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A numerical model of non-equilibrium thermal plasmas. I. Transport properties

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A self-consistent and complete numerical model for investigating the fundamental processes in a non-equilibrium thermal plasma system consists of the governing equations and the corresponding physical properties of the plasmas. In this paper, a new kinetic theory of the transport properties of two-temperature (2-T) plasmas, based on the solution of the Boltzmann equation using a modified Chapman–Enskog method, is presented. This work is motivated by the large discrepancies between the theories for the calculation of the transport properties of 2-T plasmas proposed by different authors in previous publications. In the present paper, the coupling between electrons and heavy species is taken into account, but reasonable simplifications are adopted, based on the physical fact that $m_e/m_h \ll 1$, where m_e and m_h are, respectively, the masses of electrons and heavy species. A new set of formulas for the transport coefficients of 2-T plasmas is obtained. The new theory has important physical and practical advantages over previous approaches. In particular, the diffusion coefficients are complete and satisfy the mass conversation law due to the consideration of the coupling between electrons and heavy species. Moreover, this essential requirement is satisfied without increasing the complexity of the transport coefficient formulas. Expressions for the 2-T combined diffusion coefficients are obtained. The expressions for the transport coefficients can be reduced to the corresponding well-established expressions for plasmas in local thermodynamic equilibrium for the case in which the electron and heavy-species temperatures are equal. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4794969]

NOMENCLATURE

$b =$ impact parameter
$b_i =$ number of atoms in a molecule of species i
$\vec{c}_i =$ velocity of species i
$\vec{C}_i =$ peculiar particle velocity of species i
$\vec{d}_i =$ diffusion driving force of species i
$\vec{d}_i^{\,\prime} =$ expression given by Eqs. (49) and (50)
$D = 1 + x_1(\theta - 1)$
$D_{ij} =$ ordinary diffusion coefficient
$D_i^T =$ thermal diffusion coefficient
$D_{ij}^\theta, D_i^{\theta^*} =$ thermal non-equilibrium diffusion coefficient
$D_i^\theta =$ coefficient given by Eq. (36)
$D_{ij}^a =$ ambipolar ordinary diffusion coefficient
$D_i^{Ta} =$ ambipolar thermal diffusion coefficient
$D_{ij}^{\theta a}, D_i^{\theta a^*} =$ ambipolar non-equilibrium diffusion coefficient
$\overline{D_{AB}^x} =$ combined ordinary diffusion coefficient
$\overline{D_{AB}^p} =$ combined pressure diffusion coefficient
$\overline{D_{AB}^T} =$ combined thermal diffusion coefficient
$\overline{D_{AB}^\theta}, \overline{D_{AB}^{\theta*}} =$ combined diffusion coefficients due to the gradient of the non-equilibrium parameter
$e =$ elementary charge
$\vec{E}^e =$ externally applied electric field
$\vec{E}^a =$ internal electric field
$E_{jk} =$ element of inverse of the matrix whose general element is $D_{ij}m_j$
$f_i =$ distribution function of species i
$f_i' =$ distribution function after collision of species i
$f_i^{(0)} =$ zero-order approximation of the distribution function
$f_i^{(1)} =$ first-order approximation of the distribution function
$g =$ relative speed of species i and j
$\vec{g}_i =$ number flux of species i
$\vec{g}_A; \vec{g}_B =$ number flux of gas A; number flux of gas B
$\overleftrightarrow{I} =$ unit tensor
$\vec{j} =$ current density
$k_B =$ Boltzmann constant
$m_i =$ mass of species i
$\overline{m_A}; \overline{m_B} =$ average mass of heavy species in gas A; average mass of heavy species in gas B
$n_i; n_t =$ species number density; total number density
$p_i; p =$ partial pressure; total pressure
$\overleftrightarrow{P} =$ pressure tensor
$\vec{q} =$ energy flux vector

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$Q_1^{(0)}$ = change of average kinetic energy of electrons via elastic collision with heavy particles
$Q_1^{mp}, \tilde{Q}_{ij}^{mp}, \tilde{Q}_{i1}^{mp*}$ = terms of the collision integrals
$Q_{ij}^{(l)}$ = gas-kinetic cross section
$\bar{Q}_{ij}^{(l,s)}$ = reduced collision integral
$\vec{r}$ = displacement vector
$\overleftrightarrow{R}_i^{(s,k)}$ = tensors listed in Table I of the supplementary material
$R_{im}^{(s,k)}$ = listed in Table II of the supplementary material
s_i = stoichiometric coefficient
t = time
$t_{ip}^{(s,k)}$ = unknown coefficient listed in Table II of the supplementary material
T_e; T_h = electron temperature; heavy-particle temperature
T_{ij}^* = effective temperature of collisions
$\vec{v}_0$ = mass-averaged velocity
$\vec{V}_i$ = diffusion velocity of species i
$\vec{W}_i$ = reduced velocity of species i
x_i = mole fraction of species i ($x_i = n_i/n_t$)
$\overline{x_A}$; $\overline{x_B}$ = relative concentration of gas A; relative concentration of gas B
$\vec{X}_i$ = external force acting on species i
Z_i = electric charge number of species i

Greek

α_i, β = given by Eqs. (55) and (56)
θ = thermal non-equilibrium coefficient ($\theta = T_e/T_h$)
$\overleftrightarrow{\Theta}_i$ = tensor listed in Table II of the supplementary material
λ_i = translational thermal conductivity
λ_i^θ = non-equilibrium thermal conductivity
$\lambda_i', \lambda_i'^\theta, \lambda_{ij}^D$ = coefficients given by Eqs. (30)–(32)
ρ_i; ρ = mass density of species i; total mass density
μ = viscosity
μ_{ij} = reduced mass
γ = reduced relative speed
χ = deflection angle
ϕ_i = perturbation function
$\overleftrightarrow{\psi}_i^{(s,k)}$ = tensors listed in Table I of the supplementary material
ε = perturbation
ε_i^r = reaction energy per unit mass of species i in the reaction r
ε_i^{in} = internal energy per unit mass of species i
ξ = level of approximation to the transport coefficients
σ = electrical conductivity
σ_{ij} = differential collision cross section
$\omega_1 = x_1 p(1-x_1)/D^2$
$\omega_i\ (i \geq 2) = -x_i x_1 p/D^2$
Ω = solid angle
$\Omega_{ij}^{(l,s)}$ = collision integral
$\Omega_{ij}^{(l,s)*}$ = reduced collision integral

Subscripts

1 or e = electron
$I \geq 2$ or h = heavy species

Superscripts

a = ambipolar
e = external
in = internal
r = reaction

I. INTRODUCTION

Thermal plasmas, which are characterized by high temperatures, heat fluxes, chemical activity, and flexibility, are widely used in industry and aerospace for applications such as arc welding, plasma cutting, plasma spraying, metallurgy, micro- or nano-scale materials preparation and processing, chemical production, waste treatment, and gasification (c.f., Refs. 1–6). Understanding of the heat transfer and fluid flow in thermal plasmas is critically important for the control of plasma processes and optimization of plasma devices, and modeling plays an increasingly significant role in developing this understanding. In the past few decades, many sophisticated numerical models have been developed to simulate the physical-chemical processes occurring in thermal plasma systems. However, the reliability of the modeling results strongly depends on using accurate values of the physical properties, in particular the thermodynamic and transport coefficients, of the plasma, which may be formed from a pure gas or a mixture of gases.

The calculation of transport coefficients of plasmas in the local thermodynamic equilibrium (LTE) state can be achieved by solving the Boltzmann equation using the well-known Chapman–Enskog method, which assumes that the particle distribution function is a first-order perturbation to a Maxwellian distribution; the transport coefficients are expressed in terms of Sonine polynomials.[7,8] Devoto[9] proposed simplified expressions for the transport coefficients of plasmas using a treatment that takes into account the significant mass difference between electrons and heavy species. Subsequently, many results have been reported on the basis of this simplified approach for different pure or mixed gas plasmas in LTE (e.g., Refs. 10–15). However, in thermal plasma applications, deviations from the LTE, in particular significant differences between the electron and heavy-species temperatures, are unavoidable. For example, deviations from LTE inevitably occur in the fringes of the plasmas, in the regions in which the plasma interacts with the workpiece, and in the vicinity of the cold electrode walls.[16–18] In addition, thermal non-equilibrium plasmas can be directly generated at atmospheric pressure by microwave discharges, non-thermal arc discharges (arc current less than the order of 10 A), or forced convection arc discharges.[19–21] As a result, numerical simulations are increasingly conducted under thermal non-equilibrium conditions.

