

Thermodynamic Functions of Nonideal Hydrogen Plasmas

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Abstract. The contribution of the charged components to the thermodynamic functions is analysed on the basis of the present theoretical knowledge. In the high-temperature low-density limit the Debye formula with quantum corrections is used. In the low-temperature high-density limit the Gellman-Brueckner formula for the electrons and a lattice-energy formula for the protons is used. Padé-approximants are constructed which contain these limiting situations as special cases and describe also the region between them in certain approximation.

Thermodynamische Funktionen eines nichtidealen Wasserstoffplasmas

Inhaltsübersicht. Auf der Grundlage der derzeit verfügbaren Kenntnisse wird der Beitrag der geladenen Komponenten zu den thermodynamischen Funktionen untersucht. Für die Hochtemperatur-Niedrigdichte-Grenze wird das Debye-Gesetz mit Quantenkorrekturen benutzt. In der Tieftemperatur-Hochdichte-Grenze werden für die Elektronen die Theorie von Gell-Mann und Brueckner und für die Protonen die Gitterenergie ausgenutzt. Es werden Padé-Approximationen konstruiert, welche dieses Grenzverhalten als Spezialfälle enthalten und das Verhalten im Zwischenbereich angenähert wiedergeben.

1. Introduction

The correct thermodynamic description of hydrogen plasmas is important for many applications connected e.g. with the fusion problem and with astrophysical calculations. We remember that a large fraction of the matter in the universe is a dense hydrogen plasma. Therefore many theoretical and experimental work has been devoted to the problem of finding the corresponding equation of state and the thermodynamic functions [1–5]. In a first approximation a hydrogen plasma may be considered to be a mixture of two fluids: the fluid of light electrons and the fluid of the heavy protons. The nonideality of these fluids is given by the relations of the mean kinetic and potential energies respectively (Fig. 1)

$$\Gamma_e = \frac{e^2}{2d\Theta_e}; \quad \Gamma_p = \frac{e^2}{2d\Theta_p} \quad (1)$$

where

$$d = \left(\frac{3}{4\pi n} \right)^{1/3}; \quad \Theta_k = k_B T I_{3/2}(\alpha_k) / n_k A_k^3. \quad (2)$$

Here n is the density of free electrons or free protons respectively I_k are the Fermi-functions, A_k the thermal De Broglie wave-length and α_k the ideal chemical potentials determined by the equations

$$I_{1/2}(\alpha_k) = \frac{1}{2} n A_k^3; \quad A_k = h[2\pi m_k k_B T]^{-1/2}. \quad (3)$$

For sufficiently low densities the mean kinetic energy per degree of freedom is $k_B T/2$.

That is why $\Gamma_e \approx \Gamma_p \approx \Gamma$ holds, with

$$\Gamma = (e^2/k_B T d). \quad (4)$$

In the opposite limit of strong degeneration there is another relation

$$\Theta_k = (\alpha_k k_B T / \bar{\epsilon}) \quad (\alpha_k k_B T = \varepsilon_F \text{ the Fermienergy}).$$

