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Technical Notes

Influence of Electronic Excitation on the Thermodynamic Properties of Hydrogen Plasmas

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Nomenclature

a_0 = Bohr radius
c_{int} = internal contribution to c_{pf}
c_p = specific heat at constant pressure
c_{pf} = frozen specific heat
c_{pr} = reactive specific heat
c_{p_nl} = specific heat neglecting the electronic degree of freedom
$c_{V_{\mathrm{int}}}$ = internal contribution to c_V of a single species
c_v = specific heat at constant volume
D = dissociation energy
E = internal energy
EI = ionization energy
f = internal partition function
g_i = degeneracy of the ith level
H = total enthalpy
H_i = enthalpy of the ith species
H_{int} = internal enthalpy
h = Planck constant
K_p = equilibrium constant
k = Boltzmann constant
m_i = mass of the ith species
N = particle density
n_i = number density of the ith species
n'_i = number density per unit of mass of the ith species
P_i = pressure of the ith species
P_{tot} = total pressure
T = temperature
ΔI = lowering of ionization potential
ε_i = energy of the ith level
ρ = mass density

I. Introduction

THE influence of electronic excitation on the thermodynamic properties of local thermodynamic equilibrium (LTE) plasmas is widely studied and largely underestimated.[1–3] This situation is due to a sort of compensation between the different contributions to a given thermodynamic property calculated inserting and neglecting the electronically excited states in the relevant partition function. As an example, the total specific heat of a LTE plasma can be thought as the sum of two contributions, the frozen and reactive ones. Comparison of the total specific heat calculated with and without internal excitation of the different species (atoms and ions) shows very small differences (not exceeding a few percent) with the corresponding quantities calculated inserting the internal excitation. In a series of papers,[1–3] it has been shown that the internal excitation strongly affects the two contributions (frozen and reactive) of the total specific heat, although in opposite directions. In particular, the insertion of electronically excited states in the whole thermodynamic scheme increases the frozen specific heat compared with the corresponding quantity calculated by neglecting the electronically excited states, the reverse being true for the reactive contribution. This largely explains the insensitivity of the total thermodynamic quantities to the internal excitation of atomic species and the limited interest of the scientific community to this subject. On the other hand, electronically excited states are of paramount importance in determining the emissivity properties of atomic plasmas, so that we still support a refinement of the partition functions of these species.[4] In addition, very recently one of the present authors has shown the role of electronically excited states with their abnormous cross sections in decreasing the transport properties of LTE plasmas as compared with the same quantities calculated by treating each electronically excited state with the same transport cross section of the ground state.[5,6]

The aim of this work is to reexamine the role of excited states in affecting the thermodynamic properties of LTE plasmas. Particular emphasis will be given to high-pressure–high-temperature plasmas when the ionization degree decreases, thus allowing to the excited states to increase their role in affecting the thermodynamic properties of the plasma.[7,8] High-pressure plasmas can be important for high-power switches, as well as for high-power laser-generated plasmas.

We will consider atomic H plasmas (H, H^+, e) in the temperature range 5000–50,000 K and in the pressure range 10^2–10^8 Pa. The choice of hydrogen plasmas, apart from their strategic importance, is due to the simplicity of the energy levels of atomic hydrogen, as well as by the lack of structure in the proton component. The bulk of the results have been obtained by a very simple cutoff criterion of the electronic partition, that one which considers the size of the highest bound level of atomic hydrogen equal to average distance between the particles. Moreover, we will compare these results with the corresponding ones obtained by using the Debye–Huckel theory (see Refs. 7–10). In general the Debye–Huckel criterion should better describe moderate pressure plasmas, whereas the density cutoff criterion can be better used for high pressures.

II. Method of Calculation

The themodynamic properties of atomic hydrogen plasmas are simply calculated by summing the contributions to the relevant quantities of the different components. Let us consider a three-component plasma (H, H^+, e), denoting with n_i the number density per unity of volume and with n'_i the number density per unity of mass, that is, $n'_i = n_i/\rho$, where ρ is the mass density of the plasma, of the different species. We can write for the total enthalpy H per

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unity of mass of the mixture as

$$H = n'_{\mathrm{H}} H_{\mathrm{H}} + n'_{\mathrm{H}^+} H_{\mathrm{H}^+} + n'_{\mathrm{e}} H_{\mathrm{e}} \tag{1}$$

