A Statistical Mechanical View of the Determination of the Composition of Multi-Temperature Plasmas

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It is important that plasma composition is calculated in a manner consistent with statistical mechanics, particularly since the Boltzmann equation is the basis from which transport coefficients and the fluid-dynamic equations are derived. It is shown from statistical mechanical considerations based on the Boltzmann equation and the H-theorem that it is (i) not possible for a plasma to have more than one temperature in equilibrium in the absence of external forces and gradients, and (ii) not possible to draw conclusions about the change in entropy of a plasma in the presence of external forces and gradients. Derivations of the two-temperature Saha equation, and more generally calculations of the composition of a multi-temperature plasma, that are based on entropy maximization are therefore invalid. A thermodynamic derivation of the composition of a multi-temperature plasma that is consistent with the statistical mechanical results is presented. The derivation shows that the equilibrium composition of a plasma can be correctly calculated by minimization of the internal or free energy.

KEY WORDS: Multi-temperature plasmas; composition; calculations; thermodynamics.

1. INTRODUCTION

Knowledge of the composition of thermal plasmas is important in many applications. In particular, it is the starting point for the calculation of the thermodynamic properties and transport coefficients of the plasma, which are required for computational fluid-dynamic modeling of the plasma. For plasmas that can be described by a single temperature T, the method of calculation of the composition is well understood. For example, for a plasma composed of atoms A of a monatomic gas, and ions A^+ and electrons e^-

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resulting from ionization of the atoms, the composition is given by the Saha equation:[1]

$$\frac{n_e n_i}{n_a} = \frac{2Q_i(T)}{Q_a(T)} \left(\frac{2\pi m_e k_B T}{h^2}\right)^{3/2} \exp\left(-\frac{E_I}{k_B T}\right) \tag{1}$$

where n_e, n_i, and n_a are number densities of the electrons, atoms, and ions, respectively, Q_i and Q_a are the internal partition functions of the ions and atoms, respectively, E_I is the effective gas ionization energy, m_e is the electron mass, k_B is Boltzmann's constant, and h is Planck's constant.

In many types of thermal plasmas, such as dc and microwave jets and dc arcs, and in other high-temperature flows, a single temperature description is inadequate, either throughout the plasma (as in microwave jets[2]) or at least in some regions (such as those close to electrodes in dc arcs[3] or in the fringes of dc jets[4]). In such cases, it is necessary to consider at least two distinct temperatures, the electron temperature and the heavy-particle temperature, and sometimes more. For example, if molecular species are present, their vibrational and rotational temperatures may differ from the translational temperatures.

The correct method of calculation of composition of such multi-temperature plasmas has long been a subject of debate. For the case equivalent to Eq. (1), with atoms and ions at heavy-particle temperature T_h and electrons at temperature T_e, two particular forms of the Saha equation have been obtained:

$$n_e \left(\frac{n_i}{n_a}\right)^{T_h/T_e} = \frac{2Q_i(T_e)}{Q_a(T_e)} \left(\frac{2\pi m_e k_B T_e}{h^2}\right)^{3/2} \exp\left(-\frac{E_I}{k_B T_e}\right) \tag{2}$$

and

$$\frac{n_e n_i}{n_a} = \frac{2Q_i(T_e)}{Q_a(T_e)} \left(\frac{2\pi m_e k_B T_e}{h^2}\right)^{3/2} \exp\left(-\frac{E_I}{k_B T_e}\right) \tag{3}$$

Equation (2) was first derived by Prigogine[5] based on the thermodynamic criterion that the Helmholtz free energy would assume its minimum value at equilibrium in a process with constant temperatures and constant volumes. A more detailed derivation, based on a similar thermodynamic approach, was given by Potapov.[6]

Equation (3) differs from Eq. (2) in that there is no exponent T_h/T_e on the left-hand side. It was first derived[7-9] from kinetic theory by assuming that, since that average thermal speed of the electrons is much greater than that of the heavy particles, electrons will dominate in ionization and recombination reactions. The equilibrium constant $K = n_e n_i/n_a$ will then

depend only on T_e, which can be used to replace T on the right-hand side of Eq. (1).

