

# Problems of Bound States in Plasmas— Physical and Chemical Picture Revisited<sup>1</sup> ¶

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**Abstract**—We discuss several problems of plasma physics which were in the center of interest of the Rostock group and the research activities of Gerd Röpke who was appointed a docent in 1977 by Rostock University. In particular we will consider the problem of bound states and several approaches to treat bound states in dense systems.

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## 1. INTRODUCTION

The problem of bound states in dense systems belongs to the most difficult tasks of theoretical physics. Beginning with the classical works of Planck, Brillouin, Bethe, and Salpeter, this is a topic which has raised many theoretical and experimental investigations. When the 36-year-old Gerd Röpke started his professional career as Docent of Theoretical Physics at Rostock University, the Rostock group headed by Günther Kelbg was deeply involved in this problem. The members of the group at that time were Klaus Kilimann, Wolf-Dietrich Kraeft, Dietrich Kremp, Hartmut Krienke, Rainer Sändig, and Heinz Ulbricht, in collaboration with several younger coworkers such as Norbert Ahlbehrendt, Harald Engel, Wolfgang Fennel, Reinhard Mahnke, Claudia-Veronika Meister, Lutz Schimansky-Geier, Manfred Schlanges, Gerhard Schmitz, Wilfried Zimdahl, and others.

The state of understanding the problem of bound states was reflected in book [1] and in several articles [2–4]. When Gerd Röpke became associated with the group, the Greens function methods were extended [6] and new methods were developed such as the Bethe–Salpeter equation [5] and the Zubarev transport theory. In the present paper, we will give a critical discussion of several approaches to calculate the bound state contributions to the thermodynamic functions. First, we compare density expansions with grand canonical representations by fugacity expansions. Such expansions are conceptually simple but are, nevertheless, able to describe bound state phenomena as demonstrated by several authors [1, 3, 4, 8]. In the case of solar plasmas, the fugacity expansion method (ACTEX) has proven to

be very reliable [8]. Next, we develop a new summed-up density representation which includes the advantages of density and fugacity expansions and show that it includes not only the bound state effects but also the transition to the fully ionized Fermi gas at high densities. Finally, we compare these approaches with an advanced version of the chemical approach. Recently, we derived in the framework of the chemical description a quite advanced expression for the free energy [10, 11, 12]. By minimization of the free energy with respect to the degree of ionization  $\alpha$  and the degree of dissociation  $\beta$ , we calculate here the isothermal equation of state (EOS) and compare it with the other approaches.

## 2. FUGACITY AND DENSITY EXPANSIONS

As is well known from statistical thermodynamics since Mayer and others, there are two basic types of expansions for fluid systems:

(i) fugacity expansions

$$\beta p = z + b_2 z^2 + b_3 z^3 + \dots, \quad (1)$$

$$n = z + 2b_2 z^2 + 3b_3 z^3 + \dots, \quad (2)$$

where  $n$  is the density and  $z$  is the fugacity;

(ii) density expansions

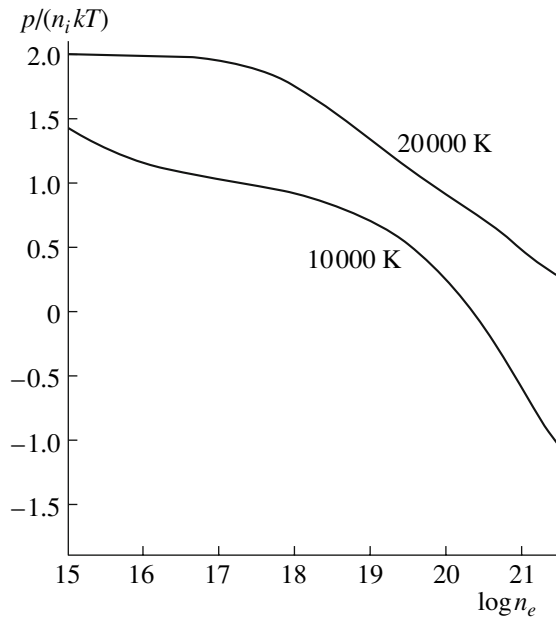
$$\beta p = n + B_2 n^2 + B_3 n^3 + \dots, \quad (3)$$