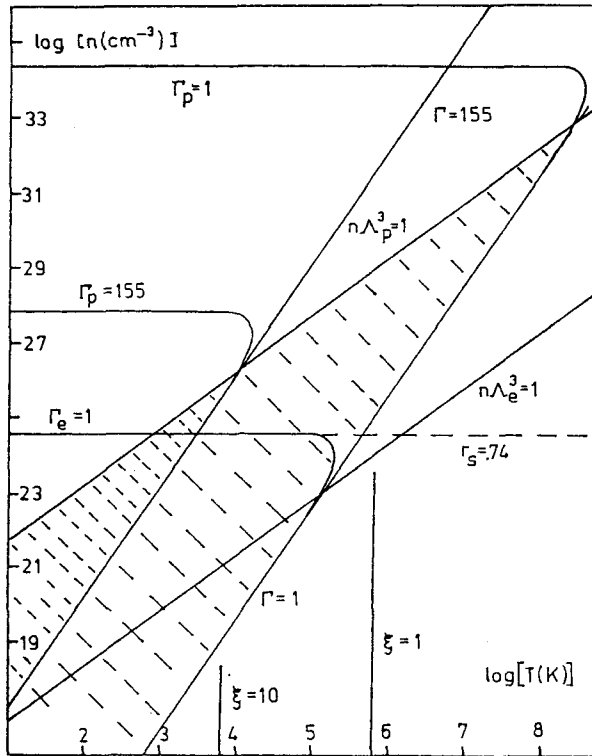


Fig. 1. The dashed area indicates the region of nonideality considered in this papers, the borders of which are given by $\Gamma = 1$ (inset of plasma ideality) and by $n\Lambda_p^3 = 1$ (inset of proton degeneracy). Above the fluid-solid transition line $\Gamma \approx 155$ the protons form a lattice. At densities above 10^{25} cm^{-3} or more precisely $r_s \lesssim 0.74$ we have strongly interacting protons imbedded in an ideal electron gas

The nonideality parameter is now temperature-independent

$$\Gamma_e = 5r_s(\alpha')^2, \quad \alpha' = (4/9\pi)^{1/3}$$

$$\Gamma_p = 1836.15 \Gamma_e$$

r_s is the usual dimensionless density parameter

$$r_s = d/a_B, \quad a_B = \hbar^2/mc^2.$$

In the following we restrict ourselves to the hatched region in the temperature-density plane where the electron fluid is non-ideal. Due to the big masses the protons may be treated classically here due to the inequality

$$n\Lambda_p^3 \ll 1$$

The two limiting states for the proton fluid are a bcc-lattice state (if the temperatures are sufficiently low) and a Debye-gas-state (if the temperatures are sufficiently high). For the electron fluid we need expressions which cover the degenerate as well as the nondegenerate region. Here we may use expressions which were developed in an earlier work on the basis of Padé-approximants for the thermodynamic functions of electron gases [6].

2. Basic Formulae for the Limiting Situations

Let us consider a hydrogen plasma consisting of n electrons, n protons and n_H atoms per cm^3 . A basic quantity for the description of such a plasma is the chemical potential of the charged components which is defined as the sum of the chemical potentials of the electrons and the protons

$$\mu = \mu_e + \mu_p. \quad (5)$$

This quantity determines the chemical equilibrium between free charges and atoms

$$\mu = \mu_H. \quad (6)$$

Therefore μ is a central quantity. The plasma contributions to the pressure and to the free energy may be obtained by the following thermodynamic relations [7]

$$p = n\mu - f; \quad \mu = \partial f / \partial n. \quad (7)$$

Here f is the free energy density $f = F/V$.

The chemical plasma potential may be splitted into the ideal part, the Hartree-Fock part and the correlation part

$$\begin{aligned} \mu &= \mu_{id} + \mu_{HF} + \mu_{corr} \\ \mu_{id} &= k_B T \alpha_e + k_B T \alpha_p \\ \mu_{HF} &= -(e^2/\Lambda_e) I_{-1/2}(\alpha_e) - (e^2/\Lambda_p) I_{-1/2}(\alpha_p). \end{aligned} \quad (8)$$

The correlation part is analytically known only in limiting cases. At very low densities and high temperatures we may write (following earlier work [5])

$$\begin{aligned} \mu_{corr}/Ryd &= -2\bar{n}^{1/2}(4k_B T/\pi Ryd)^{1/4} + \bar{n}(1+\gamma)^{1/2} K + \dots, \\ Ryd &= e^2/2a_B; \quad \bar{n} = n\Lambda_e^3; \quad \gamma = m_e/m_p, \\ K &= \frac{1}{2} + \frac{1}{4} (2/1 + \gamma)^{1/2} (1 + \ln 2) (1 + \sqrt{\gamma}) - (\xi/3 \sqrt{\pi}) \ln(2\sqrt{\gamma}/1 + \gamma) \\ &\quad + 4\xi^{-2} Q(-\xi) - 2\xi^{-2} (2/(1 + \gamma))^{3/2} \left\{ Q(-\xi \sqrt{(1 + \gamma)/2}) \right. \\ &\quad \left. + \gamma^{3/2} Q(-\xi \sqrt{(1 + \gamma)/2\gamma}) - \frac{1}{2} E(-\xi \sqrt{(1 + \gamma)/2}) \right. \\ &\quad \left. - \frac{\gamma^{3/2}}{2} E(-\xi \sqrt{(1 + \gamma)/2\gamma}) \right\}. \end{aligned} \quad (9)$$

