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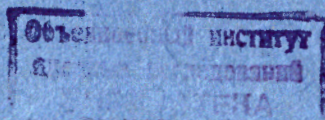
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W.Ebeling

STATISTICAL THERMODYNAMICS  
OF FLUID HYDROGEN  
AT HIGH ENERGY DENSITY

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## 1. INTRODUCTION

At high energy densities where no bound states exist, hydrogen may be considered as a mixture of two Fermi fluids which may be treated by the methods of quantum statistics<sup>/1/</sup>. The thermodynamic functions for compressed hydrogen are of interest for the study of planetary and stellar interiors as well as for several hypothetical technical applications. Therefore, much work has been done to calculate these functions in several approximations<sup>/2-18/</sup>. Here our interest is restricted to the fully ionized fluid branch shown in Fig.1. In the degenerate region (above the dotted line in Fig.1) the system forms a metallic liquid with very interesting physical properties, below the degeneration line a usual plasma is obtained. The possibility of a fluid phase even at T=0 (see<sup>/8,9,15/</sup>) is not considered here. In order to describe the thermodynamic properties in the whole (high-temperature) fluid phase region the system is considered as a two-component Fermi fluid consisting of light electrons and heavy protons  $\gamma = m_e/m_p = 1836$ . The thermodynamic functions may be considered as

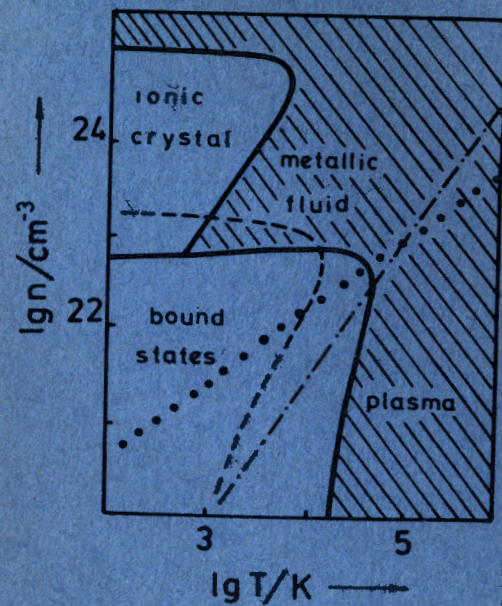


Fig.1. The region of fluid hydrogen where the theory given here may be applied. (Dashed line - border of stability, dotted line - border of degeneracy, dash-dotted line - border of strong coupling).

## 2. STRUCTURE OF THE THERMODYNAMIC FUNCTIONS

The calculation of the grand potential may be based on the formula

$$\Omega(\mu_e, \mu_i, T) = \Omega_{id} + \int_0^1 \frac{d\lambda}{\lambda} \langle V(\lambda, \mu_e, \mu_i) \rangle, \quad (1)$$

where  $\mu_e, \mu_i$  are the chemical potentials of the electrons and ions respectively and  $V$  is the potential energy. By means of the relation  $N_a = -(\partial\Omega/\partial\mu_a)$ ,  $a=e, i$  and expanding around the ideal chemical potentials  $\alpha_a(n_a, T) = \mu_a^{id}/k_B T$  which are assumed to be known we obtain the chemical potential as a function of the density ( $I_n$  - Fermi functions)

$$\mu_a(n_e, n_i, T) = k_B T \alpha_a - e_a^2 \Lambda_a^{-1} I_{-1/2}(\alpha_a) + \Lambda_a^3 [V(2s_a + 1) I_{-1/2}(\alpha_a)]^{-1} \frac{\partial}{\partial \alpha_a} \int_0^1 \frac{d\lambda}{\lambda} \langle V(\lambda, \alpha_e, \alpha_i) \rangle_c. \quad (2)$$

By using this formula the chemical potentials may be calculated at least in principle for any temperature and density value<sup>/23/</sup>. Since explicit results however are available only for limiting situations let us start with some general assumptions about the structure of the thermodynamic functions following from eqs. (1-2). As the basic quantity we shall consider the Gibbs potential (free enthalpy) which is represented as

$$G = N_e \mu_e + N_i \mu_i, \quad \mu_a = k_B T \alpha_a + \mu_a^{xc}, \quad a=e, i. \quad (3)$$

