

Account of Atomic and Molecular Contributions in the Equation-of-State for a Weakly Non-Ideal Hydrogen Plasmas

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Convergent partition function for atomic and molecular bound states is derived for weakly non-ideal hydrogen plasmas. Corrections due to charged-neutral particles interactions are also described. These contributions have been realized in the model equation of state of hydrogen plasmas and the HEOS code. The physical model EOS also includes the Coulomb and diffraction corrections, contributions of the scattering states, electron and ion interactions, and the radiation pressure. The calculated dependences of the heat capacity, the ionization degree, and partial pressures are presented.

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1 Introduction

Due to the accurate inversion of local sound velocity from optical observations the achievements of helioseismology provide possibility to check the equation of state (EOS) of weakly-nonideal hydrogen plasmas within reasonably high accuracy [1–3]. The comparison of different theoretical models with experiment permits to check the existing ways to count contributions presented in physical literature for the second virial coefficient (SVC) [4–6].

We continue the development of the model EOS of weakly-nonideal hydrogen plasmas started in [7, 8] and continued in [9–12].

Contributions to pressure for the molecular component, the negative and molecular ions, corrections for interactions of charged particles and neutrals were derived and included to the model. Expressions for partial pressures obtained in the frames of the thermodynamic perturbation theory are briefly described and the basic features of the HEOS ('hydrogen equation-of-state') code that is used for the model hydrogen EOS simulation are discussed in the following sections.

2 Thermodynamic perturbation theory

According to [13] we can calculate plasmas pressure P , using corrections to the pressure P_0 of ideal gas, consisting of electrons and protons [14]:

$$P = P_0 + P_H + P_{\text{exch}} + P_{\text{D-H}} + \delta P, \quad (1)$$

where we include the following corrections: P_H — the Hartree correction, P_{exch} — the electron-electron exchange interaction, $P_{\text{D-H}}$ — the plasma Coulomb interaction in the Debye-Hückel approximation, and the higher order correction δP , which takes into account a contribution the from ladder diagrams.

Here protons and electrons are considered as non-degenerate particles and their pressure is expressed via activities ζ_p, ζ_e : $P_p = T\zeta_p, P_e = T\zeta_e$. All pressure contributions including also the diffraction correction, the bound and the scattering states, and the radiation pressure were described in details in [9, 10]. Influence of the atomic states broadening on the contribution of the bound states has been considered in [11]. Account of the

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electrons degeneracy on the bound states pressure has been studied recently in [12], but here it is not taken into account, since it requires much more computational efforts and we would like to concentrate on the effect of corrections introduced by molecules, ions and charged-neutrals interactions.

For the same reason we also consider the bound states as non-broadened, so the BS contribution may be written in the form [9]

$$P_{BS} = \zeta_e \zeta_p T \lambda_{ep}^3 \Sigma_{SRM}^{BS}. \quad (2)$$

$$\Sigma_{SRM}^{BS} = \sum_{n=1}^{\infty} n^2 e^{u_n} F_{SRM}(u_n), \quad u_n = Ry/(Tn^2) \quad (3)$$

$$F_{SRM}(u) = 1 - e^{-u} \left(4 - \frac{6}{\sqrt{\pi}} u^{1/2} + \frac{4}{\sqrt{\pi}} u^{3/2} \right) + \operatorname{erfc} \sqrt{u} \cdot (3 - 4u + 4u^2), \quad (4)$$

where $\lambda_{kj} = \sqrt{\frac{2\pi\hbar^2}{\mu_{kj}T}}$, $\mu_{kj} = \frac{m_k m_j}{m_k + m_j}$ is the reduced mass, $F_{SRM}(u_n)$ is an atomic state form-factor.

After summation the following expression can be obtained:

$$\Sigma_{SRM}^{BS} = \sum_{k=4}^{\infty} \zeta(k-2) \frac{(-\alpha)^k}{\Gamma\left(\frac{k}{2} + 1\right)} (k-2)^2 + \sum_{k=1}^{\infty} \zeta(2k+1) \frac{\alpha^{2k+3}}{\Gamma\left(k + \frac{5}{2}\right)}, \quad (5)$$

where $\zeta(n)$ is the Riemann ζ -function, $\alpha = \sqrt{Ry/T}$.