$$B_2 = -b_2, \quad B_3 = -2b_3 + 4b_2^2, \quad \dots \quad (4)$$

The last line shows the relations between the two types of virial coefficients. Both expansions are in principle completely equivalent; however, the range of convergence and, therefore, the applicability may be quite different. As is well known, for short-range repulsive forces, the density expansion gives a much better representation of the thermodynamic properties. On the other hand, for systems with bound states, the fugacity

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¶ The text was submitted by the author in English.



**Fig. 1.**  $T =$  (below) 10000 and (above) 20000 K calculated by the low density expansion which contains only classical and semiclassical contributions including screening and the Brillouin–Planck–Larkin approximation of the second virial coefficient.

expansion is more appropriate. This is to be seen from a formal reinterpretation of the fugacity expansion, which may be formulated as [1, 4]

$$\beta p = n^* + n_2^* + n_3^* + n_4^* + \dots, \quad (5)$$

$$n^* = z, \quad n_2^* = b_2 z^2, \quad n_3^* = b_3 z^3, \quad \dots \quad (6)$$

The second line of equations may be written as

$$\frac{n_2^*}{(n^*)^2} = b_2, \quad \frac{n_3^*}{(n^*)^3} = b_3, \quad \dots \quad (7)$$

Here we may interpret  $n^*$  as the density of free particles,  $n_2^*$  as the density of bound pair states,  $n_3^*$  as the density as bound triple states, etc. The relations between them may be considered as mass action laws. The chemical reinterpretation makes sense only if the virial coefficients are large and positive. This is the case if the system forms bound pairs and bound triples and if short range repulsion is less relevant.

In plasmas the situation is much more complicated since there are repulsive and attractive forces at the same time and the coefficients may have positive and negative components.

### 3. EXPANSIONS FOR DILUTE PLASMAS

At low density and not too high temperatures, the EOS of two-component plasmas may be represented by the (i) classical ideal terms and a Debye screening con-

tribution, (ii) a second order term taking into account proton-electron bound states (atoms),

$$\beta p = (n_e + n_i) - \frac{\kappa^3}{24\pi} \left( 1 - \frac{3}{8} \sqrt{\pi} \kappa \lambda_{ie} + \dots \right) - n_e n_i \Lambda^3 \sigma(T) + \dots, \quad (8)$$

$$\sigma(T) = \sum_s s^2 [\exp(-\beta E_s) - 1 + \beta E_s]; \quad (9)$$

$$\Lambda^3 = 8\pi^{3/2} \lambda_{ie}^3 = \frac{h^3}{(2m_{ie} kT)^{3/2}},$$

where  $\kappa$  is the reciprocal Debye radius. The representation of the EOS in Fig. 1 shows that that the negative contribution of the second virial coefficient describing the bound states increases so fast with the density that the pressure reaches negative values. Therefore, we see clearly that the density expansion fails in regions where bound states dominate.

We consider now the fugacity representations for dilute plasmas [1, 3, 8] beginning with a truncated fugacity expansion that contains the same type of terms as the density representation given above ( $K$ , reciprocal Debye radius in the grand canonical ensemble):

$$\beta p = (z_e + z_i) + \frac{K^3}{12\pi} \left( 1 - \frac{3}{16} \sqrt{\pi} K \lambda_{ie} + \dots \right) + z_e z_i \Lambda^3 \sigma(T) + \dots \quad (10)$$

