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A numerical model of non-equilibrium thermal plasmas. II. Governing equations

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Governing equations and the corresponding physical properties of the plasmas are both prerequisites for studying the fundamental processes in a non-equilibrium thermal plasma system numerically. In this paper, a kinetic derivation of the governing equations used for describing the complicated thermo-electro-magneto-hydrodynamic-chemical coupling effects in non-equilibrium thermal plasmas is presented. This derivation, which is achieved using the Chapman-Enskog method, is completely consistent with the theory of the transport properties reported in the previous paper by the same authors. It is shown, based on this self-consistent theory, that the definitions of the specific heat at constant pressure and the reactive thermal conductivity of two-temperature plasmas are not necessary. The governing equations can be reduced to their counterparts under local thermodynamic equilibrium (LTE) and local chemical equilibrium (LCE) conditions. The general method for the determination of the boundary conditions of the solved variables is also discussed briefly. The two papers establish a self-consistent physical-mathematical model that describes the complicated physical and chemical processes in a thermal plasma system for the cases both in LTE or LCE conditions and under non-equilibrium conditions. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4794970]

NOMENCLATURE

$\vec{A}$ = magnetic vector potential
$\vec{B}$ = magnetic field
$\vec{c}_i$ = velocity of species i
$\vec{C}_i$ = peculiar particle velocity of species i
$\vec{d}_i$ = diffusion driving force of species i
D_{ij} = ordinary diffusion coefficient
D_i^T = thermal diffusion coefficient
$D_{ij}^{\theta}, D_i^{\theta *}$ = thermal non-equilibrium diffusion coefficient
e = elementary electric charge
e_i = specific thermal energy of species i
$\vec{E}$ = total electric field
$\vec{E}^{ext}$ = externally applied electric field
$\vec{E}^{in}$ = internal or ambipolar electric field
f_i = distribution function of species i
g = relative speed of species i and j
$\vec{g}$ = gravitational acceleration
G_{ki} = absolute value of the reaction rate
h_i = specific enthalpy of species i
h_i^* = enthalpy per particle of species i
$\overleftrightarrow{I}$ = unit tensor
$\vec{j}_{cond}$ = conduction current density
$\vec{j}_{disp}$ = displacement current density
$\vec{j}_{tot}$ = total current density
$\sum_j J_{ij}$ = collision term in the Boltzmann equation
$\sum_j J_{ij}^{el}$ = elastic collision term
$\sum_j J_{ij}^{inel}$ = inelastic collision term
k_B = Boltzmann constant
m_i = mass of species i
$n_i; n_t$ = species number density; total number density
$\dot{n}_i$ = R_i/m_i
$p_i; p$ = partial pressure; total pressure
$\overleftrightarrow{P}_i; \overleftrightarrow{P}$ = pressure tensor of species i; total pressure tensor
$\vec{q}_i; \vec{q}$ = energy flux vector of species i; total energy vector
Q_{eh}^{el} = rate of energy exchange per unit volume during elastic collisions
Q_e^{inel} = rate of electron energy exchange per unit volume during inelastic collisions
Q_h^{inel} = rate of heavy-species energy exchange per unit volume during inelastic collisions
$\vec{r}$ = displacement vector
$R_c; R_l$ = creation rate of species i; loss rate of species i
$R_{i\leftarrow j}$ = creation rate of species i in the reaction with species j as the reactant
$R_i = R_c - R_l = \sum_j R_{i\leftarrow j}$
t = time
$T_e; T_h$ = electron temperature; heavy-particle temperature
U_{rad} = radiation loss per unit volume of plasma
$\vec{v}_i$ = mean velocity of species i
$\vec{v}_0$ = mass-averaged velocity
$\vec{V}_i$ = diffusion velocity of species i
$\vec{X}_i$ = external force acting on species i
Z_i = electric charge number of species i

Greek symbols

θ = thermal non-equilibrium coefficient ($\theta = T_e/T_h$)
λ_i = translational thermal conductivity

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$\lambda_i^\theta =$ non-equilibrium thermal conductivity
$\lambda_r =$ reactive thermal conductivity
$\rho_i;\rho =$ mass density of species i; total mass density
$\rho^c =$ net charge density
$\mu_0 =$ permeability of the vacuum
$\mu_{ij} =$ reduced mass
$\nu_{m,ij} =$ momentum transfer collision frequency
$\chi =$ deflection angle
$\overleftrightarrow{\tau}_i;\overleftrightarrow{\tau} =$ viscous-stress tensor of species i; total viscous-stress tensor
$\tau_C =$ self-relaxation time of species
$\tau_E =$ relaxation time of energy exchange
$\tau_M =$ relaxation time of momentum exchange
$\tau_R =$ relaxation time of chemical reactions
$\varphi =$ total electric potential
$\varphi^{ext} =$ external electric potential
$\varphi^{in} =$ internal electric potential
$\Phi_i, \langle\Phi_i\rangle =$ arbitrary variable and its average value
$\vec{\psi}_i =$ particle number flux vector
$\varepsilon_0 =$ vacuum permittivity
$\varepsilon_i^r =$ reaction energy per unit mass of species i in the reaction r
$\varepsilon_i^{in} =$ internal energy per unit mass of species i
$\varepsilon_{ij} =$ energy difference between species i and j
$\xi_{ki} =$ coefficient corresponding to the absolute value of the reaction rate
$\sigma =$ electrical conductivity
$\sigma_{ij} =$ differential collision cross section
$\Omega =$ solid angle

Subscripts

1 or $e =$ electron
$i \geq 2$ or $h =$ heavy species
$c =$ creation
$l =$ loss

Superscripts

$el =$ elastic
$ext =$ external
$in =$ internal
$inel =$ inelastic
$r =$ reaction

I. INTRODUCTION

Thermal plasmas provide high energy densities, high temperatures, and the strong radiative emission, and consequently have been used widely in different fields including arc welding, plasma cutting, spraying, waste destruction, production of micro- or nano-structured materials, high-voltage circuit breakers, high-intensity lighting, extractive metallurgy, etc. (e.g., Refs. 1–10). With the dramatic development of the computer hardware and software, numerical simulation has become an indispensable tool in the investigation of the characteristics and applications of thermal plasmas in the past few decades. In previous studies, physical-mathematical models of thermal plasmas have been developed and applied. The models are based on simultaneous solution of the coupled mass, momentum, and energy conservation equations and electromagnetic field equations under the assumptions of local thermodynamic equilibrium (LTE) and local chemical equilibrium (LCE) conditions, and use the methods of computational fluid dynamics (CFD), taking into account the strongly temperature- and pressure-dependent physical properties of thermal plasmas (c.f. Refs. 11 and 12, and the papers cited therein). Despite the usefulness of the LTE assumptions, there are many important applications in which deviations from LTE play a significant role, including injecting a cold gas into a plasma jet,[13] low-pressure plasma spraying,[14,15] plasmas near electrodes or cold walls,[16–21] thermal plasma deposition and nano-materials production,[22,23] expanding plasma jets under soft vacuum,[24,25] simulations of plasma flowing around a spacecraft for testing the thermal protection systems,[26,27] the switching arcs in high-voltage gas circuit breakers,[28,29] and so on. In addition, deviations from the LCE state may also occur where the rates of diffusion or convection are greater than those of chemical reactions, for example, in the fringes of arcs[30] or in the near-cathode region of high-pressure argon arcs.[21]

Advanced thermal plasma modeling[12] is an indispensable tool for investigating the relatively complex fundamental processes of non-LTE/non-LCE plasmas, since complicated thermo-electro-magneto-hydrodynamic-chemical (TEMHC) coupling effects exist in such non-equilibrium plasma systems. In one approach, Benilov derived the multi-fluid governing equations for the multispecies non-equilibrium mixtures of reacting gases by treating each species of the mixture as a separate fluid with its own velocity and temperature, coexisting with the fluids made up of other species; he only focused on the momentum and energy exchange between different fluids due to elastic and inelastic collisions.[31,32]

In this paper, we consider thermal plasmas, which are a particular type of reacting gas mixture. The following aspects need to be considered.