The so-called virial functions Q and E are given by

$$\begin{aligned} Q(\xi) &= \sum_{n=4}^{\infty} \left(\frac{1}{2} \xi \right)^n \zeta(n-2)/\Gamma\left(\frac{1}{2}n+1\right) \\ E(\xi) &= \sum_{n=3}^{\infty} \left(\frac{1}{2} \xi \right)^n (1 - 2^{2-n}) \zeta(n-1)/\Gamma\left(\frac{1}{2}n+1\right) \end{aligned} \quad (10)$$

where $\zeta(x)$ is the Riemann-function, $\Gamma(x)$ the Γ -function and the Born-parameter for the electron-proton interaction is

$$\xi = (e^2/k_B T \lambda_{ep}); \quad \lambda_{ep} = \hbar(2m_{ep} k_B T)^{-1/2}. \quad (11)$$

In the limit of high density the electrons and the protons behave quite in a different way. Therefore it seems to be useful to split the plasma potential in an electron gas contribution and a proton gas contribution

$$\mu = \mu_{eg} + \mu_{pg}. \quad (12)$$

Here μ_{eg} corresponds to the chemical potential of an electron gas in a uniform positive background and μ_{pg} includes all the other contributions. From the physical point of view μ_{pg} describes a proton gas with screened interactions. The screening effect is due to some increase of the electron density in the neighborhood of each proton. We should underline that due to their definition μ_{eg} and μ_{pg} are not strictly identical to the chemical potentials of the electrons and the protons in the real plasma. Following Gellman and Brueckner the electron gas is in the high-density limit described by

$$\mu_{eg}^{\text{corr}}/Ryd = 0.0622 \ln r_s - 0.1167. \quad (13)$$

The high-density behavior of the proton gas is calculated in the adiabatic approximation [8, 9]. We start from the formula for the correlation part of the free energy density

$$f_{pg}^{\text{corr}} = -\frac{1}{2} n \alpha e^2 / a + \delta f_{pg}. \quad (14)$$

Here the first part represents the lattice energy and the second part the corrections due to the screening of the protons. Further a is the lattice constant and α the Madelung constant. In the following we choose

$$a = (3/4\pi n)^{1/3}. \quad (15)$$

Assuming a bcc-lattice the lattice energy may be written as

$$-(nk_B T) 0.89593 \Gamma \quad (16)$$

which coincides with Monte-Carlo data by about 0.15%.

As shown by DE WITT [1, 3] there are still more contributions for lower densities corresponding to the thermal energy of the protons. These additional terms in (14) were neglected in our calculations since we need here the high density behaviour only.

Now let us consider the influence of electron screening. The free energy contribution of the screening effects can be written

$$\delta f_{pg}/nk_B T = \frac{1}{3\pi} \int_0^\infty q^2 dq S^{(0)}(q) w(q) \quad (17)$$

with

$$w(q) = \frac{3\Gamma}{q^2} \left(\frac{1}{\varepsilon(q)} - 1 \right); \quad q = kd \quad (18)$$

and $S^0(q)$ is the structure factor.

This gives in a certain approximation [3]

$$\delta f/nk_B T = r_s (0.0579 + 0.971 \Gamma^{1/4} - 0.343) \quad (19)$$

The screening contribution is a function of the nonideality parameter Γ as well as of the pure density parameter $r_s = d/a_H$.

In the representation with

$$\tilde{n} = n(\beta e^2)^3 = n\tilde{r}^3 \quad (20)$$

as nonideality parameter we obtain finally for the correlation chemical potential

$$\mu_{pg}^{\text{corr}}/k_B T = -1.9228 \tilde{n}^{1/3} + r_s \tilde{n}^{1/3} (.0933 + .8206 \tilde{n}^{-1/4} - .2287 \tilde{n}^{-1/3}). \quad (21)$$

