e}{\partial T_h} \tag{25c}$$

where

$$|A| = -\left(\frac{1}{p_2p_3} + \frac{1}{p_1p_3} + \frac{1}{p_1p_2}\right) \tag{25d}$$

Substituting Eqs. (23a)–(23c) into Eq. (15a) and substituting Eqs. (25a)–(25c) into Eq. (15b), the expressions for k_{re} and k_{rh} in Eq. (14) can be rewritten as

$$\begin{aligned} k_{re} = \frac{nm_h}{\rho k_B T_h}\Bigg\{ & \Delta h_1^*\Bigg[\left(A_1D_{11}^a + A_2D_{12}^a + A_3D_{13}^a + \frac{m_e}{\theta m_h}D_{14}^a\right)\frac{\partial p_e}{\partial T_e} + (B_1D_{11}^a + B_2D_{12}^a + B_3D_{13}^a)\Bigg] \\ & + \Delta h_2^*\Bigg[\left(A_1D_{21}^a + A_2D_{22}^a + A_3D_{23}^a + \frac{m_e}{\theta m_h}D_{24}^a\right)\frac{\partial p_e}{\partial T_e} + (B_1D_{21}^a + B_2D_{22}^a + B_3D_{23}^a)\Bigg]\Bigg\} \end{aligned} \tag{26a}$$

$$\begin{aligned} k_{rh} = \frac{nm_h}{\rho k_B T_h}\Bigg\{ & \Delta h_1^*\Bigg[\left(A_1D_{11}^a + A_2D_{12}^a + A_3D_{13}^a + \frac{m_e}{\theta m_h}D_{14}^a\right)\frac{\partial p_e}{\partial T_h}\Bigg] \\ & + \Delta h_2^*\Bigg[\left(A_1D_{21}^a + A_2D_{22}^a + A_3D_{23}^a + \frac{m_e}{\theta m_h}D_{24}^a\right)\frac{\partial p_e}{\partial T_h}\Bigg]\Bigg\} \end{aligned} \tag{26b}$$

where

$$A_1 = \left(\frac{1}{p_2p_3} - \frac{2}{p_3p_4} - \frac{1}{p_2p_4}\right)\Big/\left[-\left(\frac{1}{p_2p_3} + \frac{1}{p_1p_3} + \frac{1}{p_1p_2}\right)\right] \tag{27a}$$

$$A_2 = \left(\frac{1}{p_1p_3} + \frac{2}{p_3p_4} + \frac{1}{p_1p_4}\right)\Big/\left[-\left(\frac{1}{p_2p_3} + \frac{1}{p_1p_3} + \frac{1}{p_1p_2}\right)\right] \tag{27b}$$

$$A_3 = \left(\frac{1}{p_2p_4} - \frac{1}{p_1p_4} + \frac{1}{p_1p_2}\right)\Big/\left[-\left(\frac{1}{p_2p_3} + \frac{1}{p_1p_3} + \frac{1}{p_1p_2}\right)\right] \tag{27c}$$

$$B_1 = \left[\left(\frac{1}{p_2} + \frac{1}{p_3}\right)C_1 + \frac{C_2}{p_3}\right]\Big/\left[-\left(\frac{1}{p_2p_3} + \frac{1}{p_1p_3} + \frac{1}{p_1p_2}\right)\right] \tag{27d}$$

$$B_2 = \left[-\frac{C_1}{p_3} - \left(\frac{1}{p_1} + \frac{1}{p_3}\right)C_2\right]\Big/\left[-\left(\frac{1}{p_2p_3} + \frac{1}{p_1p_3} + \frac{1}{p_1p_2}\right)\right] \tag{27e}$$

$$B_3 = \left[-\frac{C_1}{p_2} + \frac{C_2}{p_1}\right]\Big/\left[-\left(\frac{1}{p_2p_3} + \frac{1}{p_1p_3} + \frac{1}{p_1p_2}\right)\right] \tag{27f}$$

The partial pressure of electrons can be expressed by

$$p_e = n_e k_B T_e \tag{28}$$

For a fixed total pressure,

$$\frac{\partial p_e}{\partial T_e} = k_B T_e \frac{\partial n_e}{\partial T_e} + n_e k_B \tag{29a}$$

$$\frac{\partial p_e}{\partial T_h} = k_B T_e \frac{\partial n_e}{\partial T_h} \tag{29b}$$

Substituting Eq. (29a) into Eq. (26a) and substituting Eq. (29b) into Eq. (26b), results in

$$\begin{aligned} k_{re} = \frac{nm_h}{\rho k_B T_h}\Bigg\{ & \Delta h_1^*\Bigg[\left(A_1D_{11}^a + A_2D_{12}^a + A_3D_{13}^a + \frac{m_e}{\theta m_h}D_{14}^a\right) \times \left(k_B T_e \frac{\partial n_e}{\partial T_e} + n_e k_B\right) + (B_1D_{11}^a + B_2D_{12}^a + B_3D_{13}^a)\Bigg] \\ & + \Delta h_2^*\Bigg[\left(A_1D_{21}^a + A_2D_{22}^a + A_3D_{23}^a + \frac{m_e}{\theta m_h}D_{24}^a\right) \times \left(k_B T_e \frac{\partial n_e}{\partial T_e} + n_e k_B\right) + (B_1D_{21}^a + B_2D_{22}^a + B_3D_{23}^a)\Bigg]\Bigg\} \end{aligned} \tag{30a}$$