The exchange-correlation contribution to the chemical potential may still be splitted into the Hartree-Fock part and the correlation part as to be seen from eq.(2). The Hartree-Fock part is even exactly known. However due to the strong compensation effects between both contributions (see, e.g.,<sup>/19/</sup>) a unified treatment is recommended. For symmetry reasons let us assume in the following that the electrons and the ions may be represented by the same dimensionless function

$$\mu_a^{xc} = R y_a \mu(\rho_a, r_a, \gamma_a), \quad \mu_i^{xc} = R y_i \mu(\rho_i, r_i, \gamma_i), \quad (4)$$

$$R y_e = R y = m_e e^4 / h^2, \quad R y_i = R y / \gamma, \quad \gamma_e = \gamma = m_e / m_i, \quad \gamma_i = \gamma^{-1},$$

$$\rho_e = r_s = (3/4\pi n a_B^3), \quad \rho_i = t_s / \gamma, \quad r_e = k_B T / R y = r, \quad r_i = \gamma r.$$

Here  $n = N/V$  is the atomic density,  $r_s$  the radius of the Wigner cell in units of the Bohr radius  $a_B$ . Due to the large value of



the mass relation the characteristic dimensionless temperatures and spacing parameters are quite different for electrons and ions. Therefore we need the characteristic function  $\mu(\rho, r, \gamma)$  in a quite large region of the arguments. Summarizing eqs.(3-4) we may represent the exchange-correlation contribution to the Gibbs potential per atom by Ry-units by

$$G_{xc}/N = \mu_{xc} = \mu(r_s, r, \gamma) + \gamma^{-1} \mu(r_s/\gamma, \gamma r, \gamma^{-1}). \quad (5)$$

Corresponding to eqs. (3-5) the exchange-correlation contribution to the free energy per atom will be represented by

$$F_{xc}/N = \phi_{xc} = \phi(r_s, r, \gamma) + \gamma^{-1} \phi(r_s/\gamma, \gamma r, \gamma^{-1}). \quad (6)$$

### 3. THE WIGNER REGION

Our aim is to find good approximations for the two functions  $\mu$  and  $\phi$  by using all the available informations for limiting situations. In order to unify the treatment we introduce the thermodynamic potential:  $\eta = \{\mu, \phi\}$  and specify only when giving the functions explicitly. As is well known for  $T=0$  the thermodynamic potential has the representations<sup>19-21/</sup>

$$\eta(\rho, r, \gamma) = -\frac{a_M}{\rho} + \frac{a_1}{\rho^{3/2}} + O(\rho^{-2}) \text{ if } \rho \geq 100,$$

$$\eta(\rho, r, \gamma) = -\frac{a_H}{\rho} + b_0 \ln \rho - b_1 + b_2 \rho \ln \rho \text{ if } \rho \leq 1. \quad (7)$$

The constants have the values

$$\begin{aligned} a &= 2.38914 (1.79186), & a &= 3.98586 (2.65724), \\ a &= 1.22177 (0.91633), & b &= 0.06218 (0.06218), \\ b &= 0.1140 (0.0933), & b &= 0.018 (0.018). \end{aligned}$$

Here the first number always refers to the free enthalpy and the second one (in brackets) to the free energy which is at  $T=0$  identical to the internal energy. The values for the Madelung constant given above correspond to a bcc-lattice. In our calculations we have taken into account that in the fluid state there is no perfect lattice. Following the work of Baus, Hansen, Galam and De Witt<sup>12-14/</sup> we have replaced the Madelung constant by a function of  $\rho$  and  $r$ :

$$\begin{aligned} a_M = a_H + \{ \eta_{10} - \eta_{11} \Gamma^{-3/4} + \eta_{12} \Gamma^{-1} \ln \Gamma + \eta_{13} \Gamma^{-1} \} \frac{2}{1 + (1/3\Gamma)^3} + \\ + \{ \eta_{14} + \eta_{15} \Gamma^{-3/4} - \eta_{16} \Gamma^{-1} \} \frac{2(\rho/\gamma)}{1 + (\rho/3\gamma)^3}. \end{aligned} \quad (8)$$

Here  $\Gamma = (\frac{1}{2} \rho r)^{-1}$  is the plasma parameter denoting the strength of coupling. Further  $a_H + 2\eta_{10}$  represents the limiting value of the Madelung constant for fluids which is something smaller than for lattices. The second term in the parenthesis in eq.(8) denotes the influence of screening by the same kind of charges and the last term in eq.(8) describes the screening by the counter-charges. Following the above-mentioned authors the values of the constants are

$$\begin{aligned} \eta_{10} &= 0.58436 (0.43827), & \eta_{11} &= 3.73469 (3.44741), \\ \eta_{12} &= 0.55513 (0.55513), & \eta_{13} &= 3.18102 (2.99597), \\ \eta_{14} &= 0.04506 (0.04506), & \eta_{15} &= 0.56651 (0.75534), \\ \eta_{16} &= 0.17791 (0.26687), \end{aligned}$$