First, by comparing the time scales for the self-relaxation of species (τ_C), relaxation of momentum exchange (τ_M) and energy exchange (τ_E), and the relaxation of chemical reactions (τ_R),[33–35] the following conclusions can be drawn: since $\tau_C \ll \tau_E$, two Maxwellian distribution functions, with T_e for electrons and T_h for heavy species, are established, and a two-temperature (2T) description of the plasma system can be sustained; since $\tau_M \ll \tau_E$, the electrons share the same hydrodynamic velocity as the heavy species; and since $\tau_C \ll \tau_R$, the transport properties of the plasmas are not influenced by the chemical reactions. Therefore, for non-equilibrium thermal plasmas, (i) only two translational temperatures (T_e and T_h) are necessary to describe the plasma system if the excitation, rotational, and vibrational temperatures are assumed to be related to T_e and/or T_h,[35] instead of introducing multiple temperatures corresponding to each species as in Refs. 31 and 32; (ii) the momentum conservation equation with the mass-averaged velocity as the dependent variable can be solved to obtain the macroscopic flow features of the plasma system, instead of solving for the peculiar velocities for each species; (iii) the transport properties of the plasmas can be calculated using the modified Chapman-Enskog method,[36] even though the LCE conditions are not satisfied in the plasma system.

Second, under plasma conditions, especially in the discharge region, the influences of the electric field on the plasma behavior are very important. Thus, the generalized Ohm's law needs to be considered carefully, and the current continuity equation should be consistent with other equations, such as the mass, momentum, and energy conservation equations of the plasma system.

In the past few decades, many papers have been published that study the physical-chemical processes in non-equilibrium plasma systems using a simulation method. It is self-evident that an advanced physical-mathematical model for non-equilibrium thermal plasma simulation should be self-consistent in two respects: (i) The physical-mathematical models for non-equilibrium plasmas should be consistent with their well-established counterparts for LTE plasmas if $T_e = T_h$ and LCE are satisfied. However, the governing equations used by different authors for the modeling of kinetic/chemical non-equilibrium plasmas are very different (e.g., Refs. 37–40). These discrepancies might result from unclear descriptions of the assumptions employed in obtaining the non-equilibrium models from their original forms under the specific conditions used by particular authors, or possibly from mistakes in the derivations of the non-equilibrium models. (ii) The calculation method of the physical properties of the non-equilibrium plasmas should be consistent with the mass, momentum, energy fluxes, and the current flow appearing in the governing equations, since these fluxes are associated with the diffusion coefficients, thermal diffusion coefficients, viscosity, thermal conductivity, and electrical conductivity of plasmas.

In addition, the boundary conditions for different variables under non-equilibrium conditions are difficult to specify, especially for the electron temperature and the species number densities.

The purpose of this paper is to present self-consistent theoretical derivations of a set of self-consistent governing equations for the modeling of non-equilibrium thermal plasmas, based on the Boltzmann equation, by closing the inelastic collision terms using a phenomenological approach,[37,38] and to provide a general method for the determination of the boundary conditions for each independent variable.

II. THEORETICAL DERIVATIONS USING KINETIC THEORY

A. Assumptions

In this study, the following assumptions are employed:

(1) The plasma is in kinetic and/or chemical non-equilibrium state and is optically thin.
(2) The anisotropy in the distribution function of species i is small, and the isotropic component is close to Maxwellian. Thus, the definition of the temperature for electrons (T_e) and heavy species (T_h) exists, and the partial pressure for species i (p_i) is also isotropic.
(3) Particles with the same chemical composition are regarded as different species if they are in different excited states. For example, ground-state atoms and metastables of element A are designated as different species; and ions are regarded as atoms/molecules with an excitation energy equal to the ionization energy.
(4) The viscous dissipation and pressure work terms in the energy equation are neglected, which is reasonable for cases with small Mach number.

B. Definitions of the macroscopic variables

To allow the following discussion to be followed easily, the macroscopic variables are defined in this subsection before our derivations, although these definitions are of the same form as those presented in Refs. 41–43. We denote by Φ_i an arbitrary variable that is a function of particle velocity, its average value by $\langle\Phi_i\rangle$, i.e.,

$$\langle\Phi_i\rangle \equiv \frac{1}{n_i}\int_{-\infty}^{+\infty} \Phi_i f_i \mathrm{d}\vec{c}_i, \tag{1}$$

and the average value for the plasma as a whole by

$$\langle\Phi\rangle \equiv \frac{1}{n_t}\sum_i n_i\langle\Phi_i\rangle, \tag{2}$$

where n_i, f_i, and $\vec{c}_i$ are the number density, distribution function, and velocity of species i, and n_t is the total number density of the plasma. Thus, the mean velocity, $\vec{v}_i$, and diffusion velocity, $\vec{V}_i$, of species i are given by

$$\vec{v}_i \equiv \langle\vec{c}_i\rangle = \frac{1}{n_t}\int_{-\infty}^{+\infty} \vec{c}_i f_i \mathrm{d}\vec{c}_i, \tag{3}$$

and

$$\vec{V}_i \equiv \langle\vec{C}_i\rangle = \frac{1}{n_i}\int_{-\infty}^{+\infty} \vec{C}_i f_i \mathrm{d}\vec{c}_i = \vec{v}_i - \vec{v}_0, \tag{4}$$

where $\vec{C}_i$ is the peculiar particle velocity of species i with the relationship $\vec{C}_i = \vec{c}_i - \vec{v}_0$, and $\vec{v}_0$ is the mass-averaged velocity of the plasma, which is defined as

$$\vec{v}_0 \equiv \frac{1}{\rho}\sum_i n_i m_i \vec{v}_i, \tag{5}$$

where m_i is the mass of species i, and ρ is the mass density of the plasma, i.e.,

$$\rho = \sum_i \rho_i = \sum_i n_i m_i. \tag{6}$$

From Eqs. (4) and (5), we can obtain the relationship

$$\sum_i \rho_i \vec{V}_i = 0. \tag{7}$$

It should be pointed out that in the foregoing equations, the differential $\mathrm{d}\vec{c}_i$ can be used interchangeably with $\mathrm{d}\vec{C}_i$, since $\vec{v}_0$ is a function only of position and time by virtue of the definition [Eq. (1)], and hence is a constant with respect to the indicated integration. This conclusion is very useful in our later derivations.

The temperature and scalar pressure of species i are defined as

$$\frac{3}{2}n_i k_B T_i \equiv \frac{1}{2}n_i m_i \langle C_i^2 \rangle = \frac{1}{2}m_i \int_{-\infty}^{+\infty} C_i^2 f_i \mathrm{d}\vec{c}_i \quad (8)$$

and

$$p_i = n_i k_B T_i \equiv \frac{1}{3}n_i m_i \langle C_i^2 \rangle = \frac{1}{3}m_i \int_{-\infty}^{+\infty} C_i^2 f_i \mathrm{d}\vec{c}_i, \quad (9)$$

where k_B is the Boltzmann constant. The pressure of the plasma as a whole is

$$p = \sum_i p_i. \quad (10)$$

Since the differential particle flux across a plane moving with the mass-averaged velocity $\vec{v}_0$ is

$$\vec{C}_i f_i \mathrm{d}\vec{c}_i \quad (11)$$

in the mass-averaged velocity reference frame, the integrated fluxes of the thermal energy, momentum, and particles transported by species i can be obtained by the multiplication of the differential flux [Eq. (11)] by $m_i(C_i^2/2 + \varepsilon_i^r + \varepsilon_i^{in})$, $m_i\vec{C}_i$ and 1, respectively, followed by the integration over all particle velocities, i.e.,

