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Technical Notes

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Two-Temperature Saha Equations: Effects on Thermophysical Properties of H_2 Plasmas

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Introduction

THERMODYNAMIC and transport properties of thermal plasmas can be easily calculated once the composition of the system is known, which in many cases can be described by the Saha equation. Problems, however, can arise for the so-called two-temperature plasmas, that is, plasmas characterized by different temperatures that exist because of the inefficiency of electron–molecule collisions to redistribute energy and/or entropy. For this case, several Saha equations have been presented in the literature, depending on the constraints imposed to the system.[1–3]

The purpose of this Note is to show how the choice of the Saha equation affects the thermodynamic and transport properties of H_2 plasmas.

Theoretical Aspects

The two-temperature Saha equations we are using are an adaptation of the axiomatic approach presented in Refs. 1–3 for H_2 plasma. In the present case, the arrays of the independent state parameters are $\{S_{\mathrm{H,tr}}, S_{\mathrm{H,ex}}, S_{\mathrm{H^+}}, S_{\mathrm{H_2}}, S_e, V, N_{\mathrm{H}}, N_{\mathrm{H^+}}, N_{\mathrm{H_2}}, N_e\}$ in the energetic scheme and $\{U_{\mathrm{H,tr}}, U_{\mathrm{H,ex}}, U_{\mathrm{H^+}}, U_{\mathrm{H_2}}, S_e, V, N_{\mathrm{H}}, N_{\mathrm{H^+}}, N_{\mathrm{H_2}}, N_e\}$ in the entropic scheme.[4–7] Here, S, U, V and N are entropy, internal energy, volume, and number density, respectively. Subscripts tr and ex denote translational and excitation degrees of freedom whereas subscripts H, H^+, H_2, and e denote the different species present in the plasma.

The first Saha equation we consider corresponds to the following entropic constraints:

$$S_{\mathrm{H,tr}} + S_{\mathrm{H^+}} = S^a_{h,\mathrm{tr}}, \qquad S_{\mathrm{H,ex}} + S_e = S^a_{\mathrm{ex}+e} \tag{1}$$

and reads

$$N_e\left(\frac{N_{\mathrm{H^+}}}{N_{\mathrm{H}}}\right)^{1/\vartheta} = \frac{2\cdot g_{\mathrm{H^+}}}{Q_{\mathrm{H}}(T_e)}\left(\frac{2\pi m_e k_b T_e}{h^2}\right)^{\frac{3}{2}}\exp\left(-\frac{E_I}{k_b T_e}\right) \tag{2}$$

The same equation can be obtained by minimizing the Gibbs potential as shown by several researchers.[8–10]

A slight modification of Eq. (2) has been obtained in Ref. 3 by considering the following constraints:

$$S_{\mathrm{H,tr}} + S_{\mathrm{H,ex}} + S_{\mathrm{H^+}} = S^a_h, \qquad S_e = S^a_e \tag{3}$$

which in this case result in the following equation:

$$N_e\left(\frac{N_{\mathrm{H^+}}}{N_{\mathrm{H}}}\right)^{1/\vartheta} = 2\left[\frac{g_{\mathrm{H^+}}}{Q_{\mathrm{H}}(T_h)}\right]^{1/\vartheta}\left(\frac{2\pi m_e k_b T_e}{h^2}\right)^{\frac{3}{2}}\exp\left(-\frac{E_I}{k_b T_e}\right) \tag{4}$$

Note that the only difference between Eqs. (3) and (4) is the temperature at which one calculates the partition function of atomic hydrogen. In Eq. (2), the electrons are considered responsible for both ionization and excitation processes, whereas in Eq. (4), the electrons are responsible only for the ionization process.

Let us examine the Saha equations that derive from energetic constraints. By imposing

$$U_{\mathrm{H,tr}} + U_{\mathrm{H^+}} = U^a_{h,\mathrm{tr}}, \qquad U_{\mathrm{H,ex}} + U_e = U^a_{\mathrm{ex}+e} \tag{5}$$

we obtain[11]

$$\frac{N_e N_{\mathrm{H^+}}}{N_{\mathrm{H}}} = \frac{2\cdot g_{\mathrm{H^+}}}{Q_{\mathrm{H}}(T_e)}\left(\frac{2\pi m_e k_b T_e}{h^2}\right)^{\frac{3}{2}}\exp\left(-\frac{E_I}{k_b T_e}\right) \tag{6}$$