3. Padé-Approximants

Following earlier work [6] we are able to describe the correlation part of the chemical potential of an electron gas with the aid of a special Padé approximant on the basis of the analytical formulae in the regions of low and high degeneracy respectively. As shown in [6] the following limiting formulae are exactly known [1, 4, 5]

$$-\frac{\mu_{eg}^{\text{corr}}}{Ryd} = \mu_0 \bar{n}^{1/2} + \mu_1 \bar{n} \quad \text{if } \bar{n} \ll 1 \quad (22)$$

$$-\frac{\mu_{eg}^{\text{corr}}}{Ryd} = \mu_2 \ln \bar{n} + \mu_3 \quad \text{if } \bar{n} \gg 1. \quad (23)$$

The coefficients are defined as follows $\mu_0 = (k_B T / \pi Ryd)^{1/4}$, $\mu_1 = -(1/2 \sqrt{2})$, $\mu_2 = 2(1 - \ln 2)/3\pi^2$,

$$\mu_3 = \mu_2 + 0.096 - (3\mu_2/2) \ln \{(36\pi)^{1/3} Ryd/k_B T\}. \quad (24)$$

Taking into account eqs. (24–25) we proposed the following Padé-approximation for the chemical potential [6]

$$-\frac{\mu_{eg}^{\text{corr}}}{Ryd} = \frac{\mu_0 \bar{n}^{1/2} + (a_2 \mu_2 / q) \ln [1 + \bar{n}^q \exp(\mu_3 q / \mu_2)]}{1 - (\mu_1 \bar{n}^{1/2} / \mu_0) + a_2 \bar{n}^{3/2}}. \quad (25)$$

The two free parameters a_2 and q in eq. (25) have been adjusted to numerical values for the chemical potential [6]. The parameter values $a_2 = 3/4$ and $q = 1/4$ yield maximum deviations less than 6% for the region of intermediate densities. The agreement with the numerical values for the electron gas may be improved a little bit with the choice $q = 7/10$ [6].

Now it remains to find a Padé-approximation for the proton gas contribution. Again we know analytical expressions for the limits of low and high densities respectively which are given by eqs. (9) and (21). Assuming that the transition from the $n^{1/2}$ -behaviour to the $n^{1/3}$ -behaviour occurs in the region where $\tilde{n} = n l^3 = 1$ we propose for the correlation part of the chemical potential the following Padé-approximation

$$-\frac{\mu_{pg}^{\text{corr}}}{k_B T} = \frac{p_0 \tilde{n}^{1/2} [1 - p_1 \tilde{n} (1.9228 + A)]}{1 - p_1 [(\tilde{n}^{1/2}/p_0) + p_0 \tilde{n}^{7/6}]} \quad (26)$$

$$p_0 = 3.2408, \quad p_1 = -[(1 + \gamma)^{1/2} K - (1/2 \sqrt{2})] (\pi^3 k_B T / Ryd)^{1/2}, \\ A = (r_s/1 + r_s^2) (-0.0933 - 0.8206 \tilde{n}^{-1/4} + 0.2287 \tilde{n}^{-1/3}). \quad (27)$$

For the definition of the function K see eq. (9). Finally we note that the high density behaviour of the Padé-approximation can be improved if the region of validity is restricted to the fluid phase $\Gamma < 155$. Then instead of eq. (14) the semiempirical formulae for the proton gas proposed by DE WITT [3] have to be used.

The several contributions to the plasma potential may be easily calculated now in a wide temperature density-range. For example Fig. 2 shows various contributions at the relative low temperature $T = 3420$ K in dependence on the free electron density n . The density region covers (as can be seen from Fig. 1) the region from $\Gamma \approx 1$ up to $\Gamma \approx 155$.

One important result is that the correlation part comes into the order of magnitude of the ideal part at densities $n \approx 10^{21} \text{ cm}^{-3}$. Further the Hartree-Fock contribution of the electrons and the correlation contribution of the protons are of certain importance. For densities less than 10^{24} cm^{-3} the protons can be considered as classical particles with a classical ideal part and an correlation part. The density of degeneracy for the electrons is about 10^{21} cm^{-3} . For this reason we have to take into account the Hartree-Fock contribution and quantum expressions for the other terms of the thermodynamical functions.

We want to emphasize here the smoothness of the sum of the exchange and correlation contributions (j — in Fig. 2).