$$\vec{q}_i = \rho_i \left[\frac{1}{2}\langle C_i^2 \vec{C}_i \rangle + \langle \varepsilon_i^r \vec{C}_i \rangle + \langle \varepsilon_i^{in} \vec{C}_i \rangle \right], \quad (12)$$

$$\overleftrightarrow{P}_i = \rho_i \langle \vec{C}_i \vec{C}_i \rangle, \quad (13)$$

and

$$\vec{\psi}_i = n_i \vec{V}_i = n_i \langle \vec{C}_i \rangle, \quad (14)$$

where ε_i^r and ε_i^{in} represent, respectively, the related reaction energy and the internal energy per unit mass of species i. The species viscous-stress tensor $\overleftrightarrow{\tau}_i$ is defined as the negative of the species momentum-flux tensor with the scalar pressure subtracted from each of its diagonal components, i.e.,

$$\overleftrightarrow{\tau}_i \equiv -(\overleftrightarrow{P}_i - p_i \overleftrightarrow{I}) = -\left[\rho_i \langle \overleftrightarrow{C}_i \overleftrightarrow{C}_i \rangle - \frac{1}{3}\rho_i \langle C_i^2 \rangle \overleftrightarrow{I}\right], \quad (15)$$

where $\overleftrightarrow{I}$ is the unit tensor. Thus, the viscous-stress tensor for the plasma as a whole is expressed as

$$\overleftrightarrow{\tau} = \sum_i \overleftrightarrow{\tau}_i = -(\overleftrightarrow{P} - p\overleftrightarrow{I}). \quad (16)$$

The specific thermal energy of species i for a reacting gas mixture is expressed as[41,42]

$$e_i = \frac{1}{n_i}\int_{-\infty}^{+\infty} \frac{1}{2}C_i^2 f_i \mathrm{d}\vec{C}_i + \varepsilon_i^r + \varepsilon_i^{in}. \quad (17)$$

The specific enthalpy of species i is given by

$$h_i = e_i + \frac{p_i}{\rho_i} = \frac{5}{2m_i}k_B T_i + \varepsilon_i^r + \varepsilon_i^{in}. \quad (18)$$

The conduction current density $\vec{j}_{cond}$ is defined as

$$\vec{j}_{cond} \equiv \sum_i (eZ_i n_i \vec{V}_i), \quad (19)$$

where e is the elementary charge and Z_i is the electric charge number of species i.

C. General forms of the conservation equations for species *i*

The general form of the Boltzmann equation for species i in $(\vec{r}, \vec{c}_i, t)$ coordinates can be expressed as

$$\frac{\partial f_i}{\partial t} + \vec{c}_i \cdot \vec{\nabla} f_i + \frac{\vec{X}_i}{m_i}\cdot \vec{\nabla}_{\vec{c}_i} f_i = \sum_j J_{ij}. \quad (20)$$

Substituting the relationship $\vec{C}_i = \vec{c}_i - \vec{v}_0$ into Eq. (20), the Boltzmann equation in $(\vec{r}, \vec{C}_i, t)$ coordinates can be rewritten as[41]

$$\frac{\partial f_i}{\partial t} + (\vec{v}_0 + \vec{C}_i)\cdot \vec{\nabla} f_i + \left(\frac{\vec{X}_i}{m_i} - \frac{\mathrm{d}\vec{v}_0}{\mathrm{d}t}\right) \cdot \vec{\nabla}_{\vec{C}_i} f_i - \vec{C}_i \cdot \vec{\nabla}_{\vec{C}_i} f_i \cdot \vec{\nabla}\vec{v}_0 = \sum_j J_{ij}, \quad (21)$$

where $\mathrm{d}/\mathrm{d}t = \partial/\partial t + \vec{v}_0 \cdot \vec{\nabla}$, and $\vec{X}_i$ is denoted as the force acting on a particle of species i. The collision term, $\sum_j J_{ij}$, can be divided into two parts, i.e., the elastic collision term, $\sum_j J_{ij}^{el}$, and the inelastic collision term, $\sum_j J_{ij}^{inel}$. The elastic collision term can be expressed as

$$\sum_j J_{ij}^{el} = \sum_j \int_{-\infty}^{+\infty}\int_{\mathrm{d}\Omega} (f_i' f_j' - f_i f_j) g \sigma_{ij} \mathrm{d}\Omega\, \mathrm{d}\vec{C}_j, \quad (22)$$

where 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.

A moment of the Boltzmann equation, which is obtained by the multiplication of Eq. (21) by some function Φ_i, and integration of the resulting equation over velocity space,[42,43] is expressed as

$$\int_{-\infty}^{+\infty} \Phi_i \left[\frac{\partial f_i}{\partial t} + (\vec{v}_0 + \vec{C}_i)\cdot \vec{\nabla} f_i + \left(\frac{\vec{X}_i}{m_i} - \frac{\mathrm{d}\vec{v}_0}{\mathrm{d}t}\right) \cdot \vec{\nabla}_{\vec{C}_i} f_i - \vec{C}_i \cdot \vec{\nabla}_{\vec{C}_i} f_i \cdot \vec{\nabla}\vec{v}_0\right] \mathrm{d}\vec{C}_i = \int_{-\infty}^{+\infty} \Phi_i \sum_j J_{ij} \mathrm{d}\vec{C}_i. \quad (23)$$

Based on the foregoing discussion and Eq. (22), the right-hand side of Eq. (23) can be written as

$$\int_{-\infty}^{+\infty} \Phi_i \sum_j J_{ij} \mathrm{d}\vec{C}_i = \Delta_i^{el}[\Phi_i] + \Delta_i^{inel}[\Phi_i], \tag{24}$$

where

$$\Delta_i^{el}[\Phi_i] = \sum_j \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{\mathrm{d}\Omega} (\Phi_i' - \Phi_i) f_i f_j g \sigma_{ij} \mathrm{d}\Omega \mathrm{d}\vec{C}_j \mathrm{d}\vec{C}_i, \tag{25}$$

$$\Delta_i^{inel}[\Phi_i] = \sum_j \int_{-\infty}^{+\infty} \Phi_i J_{ij}^{inel} \mathrm{d}\vec{C}_i. \tag{26}$$

The species conservation equations may be obtained by means of successively setting $\Phi_i = m_i,\ m_i\vec{C}_i,\ m_i(C_i^2/2 + \varepsilon_i^r + \varepsilon_i^{in})$ in the moment Eq. (23), and are expressed as

$$\frac{\partial \rho_i}{\partial t} + \vec{\nabla}\cdot(\rho_i \vec{v}_0) = -\vec{\nabla}\cdot(\rho_i \vec{V}_i) + \Delta_i^{el}[m_i] + \Delta_i^{inel}[m_i], \tag{27}$$

$$\begin{aligned}\frac{\partial}{\partial t}(\rho_i \vec{v}_i) + \vec{\nabla}\cdot(\rho_i \vec{v}_i \vec{v}_0) &= -\vec{\nabla}\cdot \vec{P}_i - \vec{\nabla}\cdot(\rho_i \vec{V}_i \vec{v}_0) + n_i \langle \vec{X}_i \rangle \\ &\quad + \vec{v}_0 \cdot \Delta_i^{inel}[m_i] + \Delta_i^{el}[m_i \vec{C}_i] + \Delta_i^{inel}[m_i \vec{C}_i],\end{aligned} \tag{28}$$

$$\begin{aligned}&\frac{\partial}{\partial t}(\rho_i h_i) + \vec{\nabla}\cdot(\rho_i h_i \vec{v}_0) \\ &= \frac{\mathrm{d}p_i}{\mathrm{d}t} - \vec{\nabla}\cdot\vec{q}_i - (\rho_i \vec{V}_i)\cdot\frac{d\vec{v}_0}{dt} + n_i\langle \vec{X}_i \vec{C}_i\rangle + \vec{\tau}_i : \vec{\nabla}\vec{v}_0 \\ &\quad + \Delta_i^{el}\left[m_i\left(\frac{1}{2}C_i^2 + \varepsilon_i^r + \varepsilon_i^{in}\right)\right] + \Delta_i^{inel}\left[m_i\left(\frac{1}{2}C_i^2 + \varepsilon_i^r + \varepsilon_i^{in}\right)\right].\end{aligned} \tag{29}$$