Morro and Romeo,[10] van de Sanden *et al.*[11] and, most recently, Chen and Han,[12] have presented derivations of Eq. (3) using thermodynamic methods. The derivations of van de Sanden *et al.* and Chen and Han require the assumption that energy transfer between electrons and heavy particles can be neglected. Instead of minimization of Helmholtz free energy (or, equivalently, Gibbs free energy or internal energy, depending on the thermodynamic variables used), van de Sanden *et al.* and Chen and Han use the maximization of entropy to obtain their result.

Giordano[13] and Giordano and Capitelli[14,15] have argued that the formulation that should be employed in determining the composition of a multi-temperature plasma depends on the constraints (pressure, temperatures, entropy, etc.) imposed on the system. They showed that, depending on the constraints used, both Eqs. (2) and (3), and indeed other forms of the two-temperature Saha equation, can be derived using thermodynamic methods. For example, Eq. (2) was obtained from internal or free *energy* minimization by allowing redistribution between the translational *entropies* of the atoms and ions, and between the translational *entropies* of the electrons and electronic-excitation entropies of the atoms and ions, but preventing *entropy* exchange between these two groups. Equation (3) was obtained from *entropy* maximization by allowing redistribution between the translational *internal energies* of the atoms and ions, and between the translational *internal energies* of the electrons and electronic-excitation *internal energies* of the atoms and ions, but preventing *internal energy* exchange between these two groups.[14,15]

Giordano and Capitelli[15] expressed reservations about the assumption that the transfer of energy between the electrons and heavy particles (or more specifically, between the groups (i) the translational internal energies of the atoms and ions, and (ii) the translational internal energies of the electrons and electronic-excitation internal energies of the atoms and ions) can be neglected. Chen and Han[12] justified their neglect of this energy transfer on the basis that the energy transfer is proportional to the ratio of masses m_e/m_h, and is therefore small.

We would argue that energy transfer between electrons and heavy particles cannot be neglected. In most thermal plasmas, the plasma is heated via the interaction of the electrons with an external field (dc, rf or microwave). The electrons then transfer their energy to the heavy particles, which typically reach temperatures that are close to, or at least a significant fraction of, the electron temperature. Hence, while energy transfer between electrons and heavy particles is less efficient than that between species of similar mass, it cannot be neglected in determining the energy balance between the different

species, and therefore the composition of the plasma. Giordano and Capitelli[15] present further arguments, in particular noting that electron-impact ionization (whose rate is determined by the electron temperature) does not necessarily dominate over atom-impact ionization (whose rate is determined by the heavy particle temperature).

The distribution functions that describe the behavior of gaseous mixtures are solutions of the set of Boltzmann's equations, with one such equation fully describing the behavior of each species. The H-theorem can be used to calculate the equilibrium form of these distribution functions. It is interesting to investigate the ramifications of the H-theorem for a multi-temperature plasma for two reasons. Firstly, several authors have used the Second Law of Thermodynamics as a starting point to examine the equilibrium composition of a multi-temperature plasma.[10–12] Since the H-function is a generalization of the entropy, it is instructive to examine the validity of this approach when considered in the light of the H-theorem. Secondly, Boltzmann's equation is the starting point for the fluid-dynamic description of the plasma. The fluid-dynamic equations of change are derived from Boltzmann's equation, and the transport coefficients are obtained from approximate solutions of Boltzmann's equation. It is important that the composition of the plasma, which is used in calculating the transport coefficient and the thermodynamic properties, which are in turn required in the fluid-dynamic equations, is consistent with statistical mechanical considerations.