As we see in Fig. 2 (dotted lines), there is a lowering step in the relative pressure, related to the formation of atomic bound states. This step expresses the fact that in the atomic region the number of particles is half of the number in the fully ionized region. This way, the fugacity expansion nicely describes this physical effect. Let us consider now the effect of higher order terms [1]:

$$\beta p = (z_e + z_i) + \frac{K^3}{12\pi} f(K\lambda_{ie}) + z_e z_i \Lambda^3 \sigma'(T, n) + C z_e^2 z_i^2 \exp[-\beta E_{H2}] + \dots, \quad (11)$$

$$\sigma'(T, n) = \sum_s \sum_l (2l + 1) [\exp(-\beta E'_{sl}) - 1 + \beta E'_{sl}]. \quad (12)$$

Here  $E'_{sl}$  denotes the screened energy levels, which are density-dependent [9] and  $f(x)$  is a screening function:

$$f(x) = \frac{3\sqrt{\pi}}{3} \left[ \frac{1}{2} + \frac{2}{x^2} \left( 1 - \exp\left(\frac{x^2}{4}\right) \right) + \frac{x}{3\sqrt{\pi}} F_{11}\left(1, \frac{5}{2}, \frac{x^2}{4}\right) \right]. \quad (13)$$

Including higher order terms corresponding to the fourth order virial coefficient leads to a second lowering step in the relative pressure up to nearly 25 percent. However, the transition to full ionization, which is expected to occur at high densities, is evidently not described by our approximations. In order to include this effect, we develop a new procedure based on density representations.

#### 4. NEW DENSITY REPRESENTATIONS BASED ON PARTIAL SUMMATION

The idea is the following: Density representations are appropriate descriptions at low and high densities. They are wrong just in a narrow region of densities where the bound states dominate. We start from the density expansion and include higher order terms which are—in the fugacity representation—responsible for the formation of steps in the pressure. What we need are higher orders in the partition function of atomic states. By selecting a corresponding infinite series, we find

$$\beta p(n, T) = p_e^{\text{Fermi}} + A(x) \left[ nk_B T + \frac{1}{3}(u_{ee} + u_{ei} + u_{ii}) \right] + \dots; \quad (14)$$

$$A(x) = 1 - x + 2x^2 - 5x^3 + 14x^4 + \dots; \quad (15)$$

$$x = n_e \Lambda^3 \sigma'(T, n).$$

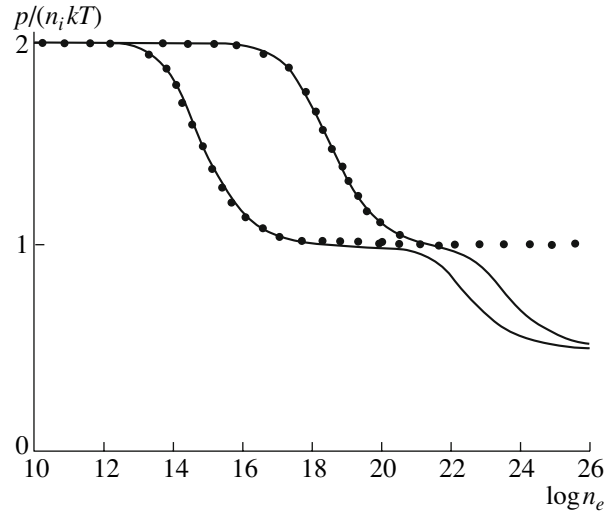
Here  $\sigma'(T, n)$  denotes again the p.f. with modified (density-dependent) energy levels [9]. The function  $A(x)$  is represented by an infinite series of higher order terms containing the atomic partition function and all its powers. By summing up this series, we got the following closed expressions and limits

$$A(x) = \frac{1}{2x} [\sqrt{1 + 4x} - 1], \quad (16)$$

$$A(x) \rightarrow 1 \quad \text{if } x \rightarrow 0, \quad (17)$$

$$A(x) \rightarrow \frac{1}{\sqrt{x}} \quad \text{if } x \rightarrow \infty. \quad (18)$$

The contributions  $u_{ee}$ ,  $u_{ei}$ ,  $u_{ii}$  denote the electron–electron, electron–ion, and ion–ion contributions to the internal energy including only the free states. These contributions, which depend only on plasma parameters and not on the atomic partition function, are well known [1, 6]. As we see from Fig. 3, the new density



**Fig. 2.**  $T = 10000$  K (upper right curves) and  $T = 20000$  K (lower left curves) calculated by fugacity expansions: (Dotted line) The expansion contains only classical contributions with quantum corrections and certain approximation of the second virial coefficient. (Full line) Higher order quantum contributions up to the fourth virial coefficient are included.