$$k_{r\mathrm{h}} = \frac{nm_\mathrm{h}}{\rho k_\mathrm{B} T_\mathrm{h}} \left\{ \Delta h_1^* \left[\left(A_1 D_{11}^\mathrm{a} + A_2 D_{12}^\mathrm{a} + A_3 D_{13}^\mathrm{a} + \frac{m_\mathrm{e}}{\theta m_\mathrm{h}} D_{14}^\mathrm{a} \right) \times k_\mathrm{B} T_\mathrm{e} \frac{\partial n_\mathrm{e}}{\partial T_\mathrm{h}} \right] + \Delta h_2^* \left[\left(A_1 D_{21}^\mathrm{a} + A_2 D_{22}^\mathrm{a} + A_3 D_{23}^\mathrm{a} + \frac{m_\mathrm{e}}{\theta m_\mathrm{h}} D_{24}^\mathrm{a} \right) k_\mathrm{B} T_\mathrm{e} \frac{\partial n_\mathrm{e}}{\partial T_\mathrm{h}} \right] \right\} \tag{30b}$$

It can be seen from Eqs. (30a) and (30b) that in order to calculate the reactive thermal conductivity, the next step should constitute the relation between $\partial n_\mathrm{e}/\partial T_\mathrm{e}$, $\partial n_\mathrm{e}/\partial T_\mathrm{h}$ and other plasma parameters, such as the number densities of the gas species, the electron temperature, heavy-particle temperature, and so on.

As is well known, the quasi-neutrality condition of the plasma gives

$$n_\mathrm{i} + 2n_\mathrm{d} - n_\mathrm{e} = 0 \tag{31}$$

Another auxiliary condition is the following relation between the number densities:

$$n = n_\mathrm{a} + n_\mathrm{i} + n_\mathrm{d} + n_\mathrm{e} \tag{32}$$

From Eqs. (31) and (32) the following partial differentiations with respect to T_e or T_h can be obtained:

$$\frac{\partial n_\mathrm{i}}{\partial T_\mathrm{e}} + 2\frac{\partial n_\mathrm{d}}{\partial T_\mathrm{e}} - \frac{\partial n_\mathrm{e}}{\partial T_\mathrm{e}} = 0 \tag{33a}$$

$$\frac{\partial n_\mathrm{i}}{\partial T_\mathrm{h}} + 2\frac{\partial n_\mathrm{d}}{\partial T_\mathrm{h}} - \frac{\partial n_\mathrm{e}}{\partial T_\mathrm{h}} = 0 \tag{33b}$$

$$\frac{\partial n_\mathrm{a}}{\partial T_\mathrm{e}} + \frac{\partial n_\mathrm{i}}{\partial T_\mathrm{e}} + \frac{\partial n_\mathrm{d}}{\partial T_\mathrm{e}} + \frac{\partial n_\mathrm{e}}{\partial T_\mathrm{e}} = \frac{\partial n}{\partial T_\mathrm{e}} \tag{33c}$$

$$\frac{\partial n_\mathrm{a}}{\partial T_\mathrm{h}} + \frac{\partial n_\mathrm{i}}{\partial T_\mathrm{h}} + \frac{\partial n_\mathrm{d}}{\partial T_\mathrm{h}} + \frac{\partial n_\mathrm{e}}{\partial T_\mathrm{h}} = \frac{\partial n}{\partial T_\mathrm{h}} \tag{33d}$$

For the 2-T argon plasma system, the relation between the total pressure and the particle number densities can be expressed as

$$p = n_\mathrm{e} k_\mathrm{B} T_\mathrm{e} + \sum_{s=1}^{3} n_s k_\mathrm{B} T_\mathrm{h} = n k_\mathrm{B} T_\mathrm{h} [(\theta - 1) x_\mathrm{e} + 1] \tag{34}$$

where $x_\mathrm{e} (= n_\mathrm{e}/n)$ is the mole fraction of electrons in the mixture. For a fixed total pressure, partial differentiations $\partial n/\partial T_\mathrm{e}$ and $\partial n/\partial T_\mathrm{h}$ can be obtained from Eq. (34) as follows:

$$\frac{\partial n}{\partial T_\mathrm{e}} = -(\theta - 1)\frac{\partial n_\mathrm{e}}{\partial T_\mathrm{e}} - \frac{n_\mathrm{e}}{T_\mathrm{h}} \tag{35a}$$

$$\frac{\partial n}{\partial T_\mathrm{h}} = n(x_\mathrm{e} - 1)\frac{1}{T_\mathrm{h}} - (\theta - 1)\frac{\partial n_\mathrm{e}}{\partial T_\mathrm{h}} \tag{35b}$$