The most widely considered type of non-equilibrium plasma is the two-temperature (2-T) plasma, in which the electron temperature (T_e) is higher than that of heavy species (T_h), while the population densities of the different excited states of the heavy species satisfy the Boltzmann distribution with the characteristic temperature $T_{ex} = T_e$ (where T_{ex} is the excitation temperature), and the chemical reactions are governed by the mass action law. Proper treatment of these 2-T regions is vital in examining phenomena such as the anode layer of high-intensity arcs (e.g., Refs. 16–18 and 22–24), the arc attachment behavior near the electrodes of high-intensity discharge (HID) lamps,[25,26] the interaction between the plasma and the cold flow, the arc root reattachment process in a non-transferred arc plasma,[27,28] and interactions between the plasma and liquid or solid surfaces.[29]

Thermal plasma applications in which deviations from LTE play a significant role include materials processing[30] using inductively coupled plasmas, plasma–assisted combustion,[31] plasma jet instabilities and plasma–surface interactions in different plasma spraying techniques,[29] low-pressure plasma spraying,[32,33] simulations of plasma flowing around spacecraft for testing the thermal protection systems,[34,35] the subsonic and supersonic plasma flow in an arcjet thruster,[36] the switching arcs in high-voltage gas circuit breakers,[37,38] thermal plasma deposition and nano–materials production,[29,39] plasma-assisted fuel conversion,[40] and so on.

Accurate physical properties of plasmas are a prerequisite for the computational modeling and simulations required in all of the preceding theoretical and application studies. However, the expressions for calculating the transport properties of 2-T plasmas proposed by different authors in previous publications differ greatly and suffer from important deficiencies. Devoto[41] developed a simplified theory assuming a complete decoupling between electrons and heavy-species, which was later modified with the redefinition of the diffusion driving force by Bonnefoi.[42,43] This simplified theory considers electrons and heavy species as two isolated subsystems with no consideration of the diffusion process between them. However, as was pointed out by Rat *et al.*,[44] the values of the diffusion coefficients obtained using this simplified theory[41–43] do not satisfy the mass conservation in the plasma system. Further, Rat *et al.* found that it was not possible to use this theory to calculate the combined diffusion coefficients, which are a very useful treatment of diffusion processes developed by Murphy.[45]

Subsequently, Rat *et al.*[46] presented a complete theory of transport coefficients without the assumption of decoupling between electrons and heavy species and redefined the 2-T diffusion driving force in order to maintain the coupling between electrons and heavy species. Although this overcomes the problems of the approaches of Devoto and Bonnefoi, the complete theory is extremely complicated and time-consuming to implement and, as a consequence, has not been widely implemented. In addition, the recent studies presented by Colombo and his co-workers[47–49] showed that the results of the simplified theory of Devoto and Bonnefoi, with the exception of diffusion coefficients, showed only slight differences from those obtained from the complete theory, after certain corrections are made.

The differences between the previous approaches indicate that it is still a major challenge to provide a unified method of calculation of, and expressions for, the transport properties of plasmas that are applicable in both LTE and 2-T plasmas. Thus, it is necessary to re-examine the assumptions and expressions previously used for the calculation of the 2-T plasma transport properties so as to strengthen the basis of modeling under 2-T plasma conditions.

In this study, new derivations of the transport coefficients of the two-temperature plasmas are conducted with the following modified assumptions, which differ from those adopted previously in Refs. 41–44 and 46. First, in contrast to the complete theory of Rat,[46] reasonable simplifications are made on the basis of the fact that the mass of electrons is much smaller than those of heavy species (ions and neutral species), i.e., $m_e \ll m_h$. For instance the change of the first-order perturbation function of heavy species is neglected compared with that of electrons in the electron–heavy-particle collisions. Second, the coupling between the subsystems of electrons and heavy species is considered in this study, instead of regarding them as two isolated systems as was assumed in the simplified theory of Devoto.[41] Although the subsystems of electrons and heavy species can be assumed to be mutually adiabatic due to the extreme weakness of the translational kinetic-energy coupling between the electrons and heavy species, work or particle transfer may take place between these two subsystems due to the occurrence of chemical reactions (e.g., ionization, excitation, and their corresponding reverse processes).[50]

The paper is organized as follows. The solutions of the Boltzmann equations for a 2-T plasma system obtained using the Chapman–Enskog method, modified in accordance with the above considerations, are presented in Sec. II. The new simplified formulas for the transport coefficients are obtained in Sec. III, and the major differences between these newly obtained formulas and the previously published results are demonstrated in Sec. IV. In addition, the combined diffusion coefficients proposed by Murphy are derived for 2-T plasmas based on the newly obtained diffusion coefficients. And finally, the main conclusions are given in Sec. V. In particular, it is pointed out in Sec. IV that these formulas for 2-T plasmas can be reduced to their counterparts for LTE plasmas with $T_e = T_h = T$ and satisfy the requirement that the diffusion flux is conserved in the plasma system. The definitions of the collision integrals and the values of some bracket integral terms are included in the Appendix.

II. METHOD OF SOLVING THE BOLTZMANN EQUATION

Using the perturbation technique of Chapman and Enskog,[7,8] the distribution function $f(\vec{r}, \vec{c}_i, t)$ of species i can be obtained from the solution of the Boltzmann equation[8]

$$\frac{\mathrm{D}f_i}{\mathrm{D}t} = \sum_{j=1}^{N} \int\int (f_i' f_j' - f_i f_j) g \sigma_{ij} \mathrm{d}\Omega \mathrm{d}\vec{c}_j, \tag{1}$$

with $\frac{\mathrm{D}f_i}{\mathrm{D}t} = \frac{\partial f_i}{\partial t} + \vec{c}_i \cdot \vec{\nabla} f_i + \frac{\vec{X}_i}{m_i} \cdot \vec{\nabla}_{\vec{c}_i} f_i$, where $\vec{c}_i$, $\vec{X}_i$, and m_i are, respectively, the velocity, external force, and mass of species i, $\vec{r}$ and t are, respectively, the displacement vector and time, f_i' is the distribution function after collision of species i, g is the relative speed of the species i and j, σ_{ij} is the differential collision cross section, and Ω is the solid angle.

The treatment used here for the 2-T plasma system is analogous to that presented in Ref. 41. Based on the assumptions listed in Sec. I, the major points for solving the Boltzmann equations are listed as follows:[51]

First, the change in the first order perturbation function of heavy species is neglected compared with that of electrons, i.e., $(\phi_i' - \phi_i) \ll (\phi_1' - \phi_1)$. The validity of this simplification can be verified by the very minor differences between the simplified theory and complete theory in comparisons presented in recent works.[47–49] Thus, we can obtain

$$\frac{\mathrm{D}f_1^{(0)}}{\mathrm{D}t} = \int\int f_1^{(0)} f^{(0)} (\phi_1' + \phi' - \phi_1 - \phi) g\sigma_{11} \mathrm{d}\Omega\, \mathrm{d}\vec{c} + \sum_{j=2}^{N} \int\int f_1^{(0)} f_j^{(0)} (\phi_1' - \phi_1) g\sigma_{1j} \mathrm{d}\Omega\, \mathrm{d}\vec{c}_j, \quad (2)$$

$$\frac{\mathrm{D}f_i^{(0)}}{\mathrm{D}t} = \int\int f_i^{(0)} f_1^{(0)} (\phi_1' - \phi_1) g\sigma_{i1} \mathrm{d}\Omega\, \mathrm{d}\vec{c}_1 + \sum_{j=2}^{N} \int\int f_i^{(0)} f_j^{(0)} (\phi_i' + \phi_j' - \phi_i - \phi_j) g\sigma_{ij} \mathrm{d}\Omega\, \mathrm{d}\vec{c}_j. \quad (3)$$

Second, it should be emphasized that the first integration term of Eq. (3), i.e., $\int\int f_i^{(0)} f_1^{(0)} (\phi_1' - \phi_1) g\sigma_{i1} \mathrm{d}\Omega\, \mathrm{d}\vec{c}_1$, is retained, unlike in the simplified theory of Devoto.[41] We will check whether it can be neglected in Sec. IV A.

Third, the definition of the diffusion driving force ($\vec{d}_i$) introduced by Rat *et al.*[46] to take into account the coupling between electrons and heavy species, i.e.,

$$\vec{d}_1 = \frac{\rho_1}{\rho} \sum_{j=1}^{N} n_j \vec{X}_j - n_1 \vec{X}_1 + \left(\frac{x_1 \theta}{D} - \frac{\rho_1}{\rho}\right) \vec{\nabla} p + \frac{\theta p}{D^2} \vec{\nabla} x_1, \quad (4)$$

$$\vec{d}_i = \frac{\rho_i}{\rho} \sum_{j=1}^{N} n_j \vec{X}_j - n_i \vec{X}_i + \left(\frac{x_i}{D} - \frac{\rho_i}{\rho}\right) \vec{\nabla} p + \frac{p}{D} \vec{\nabla} x_i - \frac{x_i(\theta - 1)p}{D^2} \vec{\nabla} x_1 \quad (i \geq 2), \quad (5)$$

where $x_i = n_i/n_t$ is the mass fraction of species $i\,(\in 1, \ldots, N)$ and $D = 1 + x_1(\theta - 1)$ is adopted. The thermal non-equilibrium coefficient is defined as $\theta = T_e/T_h$. For an arbitrary species i, the partial pressure is $p_i = n_i k_B T_i$, and $p = \sum_{i=1}^{N} p_i$ represents the total pressure.