For the elastic collision process, we consider an elastic two-body collision between species i and j. On one hand, since there are no mass changes before and after the elastic collisions between species i and j, we have $\Delta_i^{el}[m_i] = 0$; on the other hand, due to the conservation of momentum and energy in an elastic collision, Eq. (25) can be written as

$$\Delta_i^{el}[m_i\vec{C}_i] = \sum_j \int_{-\infty}^{+\infty} m_i \vec{C}_i J_{ij}^{el} \mathrm{d}\vec{C}_i = -\sum_j n_i \mu_{ij} \nu_{m,ij} (\vec{V}_i - \vec{V}_j), \tag{30}$$

$$\begin{aligned}&\Delta_i^{el}\left[m_i\left(\frac{1}{2}C_i^2 + \varepsilon_i^r + \varepsilon_i^{in}\right)\right] \\ &= \vec{v}_0 \cdot \sum_j n_i \mu_{ij} \nu_{m,ij} (\vec{V}_j - \vec{V}_i) - \sum_j \frac{2 n_i \mu_{ij}}{m_i + m_j} \nu_{m,ij} \\ &\quad \times \left[\frac{3}{2} k_B (T_i - T_j) + \frac{1}{2}(m_j - m_i)\vec{V}_i \cdot \vec{V}_j\right],\end{aligned} \tag{31}$$

where $\mu_{ij} = m_i m_j/(m_i + m_j)$ represents the reduced mass, while $\nu_{m,ij}$ is the momentum transfer collision frequency, and is given by

$$\nu_{m,ij} = n_j g \int_0^{\pi} 2\pi(1 - \cos\chi)\sigma_{ij} \sin\chi \,\mathrm{d}\chi, \tag{32}$$

where χ is the deflection angle.

For the inelastic collision processes, a phenomenological equation is employed to describe the term [Eq. (26)] that involves the integrals over the distribution function as follows:[37,38]

$$\Delta_i^{inel}[m_i] = \sum_j \int_{-\infty}^{+\infty} m_i J_{ij}^{inel} \mathrm{d}\vec{C}_i = R_c - R_l, \tag{33}$$

where R_c and R_l are the creation rate and loss rate of species i. If there are r reactions in the non-equilibrium plasma system, then, we have

$$R_i = R_c - R_l = \sum_{k=1}^{r} \xi_{ki} G_{ki}, \tag{34}$$

where G_{ki} is the absolute value of the reaction rate, while the corresponding coefficient $\xi_{ki} = 1, -1$, or 0 indicates the creation, loss, or no change for species i in reaction k, respectively.

The momentum and energy lost are related to the loss of species i in the inelastic collision process; thus, we have

$$\Delta_i^{inel}[m_i\vec{C}_i] = \sum_j \int_{-\infty}^{+\infty} m_i \vec{C}_i J_{ij}^{inel} \mathrm{d}\vec{C}_i = \sum_j R_{i\leftarrow j}(\vec{V}_i - \vec{V}_j), \tag{35}$$

where $R_{i\leftarrow j}$ represents the creation rate of species i in the reaction with species j as the reactant, and follows the relationship $R_i = \sum_j R_{i\leftarrow j}$. If we denote the energy difference between species i and j as ε_{ij}, we obtain

$$\begin{aligned}&\Delta_i^{inel}\left[m_i\left(\frac{1}{2}C_i^2 + \varepsilon_i^r + \varepsilon_i^{in}\right)\right] \\ &= \sum_j \int_{-\infty}^{+\infty} m_i\left(\frac{1}{2}C_i^2 + \varepsilon_i^r + \varepsilon_i^{in}\right) J_{ij}^{inel} \mathrm{d}\vec{C}_i \\ &= \sum_j R_{i\leftarrow j}\varepsilon_{ij} + \sum_j \left(\frac{R_{i\leftarrow j}}{m_i}\frac{3}{2}k_B T_i + \frac{R_{i\leftarrow j}}{m_j}\frac{3}{2}k_B T_j - R_{i\leftarrow j}\vec{V}_i\cdot\vec{V}_j\right).\end{aligned} \tag{36}$$

D. Conservation equations of species *i* for a non-equilibrium thermal plasma

In this subsection, we assume that the plasma system is composed of N species involved in r reactions. The subscript "e" or "1" indicates electrons, while "h" or "2, 3,…, N" represents heavy species. It is generally known that the conservation Eqs. (27)–(29) are not closed unless the unknown quantities (i.e., the diffusion velocity, the pressure tensor, and the heat flux) are given. In this study, based on the first-order approximate solutions of the Boltzmann equation using the modified Chapman–Enskog method, the preceding unknown quantities, which describe the physical and chemical processes of the non-equilibrium thermal plasma system, have been obtained as follows:[36]

$$\vec{V}_i = \frac{n_t}{n_i \rho k_B T_i} \sum_{j=1}^{N} m_j (D_{ij} \vec{d}_j + D_{ij}^{\theta} \omega_j \vec{\nabla} \ln \theta) - \frac{D_i^T}{n_i m_i} \vec{\nabla} \ln T_h - \frac{D_i^{\theta *}}{n_i m_i} \vec{\nabla} \ln \theta, \quad (37)$$

$$\overleftrightarrow{P} = p\overleftrightarrow{I} - \overleftrightarrow{\tau} = p\overleftrightarrow{I} - 2\mu\overleftrightarrow{S}, \quad (38)$$

$$\vec{q}_i = -\lambda_i \vec{\nabla} T_h - \lambda_i^{\theta} T_i \vec{\nabla} \ln \theta + n_i h_i^* \vec{V}_i - \frac{\rho k_B}{n_t} \sum_{j,k=1}^{N} \frac{\lambda_{ij}^D n_k T_k E_{jk}}{n_j m_j} \vec{V}_k, \quad (39)$$

where $\theta = T_e/T_h$, the coefficients D_{ij} and D_i^T are the ordinary diffusion coefficients and thermal diffusion coefficients, respectively, while D_{ij}^{θ} and $D_i^{\theta *}$ are the thermal non-equilibrium diffusion coefficients, and

$$\overleftrightarrow{S} = \frac{1}{2}\left[\vec{\nabla}\vec{v}_0 + (\nabla \vec{v}_0)^T\right] - \frac{1}{3}(\nabla \vec{v}_0 : \overleftrightarrow{I})\overleftrightarrow{I}, \quad (40)$$

while λ_i and λ_i^{θ} are the translational thermal conductivity and the non-equilibrium thermal conductivity, respectively, while h_i^* is the enthalpy per particle of species i expressed as

$$h_i^* = \frac{5}{2} k_B T_i + m_i \varepsilon_i^r + m_i \varepsilon_i^{in}. \quad (41)$$

The expressions for the transport coefficients and the diffusion driving force, $\vec{d}_i$, are available in Ref. 36, and the fourth term in Eq. (39) can usually be neglected compared to the others.[44] In the LTE condition, it's convenient to treat the third term of Eq. (39) as the reactive thermal conductivity. However, the definition of the non-equilibrium reactive thermal conductivity is still ambiguous in the literatures.[45–47]