On the other hand, the following partial differentiation expressions can be obtained from the 2-T Saha equations, i.e. Eqs. (5a) and (5b):

$$\frac{1}{n_\mathrm{e}}\frac{\partial n_\mathrm{e}}{\partial T_\mathrm{e}} + \frac{1}{n_\mathrm{i}}\frac{\partial n_\mathrm{i}}{\partial T_\mathrm{e}} - \frac{1}{n_\mathrm{a}}\frac{\partial n_\mathrm{a}}{\partial T_\mathrm{e}} = D_1 \tag{36a}$$

$$\frac{1}{n_\mathrm{e}}\frac{\partial n_\mathrm{e}}{\partial T_\mathrm{e}} + \frac{1}{n_\mathrm{d}}\frac{\partial n_\mathrm{d}}{\partial T_\mathrm{e}} - \frac{1}{n_\mathrm{i}}\frac{\partial n_\mathrm{i}}{\partial T_\mathrm{e}} = D_2 \tag{36b}$$

$$\frac{1}{n_\mathrm{e}}\frac{\partial n_\mathrm{e}}{\partial T_\mathrm{h}} + \frac{1}{n_\mathrm{i}}\frac{\partial n_\mathrm{i}}{\partial T_\mathrm{h}} - \frac{1}{n_\mathrm{a}}\frac{\partial n_\mathrm{a}}{\partial T_\mathrm{h}} = 0 \tag{36c}$$

$$\frac{1}{n_\mathrm{e}}\frac{\partial n_\mathrm{e}}{\partial T_\mathrm{h}} + \frac{1}{n_\mathrm{d}}\frac{\partial n_\mathrm{d}}{\partial T_\mathrm{h}} - \frac{1}{n_\mathrm{i}}\frac{\partial n_\mathrm{i}}{\partial T_\mathrm{h}} = 0 \tag{36d}$$

where

$$D_1 = \frac{3}{2}\frac{1}{T_\mathrm{e}} + \frac{\partial \ln z_{\mathrm{ex},i}^0}{\partial T_\mathrm{e}} - \frac{\partial \ln z_{\mathrm{ex},a}^0}{\partial T_\mathrm{e}} + \frac{E_\mathrm{i}}{k_\mathrm{B} T_\mathrm{e}^2} \tag{37a}$$

$$D_2 = \frac{3}{2}\frac{1}{T_\mathrm{e}} + \frac{\partial \ln z_{\mathrm{ex},d}^0}{\partial T_\mathrm{e}} - \frac{\partial \ln z_{\mathrm{ex},i}^0}{\partial T_\mathrm{e}} + \frac{E_\mathrm{d} - E_\mathrm{i}}{k_\mathrm{B} T_\mathrm{e}^2} \tag{37b}$$

After substituting $\partial n/T_\mathrm{e}$ given by Eq. (35a) into Eq. (33c) and $\partial n/\partial T_\mathrm{h}$ by Eq. (35b) into Eq. (33d), respectively, the following two sets of linear equations with $\partial n_j/\partial T_\mathrm{e}$ or $\partial n_j/\partial T_\mathrm{h} (j = 1, 2, 3, 4)$ as the dependent variables can be obtained:

$$FY_1 = b_3 \tag{38a}$$

$$FY_2 = b_4 \tag{38b}$$

where

$$F = \begin{bmatrix} 1 & 1 & 1 & \theta \\ 0 & 1 & 2 & -1 \\ -1/n_\mathrm{a} & 1/n_\mathrm{i} & 0 & 1/n_\mathrm{e} \\ 0 & -1/n_\mathrm{i} & 1/n_\mathrm{d} & 1/n_\mathrm{e} \end{bmatrix},$$

$$Y_1 = \begin{bmatrix} \partial n_\mathrm{a}/\partial T_\mathrm{e} \\ \partial n_\mathrm{i}/\partial T_\mathrm{e} \\ \partial n_\mathrm{d}/\partial T_\mathrm{e} \\ \partial n_\mathrm{e}/\partial T_\mathrm{e} \end{bmatrix}, \quad Y_2 = \begin{bmatrix} \partial n_\mathrm{a}/\partial T_\mathrm{h} \\ \partial n_\mathrm{i}/\partial T_\mathrm{h} \\ \partial n_\mathrm{d}/\partial T_\mathrm{h} \\ \partial n_\mathrm{e}/\partial T_\mathrm{h} \end{bmatrix} \tag{39a}$$

$$b_3 = \begin{bmatrix} -n_\mathrm{e}/T_\mathrm{h} \\ 0 \\ D_1 \\ D_2 \end{bmatrix}, \quad b_4 = \begin{bmatrix} n(x_\mathrm{e} - 1)/T_\mathrm{h} \\ 0 \\ 0 \\ 0 \end{bmatrix} \tag{39b}$$

According to Cramer's rule, the solutions of the Eqs. (38a) and (38b) can be expressed as follows:

$$\frac{\partial n_\mathrm{e}}{\partial T_\mathrm{e}} = \frac{|F_1|}{|F|} \tag{40a}$$

$$\frac{\partial n_\mathrm{e}}{\partial T_\mathrm{h}} = \frac{|F_2|}{|F|} \tag{40b}$$

where $|F|$ denotes the determinant of matrix F, whereas the determinants $|F_1|$ and $|F_2|$ can be expressed as

$$|F_1| = \begin{vmatrix} 1 & 1 & 1 & -n_\mathrm{e}/T_\mathrm{h} \\ 0 & 1 & 2 & 0 \\ -1/n_\mathrm{a} & 1/n_\mathrm{i} & 0 & D_1 \\ 0 & -1/n_\mathrm{i} & 1/n_\mathrm{d} & D_2 \end{vmatrix} \tag{41a}$$

$$|F_2| = \begin{vmatrix} 1 & 1 & 1 & n(x_e-1)/T_h \\ 0 & 1 & 2 & 0 \\ -1/n_a & 1/n_i & 0 & 0 \\ 0 & -1/n_i & 1/n_d & 0 \end{vmatrix} \tag{41b}$$