This equation is commonly understood to be a result of the maximization of the plasma entropy. A similar equation has been obtained by Morro and Romeo[12,13] by allowing the following constraints:

$$U_{\mathrm{H,tr}} + U_{\mathrm{H,ex}} + U_{\mathrm{H^+}} = U^a_h, \qquad U_e = U^a_e \tag{7}$$

$$\frac{N_e N_{\mathrm{H^+}}}{N_{\mathrm{H}}} = \frac{2\cdot g_{\mathrm{H^+}}}{Q_{\mathrm{H}}(T_h)}\left(\frac{2\pi m_e k_b T_e}{h^2}\right)^{\frac{3}{2}}\exp\left(-\frac{E_I}{k_b T_h}\right) \tag{8}$$

Again, the differences in Eqs. (6) and (8) are due to the role of the electrons in the ionization and excitation processes.

We consider the molecular degrees of freedom of H_2 in mutual thermal equilibrium at T_h. To get the composition, we couple the Saha equation for ionization and a similar equation for dissociation to the conditions of electroneutrality and species conservation. We consider only a four-component system (H_2, H, H^+, and e) disregarding in particular the H_2^+ and H^- species. The thermodynamic properties of the mixture are then obtained by averaging the component-property thermodynamic functions with the relevant molar fractions.[14] Note, however, that in the present study we do not consider the lowering of the ionization potential as we calculate the internal partition function of atomic hydrogen by considering levels with principal quantum numbers up to $n = 12$ irrespective of

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the pressure. The internal partition function of molecular hydrogen is calculated by summing over all of the rotational states up to the dissociation limit for each vibrational level of the ground electronic state; this procedure is repeated for all of the 14 vibrational levels sustained by the ground-state potential curve. No electronically excited states are considered in the calculation of H_2 partition function. The first bound electronic level of molecular hydrogen is excited when the molecule is practically dissociated.

For the transport properties of multitemperature plasmas, we have used the same formulation as that developed for the one-temperature case, that is, the solution of Boltzmann equation according to the Chapman–Enskog method (see Ref. 15). The procedure is correct because the heavy-particle Boltzmann equation can be decoupled from the Boltzmann equation for electrons. As a consequence, we can calculate the translational thermal conductivity of heavy components and the viscosity of plasma by inserting the composition, calculated according to the multitemperature thermodynamics, into the relevant equations. In this case, the transport cross sections for heavy-particle–heavy-particle interactions are calculated at T_h whereas those involving electron–electron and electron–heavy-particle collision are calculated at T_e.

In our case, it is possible to express the total thermal conductivity as

$$\lambda = \lambda_{\mathrm{tr}} + \lambda_{\mathrm{int}} + \lambda_R \tag{9a}$$

where the terms on the right-hand side of Eq. (9a) are the translational, internal, and reactive thermal conductivity, respectively. Translational thermal conductivity is in turn expressed as the sum of the heavy-particle contribution and of the electron contribution,

$$\lambda_{\mathrm{tr}} = \lambda_h + \lambda_e \tag{9b}$$

A different approximation of the Chapman–Enskog method must be used for λ_h and λ_e (Ref. 15). Translational thermal conductivity of the heavy particles can be calculated according to the second Chapman–Enskog approximation, whereas the third approximation of the Chapman–Enskog method must be used for electrons (see Ref. 15). The working equations may be found in Ref. 15. On the other hand, the internal thermal conductivity to a first approximation can be calculated according to the Eucken theory (see Ref. 15). Note that in our calculations the transport of internal energy for atomic hydrogen has been calculated by assuming that the diffusion coefficients of electronically excited states and H, H^+ pairs are equal.

At high temperature, gases can be partially dissociated and ionized and so they can transport their enthalpy in the temperature gradient. The so-called reactive thermal conductivity for equilibrium situations can be calculated according to the Butler and Brokaw equation. This formulation has been also extended to nonequilibrium plasmas (see Ref. 16 for the equation).