Then, the perturbation functions ϕ_1 and ϕ_i $(i \geq 2)$ for electrons and heavy species, respectively, can be expressed as

$$\phi_1 = -\vec{A}_1 \cdot \vec{\nabla} \ln T_h - \overleftrightarrow{B}_1 : \vec{\nabla} \vec{v}_0 + \sum_{j=1}^{N} \vec{C}_1^j \cdot \vec{d}_j + D_1 Q_1^{(0)} + \sum_{j=1}^{N} \vec{E}_1^j \omega_j \cdot \vec{\nabla} \ln \theta - \vec{F}_1 \cdot \vec{\nabla} \ln \theta, \quad (6)$$

$$\phi_i = -\vec{A}_i \cdot \vec{\nabla} \ln T_h - \overleftrightarrow{B}_i : \vec{\nabla} \vec{v}_0 + \sum_{j=1}^{N} \vec{C}_i^j \cdot \vec{d}_j + D_i Q_1^{(0)} + \sum_{j=1}^{N} \vec{E}_i^j \omega_j \cdot \vec{\nabla} \ln \theta - \vec{F}_i \cdot \vec{\nabla} \ln \theta, \quad (7)$$

where ω_1 and ω_i $(i \geq 2)$ are given by $\omega_1 = x_1 p(1 - x_1)/D^2$ and $\omega_i = -x_i x_1 p/D^2$, respectively, and $\vec{A}_i$, $\overleftrightarrow{B}_i$, $\vec{C}_i^j$, D_i, $\vec{E}_i^j$, and $\vec{F}_i$, where $i = 1 \cdots N$, are the unknown functions of the reduced velocity $\vec{W}_i = \sqrt{\frac{m_i}{2k_B T_i}} \vec{C}_i$, the local composition, and the local temperature. It is very important to note that the form of the third term on the right-hand side of Eq. (6), $\sum_{j=1}^{N} \vec{C}_1^j \cdot \vec{d}_j$, is equivalent to taking into account the diffusion process between electrons and heavy species, which makes the calculation of the complete set of diffusion coefficients possible. This differs from the simplified theory presented in Refs. 41–43.

Finally, solutions to the integral Eqs. (2) and (3) are obtained with a similar method to that presented in Refs. 7 and 8, in which the unknown quantities $\overleftrightarrow{\psi}_i^{(s,k)}$ are expanded in a series of Sonine polynomials

$$\overleftrightarrow{\psi}_i^{(s,k)} = \overleftrightarrow{\Theta}_i \sum_{p=0}^{\xi-1} t_{ip}^{(s,k)}(\xi) S_n^{(p)}(W_i^2), \quad (8)$$

where ξ is the so-called level of approximation to the transport coefficients and the $\overleftrightarrow{\psi}_i^{(s,k)}$ are the arbitrary unknown tensors. The value of the index n, the meaning of tensor $\overleftrightarrow{\Theta}_i$, and the unknown coefficient $t_{ip}^{(s,k)}$ are given in Table I. Eventually, it is shown that $t_{ip}^{(s,k)}(\xi)$ can be obtained by solving the following equations:

$$-R_{1m}^{(s,k)} = \sum_{p=0}^{\xi-1} Q_1^{mp} t_{1p}^{(s,k)}(\xi), \quad (9)$$

TABLE I. Expressions of $\overleftrightarrow{\Theta}_i$, $t_{ip}^{(s,k)}$, and n. Here $\vec{W}_i = \sqrt{\frac{m_i}{2k_B T_i}} \vec{C}_i$ corresponds to the reduced velocity, and $\vec{W}_i \,^\circ \vec{W}_i$ is the symmetric traceless tensor $\vec{W}_i \vec{W}_i - \frac{1}{3} W_i^2 \overleftrightarrow{I}$, with $\overleftrightarrow{I}$ as the unit tensor.

$\overleftrightarrow{\psi}_i^{(s,k)}$	n	$t_{ip}^{(s,k)}$	$\overleftrightarrow{\Theta}_i$
$\vec{A}_i$	$\frac{3}{2}$	a_{ip}	$\vec{W}_i$
$\overleftrightarrow{B}_i$	$\frac{5}{2}$	b_{ip}	$\vec{W}_i \,^\circ \vec{W}_i$
$\vec{C}_i^s - \vec{C}_i^k$	$\frac{3}{2}$	$c_{ip}^{(s,k)}$	$\vec{W}_i$
$\vec{E}_i^s - \vec{E}_i^k$	$\frac{3}{2}$	$e_{ip}^{(s,k)}$	$\vec{W}_i$
$\vec{F}_i$	$\frac{3}{2}$	f_{ip}	$\vec{W}_i$

$$-R_{im}^{(s,k)} = \sum_{p=0}^{\xi-1}\sum_{j=2}^{N}\tilde{Q}_{ij}^{mp} t_{jp}^{(s,k)}(\xi) + \sum_{p=0}^{\xi-1}\tilde{Q}_{i1}^{mp*} t_{1p}^{(s,k)}(\xi), \quad (i \geq 2), \tag{10}$$

$$Q_1^{mp} = \sum_{j=1}^{N} n_1 n_j [\overleftrightarrow{\Theta}_1 S_n^{(m)}(W_1^2); \overleftrightarrow{\Theta}_1 S_n^{(p)}(W_1^2)]_{1j} + n_1^2 [\overleftrightarrow{\Theta}_1 S_n^{(m)}(W_1^2); \overleftrightarrow{\Theta} S_n^{(p)}(\mathrm{W}^2)]_1, \tag{11}$$

with

$$\tilde{Q}_{ij}^{mp}{}_{(i\geq 2, j\geq 2)} = \begin{cases} Q_{ij}^{mp} & \text{when } t_{jp}^{(s,k)} = b_{jp} \\ Q_{ij}^{mp} - \dfrac{n_j\sqrt{m_j T_j}}{n_i\sqrt{m_i T_i}} Q_{ii}^{mp}\delta_{m0}\delta_{p0} & \text{when } t_{jp}^{(s,k)} = a_{jp}, c_{jp}^{(s,k)}, e_{jp}^{(s,k)} \text{ or } f_{ip}, \end{cases} \tag{12}$$

and

$$\tilde{Q}_{i1}^{mp*}{}_{(i\geq 2)} = \begin{cases} Q_{i1}^{mp*} & \text{when } t_{1p}^{(s,k)} = b_{1p} \\ Q_{i1}^{mp*} - \dfrac{n_1\sqrt{m_1 T_1}}{n_i\sqrt{m_i T_i}} Q_{ii}^{mp}\delta_{m0}\delta_{p0} & \text{when } t_{1p}^{(s,k)} = a_{1p}, c_{1p}^{(s,k)}, e_{jp}^{(s,k)} \text{ or } f_{1p}. \end{cases} \tag{13}$$

Q_{ij}^{mp} and Q_{i1}^{mp*} are defined as

$$Q_{ij}^{mp} = \sum_{k=2}^{N} n_i n_k \{\delta_{ij}[\overleftrightarrow{\Theta}_i S_n^{(m)}(W_i^2); \overleftrightarrow{\Theta}_i S_n^{(p)}(W_i^2)]_{ik} + \delta_{jk}[\overleftrightarrow{\Theta}_i S_n^{(m)}(W_i^2); \overleftrightarrow{\Theta}_k S_n^{(p)}(W_k^2)]_{ik}, \tag{14}$$

$$Q_{i1}^{mp*} = n_i n_1 [\overleftrightarrow{\Theta}_i S_n^{(m)}(W_i^2); \overleftrightarrow{\Theta}_1 S_n^{(p)}(W_1^2)]_{i1}. \tag{15}$$

The expressions for $R_{1m}^{(s,k)}$ and $R_{im}^{(s,k)} (i \geq 2)$ can then be obtained as listed in Table II. In Eqs. (14) and (15), the terms of form $[\overleftrightarrow{G}_{ij}; \overleftrightarrow{H}_{ij}]_{ij}$ are the bracket integrals defined by Chapman and Cowling,[8] which may be written as a linear combination of a set of collision integrals, given in the supplementary material[51] and the Appendix. Expressions for some of the bracket integrals, Q_1^{mp}, $\tilde{Q}_{ij}^{mp}$, and $\tilde{Q}_{i1}^{mp*}$, in terms of the collision integrals are given in Refs. 7–9 and 41.