Substituting $\partial n_e/\partial T_e$ and $\partial n_e/\partial T_h$ obtained from the solution of Eqs. (40a) and (40b) into Eqs. (30a) and (30b), the values of k_{re} and k_{rh} can be calculated.

For a given electron/heavy-particle temperature ratio, i.e. $\theta = T_e/T_h = const.$, the reactive thermal conductivity of the 2-T argon plasma, defined with respect to the gradient of heavy-particle temperature, ∇T_h, could be calculated by

$$\lambda_R = (k_{rh} + \theta k_{re}) \tag{42}$$

4. Theoretical derivation (the second approach)

4.1. The Van't Hoff's equation modified to the 2-T argon plasma

In a way similar to that used in Ref. [10] for a non-ionized gas, the equilibrium constant for each of the reactions (18a) and (18b) can be defined as

$$K_{p,r} = \prod_{j=1}^{4} p_j^{v_{rj}} \quad (r = 1,2) \tag{43}$$

where p_j $(j = 1,2,3,4)$ is the partial pressure of the jth component, whereas $v_{11} = -1$, $v_{12} = 0$, $v_{13} = 1$, $v_{14} = 1$ for the reaction (18a); $v_{21} = 0$, $v_{22} = -1$, $v_{23} = 1$ $v_{24} = -1$ for the reaction (18b). Taking logarithms on both sides of Eq. (43) and then calculate their gradients, we obtain

$$\nabla(\ln K_{p,r}) = \sum_{j=1}^{4} v_{rj} \nabla \ln p_j \quad (r = 1,2) \tag{44}$$

The left-hand sides of Eq. (44) can be expressed as

$$\nabla(\ln K_{p,1}) = \frac{\partial}{\partial T_e}(\ln K_{p,1})\nabla T_e + \frac{\partial}{\partial T_h}(\ln K_{p,1})\nabla T_h \tag{45a}$$

$$\nabla(\ln K_{p,2}) = \frac{\partial}{\partial T_e}(\ln K_{p,2})\nabla T_e + \frac{\partial}{\partial T_h}(\ln K_{p,2})\nabla T_h \tag{45b}$$

While the right-hand side of Eq. (44) can be calculated using Eqs. (19a)–(19d). Thus the following Van't Hoff equations modified to the 2-T argon plasma can be obtained:

$$\frac{\partial \ln K_{p,1}}{\partial T_e} = \frac{\Delta h_1^*}{k_B T_e^2}; \quad \frac{\partial \ln K_{p,1}}{\partial T_h} = 0 \tag{46a}$$

$$\frac{\partial \ln K_{p,2}}{\partial T_e} = \frac{\Delta h_2^*}{k_B T_e^2}; \quad \frac{\partial \ln K_{p,2}}{\partial T_h} = 0 \tag{46b}$$

where Eqs. (10a) and (10b) have been used.

4.2. Derivation of the reactive thermal conductivity (approach 2)

In Eq. (7), if we define A_{sj} as the element of the matrix A as

$$A_{sj} = \frac{n}{\rho k_B T_j} m_j D_{sj}^a \quad (s, j = 1,2,3,4) \tag{47}$$

then, according to Cramer's rule, one can obtain:

$$\nabla p_j = \frac{|A_j|}{|A|} \quad (j = 1,2,3,4) \tag{48}$$

where $|A_j|$ and $|A|$ are the determinants of the matrix A_j and A. The determinant $|A_j|$ can be written as

$$|A_1| = \begin{vmatrix} \vec{\psi}_1 & A_{12} & A_{13} & A_{14} \\ \vec{\psi}_2 & A_{22} & A_{23} & A_{24} \\ \vec{\psi}_3 & A_{32} & A_{33} & A_{34} \\ \vec{\psi}_4 & A_{42} & A_{43} & A_{44} \end{vmatrix}$$

$$|A_2| = \begin{vmatrix} A_{11} & \vec{\psi}_1 & A_{13} & A_{14} \\ A_{21} & \vec{\psi}_2 & A_{23} & A_{24} \\ A_{31} & \vec{\psi}_3 & A_{33} & A_{34} \\ A_{41} & \vec{\psi}_4 & A_{43} & A_{44} \end{vmatrix} \tag{49a}$$

$$|A_3| = \begin{vmatrix} A_{11} & A_{12} & \vec{\psi}_1 & A_{14} \\ A_{21} & A_{22} & \vec{\psi}_2 & A_{24} \\ A_{31} & A_{32} & \vec{\psi}_3 & A_{34} \\ A_{41} & A_{42} & \vec{\psi}_4 & A_{44} \end{vmatrix}$$

$$|A_4| = \begin{vmatrix} A_{11} & A_{12} & A_{13} & \vec{\psi}_1 \\ A_{21} & A_{22} & A_{23} & \vec{\psi}_2 \\ A_{31} & A_{32} & A_{33} & \vec{\psi}_3 \\ A_{41} & A_{42} & A_{43} & \vec{\psi}_4 \end{vmatrix} \tag{49b}$$