The electrical conductivity of a partially ionized gas can be calculated by the third approximation of the Chapman–Enskog method. It assumes a form very similar to the translational thermal conductivity of electrons.[15]

Transport cross sections (collision integrals) for the relevant interactions are tabulated in Ref. 17. Note that charged–charged collision

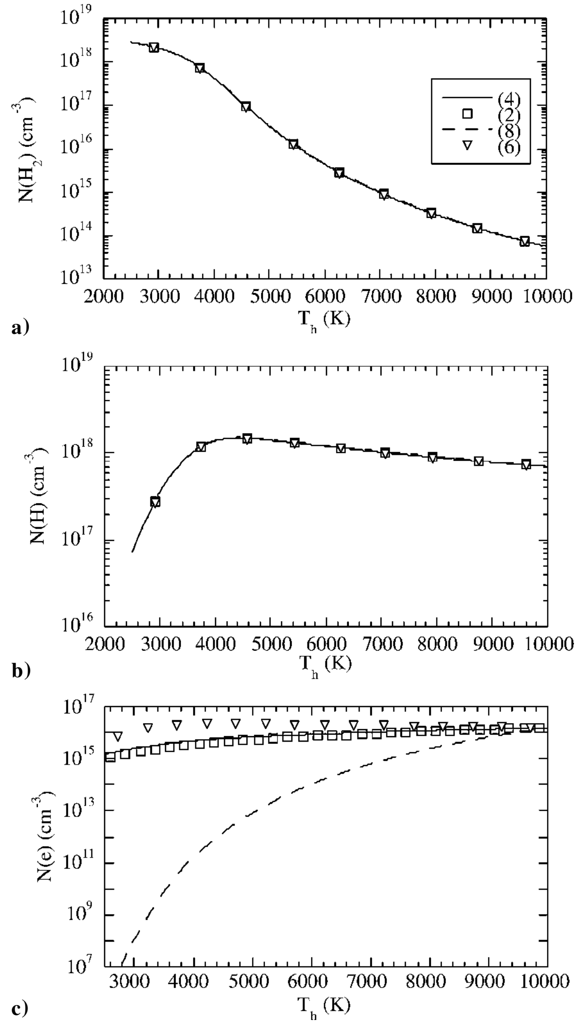
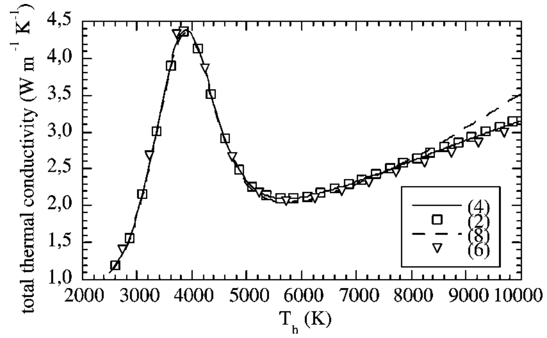
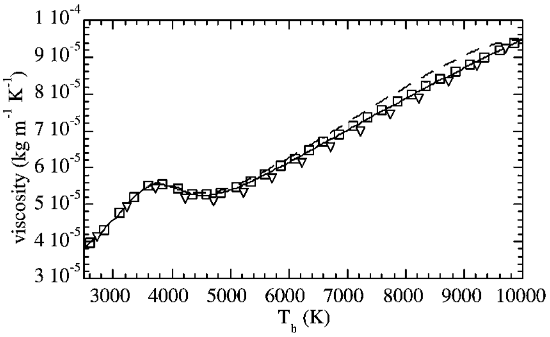


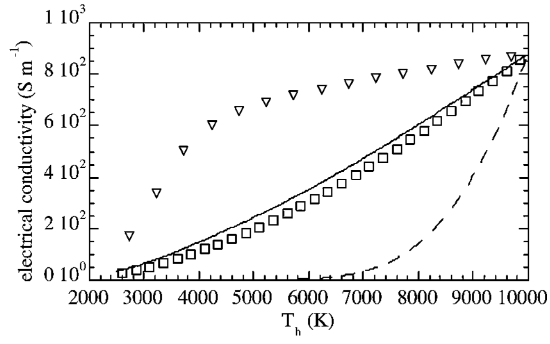
Fig. 1 Comparisons of equilibrium number densities from different Saha equations vs T_h at T_e = 10,000 K: a) molecular hydrogen, b) atomic hydrogen, and c) electrons. (Numbers in parentheses correspond to equations in text.)



a) Total thermal conductivity



b) Viscosity



c) Electrical conductivity

Fig. 2 Comparisons of transport properties vs T_h at T_e = 10,000 K.

integrals have been obtained by interpolation of Mason et al. values[18] considering the screening in the Debye length due only to electrons.