Since the expressions given by Baus, Galam, Hansen and De Witt<sup>12-14/</sup> are justified only at  $r_s \leq 3$  and  $\Gamma \geq 1/3$ , we have introduced cutting factors. This is an artificial assumption which has no theoretical justification but avoids unrealistic high contributions to the Madelung constants in regions where eq.(8) is not valid. In order to condense the analytical information given so far into one formula we propose the following Pade approximant value at small temperatures (Wigner region)

$$\begin{aligned} \eta^{(0)}(\rho, r, \gamma) = -\frac{a_H}{\rho} - \frac{1}{2} \eta_1 \ln \left( 1 + \frac{\eta_3^2}{\rho} \right) \\ \cdot \left[ \eta_0 \left( \frac{\eta_4 \rho + ((\eta_2 + 1)/\eta_0)^2}{\eta_4 \rho + 1} \right)^{1/2} - \eta_2 \left( \frac{1}{1 + \rho} \right)^{1/2} \right]. \end{aligned} \quad (9)$$

The 5 free parameters in eq.(9) are given by

$$\eta_1 = 2b_0; \quad \eta_2 = 2a_1 \eta_1^{-1} \eta_3^{-2}, \quad \eta_3 = \exp(b_1/2b_0), \quad \eta_0 = (a_M - a_H) b_0^{-1} \eta_3^{-2}, \quad (10)$$

$$\eta_4 = (\eta_2 + 1) [(2b_2/b_0) - \eta_2] \cdot [(a_0 \eta_2/a_1) - (\eta_2 + 1)^2]^{-1}.$$

By expanding eq.(9) with respect to  $\rho$  or  $\rho^{-1}$  respectively we may show that with the given choice of parameters eqs.(7) are satisfied. We note that eq.(9) does not contain free parameters since the constants  $\eta_0, \eta_1, \eta_2, \eta_3, \eta_4$  are given by the known coefficients of the expansion (7). For  $T=0$  the values for the ground state energy given by eq.(9) are in good agreement with the Monte-Carlo data of Ceperley and Adler<sup>22/</sup> for one-component plasmas as well as the three-parameter formula given in earlier work

$$\eta^{(0)}(\rho, r, \gamma) = -\frac{a_H}{\rho} - \eta_1 \ln \left[ 1 + \frac{\eta_3 \rho^{-1/2}}{1 + \eta_0^{-1} \rho^{1/2}} \right]. \quad (11)$$



The simpler Pade formula (11) is of equal accuracy, however, it does not represent the coefficients  $a_1$  and  $b_2$  in the expansion (7) in a correct way. Therefore we have used here eq. (9). In the region of moderate temperatures but  $\rho \leq 3$  and  $\Gamma \geq 1/3$  eqs. (9) or (11) respectively are in good agreement with the Monte-Carlo data for proton fluids <sup>12-14</sup>. We note that eqs. (9-10) or (10-11) respectively cover most of the region of the degenerate metallic liquid (see Fig.1). In order to describe the remaining part too, we have to take into account the Debye limiting law with quantum corrections <sup>18,19,23</sup>.

#### 4. THE DEBYE REGION

At higher temperatures, i.e., in the nondegenerate and weakly coupled plasma region shown in Fig.1 the Debye law holds. This region is characterized by the parameter

$$\mu_D = 3^{1/2} \Gamma^{3/2} \leq 1. \quad (12)$$

Up to the order  $O(\mu_D^2)$  the quantum corrections to the Debye law are exactly known <sup>18,19,23</sup> and we have the following representation (Ry-units)

$$\eta(\rho, r, \gamma) = -\eta_5 \mu_D r [1 - \eta_7 \mu_D r^{1/2} K(\xi, \gamma)] - \eta_6 (\mu_D r)^2 + O(\mu_D^{3/2}), \quad (13)$$

$$\eta_5 = 0.70711(0.47140), \quad \eta_7 = 1(0.75), \quad \eta_6 = 0.125(0.0625).$$