III. FORMULATION OF THE TRANSPORT COEFFICIENTS

The expressions for the flux of mass, momentum, and energy of species i can be obtained with the first-order approximation of the distribution function

$$f_i = f_i^{(0)}(1 + \phi_i). \tag{16}$$

TABLE II. Expressions for $R_{1m}^{(s,k)}$ and $R_{im}^{(s,k)}$.

$t_{ip}^{(s,k)}$	$R_{1m}^{(s,k)}$	$R_{im}^{(s,k)}$ $(i \geq 2)$
a_{ip}	$\frac{15}{2} n_1 \sqrt{\frac{k_B T_1}{2m_1}}\delta_{m1}$	$\frac{15}{2} n_i \sqrt{\frac{k_B T_i}{2m_i}}\delta_{m1}$
b_{ip}	$-5n_1\delta_{m0}$	$-5n_i\delta_{m0}$
$c_{ip}^{(s,k)}$	$3\sqrt{\frac{k_B T_1}{2m_1}}\frac{(\delta_{1s} - \delta_{1k})}{k_B T_1}\delta_{m0}$	$3\sqrt{\frac{k_B T_i}{2m_i}}\frac{(\delta_{is} - \delta_{ik})}{k_B T_i}\delta_{m0}$
$e_{ip}^{(s,k)}$	$3\sqrt{\frac{k_B T_1}{2m_1}}\frac{(\delta_{1s} - \delta_{1k})}{k_B T_h}\delta_{m0}$	$3\sqrt{\frac{k_B T_i}{2m_i}}\frac{\theta(\delta_{is} - \delta_{ik})}{k_B T_h}\delta_{m0}$
f_{ip}	$\frac{15}{2} n_1 \sqrt{\frac{k_B T_1}{2m_1}}\delta_{m1}$	0

Using the expression given for ϕ_i, the diffusion velocity, the pressure tensor, and the heat flux vector can be written in terms of the expansion coefficients $t_{ip}^{(s,k)}$. For simplicity, let

$$\phi_i = -\vec{A}_i \cdot \vec{\nabla}\ln T_h - \overleftrightarrow{B}_i : \vec{\nabla}\vec{v}_0 + \sum_{j=1}^{N}\vec{C}_i^j \cdot \vec{d}_j + D_i Q_1^{(0)} + \sum_{j=1}^{N}\vec{E}_i^j\omega_j \cdot \vec{\nabla}\ln\theta - \vec{F}_i \cdot \vec{\nabla}\ln\theta \quad (i = 1\cdots N). \tag{17}$$

A. Diffusion coefficients

The diffusion velocity of species i is given by

$$\vec{V}_i = \frac{1}{n_i}\int \vec{C}_i f_i d\vec{C}_i. \tag{18}$$

Substituting Eq. (17) into Eq. (16) and then into Eq. (18) and also with the help of the Sonine polynomial expansions [Eq. (8)], we obtain

$$\vec{V}_i = \frac{n_t}{n_i \rho k_B T_i}\sum_{j=1}^{N} m_j (D_{ij}\vec{d}_j + D_{ij}^{\theta}\omega_j \vec{\nabla}\ln\theta) - \frac{D_i^T}{n_i m_i}\vec{\nabla}\ln T_h - \frac{D_i^{\theta*}}{n_i m_i}\vec{\nabla}\ln\theta, \tag{19}$$

where

$$D_{ij} = \frac{n_i \rho k_B T_i}{n_t m_j}\sqrt{\frac{k_B T_i}{2m_i}} c_{i0}^{(j,i)}(\xi), \tag{20}$$

$$D_i^T = n_i m_i \sqrt{\frac{k_B T_i}{2m_i}} a_{i0}(\xi), \tag{21}$$

$$D_{ij}^{\theta} = \frac{n_i \rho k_B T_i}{n_t m_j}\sqrt{\frac{k_B T_i}{2m_i}} e_{i0}^{(j,i)}(\xi), \tag{22}$$

and

$$D_i^{\theta*} = n_i m_i \sqrt{\frac{k_B T_i}{2m_i}} f_{i0}(\xi). \qquad (23)$$

The expansion coefficients $c_{i0}^{(j,i)}(\xi)$, $a_{i0}(\xi)$, $e_{i0}^{(j,i)}(\xi)$, and $f_{i0}(\xi)$ can be calculated from the sets of linear Eqs. (9) and (10); the results are given in the supplementary material.[51]

In Eq. (20), the coefficients D_{ij} are the ordinary diffusion coefficients for the 2-T plasma, which are complete for arbitrary species i and j. The coefficients D_i^T are the 2-T thermal diffusion coefficients. As a consequence of the new definition of $\vec{d}_j$ by Rat *et al.*,[46] the thermal non-equilibrium diffusion coefficients D_{ij}^θ and $D_i^{\theta*}$ are introduced so as to ensure the exact mass conservation in the plasma system.

B. Viscosity

The pressure tensor representing the momentum flux in the plasma system is given by

$$\overleftrightarrow{P} = \sum_{i=1}^{N} m_i \int f_i \vec{C}_i \vec{C}_i \mathrm{d}\vec{C}_i. \qquad (24)$$

Introducing Eq. (16) due to Eq. (17) into Eq. (24) and using the Sonine polynomial expansions [Eq. (8)], one can obtain

$$\overleftrightarrow{P} = p\overleftrightarrow{I} - 2\mu\overleftrightarrow{S}, \qquad (25)$$

where

$$\overleftrightarrow{S} = \frac{1}{2}\left[\vec{\nabla}\vec{v}_0 + (\nabla\vec{v}_0)^T\right] - \frac{1}{3}(\nabla\vec{v}_0 : \overleftrightarrow{I})\overleftrightarrow{I}. \qquad (26)$$

The total viscosity μ is expressed as

$$\mu = \frac{1}{2} k_B \sum_{i=2}^{N} n_i T_i b_{i0}(\xi), \qquad (27)$$

where the contribution of electrons to the viscosity is neglected. The expansion coefficients $b_{i0}(\xi)$ are calculated as discussed in the supplementary material.[51]

C. Translational thermal conductivity

Considering the occurrence of chemical reactions (e.g., dissociation, ionization, recombination, etc.) and the internal energy of species due to internal degrees of freedom (e.g., electronic, rotational, or vibrational excitation), the energy flux vector may be written as

$$\vec{q} = \sum_{i=1}^{N} m_i \int \left(\frac{1}{2}C_i^2 + \varepsilon_i^r + \varepsilon_i^{in}\right)\vec{C}_i f_i \mathrm{d}\vec{C}_i, \qquad (28)$$

where ε_i^r and ε_i^{in} represent, respectively, the related reaction energy and the internal energy per unit mass of species i. Using a similar method to that discussed in the foregoing sub-sections, the energy flux can be re-written as

$$\vec{q} = \sum_{i=1}^{N}\frac{5}{2}n_i k_B T_i \vec{V}_i + \sum_{i=1}^{N} n_i m_i \varepsilon_i^r \vec{V}_i + \sum_{i=1}^{N} n_i m_i \varepsilon_i^{in}\vec{V}_i - \sum_{i=1}^{N}\lambda_i'\vec{\nabla}T_h - \sum_{i=1}^{N}\lambda_i'^{\theta} T_i \vec{\nabla}\ln\theta - \sum_{i=1}^{N}\sum_{j=1}^{N}\frac{1}{n_j m_j}\lambda_{ij}^D \cdot \vec{d}_j, \qquad (29)$$

where

$$\lambda_i' = -\frac{5}{4}k_B \frac{T_i}{T_h} n_i \sqrt{\frac{2kT_i}{m_i}} a_{i1}(\xi), \qquad (30)$$

$$\lambda_i'^{\theta} = -\frac{5}{4}k_B n_i \sqrt{\frac{2k_B T_i}{m_i}}\left[f_{i1}(\xi) - \sum_{j=1}^{N} e_{i1}^{(j,i)}(\xi)\omega_j\right], \qquad (31)$$

$$\lambda_{ij}^D = \frac{5}{4} n_i n_j m_j k_B T_i \sqrt{\frac{2k_B T_i}{m_i}} c_{i1}^{(j,i)}(\xi). \qquad (32)$$