As discussed in Sec. I, for non-equilibrium thermal plasmas, the electron and heavy-particle temperatures in the plasma system are considered to be different. The kinetic temperature of electrons is close to their excitation temperature, i.e., $T_1 = T_e = T_{ex}$, while the kinetic temperatures of different heavy species are close to each other, and can be represented by the same value of T_h, i.e., $T_i|_{i=2,3,\ldots,N} = T_h$. Thus, based on the foregoing discussions, the mass conservation equations for species i can be expressed as

$$\frac{\partial \rho_i}{\partial t} + \vec{\nabla} \cdot (\rho_i \vec{v}_0) = -\vec{\nabla} \cdot (\rho_i \vec{V}_i) + \sum_{k=1}^{r} \xi_{ki} G_{ki}. \quad (42)$$

Similarly, the mass-averaged momentum conservation equation can be written as

$$\frac{\partial}{\partial t}(\rho \vec{v}_0) + \vec{\nabla} \cdot (\rho \vec{v}_0 \vec{v}_0) = -\vec{\nabla} p + \vec{\nabla} \cdot \overleftrightarrow{\tau} + \vec{j}_{cond} \times \vec{B} + \rho^c (\vec{E} + \vec{v}_0 \times \vec{B}), \quad (43)$$

where ρ^c is the net charge density, $\vec{B}$ and $\vec{E}$ are the magnetic field and the total electric field, respectively. In this study, no external magnetic field is considered, and thus, $\vec{B}$ represents the self-induced magnetic field. A detailed discussions on the expressions of ρ^c, $\vec{B}$, and $\vec{E}$ will be presented later in this paper.

For the electron sub-system, the species energy conservation equation [Eq. (29)] can be expressed as

$$\begin{aligned}\frac{\partial(\rho_e h_e)}{\partial t} + \vec{\nabla} \cdot (\rho_e h_e \vec{v}_0) &= \vec{\nabla} \cdot (\lambda_e \vec{\nabla} T_h) + \vec{\nabla} \cdot (\lambda_e^{\theta} T_e \vec{\nabla} \ln \theta) - \vec{\nabla} \cdot (n_e h_e^* \vec{V}_e) \\ &+ \frac{dp_e}{dt} - (\rho_e \vec{V}_e) \cdot \frac{d\vec{v}_0}{dt} + n_e \langle \vec{X}_e \vec{C}_e \rangle + \overleftrightarrow{\tau}_e : \vec{\nabla} \vec{v}_0 + \vec{v}_0 \cdot \sum_{j=1}^{N} n_e \mu_{ej} \nu_{m,ej} (\vec{V}_j - \vec{V}_e) \\ &- \sum_{j=1}^{N} \frac{2 n_e \mu_{ej}}{m_e + m_j} \nu_{m,ej} \left[\frac{3}{2} k_B (T_e - T_j) + \frac{1}{2}(m_j - m_e) \vec{V}_e \cdot \vec{V}_j\right] \\ &+ \sum_{j=1}^{N} R_{e\leftarrow j} \cdot \varepsilon_{ej} + \sum_{j=1}^{N} \left[\frac{R_{e\leftarrow j}}{m_e} \cdot \frac{3}{2} k_B T_e + \frac{R_{e\leftarrow j}}{m_j} \cdot \frac{3}{2} k_B T_j - R_{e\leftarrow j} \vec{V}_e \cdot \vec{V}_j\right]. \end{aligned} \quad (44)$$

For low-speed plasma flows, the terms dp_e/dt, $(\rho_e \vec{V}_e) \cdot d\vec{v}_0/dt$, and $\overleftrightarrow{\tau}_e : \vec{\nabla} \vec{v}_0$ can be neglected.[6] If we also neglect the contribution of current induced by the self-induced magnetic field to the energy of the electron sub-system, the sixth term on the right hand side of Eq. (44) can be expressed as $n_e \langle \vec{X}_e \vec{C}_e \rangle = e n_e Z_e \vec{V}_e \cdot \vec{E}$. Also, in this section, we denote

$$Q_{eh}^{el} = -\sum_{j=1}^{N} \frac{2 n_e \mu_{ej}}{m_e + m_j} \nu_{m,ej} \left[\frac{3}{2} k_B (T_e - T_j) + \frac{1}{2}(m_j - m_e) \vec{V}_e \cdot \vec{V}_j\right] + \vec{v}_0 \cdot \sum_{j=1}^{N} n_e \mu_{ej} \nu_{m,ej} (\vec{V}_j - \vec{V}_e), \quad (45)$$

$$Q_e^{inel} = \sum_{j=1}^{N} R_{e\leftarrow j} \cdot \varepsilon_{ej} + \sum_{j=1}^{N} \left[\frac{R_{e\leftarrow j}}{m_e} \cdot \frac{3}{2} k_B T_e + \frac{R_{e\leftarrow j}}{m_j} \cdot \frac{3}{2} k_B T_h - R_{e\leftarrow j} \vec{V}_e \cdot \vec{V}_j\right], \quad (46)$$

where Q_{eh}^{el} and Q_e^{inel} represent the rates of energy exchange per unit volume during elastic and inelastic collisions, respectively, between electrons and heavy particles. Therefore, the electron energy conservation equation can be written as

$$\frac{\partial(\rho_e h_e)}{\partial t}+\vec{\nabla}\cdot(\rho_e h_e \vec{v}_0) = \vec{\nabla}\cdot(\lambda_e \vec{\nabla} T_h)+\vec{\nabla}\cdot(\lambda_e^{\theta} T_e \vec{\nabla}\ln\theta)-\vec{\nabla}\cdot(n_e h_e^* \vec{V}_e) + e n_e Z_e \vec{V}_e\cdot\vec{E}+Q_{eh}^{el}+Q_e^{inel}, \tag{47}$$

where h_e and h_e^* can be expressed as $h_e=\frac{5}{2m_e}k_B T_e$ and $h_e^*=\frac{5}{2}k_B T_e$, respectively, using Eqs. (18) and (41).

If we sum both sides of Eq. (29) over all heavy species, we obtain

$$\sum_{i=2}^{N}\frac{\partial(\rho_i h_i)}{\partial t}+\sum_{i=2}^{N}\vec{\nabla}\cdot(\rho_i h_i \vec{v}_0)=\sum_{i=2}^{N}\vec{\nabla}\cdot(\lambda_i \vec{\nabla}T_h)+\sum_{i=2}^{N}\vec{\nabla}\cdot(\lambda_i^{\theta} T_i \vec{\nabla}\ln\theta) -\sum_{i=2}^{N}\vec{\nabla}\cdot(n_i h_i^* \vec{V}_i)+\sum_{i=2}^{N}\frac{\mathrm{d}p_i}{\mathrm{d}t}-\sum_{i=2}^{N}(\rho_i\vec{V}_i)\cdot\frac{\mathrm{d}\vec{v}_0}{\mathrm{d}t}+\sum_{i=2}^{N}n_i\langle\vec{X}_i\vec{C}_i\rangle+\sum_{i=2}^{N}\overleftrightarrow{\tau}_i:\vec{\nabla}\vec{v}_0 +\vec{v}_0\cdot\sum_{i=2}^{N}\sum_{j=1}^{N}n_i\mu_{ij}\nu_{m,ij}(\vec{V}_j-\vec{V}_i)-\sum_{i=2}^{N}\sum_{j=1}^{N}\frac{2n_i\mu_{ij}}{m_i+m_j}\nu_{m,ij}\left[\frac{3}{2}k_B(T_i-T_j)+\frac{1}{2}(m_j-m_i)\vec{V}_i\cdot\vec{V}_j\right] +\sum_{i=2}^{N}\sum_{j=1}^{N}R_{i\leftarrow j}\cdot\varepsilon_{ij}+\sum_{i=2}^{N}\sum_{j=1}^{N}\left[\frac{R_{i\leftarrow j}}{m_i}\cdot\frac{3}{2}k_B T_i+\frac{R_{i\leftarrow j}}{m_j}\cdot\frac{3}{2}k_B T_j-R_{i\leftarrow j}\vec{V}_i\cdot\vec{V}_j\right]. \tag{48}$$