In Section 2, we use the H-theorem, applied to a thermal plasma, to show that it is not possible for the species in a spatially-uniform thermal plasma to have more than one temperature if there are no external forces. We then consider the influence of external forces and spatial gradients, finding that it is not possible to draw conclusions about changes in the plasma entropy in the presence of external forces or gradients. We use these two results to indicate the shortcomings of derivations of the two-temperature Saha equation, and more generally descriptions of the equilibrium composition of a multi-temperature plasma, that are based on entropy maximization. In Section 3, we develop a model from classical thermodynamics that is consistent with the results obtained from statistical mechanics, and that allows the determination of the plasma composition. Conclusions are presented in Section 4.

2. THE H-THEOREM FOR A THERMAL PLASMA

The H-theorem, or Boltzmann's H-theorem, is a demonstration of the tendency of the particles of an isolated system to approach their equilibrium distribution. The H-function for a mixture of species i with distribution

functions $f_i(\vec{r}, \vec{v}_i, t)$, where $\vec{r}$ is the position, $\vec{v}_i$ is the velocity of species i, and t is the time, is defined as

$$H(t) = \sum_i \iint f_i(\vec{r}, \vec{v}_i, t) \ln[f_i(\vec{r}, \vec{v}_i, t)] \, d\vec{v}_i \, d\vec{r} \tag{4}$$

The distribution function $f_i(\vec{r}, \vec{v}_i, t)$ must satisfy the Boltzmann equation:[16,17]

$$\frac{\partial f_i}{\partial t} + \left(\vec{v}_i \cdot \frac{\partial f_i}{\partial \vec{r}}\right) + \frac{1}{m_i}\left(\vec{X}_i \cdot \frac{\partial f_i}{\partial \vec{v}_i}\right) = \sum_j \iiint (f_i' f_j' - f_i f_j) g_{ij} \, b \, db \, d\varepsilon \, d\vec{v}_j \tag{5}$$

where $\vec{X}_i$ is an external force applied on the particle of the ith species, b is the impact parameter, g_{ij} is the initial relative velocity, and ε is the angle over which integration takes place. The dash notation denotes the value of a quantity after a collision.

It can be shown (e.g. Ref. 18) that $H = -S_v/k_B$, where S_v is the entropy per unit volume, and k_B is Boltzmann's constant. The H-function can be viewed as generalization of the entropy, since, unlike entropy defined on a strictly thermodynamic basis, it is defined in non-equilibrium situations. The H-theorem states that $dH/dt \le 0$ for an isolated system, and is hence a statement of the second law of thermodynamics.

Using the H-function, it can be shown that the equilibrium distribution function for an adiabatically-isolated spatially-uniform gas with no external forces is Maxwellian.[16,17] Here we follow the derivation as given by Hirschfelder, Curtiss and Bird[16] and examine the consequences for a thermal plasma.

2.1. Uniform Plasma without External Forces under Uniform Conditions

We assume in this section the plasma to be spatially uniform, so there is no dependence on $\vec{r}$. The H-function, $H(t)$, is then given by

$$H(t) = \sum_i \int f_i(\vec{v}_i, t) \ln[f_i(\vec{v}_i, t)] \, d\vec{v}_i \tag{6}$$

In the absence of external forces and under uniform conditions, the time rate of change of the distribution function f_i has to satisfy the following relation:

$$\frac{\partial f_i}{\partial t} = \sum_j \iiint (f_i' f_j' - f_i f_j) g_{ij} \, b \, db \, d\varepsilon \, d\vec{v}_j \tag{7}$$

Differentiating $H(t)$ and making use of Eq. (7), it can be shown that

$$\frac{dH(t)}{dt} = -\frac{1}{4} \sum_{ij} \iiint \int \left[\ln\left(\frac{f_i' f_j'}{f_i f_j}\right)\right] (f_i' f_j' - f_i f_j) g_{ij} \, b \, db \, d\varepsilon \, d\vec{v}_i d\vec{v}_j \tag{8}$$