By use of Eqs. (8a) and (8b), Eqs. (49a) and (49b) can be rewritten as

$$|A_1| = \begin{vmatrix} 1 & A_{12} & A_{13} & A_{14} \\ 0 & A_{22} & A_{23} & A_{24} \\ -1 & A_{32} & A_{33} & A_{34} \\ -1 & A_{42} & A_{43} & A_{44} \end{vmatrix} \vec{\psi}_1 + \begin{vmatrix} 0 & A_{12} & A_{13} & A_{14} \\ 1 & A_{22} & A_{23} & A_{24} \\ -1 & A_{32} & A_{33} & A_{34} \\ 1 & A_{42} & A_{43} & A_{44} \end{vmatrix} \vec{\psi}_2$$
$$= |A_1^1|\vec{\psi}_1 + |A_1^2|\vec{\psi}_2 \tag{50a}$$

$$|A_2| = \begin{vmatrix} A_{11} & 1 & A_{13} & A_{14} \\ A_{21} & 0 & A_{23} & A_{24} \\ A_{31} & -1 & A_{33} & A_{34} \\ A_{41} & -1 & A_{43} & A_{44} \end{vmatrix} \vec{\psi}_1 + \begin{vmatrix} A_{11} & 0 & A_{13} & A_{14} \\ A_{21} & 1 & A_{23} & A_{24} \\ A_{31} & -1 & A_{33} & A_{34} \\ A_{41} & 1 & A_{43} & A_{44} \end{vmatrix} \vec{\psi}_2$$
$$= |A_2^1|\vec{\psi}_1 + |A_2^2|\vec{\psi}_2 \tag{50b}$$

$$|A_3| = \begin{vmatrix} A_{11} & A_{12} & 1 & A_{14} \\ A_{21} & A_{22} & 0 & A_{24} \\ A_{31} & A_{32} & -1 & A_{34} \\ A_{41} & A_{42} & -1 & A_{44} \end{vmatrix} \vec{\psi}_1 + \begin{vmatrix} A_{11} & A_{12} & 0 & A_{14} \\ A_{21} & A_{22} & 1 & A_{24} \\ A_{31} & A_{32} & -1 & A_{34} \\ A_{41} & A_{42} & 1 & A_{44} \end{vmatrix} \vec{\psi}_2$$

$$= |A_3^1|\vec{\psi}_1 + |A_3^2|\vec{\psi}_2 \tag{50c}$$

$$|A_4| = \begin{vmatrix} A_{11} & A_{12} & A_{13} & 1 \\ A_{21} & A_{22} & A_{23} & 0 \\ A_{31} & A_{32} & A_{33} & -1 \\ A_{41} & A_{42} & A_{43} & -1 \end{vmatrix} \vec{\psi}_1 + \begin{vmatrix} A_{11} & A_{12} & A_{13} & 0 \\ A_{21} & A_{22} & A_{23} & 1 \\ A_{31} & A_{32} & A_{33} & -1 \\ A_{41} & A_{42} & A_{43} & 1 \end{vmatrix} \vec{\psi}_2$$

$$= |A_4^1|\vec{\psi}_1 + |A_4^2|\vec{\psi}_2 \tag{50d}$$

Substituting Eqs. (48), (49a), (49b), (50a)–(50d) into Eq. (44), we can get

$$\frac{\partial \ln K_{p,1}}{\partial T_e}\theta\nabla T_h = \frac{1}{|A|}\sum_{j=1}^{4}\frac{\nu_{1j}|A_j^1|}{p_j}\vec{\psi}_1 + \frac{1}{|A|}\sum_{j=1}^{4}\frac{\nu_{1j}|A_j^2|}{p_1}\vec{\psi}_2 \tag{51a}$$

$$\frac{\partial \ln K_{p,2}}{\partial T_e}\theta\nabla T_h = \frac{1}{|A|}\sum_{j=1}^{4}\frac{\nu_{2j}|A_j^1|}{p_j}\vec{\psi}_1 + \frac{1}{|A|}\sum_{j=1}^{4}\frac{\nu_{2j}|A_j^2|}{p_j}\vec{\psi}_2 \tag{51b}$$

From Eqs. (46a), (46b), (51a) and (51b), the following set of linear equations can be obtained:

$$\frac{\theta\Delta h_1^*}{k_B T_e^2}\nabla T_h = H_{11}\vec{\psi}_1 + H_{12}\vec{\psi}_2 \tag{52a}$$

$$\frac{\theta\Delta h_2^*}{k_B T_e^2}\nabla T_h = H_{21}\vec{\psi}_1 + H_{22}\vec{\psi}_2 \tag{52b}$$

where $H_{ij}(i,j=1,2)$ is the element of the matrix H and can be expressed as

$$H_{11} = \frac{1}{|A|}\sum_{j=1}^{4}\frac{\nu_{1j}|A_j^1|}{p_j} \tag{53a}$$

$$H_{12} = \frac{1}{|A|}\sum_{j=1}^{4}\frac{\nu_{1j}|A_j^2|}{p_j} \tag{53b}$$

$$H_{21} = \frac{1}{|A|}\sum_{j=1}^{4}\frac{\nu_{2j}|A_j^1|}{p_j} \tag{53c}$$

$$H_{22} = \frac{1}{|A|}\sum_{j=1}^{4}\frac{\nu_{2j}|A_j^2|}{p_j} \tag{53d}$$

the determinant of the matrix H is

$$|H| = \begin{vmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{vmatrix} \tag{54}$$