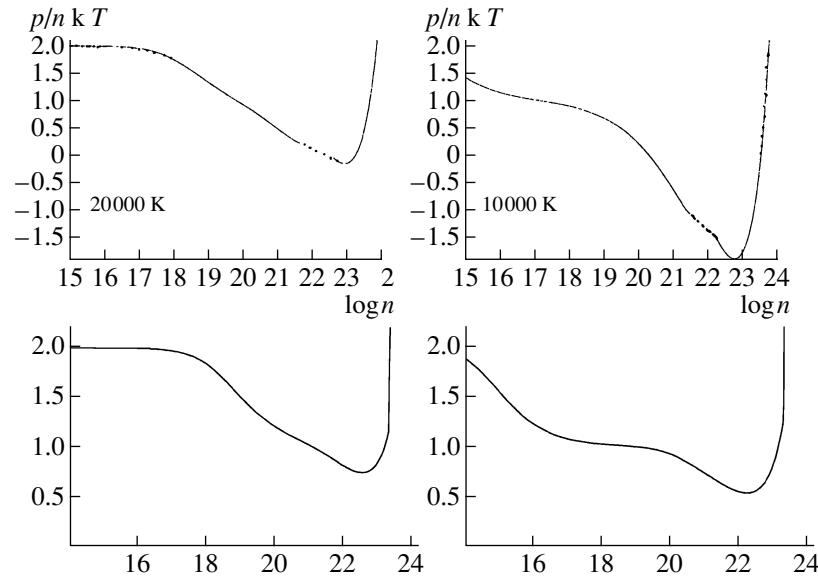
representations show indeed the desired behavior that is known from the highly developed chemical representations. At intermediate densities some open problems arise. In spite of a qualitatively correct picture, we need here further improvements of the summing-up procedure.

#### 5. EQUATION OF STATE IN THE CHEMICAL PICTURE

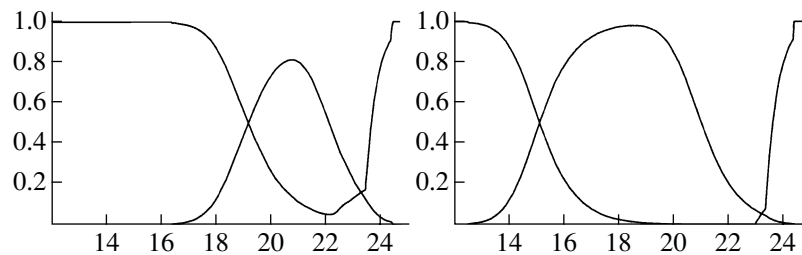
We are using the chemical approach to the free energy of dense hydrogen plasmas which recently was applied to temperatures between 2000 and 10000 K [10, 11]. The effects of pressure dissociation,  $H_2 \rightleftharpoons 2H$ , and ionization,  $H \rightleftharpoons e + p$ , are taken into account so that the transition from a molecular fluid at low temperatures and pressures through a partly dissociated, warm fluid at medium temperatures of some thousand Kelvin to a fully ionized, hot plasma above 10000 K can be explained. In the chemical picture, we consider hydrogen as a two-component system consisting of the plasma (electrons and protons) and the neutral fluid (atoms and molecules). Correspondingly, the free energy expression for a two-component system of neutral ( $F_{nl}$ ) and charged particles ( $F_{pl}$ ),

$$F(V, T, N) = F_{ne}(V, T, N) + F_{pl}(V, T, N), \quad (19)$$

combines results for the fully ionized plasma domain [1, 7] with improved data for the dense, neutral fluid calculated within a dissociation model [10]. Both contributions to the free energy are split into ideal and interaction parts. We take into account the interactions in the neutral and in the charged subsystem, respec-



**Fig. 3.**  $T = 10000$  K and  $T = 20000$  K: (i) (Above) The data were calculated by the new extended density expansion. (ii) (Below) Data calculated in the chemical picture for  $T = 20000$  K (left) and for  $T = 10000$  K (right).