The integrand of each of the integrals of the right hand of this equation is always positive or zero.[16] dH/dT is thus negative or zero, so that $H(t)$ can never increase. (This is a proof of the H-theorem under these conditions.) From the definition of $H(t)$ (Eq. (6)), it can be shown[16] that $H(t)$ is bounded and approaches a limit for large values of t. In this limit, the distribution functions are such that the integrands of each of the integrals of Eq. (8) are zero. Hence, at equilibrium,

$$\ln f_i + \ln f_j = \ln f_i' + \ln f_j' \qquad (9)$$

i.e., the sum of the logarithms of the distribution functions of two molecules is invariant in a collision. It can be shown that the only such summational invariants are linear combinations of the mass m_i, the momentum $m_i\vec{v}_i$, and the kinetic energy $\frac{1}{2}m_i v_i$. Therefore, at equilibrium, the most general expression for the logarithm of the distribution function is

$$\ln f_i = a_i m_i + [\vec{b}_i \cdot (m_i \vec{v}_i)] + c_i \left(\frac{1}{2} m_i v_i^2 \right) \qquad (10)$$

where a_i, $\vec{b}_i$, and c_i are constants.

Chapman and Cowling[17] have shown that $a_i = n_i(2\pi/m_i c)^{3/2}$, $\vec{b}_i = \vec{v}_0 c_i$, where $\vec{v}_0 = \sum_i n_i m_i \vec{v}_i / \rho$ is the mass average velocity, and $c_i = 1/kT_i$. From these expressions, the usual form of Maxwell's velocity-distribution function, $f_i = n_i \left(\frac{m_i}{2\pi k T_i} \right)^{3/2} \exp(-m_i V_i^2 / 2k_B T_i)$, is obtained, where $\vec{V}_i$ is the peculiar velocity, defined as $\vec{V}_i = \vec{v}_i - \vec{v}_0$.

We obtain from Eq. (9)

$$a_i m_i + a_j m_j + \vec{b}_i \cdot m_i \vec{v}_i + \vec{b}_j \cdot m_j \vec{v}_j + c_i \frac{1}{2} m_i v_i^2 + c_j \frac{1}{2} m_j v_j^2$$

$$= a_i m_i + a_j m_j + \vec{b}_i \cdot m_i \vec{v}_i' + \vec{b}_j \cdot m_j \vec{v}_j' + c_i \frac{1}{2} m_i v_i'^2 + c_j \frac{1}{2} m_j v_j'^2 \qquad (11)$$

Using the above expression for $\vec{b}_i$, we obtain

$$\vec{v}_0 \cdot (c_i m_i \vec{v}_i + c_j m_j \vec{v}_j) + c_i \frac{1}{2} m_i v_i^2 + c_j \frac{1}{2} m_j v_j^2$$

$$= \vec{v}_0 \cdot (c_i m_i \vec{v}_i' + c_j m_j \vec{v}_j') + c_i \frac{1}{2} m_i v_i'^2 + c_j \frac{1}{2} m_j v_j'^2 \qquad (12)$$

Conservation of momentum

$$m_i \vec{v}_i + m_j \vec{v}_j = m_i \vec{v}_i' + m_j \vec{v}_j' \qquad (13)$$

and conservation of energy

$$\frac{1}{2} m_i v_i^2 + \frac{1}{2} m_j v_j^2 = \frac{1}{2} m_i v_i'^2 + \frac{1}{2} m_j v_j'^2 \qquad (14)$$

can only be satisfied for all collisions if $c_i = c_j$, i.e., if $T_i = T_j$. We conclude that, in the absence of external forces, a spatially-uniform plasma has only a unique temperature when equilibrium is reached.