Here, we define

$$\rho_h h_h=\sum_{i=2}^{N}\rho_i h_i, \tag{49}$$

$$\lambda_h=\sum_{i=2}^{N}\lambda_i, \tag{50}$$

where ρ_h, h_h, and λ_h are the mass density, specific enthalpy, and translational thermal conductivity of the heavy species, respectively. Similarly, with the neglect of the contribution of the magnetic-field-induced current to the energy of the heavy-particle sub-system, the sixth term on the right-hand side of Eq. (48) can be expressed as $\sum_{i=2}^{N}n_i\langle\vec{X}_i\vec{C}_i\rangle=\sum_{i=2}^{N}(en_iZ_i\vec{V}_i)\cdot\vec{E}$; and for the low-speed plasma flows, the relations $\sum_{i=2}^{N}\mathrm{d}p_i/\mathrm{d}t=0$, $\sum_{i=2}^{N}(\rho_i\vec{V}_i)\cdot\mathrm{d}\vec{v}_0/\mathrm{d}t=0$ and $\sum_{i=2}^{N}\overleftrightarrow{\tau}_i:\vec{\nabla}\vec{v}_0=0$ in Eq. (48) are also satisfied.[6] The eighth and ninth terms on the right-hand side of Eq. (48) represent the sum of the energy exchange per unit volume during elastic collisions between electrons and heavy-particles. Thus, the sum of these two terms is equal to $-Q_{eh}^{el}$. For the inelastic collision process, we denote

$$Q_h^{inel}=\sum_{i=2}^{N}\sum_{j=1}^{N}R_{i\leftarrow j}\cdot\varepsilon_{ij} +\sum_{i=2}^{N}\sum_{j=1}^{N}\left[\frac{R_{i\leftarrow j}}{m_i}\cdot\frac{3}{2}k_B T_i+\frac{R_{i\leftarrow j}}{m_j}\cdot\frac{3}{2}k_B T_j-R_{i\leftarrow j}\vec{V}_i\cdot\vec{V}_j\right]. \tag{51}$$

Therefore, based on the foregoing discussions, the energy conservation equation for heavy particles can be expressed as

$$\frac{\partial(\rho_h h_h)}{\partial t}+\vec{\nabla}\cdot(\rho_h h_h\vec{v}_0) =\vec{\nabla}\cdot(\lambda_h\vec{\nabla}T_h)+\sum_{i=2}^{N}\vec{\nabla}\cdot(\lambda_i^{\theta}T_i\vec{\nabla}\ln\theta)-\sum_{i=2}^{N}\vec{\nabla}\cdot(n_i h_i^*\vec{V}_i) +\sum_{i=2}^{N}(en_iZ_i\vec{V}_i)\cdot\vec{E}-Q_{eh}^{el}+Q_h^{inel}. \tag{52}$$

Analogously, the expression of $\rho_h h_h$ can be read as

$$\rho_h h_h=\frac{5}{2}n_h k_B T_h+\rho_h\varepsilon_h^{r}+\rho_h\varepsilon_h^{in}. \tag{53}$$

The current continuity equation is obtained as follows. After division by m_i, the mass conservation equation for species i can be re-expressed as

$$\frac{\partial n_i}{\partial t}+\vec{\nabla}\cdot(n_i\vec{v}_0)=-\vec{\nabla}\cdot(n_i\vec{V}_i)+\dot{n}_i, \tag{54}$$

where Eq. (34) has been used, and $\dot{n}_i=R_i/m_i$. In a plasma system, the charge conservation condition is satisfied, i.e.,

$$\sum_j(eZ_i\dot{n}_i)=0, \tag{55}$$

and using the expression for the conduction current [Eq. (19)], Eq. (54) can be re-written as

$$\frac{\partial\rho^c}{\partial t}+\vec{\nabla}\cdot(\rho^c\vec{v}_0)=-\vec{\nabla}\cdot\vec{j}_{cond} \tag{56}$$

or

$$\vec{\nabla}\cdot(\vec{j}_{cond}+\rho^c\vec{v}_0)=-\frac{\partial\rho^c}{\partial t}, \tag{57}$$

where ρ^c is the net charge density, which is expressed as

$$\rho^c = \sum_j (eZ_i n_i). \quad (58)$$

In a conducting substance, the total current density can be expressed as[48]

$$\vec{j}_{tot} = \vec{j}_{cond} + \vec{j}_{disp} + \rho^c \vec{v}_0, \quad (59)$$

where $\vec{j}_{disp}$ is the displacement current and reads[48]

$$\vec{j}_{disp} = \varepsilon_0 \frac{\partial \vec{E}}{\partial t}, \quad (60)$$

where ε_0 is the vacuum permittivity, and $\vec{E}$ is the total electric field. The net charge density, ρ^c, is related to the electric field by

$$\rho^c = \varepsilon_0 \vec{\nabla} \cdot \vec{E}. \quad (61)$$

It can, therefore, be seen that the current continuity equation can be re-expressed as

$$\vec{\nabla} \cdot \vec{j}_{tot} = 0. \quad (62)$$

In a plasma system, electrons diffuse more rapidly than ions because of their smaller mass; the subsequent charge separation induces an electric field which is known as the ambipolar electric field. This slows the diffusion of electrons and increases the rate of diffusion of ions. Therefore, the total electric field, $\vec{E}$, "seen" by a charged particle in the plasma system, can be divided into two parts, the externally applied electric field ($\vec{E}^{ext}$) and the internal, or ambipolar, electric field ($\vec{E}^{in}$), i.e.,

$$\vec{E} = \vec{E}^{ext} + \vec{E}^{in}. \quad (63)$$

Since the conduction current is related with the external electric field, we have

$$\vec{j}_{cond} = \sigma \vec{E}^{ext}, \quad (64)$$

where σ is the electrical conductivity of the plasmas. If we define the external electric field as the gradient of the external electric potential, i.e.,

$$\vec{E}^{ext} = -\vec{\nabla} \varphi^{ext}, \quad (65)$$

Then, φ^{ext} represents the electric potential distribution attributed to the externally applied electric field, which drives the current flows in the plasma system. Substituting Eqs. (64) and (65) into Eq. (56), we obtain

$$\vec{\nabla} \cdot (\sigma \vec{\nabla} \varphi^{ext}) = \frac{\partial \rho^c}{\partial t} + \vec{\nabla} \cdot (\rho^c \vec{v}_0). \quad (66)$$

If we denote the total electric potential by $\varphi (= \varphi^{in} + \varphi^{ext})$, we can obtain the following equations from Eq. (61):

$$\nabla^2 \varphi = -\frac{\rho^c}{\varepsilon_0} \quad (67)$$

or

$$\nabla^2 \varphi^{in} = -\frac{\rho^c}{\varepsilon_0} - \nabla^2 \varphi^{ext}. \quad (68)$$

It can be seen from Eqs. (66)–(68) that:

First, if the plasma system is in a steady state with no externally applied electric field and satisfies the quasi-charge-neutrality condition, we have $\varphi = \varphi^{in} = \varphi^{ext} = 0$, which means that there are no current flows in the plasma system.

Second, if the plasma system is in a steady state with no externally applied electric field, but the quasi-charge neutrality condition is no longer satisfied (e.g., in the sheath region near the cold walls), then, $\varphi^{ext} = 0$ and $\nabla^2 \varphi = \nabla^2 \varphi^{in} = -\frac{\rho^c}{\varepsilon_0}$, which implies that $\varphi = \varphi^{in} \neq 0$.