For the present case electrons and protons have only translational enthalpy, whereas atomic hydrogen possesses also internal energy E. Protons and atoms also have dissociation D and ionization EI energy. We can write the following equations for the single species:

$$H_{\mathrm{H}} = \tfrac{5}{2}kT + E + D/2 \tag{2}$$

$$H_e = \tfrac{5}{2}kT \tag{3}$$

$$H_{\mathrm{H}^+} = \tfrac{5}{2}kT + D/2 + EI \tag{4}$$

The total enthalpy is then written as

$$H = n'_{\mathrm{H}}\left(\tfrac{5}{2}kT + E + D/2\right) + n'_{\mathrm{H}^+}\left(\tfrac{5}{2}kT + D/2 + EI\right) + n'_{\mathrm{e}}\left(\tfrac{5}{2}kT\right) \tag{5}$$

The internal enthalpy in this simple case is given by

$$H_{\mathrm{int}} = n'_{\mathrm{H}} E \tag{6}$$

where the internal energy per particle is given by

$$\frac{E}{N} = kT^2 \left(\frac{\partial \ln f}{\partial T}\right)_V \tag{7}$$

where f is the internal partition function given by

$$f = \sum_i g_i \exp\left(-\frac{\varepsilon_i}{kT}\right) \tag{8}$$

where the g_i and ε_i for the atomic hydrogen take the closed form, $g_i = 2i^2$ and $\varepsilon_i = 13.56 \times 1.6e - 19 \times (1 - 1/i^2)\ J$, where i represents the principal quantum number of atomic hydrogen.

When the derivative of the total enthalpy with respect to the temperature at constant pressure is formed, we must also consider the dependence of the number density on temperature. We can, therefore, define two "total" specific heats. The first one, the so-called frozen specific heat, is obtained by deriving the total enthalpy with respect to the temperature keeping constant the number densities of the different species, whereas, in the second one, called chemical–equilibrium specific heat, this constraint is eliminated. Therefore, the frozen specific heat is obtained as

$$c_{pf} = \left(\frac{\partial H}{\partial T}\right)_{P,n'_i} = n'_{\mathrm{H}}\left(\frac{5}{2}k + c_{V_{\mathrm{int}}}\right) + n'_{\mathrm{H}^+}\left(\frac{5}{2}k\right) + n'_{\mathrm{e}}\left(\frac{5}{2}k\right) \tag{9}$$

whereas the chemical–equilibrium specific heat is given by

$$c_p = \left(\frac{\partial H}{\partial T}\right)_P = c_{pf} + c_{pr} \tag{10}$$

$$c_{pr} = \left(\frac{\partial n'_{\mathrm{H}}}{\partial T}\right)_P \left(\frac{5}{2}kT + E + \frac{D}{2}\right) + \left(\frac{\partial n'_{\mathrm{H}^+}}{\partial T}\right)_P \left(\frac{5}{2}kT + \frac{D}{2} + EI\right) + \left(\frac{\partial n'_{\mathrm{e}}}{\partial T}\right)_P \left(\frac{5}{2}kT\right) \tag{11}$$

A simplification occurs in this equation if we remember that, from the conservation of the formation species and from electroneutrality, we can write

$$\left(\frac{\partial n'_{\mathrm{H}}}{\partial T}\right)_P = -\left(\frac{\partial n'_{\mathrm{H}^+}}{\partial T}\right)_P = -\left(\frac{\partial n'_{\mathrm{e}}}{\partial T}\right)_P \tag{12}$$

Then we can write

$$c_{pr} = \left(\frac{\partial n'_{\mathrm{H}^+}}{\partial T}\right)_P \left(\frac{5}{2}kT + EI - E\right) \tag{13}$$

Note that from Eqs. (9), (10), and (13) we recover the compensation effects included in Refs. 1–3 in the total specific heat calculated with or without electronic excitation terms. In fact, the electronic term adds a positive contribution to the frozen specific heat [$c_{V_{\mathrm{int}}}$ in Eq. (9)], having a negative effect on the reactive contribution [E in Eq. (13)]. This compensation, however, disappears at high pressures, as will be shown later. Let us now define the internal contribution to c_{pf} as

$$c_{\mathrm{int}} = n'_{\mathrm{H}} c_{V\mathrm{int}} \tag{14}$$

where $c_{V_{\mathrm{int}}}$ is given by

$$c_{V_{\mathrm{int}}} = \left(\frac{\partial E}{\partial T}\right)_V = R\left[2T\left(\frac{\partial \ln f}{\partial T}\right)_V + T^2\left(\frac{\partial^2 \ln f}{\partial T^2}\right)_V\right] \tag{15}$$