Nevertheless λ_i' and $\lambda_i'^{\theta}$ do not represent the true thermal conductivity, since the thermal conductivity is usually defined as the coefficient of the temperature gradient term when all diffusion velocities are zero. To obtain the true thermal conductivity, the expression for $\vec{d}_j$ obtained from Eq. (19) is employed in Eq. (29), giving

$$\vec{q} = \sum_{i=1}^{N}\frac{5}{2}n_i k_B T_i \vec{V}_i + \sum_{i=1}^{N} n_i m_i \varepsilon_i^r \vec{V}_i + \sum_{i=1}^{N} n_i m_i \varepsilon_i^{in}\vec{V}_i - \sum_{i=1}^{N}\frac{\rho k_B}{n_t}\sum_{j,k=1}^{N}\frac{\lambda_{ij}^D n_k T_k E_{jk}}{n_j m_j}\vec{V}_k - \sum_{i=1}^{N}\lambda_i \vec{\nabla}T_h - \sum_{i=1}^{N}\lambda_i^{\theta} T_i \vec{\nabla}\ln\theta, \qquad (33)$$

where

$$\lambda_i = \lambda_i' + \frac{\rho k_B}{n_t}\sum_{j,k=1}^{N}\frac{\lambda_{ij}^D T_k E_{jk}}{n_j m_j m_k T_h} D_k^T, \qquad (34)$$

$$\lambda_i^{\theta} = \lambda_i'^{\theta} + \frac{\rho k_B}{n_t}\sum_{j,k=1}^{N}\frac{\lambda_{ij}^D n_k T_k E_{jk}}{n_j m_j T_i} D_k^{\theta}, \qquad (35)$$

$$D_i^{\theta} = \frac{D_i^{\theta*}}{n_i m_i} - \frac{n_t}{n_i \rho k_B T_i}\sum_{j=1}^{N} m_j D_{ij}^{\theta}\omega_j, \qquad (36)$$

and E_{jk} is defined as an element of inverse of the matrix whose general element is $D_{ij}m_j$, as presented in Ref. 41. λ_i and λ_i^{θ} are the translational thermal conductivity and the non-equilibrium thermal conductivity of the 2-T plasma, respectively.[46] The expansion coefficients $c_{i1}^{(j,k)}(\xi)$, $f_{i1}(\xi)$, $e_{i1}^{(j,k)}(\xi)$, and $a_{i1}(\xi)$ are also given in the supplementary material.[51]

D. Electrical conductivity

The current density in a plasma system can be expressed as

$$\vec{j} = \sum_{i=1}^{N} eZ_i n_i \vec{V}_i, \qquad (37)$$

where eZ_i is the charge of species i, and e is the elementary electric charge. The electrostatic force acting on the ith species is

$$\vec{X}_i = eZ_i(\vec{E}^e + \vec{E}^a), \tag{38}$$

where $\vec{E}^e$ is the externally applied electric field while $\vec{E}^a$ is the internal electric field that is caused due to the tendency of electrons to diffuse more rapidly than ions. By employing the charge neutrality condition

$$\sum_{j=1}^{N} n_j Z_j = 0, \tag{39}$$

the diffusion driving force for an arbitrary particle can be written as

$$\vec{d}_j = -n_j Z_j e(\vec{E}^e + \vec{E}^a), \tag{40}$$

where for simplicity the gradient of pressure and concentration is ignored in the derivation of electrical conductivity.[8]

The internal electric field $\vec{E}^a$ slows the diffusion of electrons and speeds the diffusion of ions so that quasi-neutrality is maintained. As a result, a steady state will be reached in which the net electric current density within the plasma is due only to the externally applied electric field $\vec{E}^e$,[45] and thus

$$\sum_{i=1}^{N} eZ_i n_i \vec{V}_i = \sigma \vec{E}^e, \tag{41}$$

where σ is the 2-T electrical conductivity. Substituting Eq. (40) into the expression for the diffusion velocity (19) and then into Eq. (41) and comparing the terms containing $\vec{E}^e$ on both sides, the following expression for the electrical conductivity is obtained:

$$\sigma = -\frac{e^2 n_t}{\rho k_B} \sum_{i=1}^{N} \left[\frac{Z_i}{T_i} \sum_{j=1}^{N} (m_j n_j Z_j D_{ij}) \right]. \tag{42}$$

IV. DISCUSSIONS

A. Completeness of the diffusion coefficients and derivation of the combined diffusion coefficients

In the preceding derivations, it is seen clearly that in contrast to the simplified theory of Devoto[41] and Bonnefoi,[42,43] the coupling between electrons and heavy species is maintained; that is to say, the subsystems of electron and heavy-species are not treated in isolation from each other. This is a consequence of the introduction of the new definition of $\vec{d}_i$ given by Rat *et al.*,[46] which allows the exchange of mass, momentum, and energy between the subsystems of electrons and heavy species. According to the requirement that the sum of the mass fluxes of all species must vanish, i.e.,

$$\sum_{i=1}^{N} n_i m_i \vec{V}_i = 0, \tag{43}$$

the diffusion coefficients should satisfy the following relationships:

$$\sum_{i=1}^{N} \frac{m_i}{T_i} (m_h D_{ih} - m_k D_{ik}) = 0, \tag{44}$$

$$\sum_{i=1}^{N} D_i^T = 0, \tag{45}$$

$$\sum_{i=1}^{N} \frac{m_i}{T_i} \left(m_h D_{ik}^\theta - m_k D_{ik}^\theta \right) = 0, \tag{46}$$

$$\sum_{i=1}^{N} D_i^{\theta*} = 0. \tag{47}$$

On the other hand, since the diffusion processes between electrons and heavy species are taken into account in this study, the diffusion coefficients given in Sec. III are complete. In addition, based on the assumptions made in Sec. I, a term, $\int\int f_i^{(0)} f_1^{(0)} (\phi_1' - \phi_1) g\sigma_{i1} \mathrm{d}\Omega\, \mathrm{d}\vec{c}_1$, on the right hand side of Eq. (3) appears and leads to the bracket integral terms $\tilde{Q}_{i1}^{mp*}$. Although it can be proved that this term is of magnitude m_e/m_h or smaller (see Appendix), it is still not clear whether this term can be neglected due to the relationship of Eq. (47). This will be checked in future numerical calculations; the term is retained here. With the complete diffusion coefficients, based on the theory of Murphy,[45] the 2-T combined diffusion coefficients in a plasma system containing two non-reacting homonuclear gases A and B can be obtained as follows.

Taking into account the ambipolar diffusion process, the diffusion velocity of species i can be re-written as

$$\vec{V}_i = \frac{n_t}{n_i \rho k_B T_i} \sum_{j=1}^{N} m_j (D_{ij}^a \vec{d}_j' + D_{ij}^{\theta a} \omega_j \vec{\nabla} \ln \theta) - \frac{D_i^{Ta}}{n_i m_i} \vec{\nabla} \ln T_h - \frac{D_i^{\theta a*}}{n_i m_i} \vec{\nabla} \ln \theta, \tag{48}$$

where

$$\vec{d}_1' = p \left(\frac{x_1 \theta}{D} - \frac{\rho_1}{\rho} \right) \vec{\nabla} \ln p + \frac{p\theta}{D^2} \vec{\nabla} x_1, \tag{49}$$

and

$$\vec{d}_i' = p \left(\frac{x_i}{D} - \frac{\rho_i}{\rho} \right) \vec{\nabla} \ln p + \frac{p \vec{\nabla} x_i}{D} - \frac{p x_i (\theta - 1)}{D^2} \vec{\nabla} x_1, \quad (i \geq 2). \tag{50}$$

In Eq. (48), the corresponding ambipolar diffusion coefficients are expressed as

$$D_{ij}^a = D_{ij} + \frac{\alpha_i}{\beta} \sum_{\ell=1}^{N} \frac{Z_\ell}{T_\ell} D_{\ell j}, \tag{51}$$

$$D_{ij}^{\theta a} = D_{ij}^\theta + \frac{\alpha_i}{\beta} \sum_{\ell=1}^{N} \frac{Z_\ell}{T_\ell} D_{\ell j}^\theta, \tag{52}$$

$$D_i^{Ta} = D_i^T + \frac{\alpha_i m_i}{\beta T_i}\sum_{\ell=1}^{N}\frac{Z_\ell D_\ell^T}{m_\ell}, \qquad (53)$$

$$D_i^{\theta a*} = D_i^{\theta *} + \frac{\alpha_i m_i}{\beta T_i}\sum_{\ell=1}^{N}\frac{Z_\ell D_\ell^{\theta^*}}{m_\ell}, \qquad (54)$$

$$\alpha_i = \sum_{j=1}^{N} n_j m_j Z_j D_{ij}, \qquad (55)$$

$$\beta = -\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{Z_i}{T_i}Z_j n_j m_j D_{ij}, \qquad (56)$$

with $T_1 = T_e$ and $T_i = T_h$ if $i \geq 2$.