2.2. Inclusion of External Forces and Gradients

Differentiating the H-function in the presence of gradients, given by Eq. (4), with respect to time gives

$$\frac{dH(t)}{dt} = \sum_i \iint \{1 + \ln[f_i(\vec{r}, \vec{v}_i, t)]\} \frac{\partial f_i(\vec{r}, \vec{v}_i, t)}{\partial t} d\vec{v}_i \, d\vec{r} \tag{15}$$

which, taking into account the Boltzmann equation (5), and retaining the gradient and external force terms, becomes

$$\frac{dH(t)}{dt} = \sum_i \iint \left[\{1 + \ln[f_i(\vec{r}, \vec{v}_i, t)]\} \left\{ \sum_j \iiint (f_i'f_j' - f_i f_j) g_{ij} b \, db \, d\varepsilon \, d\vec{v}_j \right. \right.$$
$$\left. \left. - \left(\vec{v}_i \cdot \frac{\partial f_i}{\partial \vec{r}} \right) - \frac{1}{m_i} \left(\vec{X}_i \cdot \frac{\partial f_i}{\partial \vec{v}_i} \right) \right\} \right] d\vec{v}_i \, d\vec{r} \tag{16}$$

This reduces to Eq. (8) in the absence of external forces and gradients. However, in the presence of the terms describing external forces and gradients, the distribution function is no longer Maxwellian, and furthermore the sign of the evolution of $H(t)$ cannot be determined. Nevertheless, when equilibrium is reached, the functions f_i no longer vary with time (if we consider a time scale larger than the duration of a collision), and thus

$$\frac{\partial f_i}{\partial t} = 0 \tag{17}$$

which implies, from Eq. (15), that

$$\frac{dH(t)}{dt} = 0 \tag{18}$$

Since the entropy is directly related to the H-function, we can write as a consequence of Eq. (16) that

$$S = \sum_i \left(S_i^{\text{int}} + S_i^{\text{ext}} \right) \tag{19}$$

where S is the entropy of the whole system, S_i^{int} is the entropy related to the distribution function and exchanges between the different species during collisions, and S_i^{ext} is the entropy related to the external forces and gradients.

From Eq. (18) we obtain:

$$\frac{dS}{dt} = 0 \tag{20}$$

In equilibrium, therefore, the entropy of the total system, taking into account external forces and gradients, is stable in time. However, it is not possible to draw any conclusions about the evolution of S_i^{int} or $\sum_i S_i^{int}$ in the presence of external forces or gradients.

2.3. Consequences for the Calculation of Plasma Composition

In the preceding parts of Section 2, we have considered some of the consequences of statistical mechanics, including Boltzmann's H-theorem, for multi-temperature plasma composition calculations. We showed in Section 2.1 that it is not possible for plasma species to be at more than one temperature in an isolated, spatially-uniform system, i.e., in the absence of external forces or gradients. Further, we demonstrated in Section 2.2 that when external forces or gradients are taken into account, it is not possible to draw any conclusions regarding changes in the internal entropy S_i^{int} of any species i, or changes in the total internal entropy $\sum_i S_i^{int}$ of any plasma.

It follows logically from these two points that it is not possible to draw conclusions about changes in the internal entropy for any multi-temperature plasma.

We noted in Section 1 that the two-temperature Saha equation (3) is obtained using derivations based on maximization of the internal entropy.[14,15] In particular, the derivations of van de Sanden *et al.*[11] and Chen and Peng,[12] and those of Giordano and Capitelli[14,15] that give Eq. (3), are based explicitly on the consideration of a two-temperature plasma under the condition that $dS_i^{int}/dt = 0$. Such derivations are clearly inconsistent with our conclusions derived from statistical mechanics.

In the following section, we investigate the determination of the plasma composition using a classical thermodynamic approach that is consistent with the consequences of the H-theorem.