Third, if the plasma system is in a transient state with no macroscopic flows and the quasi-charge neutrality condition is not satisfied, then the electric potentials and the current densities can be obtained by the following equations, which are commonly employed in the numerical modeling of low-pressure plasmas

$$\begin{cases} \vec{\nabla} \cdot (\sigma \vec{\nabla} \varphi^{ext}) = \dfrac{\partial \rho^c}{\partial t} \\ \nabla^2 \varphi = -\dfrac{\rho^c}{\varepsilon_0} \end{cases}, \quad \text{and} \begin{cases} \vec{j}_{cond} = \sigma \vec{E}^{ext} = -\sigma \vec{\nabla} \varphi^{ext} \\ \vec{j}_{disp} = \varepsilon_0 \dfrac{\partial \vec{E}}{\partial t} = -\varepsilon_0 \dfrac{\partial}{\partial t} (\vec{\nabla} \varphi) \end{cases}. \quad (69)$$

Finally, for the case in which the charge neutrality condition is satisfied, i.e., $\rho^c = 0$, we have

$$\vec{\nabla} \cdot (\sigma \vec{\nabla} \varphi^{ext}) = 0. \quad (70)$$

This is a general form of the electric potential equation for thermal plasma modeling without the consideration of the electrode sheath.

It can be seen from the mass-averaged momentum conservation equation [Eq. (43)] that the spatial distribution of the self-induced magnetic field, $\vec{B}$, need to be determined if current flows through the plasma system to take into account the Lorentz force. For the general case, the magnetic vector potential, $\vec{A}$, defined as $\vec{B} = \vec{\nabla} \times \vec{A}$, is usually introduced; then, starting from the Maxwellian equations, we can obtain the magnetic vector potential equation as[48]

$$\nabla^2 \vec{A} = -\mu_0 \vec{j}_{tot}, \quad (71)$$

where μ_0 is the permeability of the vacuum.

E. Brief discussion of the boundary conditions

For the simulation of a plasma system, the boundary conditions and the initial conditions (if any) are necessary to obtain the correct solutions. Of course, for different physical problems, the corresponding governing equations, as well as the boundary and initial conditions, may differ greatly. Hence, we discuss only the general method for the determination of the boundary conditions corresponding to the preceding partial differential equations.

First, for the mass conservation equation of species i, the number flux of species i at the boundary is imposed based on the chemical reactions, such as presented in Refs. 49 and 50.

Second, for the mass-averaged momentum conservation equation of the plasmas, the value of the mass-averaged velocity ($\vec{v}_0$) can be determined according to the physical conditions, e.g., the no-slip condition is employed along the solid walls, or the velocity distributions are determined satisfying mass conservation at the inlet and/or outlet of the calculation domain.

Third, for the energy conservation equation of species i, energy flux of species i is imposed as the boundary condition.[49,50]

Finally, for the electric potential equation, the externally applied voltage along the boundary can be imposed to solve Eq. (66), so as to obtain the distributions of the external electric field, while the total electric field can be obtained by employing Eq. (67).

III. DISCUSSIONS OF THE GOVERNING EQUATIONS UNDER SPECIFIC PLASMA STATES

A. 2T, LCE, quasi-charge-neutral (QCN) plasmas

When the characteristic time of the slowest reaction is small compared to the characteristic time of the flow, and also small compared to the diffusion time along the temperature and composition gradients, an LCE plasma can be assumed.[35] QCN is sustained in the system provided that the plasma sheath near the cold wall is ignored.

For 2T-LCE-QCN plasmas, the plasma system can be regarded as a single conducting fluid with two different temperatures, i.e.,

$$\rho^c = \sum_i (eZ_i n_i) = 0, \tag{72}$$

$$T_1 = T_e, T_i|_{i=2,3,\ldots,N} = T_h \text{ and } T_e \neq T_h. \tag{73}$$

The composition of the 2T-LCE-QCN plasma can be determined by many different methods (e.g., Refs. 51–55), and the species mass conservation equation [Eq. (27)] need not to be solved if a single homonuclear plasma gas is used. However, solution of the mass conservation equation for the plasma system is necessary if macroscopic fluid flow exists in the system. Summing both sides of Eq. (27) over all species, the mass conservation equation for the plasma system can be re-written as

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v}_0) = 0, \tag{74}$$

where the relationship $\sum_{i=1}^{N} \sum_{k=1}^{r} \xi_{ki} G_{ki} = 0$ has been applied due to the LCE condition, and Eqs. (6) and (7) have been used.

Analogously, summing both sides of Eq. (28) over all species, and using the momentum conservation law for elastic collision process, and the LCE condition, we can obtain

$$\sum_{i=1}^{N} \Delta_i^{el}[m_i \vec{C}_i] = 0, \tag{75}$$

$$\sum_{i=1}^{N} \Delta_i^{inel}[m_i \vec{C}_i] = 0. \tag{76}$$

The external forces acting on species i under plasma conditions can be written as

$$\vec{X}_i = Z_i e(\vec{E} + \vec{c}_i \times \vec{B}) + m_i \vec{g}, \tag{77}$$

where $\vec{g}$ is the gravitational acceleration, which has no contribution to the diffusion driving force. Therefore, the term involving the gravitational acceleration will not be considered in the external force. Thus, according to Eqs. (1) and (3), the sum of the average value of $\vec{X}_i$ may be written as

$$\begin{aligned} \sum_{i=1}^{N} n_i \langle \vec{X}_i \rangle &= \sum_{i=1}^{N} n_i e Z_i (\vec{E} + \vec{v}_i \times \vec{B}) \\ &= \rho^c (\vec{E} + \vec{v}_0 \times \vec{B}) + \sum_{i=1}^{N} n_i e Z_i \vec{V}_i \times \vec{B}. \end{aligned} \tag{78}$$

Using Eqs. (19) and (72), Eq. (78) can be re-written as

$$\sum_{i=1}^{N} n_i \langle \vec{X}_i \rangle = \vec{j}_{cond} \times \vec{B}. \tag{79}$$

Thus, the mass-averaged momentum conservation equation can be expressed as

$$\frac{\partial}{\partial t}(\rho \vec{v}_0) + \vec{\nabla} \cdot (\rho \vec{v}_0 \vec{v}_0) = -\vec{\nabla} p + \vec{\nabla} \cdot \vec{\vec{\tau}} + \vec{j}_{cond} \times \vec{B}. \tag{80}$$

Based on the LCE condition and taking into account the assumption that the plasma is optically thin, the inelastic collision term can be written as

$$Q_e^{inel} = -U_{rad}, \tag{81}$$

where U_{rad} is the radiation loss per unit volume of the plasma. Thus, the electron energy conversation equation [Eq. (48)] reads

$$\begin{aligned} &\frac{\partial}{\partial t}\left(\frac{5}{2} n_e k_B T_e\right) + \vec{\nabla} \cdot \left[\left(\frac{5}{2} n_e k_B T_e\right) \vec{v}_0\right] \\ &= \vec{\nabla} \cdot (\lambda_e \vec{\nabla} T_h) + \vec{\nabla} \cdot (\lambda_e^{\theta} T_e \vec{\nabla} \ln \theta) - \vec{\nabla} \cdot (n_e h_e^* \vec{V}_e) \\ &\quad + e n_e Z_e \vec{V}_e \cdot \vec{E} + Q_{eh}^{el} - U_{rad}. \end{aligned} \tag{82}$$

In Eq. (82), the term $e n_e Z_e \vec{V}_e \cdot \vec{E}$ can be rewritten as

$$e n_e Z_e \vec{V}_e \cdot \vec{E} = -e n_e \vec{V}_e \cdot (\vec{E}^{ext} + \vec{E}^{in}) = \vec{F}^{ext} \cdot \vec{V}_e + \vec{F}^{in} \cdot \vec{V}_e, \tag{83}$$

with

$$\vec{F}^{ext} = -e n_e \vec{E}^{ext} \quad \text{and} \quad \vec{F}^{in} = -e n_e \vec{E}^{in}. \tag{84}$$

We consider, as an example, the one-dimensional case. The physical meaning of Eq. (83) can be illustrated in Fig. 1. It can be seen that the first term $\vec{F}^{ext} \cdot \vec{V}_e$ on the right hand side of Eq. (84) represents the positive work done by the externally applied electric field, which is the Joule heating term; while the second term $\vec{F}^{in} \cdot \vec{V}_e$ represents negative work resulting from the internal electric field. As discussed in Sec. II, the internal electric field slows the diffusion of electrons and speeds the diffusion of ions so that quasi-neutrality is maintained; this is the ambipolar diffusion effect. If there is no externally applied electric field, the ambipolar diffusion effect will not cause the macroscopic current flow and work input. In contrast, if an externally applied electric field is present, the charged particles (electrons and ions) will be forced to move in a certain direction, leading to a macroscopic current flow. Simultaneously, the internal electric field will "appear" to retard the separation of ions and electrons arising because of their motions in the external electric field, and apply negative work to the charged particles.