To proceed further, we calculate the equilibrium composition for the reaction

$$H = \mathrm{H}^+ + \mathrm{e} \tag{16}$$

We have three unknowns, so that we must write three equations. They are the equilibrium constant, the constraint on the total pressure P_{tot}, and the electroneutrality of the plasma, that is,

$$K_p = P_{\mathrm{e}} P_{\mathrm{H}^+} / P_{\mathrm{H}} \tag{17}$$

$$P_{\mathrm{tot}} = P = P_{\mathrm{H}} + P_{\mathrm{H}^+} + P_{\mathrm{e}} \tag{18}$$

$$P_{\mathrm{H}^+} = P_{\mathrm{e}} \tag{19}$$

By simple algebra we get

$$K_p = P_{\mathrm{e}}^2 \big/ (P - 2P_{\mathrm{e}}) \tag{20}$$

and, therefore, once P and T are fixed, we get P_{e} and the other partial pressures. Now we can transform partial pressure P_i in number density n_i,

$$P_i = n_i kT \tag{21}$$

Introducing the number density in this equation we get

$$K_p = n_{\mathrm{e}}^2 (kT) \big/ (n - 2n_{\mathrm{e}}) \tag{22}$$

Moreover, we can calculate the plasma mass density as

$$\rho = \sum_i n_i m_i$$

and then obtain the number density per unit of mass.

The equilibrium constant is given by the Saha equation

$$K_p = \frac{P_{\mathrm{e}} P_{\mathrm{H}^+}}{P_{\mathrm{H}}} = 2\frac{(2\pi m_{\mathrm{e}})^{\frac{3}{2}} (kT)^{\frac{5}{2}}}{h^3} \frac{f_{\mathrm{H}^+}}{f_{\mathrm{H}}} \exp\left(-\frac{EI}{kT}\right) \tag{23}$$

In the case of atomic hydrogen plasma, the only problem in the calculation of K_p is the divergence of the partition function of atomic hydrogen due to the divergence of the statistical weight.

Many procedures are adopted in the literature to overcome this problem. The simplest method is to insert in the partition function in all of the levels where the Bohr radius is equal to the interparticle distance (see Ref. 11). We can, therefore, write

$$a_0 n_{\max}^2 = \left(1\big/n^{\frac{1}{3}}\right) \tag{24}$$

$$n_{\max} = \sqrt{1\big/a_0 n^{\frac{1}{3}}} \tag{25}$$

where n is the particle density (per cubic centimeter) that for an ideal gas is linked to the pressure $P = nkT$ and $n_{\max}$ is the maximum principal quantum number included in the partition function.

Therefore, the electronic partition function depends on the pressure due to the different number of levels to be inserted in it because of the pressure-dependent cutoff. At the same time K_p depends on both T and P.

III. Results

Before discussing the results, we want to show the effect of introducing the electronic states in the partition function of atomic hydrogen and its derivatives. We select the total specific heat of the plasma, and we show in Fig. 1 the ratio of the total specific heat calculated inserting and neglecting the electronic degree of freedom. (The absolute values of total and frozen specific heats can be found in Refs. 9 and 10). We plot this ratio as a function of the temperature for selected pressures in the range 10^2–10^8 Pa. Inspection of Fig. 1 shows that this ratio does not behave monotically, presenting maximum and minimum values in the examined temperature range at fixed pressure. In any case, the differences strongly sincrease with increasing the pressure. The practical independence of this ratio for $P \leq 10^5$ Pa convinced the researchers of the possibility of neglecting the electronic degree of freedom in every step of the calculation of thermodynamic properties of the LTE plasmas.[11] As already pointed out,[1–3] the insensitivity of the total specific heat to the electronic degree of freedom was attributed in the past to compensation effects between the frozen and reactive contributions to a given total thermodynamic property. This compensation, however, fails at high pressure when the ionization process is slowed down, thus permitting the excited states to affect the thermodynamic properties of LTE plasmas.

Let us now examine the actual role of electronic excited states in affecting the thermodynamic properties of plasmas. We start with the electronic partition function as a function of temperature for selected pressures. As expected, we observe a strong increase of the electronic partition function with the temperature and a corresponding strong decrease with increasing the pressure. This last effect is due to the used cutoff criterion for truncating the partition function, that is, the increase of pressure decreases the number of electronic levels to be inserted in the partition function. Note that the electronic partition function at 50,000 K approximately decreases by three orders of magnitude, passing from 10^2 to 10^8 Pa.