Thus, the number flux of species i, $\vec{g}_i$, can be expressed as

$$\vec{g}_i = n_i\vec{V}_i = \frac{n_t}{\rho k_B T_i}\sum_{j=1}^{N} m_j(D_{ij}^a\vec{d}_j' + D_{ij}^{\theta a}\omega_j\vec{\nabla}\ln\theta) - \frac{D_i^{Ta}}{m_i}\vec{\nabla}\ln T_h - \frac{D_i^{\theta a^*}}{m_i}\vec{\nabla}\ln\theta, \qquad (57)$$

where the same notation as that in Ref. 45 is used, i.e., subscript 1 corresponds to electrons, subscripts $i = 2, \ldots, p$ represent the species derived from gas A, and subscripts $i = p+1, \ldots, N$ denote the species derived from gas B. With the assumption that the plasma composition is defined as a function of the temperature of heavy species (T_h), the non-equilibrium parameter (θ), pressure (p), and the relative mass fractions of the two gases ($\overline{x_A}$ and $\overline{x_B}$), the number flux of gas A is given by

$$\vec{g}_A = \sum_{i=1}^{p} s_i\vec{g}_i = \frac{n_t p}{\rho k_B T_h}\overline{m_B}(\overline{D_{AB}^x}\vec{\nabla}\overline{x_B} + \overline{D_{AB}^p}\vec{\nabla}\ln p) - \frac{\overline{D_{AB}^T}}{\overline{m_A}}\vec{\nabla}\ln T_h + \left(\frac{n_t p}{\rho k_B T_h}\overline{m_B}\,\overline{D_{AB}^\theta} - \frac{\overline{D_{AB}^{\theta^*}}}{\overline{m_A}}\right)\vec{\nabla}\ln\theta, \qquad (58)$$

where the coefficients $\overline{D_{AB}^x}$, $\overline{D_{AB}^p}$, and $\overline{D_{AB}^T}$ are the combined ordinary diffusion coefficient, the combined pressure diffusion coefficient, and the combined thermal diffusion coefficient of 2-T plasmas, respectively, and $\overline{D_{AB}^\theta}$ and $\overline{D_{AB}^{\theta^*}}$ are the combined diffusion coefficients due to the gradient of the non-equilibrium parameter. They can be expressed as

$$\overline{D_{AB}^x} = \frac{1}{\overline{m_B}}\sum_{i=1}^{p} s_i\sum_{j=2}^{N}\left(\frac{m_j D_{ij}^a}{D} + \frac{(\theta-1)A_i}{D^2} - \frac{m_1 D_{i1}^a\theta}{D^2}\right)\left(\frac{\partial x_j}{\partial\overline{x_B}}\right), \qquad (59)$$

$$\overline{D_{AB}^p} = \frac{1}{\overline{m_B}}\sum_{i=1}^{p} s_i\left\{m_1 D_{i1}^a\left(\frac{x_1\theta}{D} - \frac{\rho_1}{\rho}\right) + \sum_{j=2}^{N}\left[m_j D_{ij}^a\left(\frac{x_j}{D} - \frac{\rho_j}{\rho}\right) + p\left(\frac{m_j D_{ij}^a}{D} + \frac{(\theta-1)A_i}{D^2} - \frac{m_1 D_{i1}^a\theta}{D^2}\right)\left(\frac{\partial x_j}{\partial p}\right)\right]\right\}, \qquad (60)$$

$$\overline{D_{AB}^T} = \overline{m_A}\sum_{i=1}^{p} s_i\left[\frac{D_i^{Ta}}{m_i} - \frac{n_t p}{\rho k_B T_h}\sum_{j=2}^{N}\times\left(\frac{m_j D_{ij}^a}{D} + \frac{(\theta-1)A_i}{D^2} - \frac{m_1 D_{i1}^a\theta}{D^2}\right)T_h\left(\frac{\partial x_j}{\partial T_h}\right)\right], \qquad (61)$$

$$\overline{D_{AB}^\theta} = \frac{1}{\overline{m_B}}\sum_{i=1}^{p} s_i\left[\frac{1}{p}\sum_{j=2}^{N}(m_j D_{ij}^{\theta a} - m_1 D_{i1}^{\theta a})\omega_j + \sum_{j=2}^{N}\left(\frac{m_j D_{ij}^a}{D} + \frac{(\theta-1)A_i}{D^2} - \frac{m_1 D_{i1}^a\theta}{D^2}\right)\theta\left(\frac{\partial x_j}{\partial\theta}\right)\right], \qquad (62)$$

$$\overline{D_{AB}^{\theta^*}} = \overline{m_A}\sum_{i=1}^{p} s_i\frac{D_i^{\theta a^*}}{m_i}, \qquad (63)$$

where

$$\overline{m_A} = \sum_{i=2}^{p} m_i x_i \Big/ \sum_{i=2}^{p} x_i, \qquad (64)$$

$$\overline{m_B} = \sum_{i=p+1}^{N} m_i x_i \Big/ \sum_{i=p+1}^{N} x_i, \qquad (65)$$

$$\overline{x_A} = \sum_{i=2}^{p}(1+Z_i)x_i, \qquad (66)$$

$$\overline{x_B} = \sum_{i=p+1}^{N}(1+Z_i)x_i = 1 - \overline{x_A}, \qquad (67)$$

are, respectively, the average masses of the heavy species of gas A and gas B, and the relative concentrations of gas A and gas B.

Similarly, the number flux of gas B is given by

$$\vec{g}_B = \sum_{i=p+1}^{N} s_i\vec{g}_i = \frac{n_t p}{\rho k_B T_h}\overline{m_A}(\overline{D_{BA}^x}\vec{\nabla}\overline{x_A} + \overline{D_{BA}^p}\vec{\nabla}\ln p) - \frac{\overline{D_{BA}^T}}{\overline{m_B}}\vec{\nabla}\ln T_h + \left(\frac{n_t p}{\rho k_B T_h}\overline{m_A}\,\overline{D_{BA}^\theta} - \frac{\overline{D_{BA}^{\theta *}}}{\overline{m_B}}\right)\vec{\nabla}\ln\theta, \qquad (68)$$

and the expressions of the 2-T combined diffusion coefficients can be calculated by

$$\overline{D_{BA}^x} = -\frac{1}{\overline{m_A}}\sum_{i=p+1}^{N} s_i\sum_{j=2}^{N}\left(\frac{m_j D_{ij}^a}{D} + \frac{(\theta-1)A_i}{D^2} - \frac{m_1 D_{i1}^a\theta}{D^2}\right)\left(\frac{\partial x_j}{\partial\overline{x_B}}\right), \qquad (69)$$

$$\overline{D_{BA}^p} = \frac{1}{\overline{m_A}}\sum_{i=p+1}^{N} s_i\left\{m_1 D_{i1}^a\left(\frac{x_1\theta}{D} - \frac{\rho_1}{\rho}\right) + \sum_{j=2}^{N}\left[m_j D_{ij}^a\left(\frac{x_j}{D} - \frac{\rho_j}{\rho}\right) + p\left(\frac{m_j D_{ij}^a}{D} + \frac{(\theta-1)A_i}{D^2} - \frac{m_1 D_{i1}^a\theta}{D^2}\right)\left(\frac{\partial x_j}{\partial p}\right)\right]\right\}, \qquad (70)$$

$$\overline{D_{BA}^T} = \overline{m_B}\sum_{i=p+1}^{N} s_i\left[\frac{D_i^{Ta}}{m_i} - \frac{n_t p}{\rho k_B T_h}\sum_{j=2}^{N}\left(\frac{m_j D_{ij}^a}{D} + \frac{(\theta-1)A_i}{D^2} - \frac{m_1 D_{i1}^a\theta}{D^2}\right)T_h\left(\frac{\partial x_j}{\partial T_h}\right)\right], \qquad (71)$$

$$\overline{D_{BA}^{\theta}} = \frac{1}{\overline{m_A}} \sum_{i=p+1}^{N} s_i \left[\frac{1}{p} \sum_{j=2}^{N} (m_j D_{ij}^{\theta a} - m_1 D_{i1}^{\theta a}) \omega_j + \sum_{j=2}^{N} \left(\frac{m_j D_{ij}^{a}}{D} + \frac{(\theta-1)A_i}{D^2} - \frac{m_1 D_{i1}^{a} \theta}{D^2} \right) \theta \left(\frac{\partial x_j}{\partial \theta} \right) \right], \quad (72)$$

$$\overline{D_{BA}^{\theta^*}} = \overline{m_B} \sum_{i=p+1}^{N} s_i \frac{D_i^{\theta a^*}}{m_i}. \quad (73)$$

In the preceding equations, the variable s_i is the stoichiometric coefficient, which is defined as[45,52]

$$s_1 = (m_e/\overline{m_A}) \sum_{k=2}^{p} Z_k x_k / x_e, \quad (74)$$

$$s_i = b_i \sum_{k=2}^{p} x_k \Big/ \sum_{k=2}^{p} b_k x_k, \; 2 \le i \le p, \quad (75)$$

$$s_i = b_i \sum_{k=p+1}^{N} x_k \Big/ \sum_{k=p+1}^{N} b_k x_k, \; p+1 \le i \le N, \quad (76)$$

where b_i is the number of atoms in a molecule of species i.