Pressure of hydrogen molecules is derived using the ‘harmonic oscillator’-‘rigid rotator’ approximation [14]

$$P_m = T \zeta_m, \quad \zeta_m = \zeta_a^2 \lambda_{aa}^3 \Sigma_m, \quad \zeta_a = P_{BS}/T \quad (6)$$

and the molecular partition function Σ_m has the following general form:

$$\Sigma_m = \sum_{n_1, n_2, J, v} n_1^2 F_{SRM}(\beta I_{n_1}) e^{\beta I_{n_1}} n_2^2 F_{SRM}(\beta I_{n_2}) e^{\beta I_{n_2}} \times \left\{ \exp \left(\beta \left(D_{n_1, n_2} - \hbar \omega_{n_1, n_2} v - \frac{\hbar^2 J^2}{2I_{n_1, n_2}} \right) \right) - 1 \right\}, \quad (7)$$

where summation is performed over atomic states with principal quantum numbers n_1, n_2 , vibrational (v) and rotational (J) states. I_{n_1}, I_{n_2} are the ionization energies of these atomic states, D_{n_1, n_2} is the dissociation energy of corresponding molecule, I_{n_1, n_2} is the moment of inertia, $\beta = T^{-1}$. For our applications a simplified expression as a product of vibrational and rotational partition functions was used:

$$\Sigma_m = \Sigma_r \Sigma_v = \frac{T}{B_r} \left(\frac{e^{D/T} - 1}{1 - e^{-\hbar\omega/T}} - \frac{D}{\hbar\omega} - \frac{D^2}{2\hbar\omega T} \right) \quad (8)$$

where $D \approx 4.52$ eV is the dissociation energy for hydrogen molecule, $B_r = \hbar^2/2I_{1,1} \approx 0.00736$ eV is the characteristic rotational energy, $\hbar\omega \approx 0.546$ eV is the characteristic vibrational energy. The authors believe that the last term in brackets in (8) is introduced for the first time.

Corrections due to interactions of charged and neutral particles are considered in the following simple form:

$$P_{en} = c_{en} \zeta_e \zeta_n, \quad P_{p,pn} = c_{p,pn} \zeta_p \zeta_n, \quad (n = a, m), \quad (9)$$

where the subscript p means account of polarization of atoms and molecules by charged particles and

$$c_{en} = -\frac{2\pi\hbar^2}{\mu_{en}} l_{0,n}, \quad c_{p,pn} = 2\pi e^2 \alpha_n / r_0, \quad (10)$$

where $l_{0,n}$ is the scattering length for particle n : $l_{0,a} = 3.125a_0$, $l_{0,m} = 1.6a_0$, $\alpha_a = 6.67 \cdot 10^{-25}$, $\alpha_m = 8.17 \cdot 10^{-25}$ and $a_0 = \hbar^2/(m_e e^2)$, $r_0 = e^2/I$, here I is the ionization potential of the neutral component.

There are also two types of hydrogen ions that have to be accounted in low-temperature hydrogen plasma EOS - the negative (or atomic) ion $H^- = (ep, e)$ and the molecular ion $H_2^+ = (ep, p)$. (For generality we shall use the notations ‘ae’ and ‘ap’ respectively.) The contributions to pressure for these ions are calculated as follows:

$$P_{ac} = T \zeta_{ac}, \quad \zeta_{ac} = \zeta_a \zeta_c \lambda_{ac}^3 \Sigma_{ac}, \quad \Sigma_{ac} = e^{I_{ac}/T} - 1, \quad (11)$$

where $c = e, p$ and $I_{ae} \approx 0.75$ eV, $I_{ap} \approx 2.69$ eV.

3 Hydrogen weakly-nonideal plasmas EOS: physical model

We consider weakly-nonideal hydrogen plasmas in the frames of physical model that assumes two types of independent particles - electrons and protons. To calculate thermodynamic functions of weakly-nonideal hydrogen plasmas for given ρ and T one needs to determine two unknown chemical potentials for these types μ_e and μ_p from the system of two nonlinear equations. The first one is the equation for the total pressure:

$$\frac{\partial P}{\partial \mu_e} + \frac{\partial P}{\partial \mu_p} = 2n_0T, \quad (12)$$

where $n_0 = \rho N_A / \langle A \rangle$, N_A — the Avogadro number, $\langle A \rangle = 1.00794$ — the hydrogen atomic weight. The 2nd equation imposed by the model is the condition of neutrality in activities $\zeta_e = \zeta_p$ to provide finite (zero) value of the Hartree correction [9]. Notice that in this case concentrations of all electrons and protons (free and bound ones) can not be defined as the derivatives of the total pressure on chemical potentials as it is valid in the chemical model.