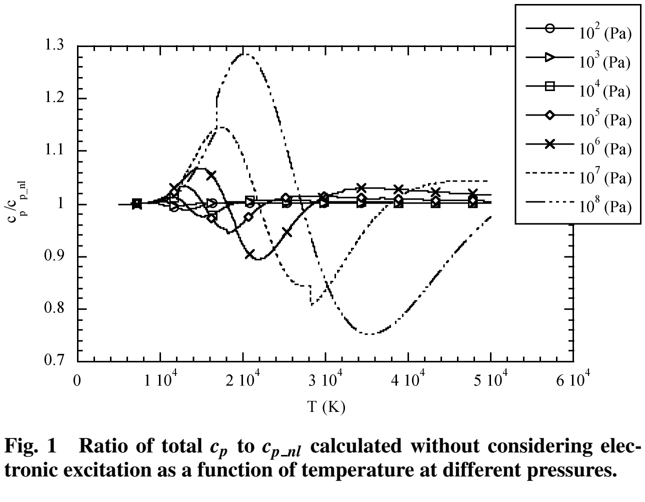

Fig. 1 Ratio of total c_p to c_{p_nl} calculated without considering electronic excitation as a function of temperature at different pressures.

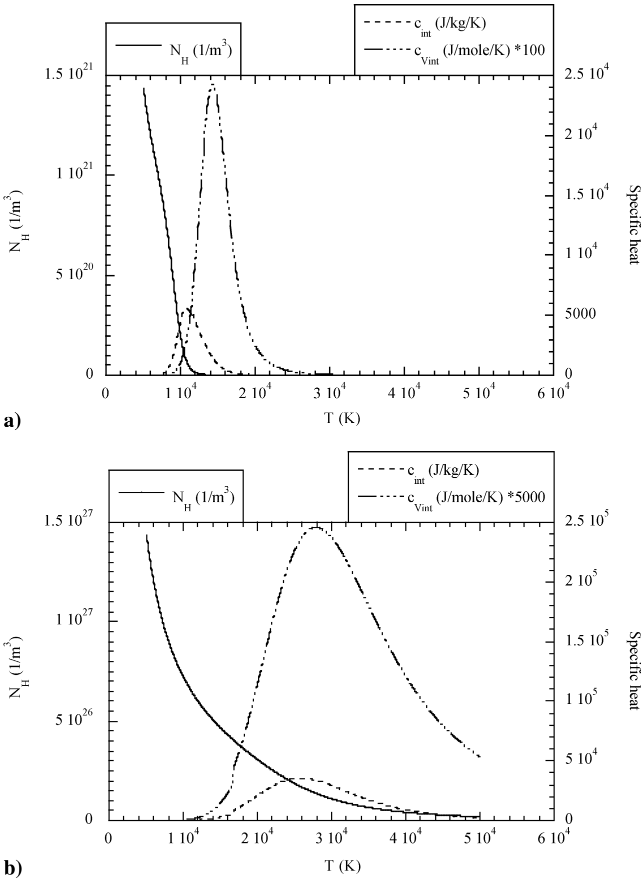

Fig. 2 Values of $c_{V_{\mathrm{int}}}$, N_{H}, and c_{int} as function of temperature at a) 10^3 Pa and b) 10^8 Pa.

Let us now consider the internal specific heat of atomic hydrogen, $c_{V_{\mathrm{int}}}$, which is plotted as a function of temperature for two different pressures in Figs. 2a and 2b. We observe the typical form of any specific heat calculated with a finite number of levels, that is, the specific heat of atomic hydrogen presents a maximum that then tends to become zero. This trend is accelerated by the low pressure, as can be appreciated by comparing the results shown in Figs. 2a and 2b. In Figs. 2a and 2b, we also show the behavior of the atom number density N_{H} and of the contribution of the internal energy to the specific heat calculated as the product of the number density and of specific heat of atomic hydrogen, c_{int}.

Inspection of Figs. 2a and 2b shows that the overlapping between the number density of atomic hydrogen and the corresponding specific heat increases with the pressure so that one should expect a major role of the internal specific heat in affecting the total properties with the increase of the pressure. This is indeed the case as one can appreciate by examining the ratios c_{int}/c_{pf} and c_{int}/c_p as a function of temperature for the selected pressures.