Based on the relationship [Eq. (43)] and Eqs. (58) and (68), the foregoing 2-T combined diffusion coefficients should satisfy the following conditions:

$$\overline{D_{AB}^{x}} = \overline{D_{BA}^{x}}, \quad (77)$$

$$\overline{D_{AB}^{p}} = -\overline{D_{BA}^{p}}, \quad (78)$$

$$\overline{D_{AB}^{T}} = -\overline{D_{BA}^{T}}, \quad (79)$$

$$\overline{D_{AB}^{\theta}} = -\overline{D_{BA}^{\theta}}, \quad (80)$$

$$\overline{D_{AB}^{\theta^*}} = -\overline{D_{BA}^{\theta^*}}. \quad (81)$$

B. Simplicity of the expressions for the Boltzmann equations and those for the corresponding transport coefficients

The inequality $m_e/m_h \ll 1$ is, of course, a physical fact. As a consequence, some reasonable simplifications that were first proposed by Devoto are valid for the derivation of the transport coefficients under plasma conditions, and the complex theory of Rat *et al.*[46] is not necessary. Based on these simplifications, not only are the expressions for the transport coefficients obtained in this study considerably simpler than those based on the complex theory of Rat *et al.*, but there is also no need to define new bracket integrals.[46] For example, the fourth-order approximation ($\xi = 4$) for the ordinary diffusion coefficients between electrons and heavy species is given by

$$[D_{1j}]_4 = -\frac{3 n_e \rho}{\sqrt{2} n_t m_j} \frac{k_B T_e / m_e}{|Q_1|} (\delta_{1j} - 1) \cdot \begin{vmatrix} Q_1^{11} & Q_1^{12} & Q_1^{13} \\ Q_1^{21} & Q_1^{22} & Q_1^{23} \\ Q_1^{31} & Q_1^{32} & Q_1^{33} \end{vmatrix}, \quad (82)$$

where $|Q_1|$ is the determinant of the Q_1^{mp} element. Obviously, the order of the determinant is reduced in Eq. (82) compared to the full expressions (Eq. (3.3) in Ref. 46), where the order of the determinant is proportional to the number of the components (N) in a plasma system and to the order of the approximation (ξ).[9] Furthermore, Ref. 53 indicated that the higher levels of approximation in the Sonine polynomial expansion were required, particularly for the thermal conductivity, while the results from our derivation, like those in Ref. 9, still allow the use of lower levels of approximation in the heavy particle expressions, and require the higher level approximations only for the electron expressions. This significantly simplifies the calculations.

Finally, the new theory of transport properties is also applicable to LTE ($\theta = 1$) plasmas. It can easily be checked that the expressions for the transport coefficients in Sec. III and the combined diffusion coefficients in Sec. IV A can be reduced to the previously reported expressions for a plasma when $\theta = 1$.[9,45]

V. CONCLUSIONS

In this paper, a new simplified theory of the transport properties of a 2-T plasma system is proposed based on the solution of the Boltzmann equations using a modified Chapman–Enskog method. The major differences between the derivations in this study and those in previous publications are the employment of both the physical fact $m_e/m_h \ll 1$ and the inclusion of the coupling between the electron and heavy-species subsystems. While they are treated as separate systems, mass, momentum, and energy exchanges between these two subsystems are considered, which are particularly important for the treatment of the diffusion processes. Based on these two newly modified assumptions, simplified yet complete transport coefficients are obtained for 2-T plasmas.

The new theory has two particular physical and practical advantages over the previous theories:

(1) The diffusion coefficients calculated from the theory satisfy the mass conservation law in the plasma system, and the corresponding combined diffusion coefficients in a 2-T gas-mixture plasma system may also be calculated.
(2) There is no increase in the complexity of the expressions for the transport coefficients, and in particular no increase in the number of collision integrals required, which means that the new theory can easily be implemented in existing computer programs for the calculation of 2-T plasma properties.

In addition, it is noted that based on the same method of solution of the Boltzmann equation and on the same definitions for the fluxes of mass, momentum, and energy within a non-equilibrium plasma system, self-consistent derivations of the governing equations for modeling of 2-T plasmas can be conducted. This will be presented in a subsequent paper. On this basis, a self-consistent physical-mathematical model may be established to describe the complicated physical and chemical processes in a gas discharge plasma system.

Finally, it will have been noted by the reader that no examples have been presented of transport properties calculated using the formulas derived in this paper. We plan to develop the required computer codes, but this is a complicated and lengthy task, requiring calculation of the composition of the non-equilibrium plasma as well as implementation of the expressions for transport properties. It should be noted that since one of the main points of this paper is that we are able to obtain expressions that are as accurate as those of Rat *et al.*[46] but are much simpler, we would not expect to see any significant differences between the results of Rat *et al.*[46] and those obtained from our formulas, assuming that the plasma composition used in both cases was the same.

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APPENDIX: COLLISION INTEGRALS

The bracket integrals, which are in terms of the collision integrals $\Omega_{ij}^{(l,s)}$ defined by Chapman and Cowling and used for calculating the transport coefficients,[8] are expressed as follows:

$$\Omega_{ij}^{(l,s)} = \left(\frac{kT_{ij}^*}{2\pi\mu_{ij}}\right)^{\frac{1}{2}} \int_0^\infty e^{-\gamma^2}\gamma^{2s+3} Q_{ij}^{(l)} \mathrm{d}\gamma, \qquad \text{(A1)}$$

where

$$Q_{ij}^{(l)} = 2\pi \int_0^\pi \sigma_{ij}(\chi, g)(1-\cos^l\chi)\sin\chi \mathrm{d}\chi = 2\pi\int_0^\infty (1-\cos^l\chi) b\mathrm{d}b \qquad \text{(A2)}$$

is the gas-kinetic cross section, $\gamma = (\mu_{ij}/2k_B T_{ij}^*)^{\frac{1}{2}} g$ is the reduced relative speed, $\mu_{ij} = m_i m_j/(m_i+m_j)$ is the reduced mass, χ and b are the deflection angle and the impact parameter, respectively, and T_{ij}^* is the effective temperature of collisions, defined as[46]

$$T_{ij}^* = \left[\frac{1}{m_i+m_j}\left(\frac{m_i}{T_j}+\frac{m_j}{T_i}\right)\right]^{-1}. \qquad \text{(A3)}$$

Note that when i (or j) denotes the electrons and j (or i) denotes the heavy species, we can write $T_{ij}^* = T_e$ and $\mu_{ij} = m_e$, which is derived from the small value of m_e/m_h. For rigid spherical molecules of diameter σ, the preceding relation may be written as

$$[\Omega_{ij}^{(l,s)}]_{rs} = \frac{(s+1)![2l+1-(-1)^l]}{4(l+1)}\left(\frac{k_B T_{ij}^*}{2\pi\mu_{ij}}\right)^{\frac{1}{2}} \pi\sigma^2. \qquad \text{(A4)}$$

Finally, the bracket integrals are expressed with the reduced collision integrals $\bar{Q}_{ij}^{(l,s)}$ or $\Omega_{ij}^{(l,s)*}$ as

$$\bar{Q}_{ij}^{(l,s)} = \pi\sigma^2\Omega_{ij}^{(l,s)*} = \pi\sigma^2\frac{\Omega_{ij}^{(l,s)}}{[\Omega_{ij}^{(l,s)}]_{rs}} = \frac{4(l+1)}{(s+1)![2l+1-(-1)^l]}\int_0^\infty e^{-\gamma^2}\gamma^{2s+3}Q_{ij}^{(l)}\mathrm{d}\gamma. \qquad \text{(A5)}$$