Results and Remarks

Numerous data exist for the thermodynamic properties of H_2 thermal plasmas. The present results, which have been partially tabulated in Ref. 19, are in excellent agreement with those reported in Ref. 20.

The transport properties at atmospheric pressure (total thermal conductivity, viscosity, and electrical conductivity) calculated in the present Note have been compared with the recent calculations performed by Murphy[21] and with the older ones of Devoto.[22] Excellent agreement for total thermal conductivity and good agreement for viscosity and electrical conductivity have been found.

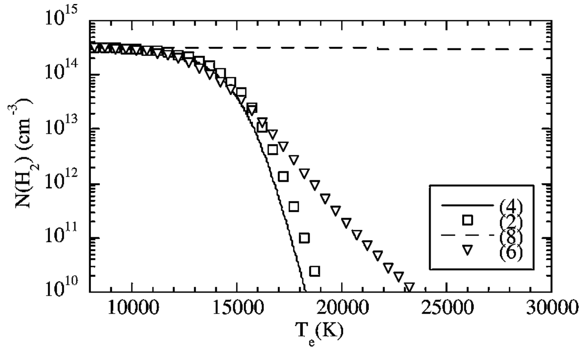
Calculations of thermodynamic and transport properties of two-temperature H_2 plasmas have been recently reported by Aubreton et al.[16] by using Eq. (4) for plasma composition. Our results reported in Ref. 19 are in good agreement with these data.

We now compare the results that can be obtained by using the different formulations, that is, Eqs. (2), (4), (6), and (8), for the ionization process. We limit the comparison to $T_e = 10{,}000$ K for different T_h values and to $T_h = 8{,}000$ K for different T_e values ($p = 1$ atm). We examine the behavior of the number densities. In the dissociation regime, where heavy particles density greatly exceeds electron density, we see Eqs. (2), (4), (6), and (8) give essentially the same values for the heavy-particles density and large differences in the electron density (Figs. 1a–1c). These differences also appear in the transport properties (Figs. 2a–2c).

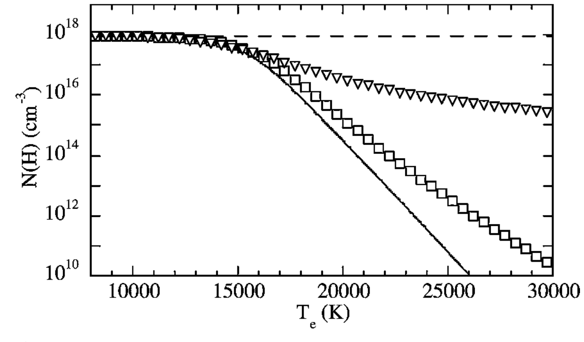
The relevant trends can be understood by recalling that electrons dominate the electrical conductivity, whereas heavy-particle behavior dominates viscosity. This is confirmed by inspection of Figs. 2b and 2c. Figures 2b and 2c show that viscosity, which depends on heavy particles, does not depend on the form of ionization reaction, whereas electrical conductivity, which depends on electrons, is strongly affected by the form of Saha equation.

Total specific heat and total thermal conductivity do not depend on the different forms of Saha equation in the dissociation regime: They have a small dependence on the form of ionization reaction at high temperatures. In the ionization regime, where electron density exceeds heavy-particle density, there are significant differences in heavy-particle densities (Figs. 3a–3c). The dependence of the total thermal conductivity on the different forms of Saha equation is more significant in the ionization regime, as shown in Figs. 4a–4c. On the other hand, electrical conductivity is weakly affected by the form of Saha equation for Eqs. (2), (4), and (6) (see Fig. 4c), whereas for Eq. (8), there is a strong difference due to the appearance of T_h in the exponential factor.

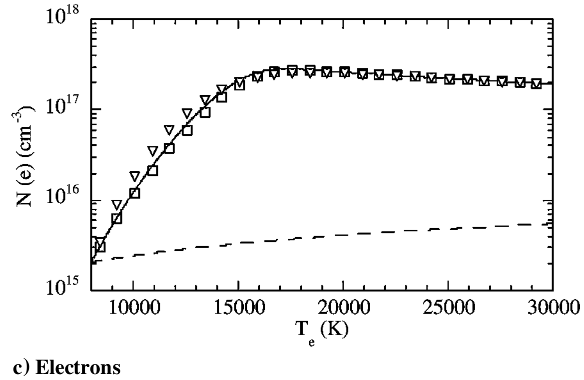
It is difficult to extend these conclusions to a wide range of pressure T_e and T_h values. The problem is which formulation of the Saha equation use. According to our work, different Saha equations