For heavy particles, the inelastic collision term vanishes, i.e., $Q_h^{inel} = 0$, due to the LCE condition; and thus, the heavy-particle energy conservation equation reads

$$\frac{\partial}{\partial t}\left(\frac{5}{2}n_h k_B T_h + \rho_h \varepsilon_h^r + \rho_h \varepsilon_h^{\text{int}}\right) + \vec{\nabla}\cdot\left[\left(\frac{5}{2}n_h k_B T_h + \rho_h \varepsilon_h^r + \rho_h \varepsilon_h^{\text{int}}\right)\vec{v}_0\right]$$
$$= \vec{\nabla}\cdot(\lambda_h \vec{\nabla} T_h) + \sum_{i=2}^{N}\vec{\nabla}\cdot(\lambda_i^\theta T_i \vec{\nabla}\ln\theta) - \sum_{i=2}^{N}\vec{\nabla}\cdot(n_i h_i^* \vec{V}_i) + \sum_{i=2}^{N}(en_i Z_i \vec{V}_i)\cdot\vec{E} - Q_{eh}^{el}. \quad (85)$$

For the 2T-LCE-QCN plasmas, the electric potential distribution corresponding to the externally applied electric field can be obtained by employing Eq. (66) and the QCN condition [Eq. (72)], i.e.,

$$\vec{\nabla}\cdot(\sigma\vec{\nabla}\varphi^{ext}) = 0. \quad (86)$$

B. LTE-LCE-QCN plasmas

In regions where the electron number density is high enough to allow sufficient transfer of energy between the electrons and heavy species, such as the core region of plasmas, LTE can exist.[35] The set of governing equations, in particular the energy conversation equation, presented previously, should reduced to the usual equations obtained for the LTE-LCE-QCN state.

For LTE-LCE-QCN plasmas, the plasma system can be regarded as a single conducting fluid with the uniform gas temperature, i.e., $\rho^c = \sum_i (eZ_i n_i) = 0$, and $T_e = T_h$ (or $\theta = 1$); and the number density of species i can be determined by the mass action law (Saha equation) for a single homonuclear plasma gas, instead of solving the species continuity equations. For such plasma system, the flow field can be determined with the mass conservation equation and the mass-averaged momentum conservation equation with the same forms as those of Eqs. (74) and (80).

By adding Eqs. (82) and (85), we obtain

$$\sum_{i=1}^{N}\frac{\partial(\rho_i h_i)}{\partial t} + \sum_{i=1}^{N}\vec{\nabla}\cdot(\rho_i h_i \vec{v}_0)$$
$$= \sum_{i=1}^{N}\vec{\nabla}\cdot(\lambda_i\vec{\nabla}T) - \sum_{i=1}^{N}\vec{\nabla}\cdot(n_i h_i^*\vec{V}_i) + \sum_{i=1}^{N}(en_i Z_i\vec{V}_i)\cdot\vec{E} - U_{rad}. \quad (87)$$

According to the definition of the reactive thermal conductivity (λ_r) of a plasma in Ref. 45, we can obtain the relationship

$$\sum_{i=1}^{N}\vec{\nabla}\cdot(n_i h_i^*\vec{V}_i) = -\vec{\nabla}\cdot(\lambda_r\vec{\nabla}T) - \frac{5}{2}\frac{k_B}{e}\cdot\vec{j}_{cond}\cdot\vec{\nabla}T. \quad (88)$$

With Eq. (19) and the definition of the specific enthalpy of the plasmas as $\rho h = \sum \rho_i h_i$, Eq. (87) can be re-written as

$$\frac{\partial(\rho h)}{\partial t} + \vec{\nabla}\cdot(\rho\vec{v}_0 h) = \vec{\nabla}\cdot(\lambda\vec{\nabla}T) + \vec{j}_{cond}\cdot\vec{E} + \frac{5}{2}\frac{k_B}{e}\cdot\vec{j}_{cond}\cdot\vec{\nabla}T - U_{rad}, \quad (89)$$

where the thermal conductivity of the plasmas is defined as $\lambda = \lambda_e + \lambda_h + \lambda_r$. Equation (89) is consistent with the well-established energy conversation equation under thermal plasma conditions in the literature (e.g., Ref. 56).

In addition, the form of the current continuity equation for LTE-LCE-QCN plasmas is the same as that of Eq. (86) if current flow occurs in the plasma system.

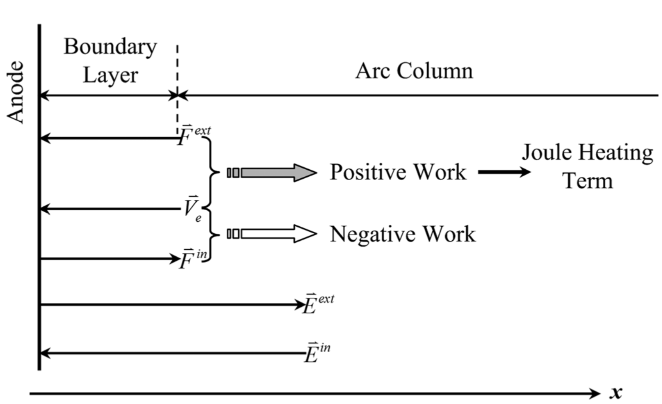

FIG. 1. Schematic of the work done by the electric field in a one-dimensional case.

IV. CONCLUSIONS

In this paper, the Chapman–Enskog method, which has been applied for the derivation of the transport properties of plasmas, has been used to derive the governing equations of a non-equilibrium plasma system. It has been shown that, in order to obtain the governing equations used for describing the complicated TEMHC coupling effects in a non-equilibrium thermal plasma system rigorously and accurately, a self-consistent treatment of the mass, momentum, energy fluxes, and the current flow used in the governing equations and for the transport property calculations is necessary. Based on this self-consistent theory, definitions of the specific heat at constant pressure and the reactive thermal conductivity of 2T plasmas, which are still ambiguous in the literature, are not required in the governing equations. As is required for any self-consistent set of governing equations used for simulation of the non-equilibrium thermal plasmas, the theoretical derivations show that these general equations can be reduced to their well-established counterparts for plasmas in both LTE and LCE states. Therefore, the established physical-mathematical model obtained in these two papers, based on a self-consistent theory of the transport properties and the governing equations, is capable of predicting the complicated physical and chemical processes in a gas discharge plasma system.

The self-consistency of the derivations of the transport coefficients and the governing equations that have been presented in Part I and here should make it possible to check the coefficients and the equations simultaneously, by means of comparing predictions of modeling results with experimental data in simple cases, such as the free-burning arc. This is an important point, since the only available measured values of transport coefficients are for LTE plasmas, and even these data are very limited.

Development of the computer codes to implement the calculation of the transport properties and the modeling of the complicated physical-chemical processes in a non-equilibrium thermal plasma system is planned for our future work, but is a complicated and long-term task.

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