The first ratio, c_{int}/c_{pf}, represents the contribution of the internal excitation of atomic hydrogen on the total frozen specific heat, that is, the sum of the internal and translational contributions. Inspection of Fig. 3a shows that this ratio presents a maximum temperature, which strongly increases with the pressure. At 10^8 Pa, the ratio reaches a value of 0.6, indicating that the contribution from electronic excitation is higher than the corresponding contribution from translational energy.

Figure 3b, on the other hand, shows the ratio c_{int}/c_p as a function of temperature for the selected pressures. The behavior is similar to that reported for c_{int}/c_{pf}, even though the corresponding maxima decrease due to the major role presented by the reactive contribution

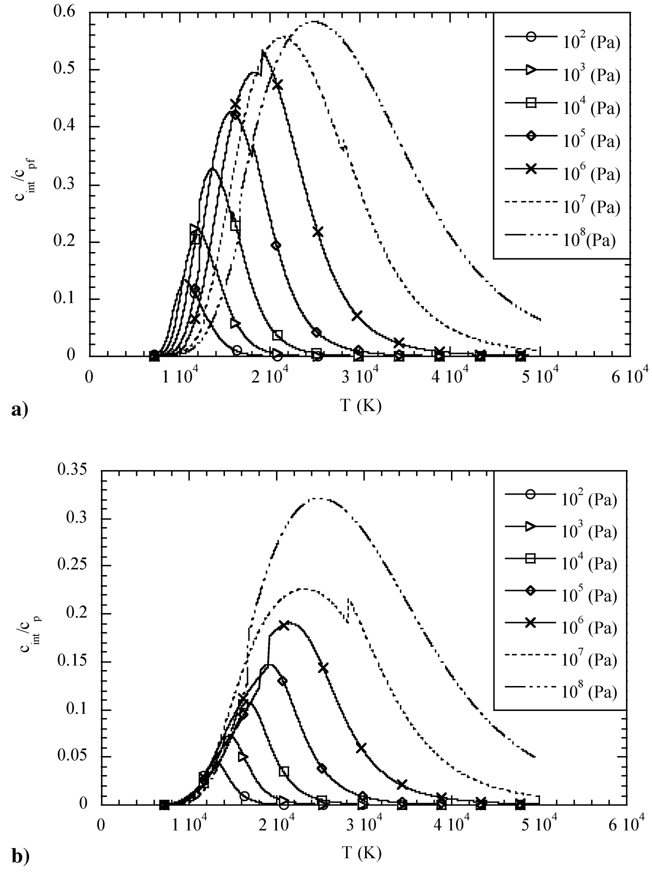

Fig. 3 Ratios as function of temperature at different pressures: a) c_{int}/c_{cf} and b) c_{int}/c_p.

to the total specific heat. We note, however, that at 10^8 Pa the ratio c_{int}/c_p reaches a maximum of 0.32, that is, the internal contribution is a nonnegligible contribution to the total specific heat of an atomic hydrogen plasma at high pressure. The small discontinuities in the ratios reported in Figs. 3a and 3b are due to the adopted cutoff criterion and will be discussed at the end of this section.

The contribution of the electronically excited states to other thermodynamic quantities are similar even though the influence decreases when the thermodynamic property depends directly on the partition function and on this first logarithmic derivative. Note in connection with this that the specific heat depends on the first and second logarithmic derivatives.

Before ending this section, we compare the present results with those obtained by a different cutoff criterion. In particular, we present results calculated by inserting in the partition function and its derivatives of atomic hydrogen all of the levels of energy that are lower than the ionization potential EI corrected by the lowering of ionization potential ΔI. In turn, ΔI is self-consistently calculated by the Debye–Huckel theory (see Refs. 9 and 10). Corresponding results are shown in Figs. 4 and 5 for the quantity c_{int}/c_{pf} and c_{int}/c_p. When these results are compared with the corresponding ones in Figs. 3a and 3b we note deviations either in the qualitative behavior of both c_{int}/c_{pf} and c_{int}/c_p as a function of pressure or in the absolute values of the relevant maxima. The maxima of c_{int}/c_{pf} calculated according the Debye–Huckel theory range in a narrow interval 0.18–0.27 vs the interval 0.1–0.6 observed with the present cutoff criterion. On the other hand, the maxima of c_{int}/c_p calculated according the Debye–Huckel theory range in the interval 0.03–0.09 vs the interval 0.04–0.32. This means that the Debye–Huckel criterion cuts off more effectively than the criterion based on the total density. As an example, at $P = 10^7$ Pa and $T = 30{,}000$ K the Debye–Huckel criterion cuts off at $n_{\max} = 4$, whereas the other method cuts off at $n_{\max} = 7$. This also explains the no-monotone behavior of both c_{int}/c_{pf} and c_{int}/c_p as a function of temperature for the different pressures, particularly observed in the values calculated by the Debye–Huckel criterion. The elimination of one level in the partition function due the quantized nature of energies is much more important in this criterion as compared with the other one due to the corresponding lower number of levels considered in the partition function. Of course, these discontinuities introduce errors up to 20% in the "puntual" values of the specific heats, having practically no effect on the global value of the relevant quantities.