Since the definition of the bracket integrals is the same as the classical one, the values of Q_1^{mp}, $\tilde{Q}_{ij}^{mp}$, and $\tilde{Q}_{i1}^{mp*}$ can be calculated using the method presented in Refs. 7–9 and 41. It is important to note that $\tilde{Q}_{i1}^{mp*}$ represents the elastic collision term between electrons and heavy species in Eq. (3). The expressions of $\tilde{Q}_{i1}^{mp*}$ ($i \geq 2$) are given by

$$\tilde{Q}_{i1}^{mp^*} = Q_{i1}^{mp^*} - \frac{n_1\sqrt{m_1T_1}}{n_i\sqrt{m_iT_i}} Q_{ii}^{mp}\delta_{m0}\delta_{p0}, \qquad \text{(A6)}$$

$$Q_{i1}^{00^*} = -8n_in_1\frac{\sqrt{m_im_e}}{m_i+m_e}\Omega_{i1}^{(1,1)}, \qquad \text{(A7)}$$

$$Q_{i1}^{01^*} = 8n_in_1\frac{m_i\sqrt{m_im_e}}{(m_i+m_e)^2}\left[-\frac{5}{2}\Omega_{i1}^{(1,1)} + \Omega_{i1}^{(1,2)}\right], \qquad \text{(A8)}$$

$$Q_{i1}^{10^*} = \frac{m_e}{m_i}Q_{i1}^{01^*}, \qquad \text{(A9)}$$

$$Q_{i1}^{11^*} = -8n_in_1\frac{(m_im_e)^{\frac{3}{2}}}{(m_i+m_e)^3}\left[\frac{55}{4}\Omega_{i1}^{(1,1)} - 5\Omega_{i1}^{(1,2)} + \Omega_{i1}^{(1,3)} - 2\Omega_{i1}^{(2,2)}\right], \qquad \text{(A10)}$$

$$Q_{i1}^{02^*} = -4n_in_1\frac{m_i^2(m_im_e)^{\frac{1}{2}}}{(m_i+m_e)^3}\left[\frac{35}{4}\Omega_{i1}^{(1,1)} - 7\Omega_{i1}^{(1,2)} + \Omega_{i1}^{(1,3)}\right], \qquad \text{(A11)}$$

$$Q_{i1}^{20^*} = \left(\frac{m_i}{m_e}\right)^3 Q_{i1}^{02^*}, \qquad \text{(A12)}$$

$$Q_{i1}^{12^*} = -8n_in_1\frac{m_i(m_im_e)^{\frac{3}{2}}}{(m_i+m_e)^4}\left[\frac{595}{16}\Omega_{i1}^{(1,1)} - \frac{189}{8}\Omega_{i1}^{(1,2)} + \frac{19}{4}\Omega_{i1}^{(1,3)} - \frac{1}{2}\Omega_{i1}^{(1,4)} - 7\Omega_{i1}^{(2,2)} + 2\Omega_{i1}^{(2,3)}\right], \qquad \text{(A13)}$$

$$Q_{i1}^{21^*} = \frac{m_e}{m_i}Q_{i1}^{12^*}. \qquad \text{(A14)}$$

[1] A. B. Murphy, M. I. Boulos, V. Colombo *et al.*, High Temp. Mater. Process. **12**, 255 (2008).
[2] P. Fauchais, T. Renault, N. Hussary *et al.*, High Temp. Mater. Process. **12**, 165 (2008).
[3] E. Pfender, Plasma Chem. Plasma Process. **19**, 1 (1999).
[4] P. Fauchais and A. Vardelle, Plasma Phys. Controlled Fusion **42**, B365 (2000).
[5] P. Bletzinger, B. N. Ganguly, D. Van Wie, and A. Garscadden, J. Phys. D: Appl. Phys. **38**, R33 (2005).
[6] I. V. Adamovich, I. Choi, N. Jiang *et al.*, Plasma Sources Sci. Technol. **18**, 034018 (2009).
[7] J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, *Molecular Theory of Gases and Liquids*, 2nd ed. (Wiley, New York, 1964).
[8] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 3rd ed. (Cambridge University Press, Cambridge, England, 1970).
[9] R. S. Devoto, Phys. Fluids **10**, 2105 (1967).
[10] R. S. Devoto, J. Plasma Phys. **2**, 617 (1968).

[11]A. B. Murphy and C. J. Arundell, Plasma Chem. Plasma Process. **14**, 451 (1994).
[12]A. B. Murphy, Plasma Chem. Plasma Process. **15**, 279 (1995).
[13]A. B. Murphy, IEEE Trans. Plasma Sci. **25**, 809 (1997).
[14]A. B. Murphy, Plasma Chem. Plasma Process. **20**, 279 (2000).
[15]W. Wang, M. Rong, A. B. Murphy *et al.*, J. Phys. D: Appl. Phys. **44**, 355207 (2011).
[16]G. Yang and J. V. Heberlein, J. Phys. D: Appl. Phys. **40**, 5649 (2007).
[17]H.-P. Li, J. Heberlein, and E. Pfender, IEEE Trans. Plasma Sci. **33**, 402 (2005).
[18]G. Yang and J. V. Heberlein, Plasma Sources Sci. Technol. **16**, 529 (2007).
[19]M. Laroussi, X. Lu, and C. M. Malott, Plasma Sources Sci. Technol. **12**, 53 (2003).
[20]Z.-B. Wang, G.-X. Chen, Z. Wang, N. Ge, H.-P. Li, and C.-Y. Bao, J. Appl. Phys. **110**, 033308 (2011).
[21]K. H. Becker, K. H. Schoenbach, and J. G. Eden, J. Phys. D: Appl. Phys. **39**, R55 (2006).
[22]D. M. Chen and E. Pfender, IEEE Trans. Plasma Sci. **9**, 265 (1981).
[23]T. Amakawa, J. Jenista, J. Heberlein, and E. Pfender, J. Phys. D: Appl. Phys. **31**, 2826 (1998).
[24]J. Haidar, J. Phys. D: Appl. Phys. **32**, 263 (1999).
[25]M. Redwitz, L. Dabringhausen, S. Lichtenberg, O. Langenscheidt, J. Heberlein, and J. Mentel, J. Phys. D: Appl. Phys. **39**, 2160 (2006).
[26]N. A. Almeida, M. S. Benilov, U. Hechtfischer, and G. V. Naidis, J. Phys. D: Appl. Phys. **42**, 045210 (2009).
[27]J. P. Trelles, J. V. R. Heberlein, and E. Pfender, J. Phys. D: Appl. Phys. **40**, 5937 (2007).
[28]S. Ghorui, M. Vysohlid, J. V. R. Heberlein, and E. Pfender, Phys. Rev. E **76**, 016404 (2007).
[29]T. Yoshida, Pure Appl. Chem. **78**, 1093 (2006).
[30]Y. Tanaka, J. Phys. D: Appl. Phys. **37**, 1190 (2004).
[31]S. A. Al-Mamun, Y. Tanaka, and Y. Uesugi, Plasma Chem. Plasma Process. **30**, 141 (2010).
[32]P. Han and X. Chen, Plasma Chem. Plasma Process. **21**, 249 (2001).
[33]Y. Bartosiewicz, P. Proulx, and Y. Mercadier, J. Phys. D: Appl. Phys. **35**, 2139 (2002).
[34]A. Kaminska, B. Lopez, B. Izrar, and M. Dudeck, Plasma Sources Sci. Technol. **17**, 035018 (2008).
[35]Y. Takahashi, H. Kihara, and K. Abe, J. Phys. D: Appl. Phys. **43**, 185201 (2010).
[36]D. M. Zube and R. M. Myers, J. Propul. Power **9**, 545 (1993).
[37]Ph. Teulet, J. J. Gonzalez, A. Mercado-Cabrera, Y. Cressault, and A. Gleizes, J. Phys. D: Appl. Phys. **42**, 185207 (2009).
[38]A. A. Iordanidis and C. M. Franck, J. Phys. D: Appl. Phys. **41**, 135206 (2008).
[39]Y. Tian, Y. Zhang, B. Wang, W. Ji, Y. Zhang, and K. Xie, Carbon **42**, 2597 (2004).
[40]K. Xie, Y. Lu, Y. Tian, and D. Wang, Energy Sources **24**, 1093 (2002).
[41]R. S. Devoto, Ph.D. dissertation, Stanford University, 1965.
[42]C. Bonnefoi, Ph.D. dissertation, University of Limoges, 1983.
[43]J. Aubreton, C. Bonnefoi, and J. M. Mexmain, Rev. Phys. Appl. **21**, 365 (1986).
[44]V. Rat, J. Aubreton, M. F. Elchinger, and P. Fauchais, Plasma Chem. Plasma Process. **21**, 355 (2001).
[45]A. B. Murphy, Phys. Rev. E **48**, 3594 (1993); **50**, 5145(E) (1994).
[46]V. Rat, P. Andre, J. Aubreton, M. F. Elchinger, P. Fauchais, and A. Lefort, Phys. Rev. E **64**, 026409 (2001).
[47]V. Colombo, E. Ghedini, and P. Sanibondi, Prog. Nucl. Energy **50**, 921 (2008).
[48]V. Colombo, E. Ghedini, and P. Sanibondi, J. Phys. D: Appl. Phys. **42**, 055213 (2009).
[49]V. Colombo, E. Ghedini, and P. Sanibondi, Plasma Sources Sci. Technol. **20**, 035003 (2011).
[50]X. Chen and P. Han, J. Phys. D: Appl. Phys. **32**, 1711 (1999).
[51]See supplementary material at http://dx.doi.org/10.1063/1.4794969 for the solution of the Boltzmann equation.
[52]A. B. Murphy, J. Phys. D: Appl. Phys. **31**, 3383 (1998).
[53]R. S. Devoto, Phys. Fluids **9**, 1230 (1966).