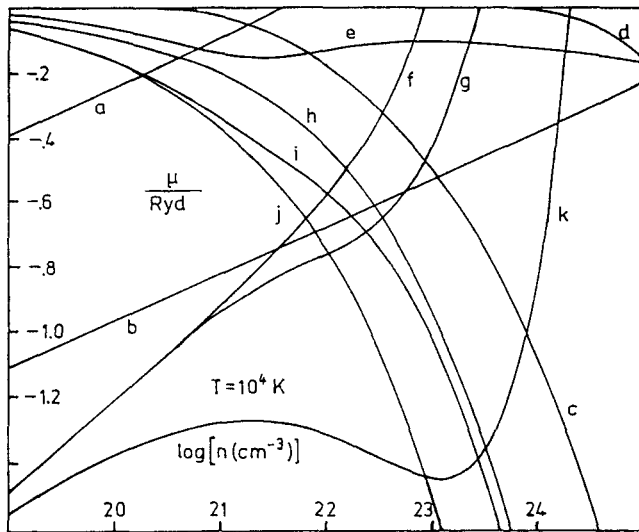


Fig. 2. Several contributions to the H -plasma potential as functions of the free electron density. The letters a to j correspond to:

$a - \mu_{id}^e$, $b - \mu_{id}^p$, $c - \mu_{HF}^e$, $d - \mu_{HF}^p$, $e - \mu_{corr}^e$, $f - \mu_{id}^e$, $g - \mu_{id}^e + \mu_{HF}^e$, $h - \mu_{corr}^p$, $i - \mu_{corr}^e$, $j - \mu_{HF}^e + \mu_{corr}^e$, $k - \mu$.

Here the indices e and p correspond to the electron gas and the proton gas; id , HF and $corr$ are the ideal, Hartree-Fock and correlation contributions respectively

4. The Ionization Equilibrium

Here we want to give an estimate of the degree of ionisation of the plasma for the region where $\alpha > 1/3$ i.e. more than 50% of the particles are charged. Taking into account in this approximation only the formation of atoms we need an expression for the atomic chemical potential. Considering an atom in first approximation as a hard sphere with internal degrees of freedom we find

$$\mu_H = k_B T \ln [n_H A_H^3 / 4 \Sigma(T, n_{tot})] + \mu_{PY}(n_H) \quad (28)$$

where n_H is the density of atoms and $n_{tot} = n + n_H$ is the total density of the protons.

The chemical potential of hard spheres of density n_H is given by [10]

$$\mu_{PY} = k_B T \eta (8 - 9\eta + 3\eta^2) (1 - \eta)^{-3} \quad (29)$$

with $\eta = 4\pi n_H R^3/3$ and R is an effective hard core radius of an H atom.

The value of R we choose after [11]

$$R = 1.54 a_B.$$

$\Sigma(T, n_{\text{tot}})$ is the atomic partition function. In order to obtain a relevant expression for Σ we assume the atom as enclosed in a sphere of radius r_0 , which is the half of the mean distance between two protons in the system.

$$(4\pi/3) (n + n_H) r_0^3 = 1. \quad (30)$$

The wave functions of bound electrons have to vanish at the surface of the sphere.

The discrete electron energies are diminished with increasing density, since there is a positive energy contribution from enclosure. The energy levels for a free electron enclosed in a spherical box reads

$$E_{sl} = (Ry) x_{sl}^2 a_B^2 / r_0^2$$

where x_{sl} are the zero-points of the Bessel functions [14]. Assuming a simple addition rule between the enclosure energy and the Coulomb-energy we shall use the approximation

$$E_{sl} = -(Ry) \left[\frac{1}{s^2} - x_{sl}^2 \frac{a_B^2}{r_0^2} \right] \quad \text{if } s^2 \leq (r_0 a_B / x_{sl})^2 \quad (31)$$

and $E_{sl} = 0$ otherwise.