According to Cramer's rule, the solutions of Eqs. (52a) and (52b) are

$$\vec{\psi}_1 = \frac{\theta}{k_B T_e^2}\frac{\begin{vmatrix} \Delta h_1^* & H_{12} \\ \Delta h_2^* & H_{22} \end{vmatrix}}{|H|}\nabla T_h \tag{55a}$$

$$\vec{\psi}_2 = \frac{\theta}{k_B T_e^2}\frac{\begin{vmatrix} H_{11} & \Delta h_1^* \\ H_{21} & \Delta h_2^* \end{vmatrix}}{|H|}\nabla T_h \tag{55b}$$

Substituting Eqs. (55a) and (55b) into Eq. (9), we obtain

$$\lambda_R = [\Delta h_1^*\vec{\psi}_1 + \Delta h_2^*\vec{\psi}_2]/\nabla T_h$$

$$= \frac{\theta\Delta h_1^*}{k_B T_e^2}\frac{\begin{vmatrix} \Delta h_1^* & H_{12} \\ \Delta h_2^* & H_{22} \end{vmatrix}}{|H|} + \frac{\theta\Delta h_2^*}{k_B T_e^2}\frac{\begin{vmatrix} H_{11} & \Delta h_1^* \\ H_{21} & \Delta h_2^* \end{vmatrix}}{|H|} \tag{56a}$$

or

$$\lambda_R = -\frac{\theta}{k_B T_e^2}\begin{vmatrix} 0 & \Delta h_1^* & \Delta h_2^* \\ \Delta h_1^* & H_{11} & H_{12} \\ \Delta h_2^* & H_{21} & H_{22} \end{vmatrix} \Big/ \begin{vmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{vmatrix} \tag{56b}$$

5. Results and discussion

The expressions derived in Sections 3 and 4 using two different approaches, i.e. Eqs. (42) and (56b) and their auxiliary equations, have been used to calculate the reactive thermal conductivity of the 2-T argon plasma. It is found that although the reactive thermal conductivity expressions derived by the two approaches are different in their formulations, sample calculations give completely the same values of the reactive thermal conductivity. However, it is also found that the Approach 1 requires appreciably less numerical effort than that involved in the Approach 2, if a personal computer is employed. It is because that more complex matrix calculation is involved in the Approach 2. Hence, the reactive thermal conductivity expressions deduced using the Approach 1, i.e. Eq. (42) and its auxiliary equations, are used in the following to calculate the values of the reactive thermal conductivity for the 2-T argon plasma. The calculated values are then compared with previous results, especially with those presented in Ref. [5].

As mentioned in Section 1, the author of Ref. [5] used the same expression as that employed in Refs. [1,2] to calculate the reactive thermal conductivity of the 2-T argon plasma. However, the expression presented in Refs. [1,2] is only applicable to a single-temperature plasma. The calculated results obtained by the present modified approach, i.e. using Eq. (42) and its auxiliary equations, are compared with those presented in Ref. [5].

The calculated results show that for the special case that the plasma is in the LTE state, the present modified approach gives the same calculated values of the reactive thermal conductivity given by Ref. [5], as shown in Fig. 1(a). For this case of single-temperature system, the present modified approach reduces to be the same like that given by Hsu [5] or by Devoto [1] if the LTE state is concerned.

However, the present modified approach gives different predicted results from those in Ref. [5] for the reactive thermal conductivity when the electron/heavy-particle temperature ratio θ is not equal to 1 (i.e. $T_e \neq T_h$), and the difference increases with the increase of θ, as shown in Fig. 1(b)–(d), the difference becomes quite significant at high electron/heavy-particle temperature ratios.

In order to check what is the source for the increasing difference between the calculated results of the reactive thermal conductivity by the present study and by Ref. [5] at larger electron/heavy-particle temperature ratios, numerical experiments are performed for the following four cases:

Case 1: Employ the Saha equations (6a) and (6b) [with the power of $1/\theta$] and the formula for the reactive thermal conductivity presented in Refs. [1,3,5,8] (without modification for the 2-T plasma) to calculate the reactive thermal conductivity of the 2-T argon plasma. This case corresponds to the approach used by Hsu [5].

Case 2: Employ the Saha equations (6a) and (6b) [with the power of $1/\theta$] and the formula for the reactive thermal conductivity derived in this paper [Eq. (42) and its auxiliary equations, with modification for the 2-T plasma] to calculate the reactive thermal conductivity of the 2-T argon plasma.