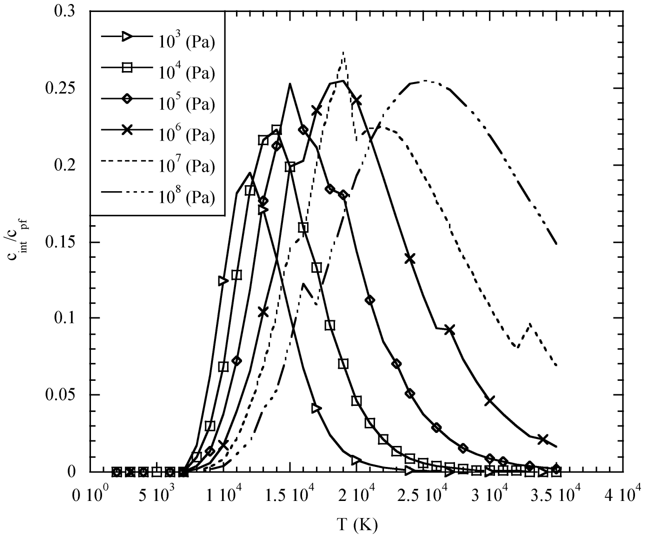

Fig. 4 Ratio of c_{int}/c_{pf} as function of temperature at different pressures, with Debye–Huckel cutoff criterion.

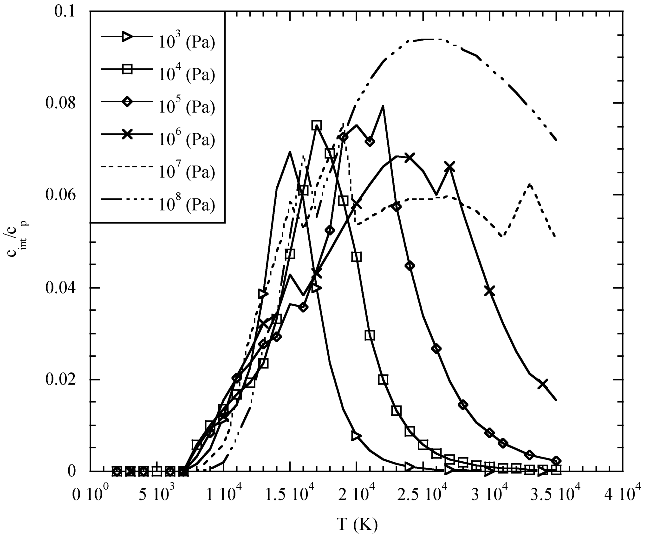

Fig. 5 Ratio of c_{int}/c_p as function of temperature at different pressures, with Debye–Huckel cutoff criterion.

The importance of internal energy in affecting the frozen and total specific heat of a plasma at high pressure is confirmed by both criteria. Future work on the subject should probably use more established approaches, such as those described in Refs. 12–14, especially for the high-pressure case. These approaches, based on quantum statistical mechanics, could also introduce a better cutoff criterion based on the density, which could also eliminate the discontinuities already discussed. On the other hand, the extension of these ideas to other atomic plasmas (N and O) should take into account the so-called low lying excited states, as well as the electronic levels above the first ionization limit of atoms, that is, the autoionization levels.[15]

IV. Conclusions

The results presented unambiguously show that electronic excitation plays a nonmarginal role in affecting the thermodynamic properties of high-temperature atomic hydrogen plasmas. In particular, they confirm and extend the compensation effects found in the past on the specific heats of nitrogen and helium plasmas, indicating, however, that this kind of compensation fails for pressure higher than 10^5 Pa. The present results, together with the corresponding results on transport coefficients,[5,6] provide new perspectives in the study of high-temperature–high-pressure LTE plasmas. Future exploration in this direction should make use of more refined cutoff criteria, valid for all pressure and temperature ranges. Corresponding results can quantitatively change the present observations without changing the qualitative nature of the present results of electronically excited states for LTE plasmas. Higher differences can be expected for non-LTE plasmas with overpopulation.