Again here the first numbers refer to the Gibbs potential and the second one (in parenthesis) to the free energy. The so-called virial function  $K(\xi, \gamma)$  is exactly known as an infinite convergent series in the parameter

$$\xi = (2/r)^{1/2}. \quad (14)$$

For our purpose the following simple approximation <sup>18</sup> is sufficient

$$K(\xi, \gamma) = \frac{(\pi/2)}{2\xi} \left\{ \frac{\xi^2 + (1 + \ln 2)(2 + 2\gamma)^{-1/2}}{\xi + 1} + \frac{1}{3\pi^{1/2}} \exp\left[ \frac{\pi^{1/2}}{2 \ln(\xi/3) - 2\xi} \right] \right\}. \quad (15)$$

With lower accuracy holds the approximation

$$K(\xi, \gamma) = \frac{(\pi/2)^{1/2}}{2\xi}. \quad (16)$$

We are searching now a Pade formula which combines our knowledge about the Debye region contained in the formulae (13-15) with that about the Wigner region which has been compressed into eqs. (9-10) or (11), respectively. Taking into account earlier experience for the electron fluid <sup>19</sup> we propose the Pade formula

$$\eta(\rho, r, \gamma) = \frac{U \eta^{(0)}(\rho, r, \gamma) - \eta_5 \mu_D r - \eta_6 (\mu_D r)^2}{1 + U + \eta_7 R}, \quad (17)$$

where

$$U = c_1 \bar{n} + c_2 \bar{n}^2 = c_1 6\pi^{-1} \rho^{-3} r^{-3} + c_2 36\pi \rho^{-6} r^{-3}, \quad (18)$$

$$R = c_3 \ln[1 + c_3^{-1} K(\xi, \gamma) \mu_D r^{1/2}].$$

Here  $c_1$ ,  $c_2$  and  $c_3$  are fitting parameters which regulate the smooth transition between the Debye region, and the Wigner region. Taking into account earlier attempts <sup>18,19</sup> we have made for our calculations the choice

$$c_1 = 10, \quad c_2 = c_3 = 8. \quad (19)$$

#### 5. DISCUSSION

The Pade formulae (9) and (17) contain the eleven constant parameters  $\eta_0$  to  $\eta_7$  and  $c_1$  to  $c_3$ . We note that eight of those constants namely  $\eta_0$  to  $\eta_7$  are fixed by our knowledge about the limiting behaviour of the thermodynamical functions for the Wigner region and the Debye region. The three free parameters  $c_1$ ,  $c_2$ ,  $c_3$  have been chosen in such a way that a smooth transition from the Debye region to the Wigner region is obtained. Due to the lack of reliable Monte-Carlo results for the transition region the question of a proper fit of these constants remains open. Since however the results are not sensitive with respect to the value of  $c_1$ ,  $c_2$ ,  $c_3$  we believe that the estimate (19) will give quite reasonable results for the transition region. Several values for the exchange-correlation contribution to the thermodynamic functions at 20 density-temperature values calculated by means of eqs. (5), (6), (9), (17) have been given in the Table. In order to simplify interpolations we have given 6 figures, i.e., more than the accuracy of the formulae would justify. Direct comparison with the results of other work is possible only at  $T=0$ , where our formulae are not valid strictly speaking (see Fig.1). In Fig.2 the result of our calculations for  $r = 0.03$  ( $T = 4737$ ) and an extrapola-



Table

Exchange and correlation contributions to the thermodynamic potentials. (1) free enthalpy per atom, (2) free enthalpy per electron, (3) free energy per atom, (4) free energy per electron

No	T=0	0.003	0.03	0.09
1	11.79724	11.74651	11.57046	11.35757
2	4.27605	4.27553	4.27375	4.27168
3	0.3	8.94397	8.89923	8.74858
4		3.23776	3.23710	3.23490
1		3.74664	3.71609	3.62630
2		1.36014	1.35817	1.35220
3	1.0	2.85634	2.83168	2.76650
4		1.03735	1.03500	1.02815
1		1.94645	1.92473	1.87296
2		0.71413	0.71063	0.70102
3	2.0	1.49131	1.47553	1.44835
4		0.54704	0.54306	0.53263
1		1.31631	1.29613	1.25155
2		0.49212	0.48759	0.47598
3	3.0	1.00874	0.99371	0.97043
4		0.37785	0.37286	0.36070
1		0.40406	0.38283	0.33731
2		0.16556	0.15866	0.14525
3	10	0.30729	0.28836	0.25126
4		0.12758	0.12073	0.10831

tion to  $T=0$  are represented. For comparison the ground state calculations of Kagan et al.<sup>4/</sup> for solid hydrogen metal, of Mon et al.<sup>8/</sup> for liquid hydrogen metal and of Grigoriev et al.<sup>24/</sup> for molecular hydrogen are represented, too. The results for the equation of state, i.e., specific volume pressure (note