Case 3: Employ the Saha equations (5a) and (5b) [without the power of $1/\theta$] and the formula for the reactive thermal conductivity presented in Refs. [1,3,5,8] (without modification for the 2-T plasma) to calculate the reactive thermal conductivity of the 2-T argon plasma.

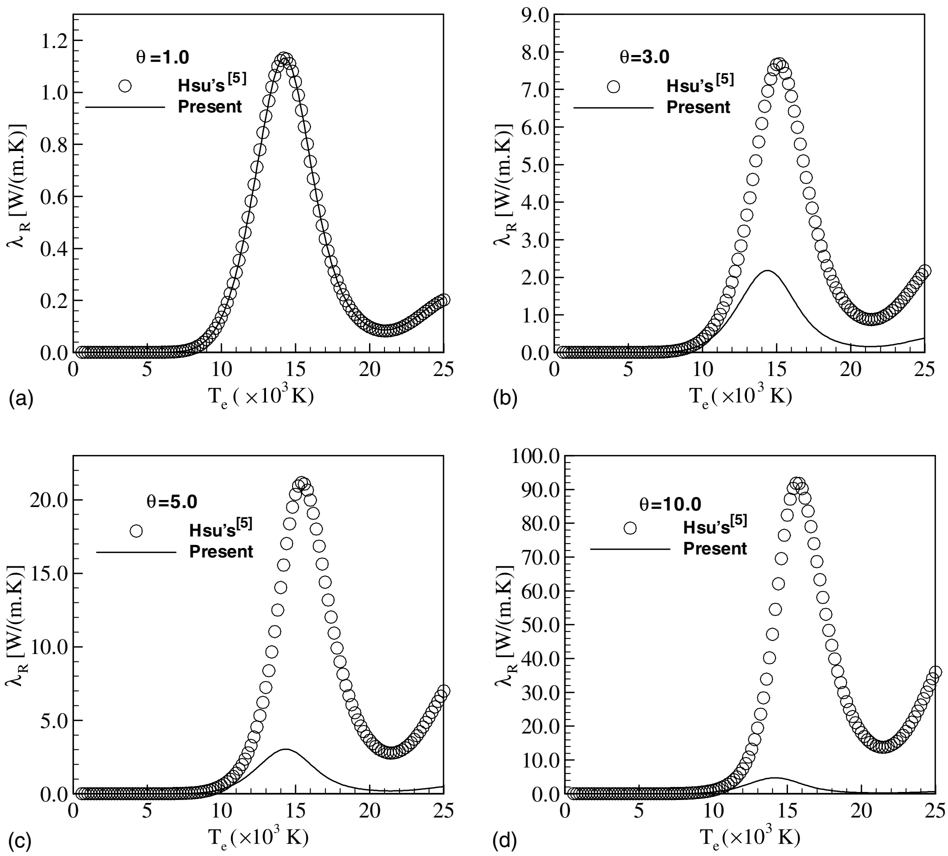

Fig. 1. Comparison of the calculated values of the reactive thermal conductivity for different electron/heavy-particle temperature ratios. Argon plasma at atmospheric pressure; continuous lines—by the present study; circles—by Hsu [5]. (a) $\theta = 1$; (b) $\theta = 3$; (c) $\theta = 5$; (d) $\theta = 10$.