In the HEOS code to solve the system in unknown variables $y_e = \mu_e/T$, $y_p = \mu_p/T$ by a kind of Newton method one need to get Jacobi matrix for the system. This means that we shall calculate derivatives on y_e , y_p up to the 2nd order and also, to calculate thermodynamic properties we need derivatives $\frac{\partial}{\partial T}$, $\frac{\partial^2}{\partial T^2}$, $\frac{\partial^2}{\partial T \partial y_e}$, $\frac{\partial^2}{\partial T \partial y_p}$, $\frac{\partial}{\partial \rho}$, $\frac{\partial^2}{\partial \rho \partial y_e}$, $\frac{\partial^2}{\partial \rho \partial y_p}$. All these twelve derivatives are calculated simultaneously with calculations of all activities and their functions, including the pressure components themselves. To simplify calculations of function products the derivatives of functions are mostly calculated for their logarithms. Special care is taken to avoid loss of accuracy, for example, in series with Riemann ζ -function.

4 Hydrogen EOS with molecular contribution and interactions of charged particles and neutrals

In this work the HEOS code was used to simulate the model equation of state for weakly-nonideal hydrogen plasma for conditions of low temperatures in the range from several thousand up to 10^5 K. Special interest was focused on obtaining the characteristic peak in density dependences of the ionization degree and the heat capacity along the lines of constant temperature. It was also interesting to account for the influence of the last term introduced in (8).

For this simulation we have included in the model the following pressure components only: protons and non-degenerated electrons, Coulomb correction, bound states (atoms), molecules, molecular and negative ions and four interactions of charged particles and neutrals.

In Fig. 1 the temperature dependences of heat capacity c_v along the lines of constant density are shown for the model EOS with (solid lines) and without (dots) last term in the molecular PF (8). As can be seen, the influence is more pronounced at higher values of density $\rho > 10^{-2}$ g·cm⁻³. The effect of introduction of the interactions of charged and neutral particles is shown in Fig. 2. The difference is observable for $T > 10^4$ K and much stronger for higher temperatures. In Fig. 3 density dependences of the ionization degree at temperatures in the range 10^4 – 10^5 K are shown for the model EOS with (solid lines) and without (dots) account of interactions of charged and neutral particles. A more complete model EOS was used to calculate partial pressures for hydrogen plasmas in conditions of the Sun. It also includes diffraction, logarithmic and electrons exchange corrections, scattering states contribution, radiation pressure, p-p and e-e interactions. Fig. 4 shows the influence of account of the last term in the molecular PF on the relative partial pressure of molecules in conditions of Solar interior in dependence on the plasma temperature inside the Sun. In the same coordinates the distribution of main relative partial pressures for Solar data is shown in Fig. 5.

5 Conclusion

The weakly-nonideal hydrogen plasmas EOS was developed to allow adequate simulation in the low-temperature range. Contributions of molecular component, negative and molecular ions and interactions of charged and neutral particles were introduced to the model. Corresponding modifications to the HEOS code were implemented.

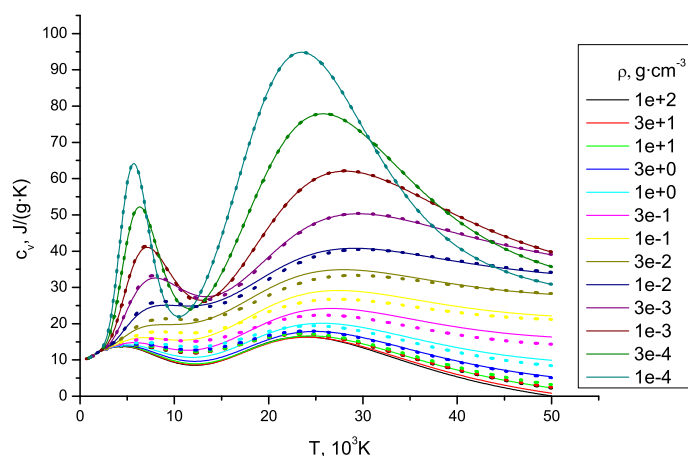


Fig. 1 Hydrogen heat capacity (c_v) at different densities with molecular contributions and interactions with (solid lines) and without (dots) last term in molecular PF 8. (Online colour: www.cppjournal.org)