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References

[1] Capitelli, M., Ficocelli, V. E., and Molinari, E., "Electronic and Thermodynamic Properties of High Temperature Gases," *Zeitschrift für Naturforschung*, Vol. 26a, No. 4, 1971, pp. 672, 683.

[2] Capitelli, M., and Ficocelli, E., "The Contribution of Electronic Excitation to the Total Specific Heats of High Temperature Gases: A misinterpreted Absence," *Journal of Plasma Physics*, Vol. 5, Pt. 1, 1971, pp. 115, 121.

[3] Capitelli, M., and Ficocelli, V. E., "Frozen" Properties and Cut-off Criteria of High Temperature Gases," *Zeitschrift für Naturforschung*, Vol. 25a, No. 6, 1970, pp. 977, 979.

[4] Wang, T. S., and Rhodes, R., "Thermophysics Characterization of Multiply Ionized Air Plasma Absorption of Laser Radiation," *Journal of Thermophysics and Heat Transfer*, Vol. 17, No. 2, 2003, pp. 217–224.

[5] Capitelli, M., Celiberto, R., Gorse, C., Laricchiuta, A., Minelli, P., and Pagano, D., "Electronically Excited States and Transport Properties of Thermal Plasmas: The Reactive Thermal Conductivity," *Physical Review E*, Vol. 66, 2002, p. 016403.

[6] Capitelli, M., Celiberto, R., Gorse, C., Laricchiuta, A., Pagano, D., and Traversa, P., "Transport Properties of Local Thermodynamic Equilibrium Hydrogen Plasmas Including Electronically Excited States," *Physical Review E*, Vol. 69, 2004, p. 026412.

[7] Kovitya, P., "Thermodynamic Properties of High-Temperature Plasmas," *IEEE Transactions on Plasma Science*, Vol. PS-13, 1985, p. 587.

[8] Patch, R. W., "Components of a Hydrogen Plasma Including Minor Species," NASA TND-4993, 1968.

[9] Capitelli, M., and Ficocelli, V. E., "Thermodynamic Properties of Ar–H_2 Plasmas," Res. Int. Hautes Temp., Rept. 14, 1977, pp. 95.

[10] Capitelli, M., Ficocelli, E., and Molinari, E., "Equilibrium Composition and Thermodynamic Properties of Mixed Plasmas. III Argon–Hydrogen Plasmas at 10^{-2}–10^3 Atmospheres Between 2000 K and 35000 K," Centro di Studio per la Chimica dei Plasmi del Consiglio Nazionale delle Ricerche, Istituto di Chimica Generale ed Inorganica, Univ. degli Studi di Bari, Bari, Italy.

[11] Gurvich, L. V., Veyts, I. V., and Alcock, C. B., *Thermodynamic Properties of Individual Substances*, Hemisphere, New York, 1989.

[12] Ebeling, W., Steinberg, M., and Ortner, J., "Ionization Equilibrium and EOS of a Low-Temperature Hydrogen Plasma in Weak Magnetic Fields," *European Physics Journal*, Vol. D 12, 2000, pp. 513–520.

[13] Khomkin, A. L., and Mulenko, I. A., "Free Energy of Nonideal Atomic Plasma," *High Temperature*, Vol. 41, No. 3, 2003, pp. 275–281.

[14] Filinov, V. S., Bonitz, M., Fortov, V. E., Ebeling, W., Levashov, P., and Schlanges, M., "Thermodynamic Properties and Plasma Phase Transition in Dense Plasmas," *Contributions to Plasma Physics*, Vol. 44, No. 5-6, 2004, pp. 388–394.

[15] Capitelli, M., Colonna, G., Giordano, D., Marraffa, L., Casavola, A., Minelli, P., Pagano, D., Pietanza, D., and Taccogna, F., "High-Temperature Thermodynamic Properties of Mars-Atmosphere Components," *Journal of Spacecraft and Rockets*, Vol. 42, No. 6, 2005, pp. 980–989.