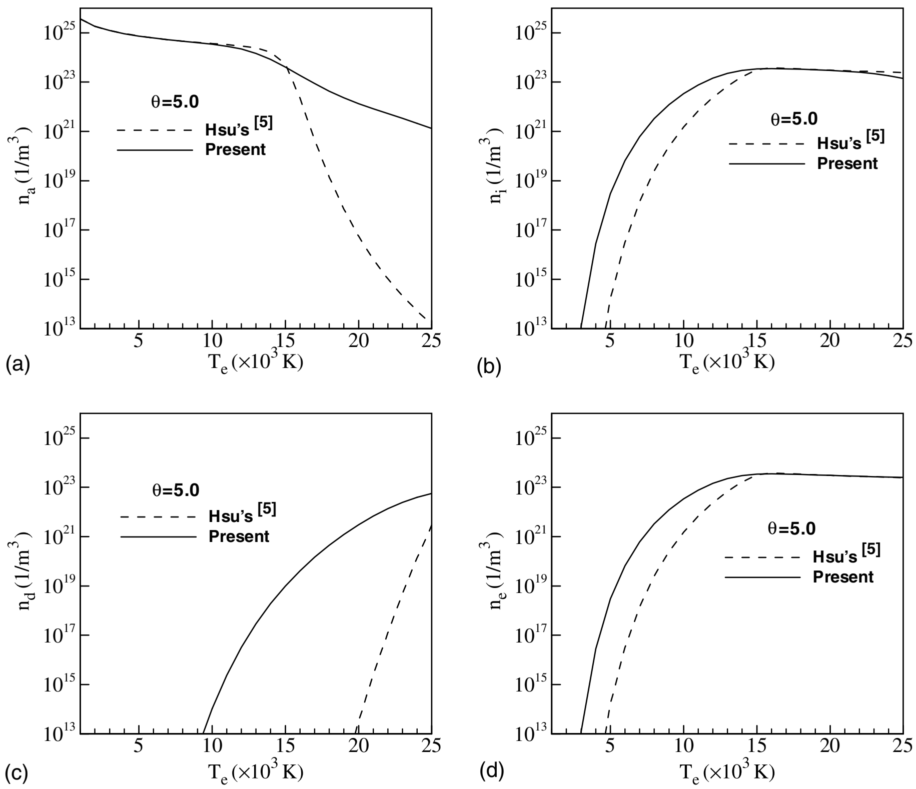

Fig. 2. Comparison of the particle number densities calculated by Eqs. (5a) and (5b) used in Case 3 or Case 4 (this study) with those by Eqs. (6a) and (6b) used in Case 1 (or Ref. [5]) and Case 2 for the 2-T argon plasma at atmospheric pressure and with $\theta = 5$. Continuous lines—this study; dash lines—by Hsu [5]. (a) Argon atom number density; (b) singly-ionized argon ion number density; (c) doubly-ionized argon ion number density; (d) electron number density.

Case 4: Employ the Saha equations (5a) and (5b) [without the power of $1/\theta$] and the formula for the reactive thermal conductivity presented in this paper [Eq. (42) and its auxiliary equations, with modification for the 2-T plasma] to calculate the reactive thermal conductivity of the 2-T argon plasma. This case represents the approach employed in the present study.

For the four different cases, the calculated number densities of atoms, singly-ionized ions, doubly-ionized ions and electrons of the 2-T argon plasma with $\theta = 5$ are plotted in Fig. 2(a)–(d), respectively, whereas the calculated reactive thermal conductivities are shown in Fig. 3. It is seen from Fig. 2(a)–(d) that the effect due to employing different Saha equations (Eqs. (5a), (5b) or Eqs. (6a), (6b)) on the number densities of atoms, ions and electrons cannot be ignored, especially for the doubly-ionized ion number density, different values of thermodynamic and transport properties (including the reactive thermal conductivity) are expected to be deduced. From the values of the reactive thermal conductivity obtained for the four different cases (Fig. 3), two conclusions can be obtained: (1) the effect of the difference in calculated species number densities due to employing different Saha equations on the reactive thermal conductivity cannot be neglected, this can be drawn from the comparison of the calculated results for the Case 1 with those for the Case 3 (or for the Case 2 with those for the Case 4), (2) the values of the reactive thermal conductivity predicted by the present modified approach (using Eq. (42) and its auxiliary equations) are appreciably smaller than those by the approach used in Ref. [5] when the electron temperature is higher than the heavy-particle temperature even the same plasma composition is used in the calculation, this can be drawn from the comparison of the calculated results for the Case 1 and the Case 2, or for the Case 3 and Case 4.

Although the derivation for the reactive thermal conductivity of 2-T plasma presented in this paper is concerned with the 2-T argon plasma. It is easy to extend the derivation to other 2-T plasmas with other monatomic gas as the working gas. In addition, only single- and double-ionization reactions are considered in this study. When triple-ionization is involved, much more numerical efforts will be required, although the present study can be extended to this more complicated case.

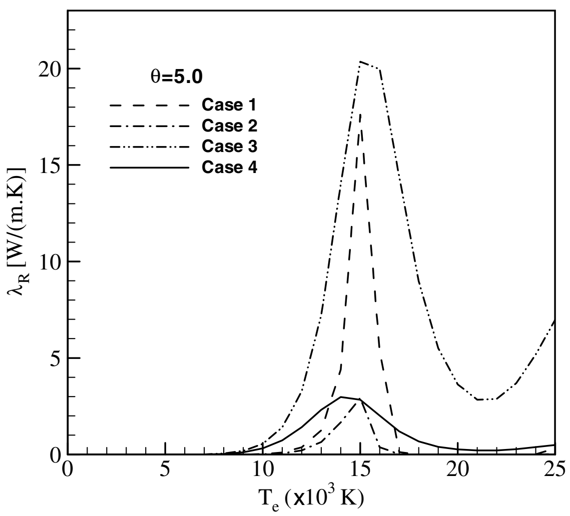

Fig. 3. Comparison of the calculated values of the reactive thermal conductivity of the 2-T argon plasma at atmospheric pressure for four different cases. Case 1—Using the Saha equations (6a) and (6b) and the reactive thermal conductivity expression used in Ref. [5]; Case 2—Using the Saha equations (6a) and (6b) and the reactive thermal conductivity expression derived in present study; Case 3—Using the Saha equations (5a) and (5b) and the reactive thermal conductivity expression used in Ref. [5]; Case 4—Using the Saha equations (5a) and (5b) and the reactive thermal conductivity expression derived in present study.

6. Conclusions

The expressions of the reactive thermal conductivity have been derived by use of two different approaches for the 2-T argon plasma. The Saha equations and the species diffusion velocities modified to the 2-T plasma have been employed in the derivation. The calculated results for the 2-T argon plasma show that the two approaches give the same calculated results of the reactive thermal conductivity.

For the special case with equal electron and heavy-particle temperatures, the present results are identical to those presented by Hsu [5]. However, the difference between the calculated values of the reactive thermal conductivity by the present study and by Hsu [5] increases with increasing electron/heavy-particle temperature ratio. The difference becomes quite significant at high electron/heavy-particle temperature ratios.

Acknowledgements

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