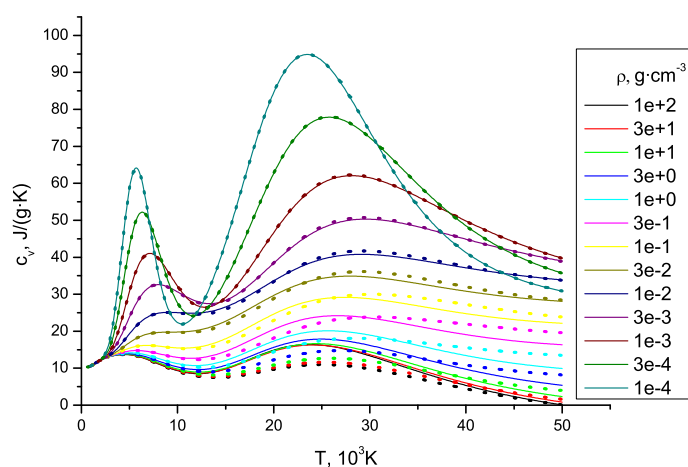


Fig. 2 Hydrogen heat capacity (c_v) at different densities with molecular contributions with (solid lines) and without (dots) interactions of charged particles and neutrals. (Online colour: www.cppjournal.org)

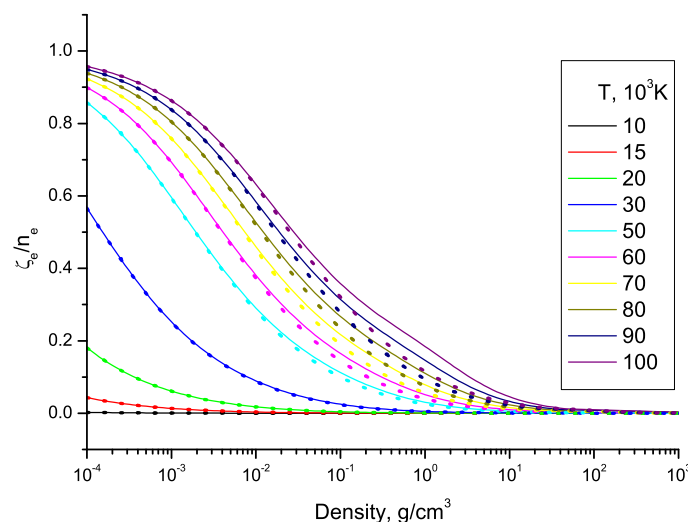


Fig. 3 Ionization degree (ζ_e/n_e) at different temperatures with (solid lines) and without (dots) interactions of charged particles and neutrals. (Online colour: www.cppjournal.org)

Several calculations were performed in the 0.2–5 eV temperature range and densities within 10^{-4} – 10^2 $\text{g}\cdot\text{cm}^{-3}$. Qualitative correspondence was observed in the changes of the ionization degree behaviour due to interaction of charged-neutral particles. Notice that the physical model uses the great canonical ensemble approach that smooths any sharp features, so it is planned to develop the chemical picture with the canonical ensemble approach within the frames of the HEOS code.

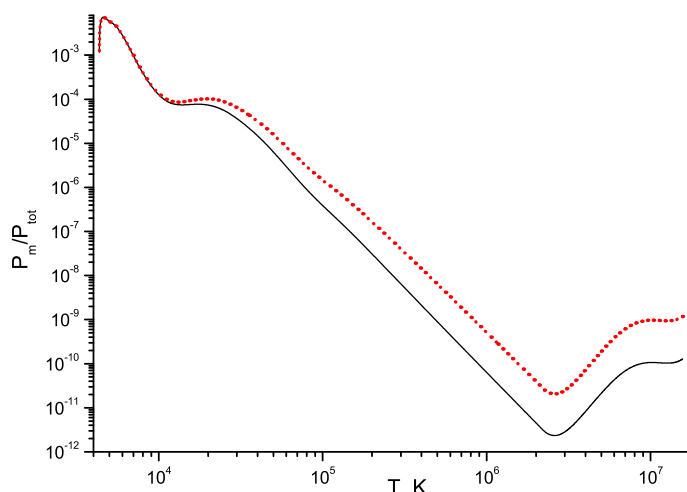


Fig. 4 Partial pressure of molecular component for the model hydrogen EOS with (solid lines) and without (dots) last term in molecular PF (8) in conditions of Solar plasma. (Online colour: www.cppjournal.org)