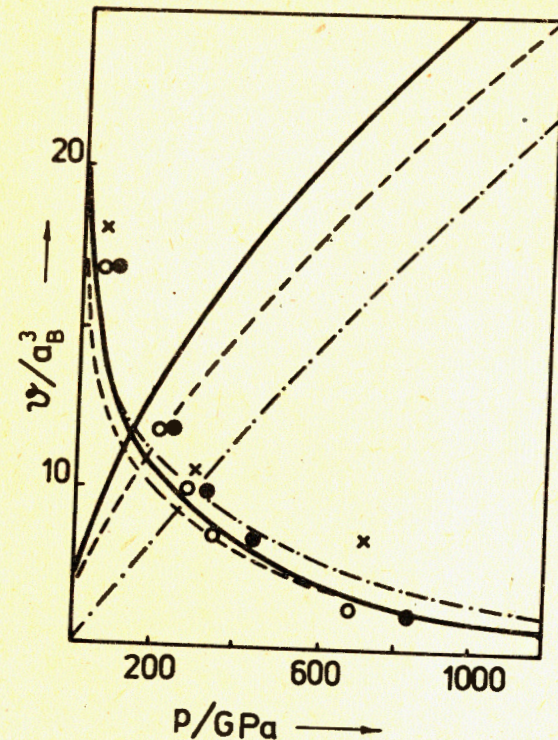


Fig.2. Equation of state and Gibbs potential per atom. (Full line - this theory for  $T=4737$  K; dashed line - extrapolation of this theory to  $T=0$ ; dash-dotted line - theory of Kagan et al.<sup>4/</sup> for crystals at  $T=0$ ; open circles - equation of state at  $T=0$  after Grigoriev et al.<sup>24/</sup>; full circles - isentropic data of the same authors<sup>24/</sup>; crosses - calculations of Mon et al.<sup>8/</sup> for liquid hydrogen at  $T=0$ .)

100 GPa = 1 Mbar) shows agreement in the overall shape, the numerical values for the pressure however, predicted by our theory are for given density somewhat lower than

those predicted by other authors for the ground state. The circles in Fig.2 correspond to the density-pressure data obtained by Grigoriev et al.<sup>24/</sup> from adiabatic compression experiments. The corresponding densities are experimental values the pressure values however were estimated by extrapolations of the equation of state for solid molecular hydrogen. Looking at the curves in Fig.2 it seems that at about 200-400 GPa (2-4 Mbar) the molecular crystal melts and forms a metallic hydrogen fluid. Let us still note that the theoretical equation of state for liquid hydrogen crosses the axis  $p=0$  at densities of about  $0.5-0.7$  g/cm<sup>3</sup>, i.e., liquid hydrogen could possibly exist in a metastable modification even at normal pressures<sup>2/</sup>. Summarizing the results obtained here for the equation of state we may state that the Pade approximation technique applied here yields reasonable results for the pressure in spite of its relative simplicity. The results for the Gibbs potential seem to be somewhat too high comparing with the ground state calculations for solid hydrogen metal by Kagan et al.<sup>4/</sup> and Hammerberg and Ashcroft<sup>7/</sup> as well as with the  $T=0$  calculations for liquid metals by Mon et al.<sup>8/</sup>. This point therefore needs further clarification. One may hope that in near future reliable Monte-Carlo calculations for liquid hydrogen metal will be available.



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Эбелинг В.

E17-84-459

Статистическая термодинамика жидкого водорода при высокой плотности энергии

Получена аппроксимация Паде для термодинамических функций, которая учитывает известную информацию о низкотемпературной области Вигнера /формулы решетки и Гелл-Манна-Бракнера/ и также для высокотемпературной области Дебая /предельный закон с квантовыми поправками/. Формулы описывают нерелятивистскую область плотностей и температур с исключением ионной решетки и связанных состояний.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

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Ebeling W.

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Statistical Thermodynamics of Fluid Hydrogen at High Energy Density

By using the available knowledge about the thermodynamic functions for the low-temperature Wigner region /lattice formulae and Gell-Mann Brueckner formulae/ as well as for the high-temperature Debye region /limiting law with quantum corrections/ Padé approximations are constructed. The formulae cover the whole nonrelativistic region of density and temperature except the region of ionic lattice and of bound states.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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