3. THERMODYNAMIC CALCULATION OF PLASMA COMPOSITION

In a plasma, the electrons (which we will denote in this section as particle system 1) gain energy in the electric field, since their mass and consequently their mobility is higher than those of the heavy particles (which we will denote as particle system 2). We can thus say that the plasma system as a whole

receives energy δW_{el} mainly through the electrons. For simplicity, we neglect energy received through the heavy particles; note that including this term would not affect the results. The electrons subsequently transfer their translational energy through collisions to the heavy particles, either by exchange of translational energy (an elastic collision) or through a chemical reaction such as electron-impact ionization (an inelastic collision). The energy lost by the electrons through collisions with heavy particles is denoted by δQ_1. Since the number of electrons, dN_1, varies in chemical reactions, the work, δL_1, due the chemical reactions has to be taken into account. The same types of energy exchange occur between the heavy particles and the electrons, and are characterized by δQ_2 and δL_2, respectively. Further, the interactions of the electrons with the heavy particles leads to the emission of energy δQ_{em}^1 to the outside by, for example, bremsstrahlung and other radiative emission. Similarly, the heavy particles lose energy δQ_{em}^2 by monatomic and diatomic line radiation, thermal conduction to walls, etc. In addition, the systems of electrons and heavy particles can exchange work with the outside, denoted by δW_1^{ext} and δW_2^{ext}, respectively. Figure 1 shows all the energy exchanges.

The first law of thermodynamics applied to particle systems 1 and 2 results in:

$$dU_1 = \delta Q_1 + \delta L_1 + \delta Q_{em}^1 + \delta W_1^{ext} + \delta W_{el} \tag{21}$$

and

$$dU_2 = \delta Q_2 + \delta L_2 + \delta Q_{em}^2 + \delta W_2^{ext} \tag{22}$$

respectively, where U_1 and U_2 are respectively the internal energies of particle systems 1 and 2. It follows that

$$dU = \delta Q_1 + \delta Q_2 + \delta L_1 + \delta L_2 + \delta Q_{em}^1 + \delta Q_{em}^2 + \delta W_1^{ext} + \delta W_2^{ext} + \delta W_{el} \tag{23}$$
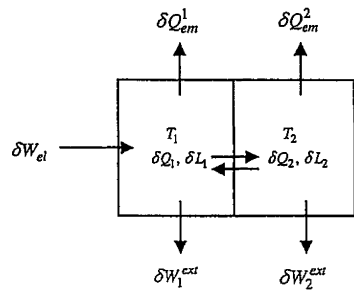
where $dU = dU_1 + dU_2$.

Fig. 1. Schematic diagram showing the energy exchanges between electrons (particle system 1), heavy species (particle system 2), and the exterior.

When the system is stable in time, it can be assumed that the energy gains are equal to the energy losses so that:

$$\delta W_{el} = -\delta Q_1^{em} - \delta Q_2^{em} - \delta W_1^{ext} - \delta W_2^{ext} \tag{24}$$

We then introduce the relations $\delta Q_1 = T_1 \, dS_1^{exch}$ and $\delta Q_2 = T_2 \, dS_2^{exch}$, where dS_1^{exch} is the entropy change associated with the energy exchanges from the electrons to the heavy species, and dS_2^{exch} is the entropy change associated with the energy exchanges from the heavy species to the electrons. The work performed on the external system is given by $\delta W_1^{ext} = -p_1 \, dV$ and $\delta W_2^{ext} = -p_2 \, dV$, where p_1 and p_2 are respectively the partial pressure of the electrons and the heavy species. The chemical work performed on the electron and heavy particle systems is given by $\delta L_1 = \mu_1 \, dN_1$ and $\delta L_2 = \mu_2 \, dN_2$, where μ_1 and μ_2 are respectively the chemical potentials of the electrons and heavy particles. Substituting these relations into Eq. (23), and using Eq. (24), dU can be written as:

$$dU = T_1 \, dS_1^{exch} + T_2 \, dS_2^{exch} + \mu_1 \, dN_1 + \mu_2 \, dN_2 \tag{25}$$