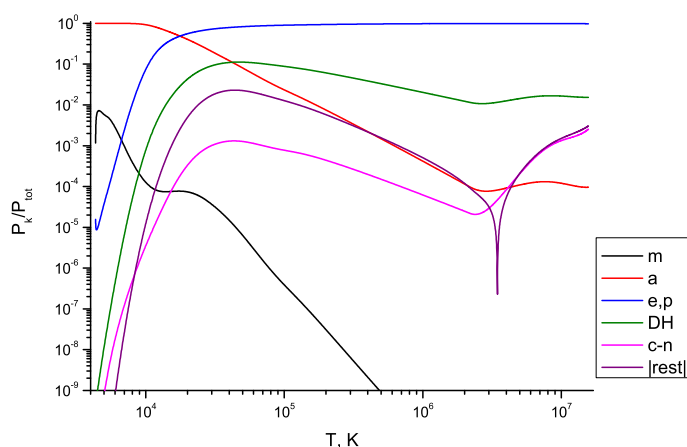


Fig. 5 Partial pressures of molecules (m), atoms (a), electrons and protons (e,p), Debye-Hückel correction (DH), charged-neutral particles interaction (c-n), and absolute value of the rest ($|\text{rest}|$) for the model hydrogen EOS in conditions of Solar plasma. (Online colour: www.cppjournal.org)

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References

- [1] J. Christensen-Dalsgaard, W. Däppen, W.A. Dziembowski, and J.A. Guzik, An introduction to helioseismology, in: Variable Stars as Important Astrophysical Tools, Proc. NATO Advanced Study Institute, Cesme, Turkey, Aug. 30 Sept. 11 1998, edited by C. Ibanoglu (Kluwer Academic, Dordrecht, 2000), pp. 59167, http://bigcat.ifa.au.dk/~jcd/solar_models/cptrho.l5bi.d.15c.
- [2] V.A. Baturin, W. Däppen, D.O. Gough, and S.V. Vorontsov, Mon. Not. R. Astr. Soc. **316**, 7183 (2000).
- [3] S. Basu, W. Däppen, and A. Nayfonov, Astrophys. J. **518**(June), 985993 (1999).
- [4] D.G. Hummer and D. Mihalas, Astrophys. J. **331**(August), 794814 (1988).
- [5] D. Mihalas, W.Däppen, and D.G. Hummer, Astrophys. J. **331**, 815825 (1988).
- [6] F.J. Rogers, F.J. Swenson, and C.A. Iglesias, Astrophys. J. **456**, 902908 (1996).
- [7] G.E. Norman and A.N. Starostin, Teplofizika vysokih temperatur **8**, 413438 (1970), [1970 Sov. Phys. High Temp. **8** 381].
- [8] A.N. Starostin, V.C. Roerich, and R.M. More, Contrib. Plasma Phys. **43**(5-6), 369372 (2003).
- [9] A.N. Starostin and V.C. Roerich, Zh. Éksp. Teor. Fiz. **127**(1), 186219 (2005), [2005 JETP 100(1) 165198].
- [10] A.N. Starostin and V.C. Roerich, J. Phys. A: Math. Gen. **39**(17), 44314439 (2006).
- [11] A.N. Starostin and V.C. Roerich, Plasma Sources Sci. Technol. **15**(3), 410415 (2006).
- [12] A.N. Starostin, V.C. Roerich, V.K. Gryaznov, V. E. Fortov, and I. L. Iosilevskiy, J. Phys. A: Math. Theor. **42**, 214009 (2009).
- [13] L. Kadanoff and G. Baym, Quantum Statistical Mechanics (W A Benjamin, Inc., New York, 1962).
- [14] L.D. Landau and E.M. Lifshitz, Statistical Physics: Part 1 (Course of Theoretical Physics, v. 5) (Butterworth-Heinemann, Oxford, 1980), (translated by J B Sykes and M J Kearsley).