Now we are able to calculate the atomic partition function in this simple approximation.

$$\Sigma(n_{\text{tot}}, T) = \sum_{s=1}^{\infty} \sum_{l=0}^{s-1} (2l+1) \cdot \{ \exp(-E_{sl}/k_B T) - 1 + (E_{sl}/k_B T) \}. \quad (32)$$

The degree of ionisation $\alpha = n/n_{\text{tot}}$ is obtained now by solving the following equation consistently.

$$\mu(n, T) = \mu_H(n, n_H, T). \quad (33)$$

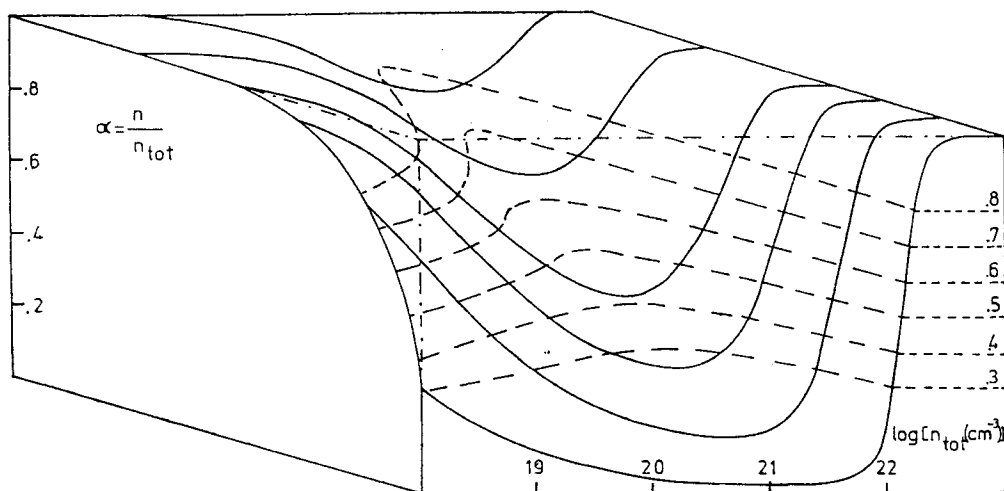


Fig. 3. The ionisation valley of the H -plasma plotted over the total proton density. The full lines are α -curves for 15000, 20000, 25000, 30000, 40000 and 50000 Kelvin (beginning in front of the cubus with the lowest temperature and the deepest valley). The dashed lines are the isocurves of constant degree of ionisation. The left hand side surface is a cut for $n_{\text{tot}} = 10^{18} \text{ cm}^{-3}$. The lowering of the ionisation degree with decreasing temperature is well visible

The result of this calculation is shown in Fig. 3. One observes firstly a lowering of the degree of ionisation with increasing total proton density and then an increase again which is called sometimes pressure ionisation. The pressure ionisation is due to the decrease of the ionisation energy caused by the correlation contributions to the plasma potential and furtheron by the influence of the repelling forces between the atoms which make the atomic state unfavourable at high densities. The main contribution is due to the shift of the electron states. The $1s$ state disappears at the total proton density $5.2 \times 10^{22} \text{ cm}^{-3}$.

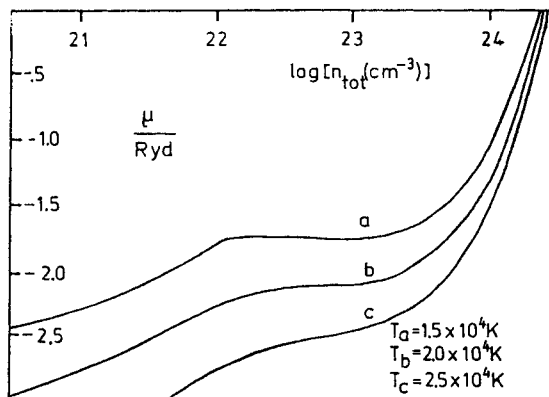


Fig. 4. The H -plasma potential vs the total proton density for three temperatures

We have to underline that the effects of hard spheres and the limitation of the wave functions are described here only approximately. The correct theory has to improve the choice of R and to handle the density dependence of the energy levels E_{si} in a more consistent way as done by GRABOSKE et al., FORTOV a.o. [15, 2] or one has to solve the Bethe-Salpeter-equation in a rigorous many body theory [16]. In Fig. 4 we present the chemical plasma potential as a function of the total proton density. As critical temperature for a phase transition we have found $T_C \approx 13000 \text{ K}$. Due to several approximations especially to the rough approximation for the interaction with neutrals the theory given here is restricted to the region where $\alpha > 1/3$ and $T > T_C$.

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