The Helmholtz free energy is given by:

$$dF = S_1^{exch} \, dT_1 + S_2^{exch} \, dT_2 + \mu_1 \, dN_1 + \mu_2 \, dN_2 \tag{26}$$

Taking Dalton's law into account, the Gibbs free energy can be written as:

$$dG = S_1^{exch} \, dT_1 + S_2^{exch} \, dT_2 + \mu_1 \, dN_1 + \mu_2 \, dN_2 - V \, dp_1 - V \, dp_2 \tag{27}$$

Immediately we see that, when the system is stable in time:

$$(dU)_{S_1^{exch}, S_2^{exch}, N_i} = (dF)_{T_1, T_2, N_i} = (dG)_{T_1, T_2, p, N_i} = 0 \tag{28}$$

This relation is similar to that proposed by Giordano and Capitelli[13–15] in their derivation of Eq. (2). It can be shown to lead to the two-temperature Saha equation in the form of Eq. (2).[5,14,15]

Taking into account the energy exchanges with the external system at temperature T_{out}, and applying Eq. (20), results in:

$$dS^{exch} = \frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} + \frac{\delta Q_1^{em}}{T_{out}} + \frac{\delta Q_2^{em}}{T_{out}} = 0 \tag{29}$$

where $\frac{\delta Q_1^{em}}{T_{out}} + \frac{\delta Q_2^{em}}{T_{out}}$ corresponds to the term $\sum_i S_i^{ext}$, and $\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2}$ corresponds to the term $\sum_i S_i^{int}$, in Eq. (19). As we showed in Section 2.2, no conclusion can be drawn about $d \sum_i S_i^{int}$; in particular it cannot be stated that $d \sum_i S_i^{int} \geq 0$, which is the relation used by van de Sanden *et al.*[11] and Chen and Han[12] to derive the two-temperature Saha equation in the form

of Eq. (3). Potapov[6] also erroneously used a similar relation, although he nevertheless obtained the two-temperature Saha equation in the form of Eq. (2).

4. CONCLUSIONS

The transport coefficients and the fluid-dynamic equations, which describe change in thermal plasmas, are derived from the Boltzmann equation. It is therefore particularly important that the composition of the plasma, which is used in calculating the transport coefficients and the thermodynamic properties, which are in turn required in the fluid-dynamic equations, is calculated in a manner consistent with statistical mechanics.

We have shown from a statistical mechanical viewpoint, using an argument based on the consequences of Boltzmann's *H*-theorem, that it is not possible for multiple temperatures to exist in a plasma in equilibrium in the absence of external forces or gradients. Using further statistical mechanical arguments, we have shown that when gradients or external forces are present, the entropy is the sum of the entropy of the plasma system, and the entropy exchanged with the surrounding external system. It is then not possible to draw any conclusions about the evolution of plasma system, only that the entropy of the total system is stable in time when the plasma is in equilibrium. Such results mean that the assumption that the entropy of the plasma system reaches a maximum value, which is made by some authors[6,11,12] in characterizing the equilibrium composition in multi-temperature plasmas, is inconsistent with statistical mechanics and therefore invalid. This problem does not affect the derivation of the two-temperature Saha equation of the form of Eq. (2) given by Prigogine,[5] or the formulation given by Giordano and Capitelli[13–15] in their derivation of Eq. (2).

We have further presented a thermodynamic calculation that includes the exchange of energy between electrons and heavy species, and between the plasma system and the external system. The calculation shows that minimization of free energy or internal energy is an appropriate method for calculating the composition of a multi-temperature plasma that is stable in time. This result is in accordance with that of Prigogine,[5] and of the Giordano and Capitelli[13–15] derivation of Eq. (2). In a plasma that is not stable in time, such as that in a sulfur hexafluoride circuit breaker arc, chemical equilibrium is not reached, and a kinetic calculation is more likely to be accurate.

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