a) Molecular hydrogen

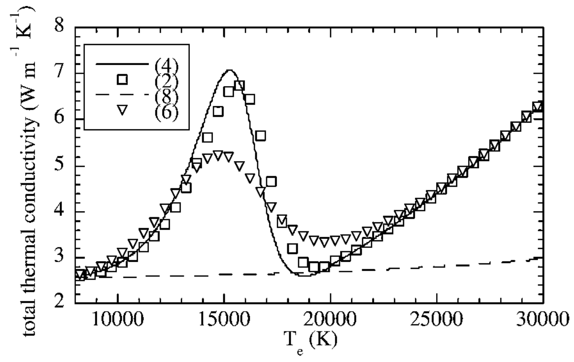


b) Atomic hydrogen

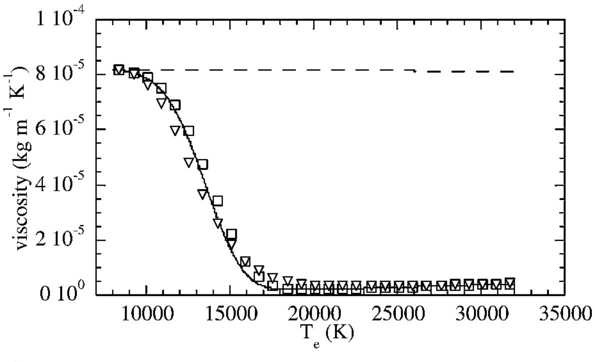


c) Electrons

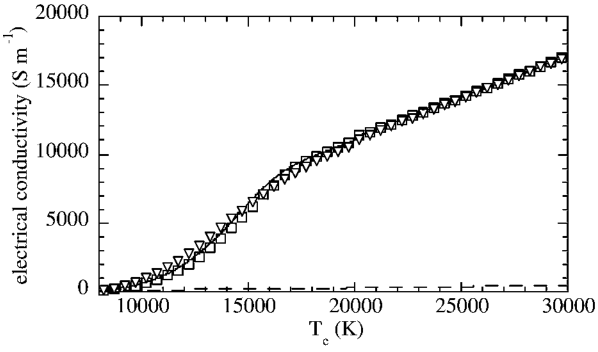
Fig. 3 Comparisons of equilibrium number densities from different Saha equations vs T_e at T_h = 8000 K.



a) Total thermal conductivity



b) Viscosity



c) Electrical conductivity

Fig. 4 Comparison of transport properties vs T_e at T_h = 8000 K.

arise from the different constraints imposed on the system, so that only experimental data can help in selecting the true Saha equation. Moreover, also accepting the maximization entropy criterion, we can have different formulations of the Saha equation depending on the definition of the relevant excitation temperatures, and these depend on the role of electrons and heavy particles in the dissociation and ionization processes.[23–27]

Conclusions

We have presented new calculations of thermodynamic and transport properties of equilibrium and nonequilibrium H_2 plasmas. In general, our results are in good agreement with those obtained by other authors.[16,21,22] The main conclusion that can be drawn from the results is that the thermodynamic and transport properties of two-temperature plasmas may depend in a nonnegligible manner on the adopted form of the Saha equation, which, in turn, is determined by the physical constraints imposed on the considered system.

Acknowledgment

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Extended Slip Boundary Conditions for Microscale Heat Transfer

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Nomenclature

Kn = Knudsen number
T = temperature, K
u_s = slip velocity, m/s
y = coordinate axis

Introduction

THE commonly used slip boundary conditions in microchannels are called the Maxwellian conditions, and they are first-order accurate in Knudsen number. In the present analysis, we develop the extended slip boundary conditions in a systematic manner to be used beyond the slip flow regime. The results are valid for early transition flows.

Analysis

A. Velocity Slip

When a gas flows over a surface, the molecules leave some of their momentum and create the shear stress on the wall. This momentum is the difference between the momentum of the incoming, M_{in}, and the reflected, M_{out}, molecules. The incoming momentum has two components: momentum of the impinging and the slipping molecules. The momentum going away from the surface is by reflection. As shown in Fig. 1, the specular reflection conserves the tangential momentum of the molecules $M_{\text{specular}} = M_{\text{in}}$, and the diffuse

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