**Fig. 4.**  $T = 20000$  K (left) and  $T = 10000$  K (right). At high densities we see the transition to full ionization.

tively, whereas the interaction between charges and neutrals is accounted for by the reduced-volume concept. Instead of going into detail, we refer to the cited papers. We consider a hydrogen plasma at fixed temperature  $T$  and proton density  $n$ . We take into account ionization processes



and dissociation processes



For simplicity, the formation of other species as  $\text{H}_2^+$  and  $\text{H}^-$  species will be neglected. The degrees of ionization and dissociation are defined by [10]:

$$\alpha = \frac{n_i}{n_i + n_a + 2n_m}, \quad \beta_a = \frac{n_a}{n_i + n_a + 2n_m}, \quad (22)$$

$$\beta_m = \frac{2n_m}{n_i + n_a + 2n_m}.$$

These are the variational parameters of our problem. The free energy has to be minimized with respect to them. We note that  $\beta_a$  is the relative amount of protons bound in atoms and  $\beta_m$ , the relative amount bound in molecules. Due to the balance relation for the total proton density

$$n = n_i + n_a + 2n_m, \quad (23)$$

we find several relations between the degrees; only one of the  $\beta$ -parameters is independent. Further, the condition of neutrality requires that electron and ion densities are always equal. The result of calculations is shown in Figs. 3 and 4.

## 6. CONCLUSIONS

We have studied in this work the problem of bound states in relation between several methods of studying the thermodynamics of dense hydrogen plasma:

- (i) density expansions,
- (ii) fugacity expansions,
- (iii) summed-up density representations,

(iv) the chemical description based on minimization of the free energy.

The density expansion overestimates the effect of bound states, leading to negative pressures at larger densities. The fugacity expansion does better in this respect, and the relative pressure goes to saturation. However, the fugacity representations fail to describe the transition to full ionization at very high densities. This effect is correctly described by the new summed-up density expansions and also by advanced chemical descriptions.

The most realistic description is given by advanced chemical descriptions, which, however, are quite complicated and still connected with open problems [12]. The new summed-up density expansions still have to be explored further; however, they seem to be a promising alternative to the chemical picture.

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#### REFERENCES

1. W. Ebeling, W.-D. Kraeft, and D. Kremp, *Theory of Bound States and Ionization Equilibrium in Plasmas and Solids* (Academie, Berlin, 1976).
2. W. Ebeling, *Ann. Phys.* **22**, 383, 392 (1969).
3. G. P. Bartsch and W. Ebeling, *Contr. Plasma Phys.* **11**, 393 (1971).
4. W. Ebeling, *Phys. A* **73**, 573 (1974).
5. R. Zimmermann, K. Kilimann, W.-D. Kraeft, et al., *Phys. Stat. Solidi B* **90**, 175 (1978).
6. W.-D. Kraeft, W. Kremp, W. Ebeling, and G. Ropke, *Quantum Statistics of Charged Particle Systems* (Akademie, Pergamon, Berlin, 1986).
7. W. Ebeling and W. Richert, *Phys. Stat. Solidi B* **128**, 467 (1985); *Phys. Lett. A* **108**, 80 (1985).
8. F. J. Rogers, *Contr. Plasma Phys.* **41**, 179 (2001).
9. W. Ebeling, D. Blaschke, H. Reinholz, et al., Preprint (University Rostock, 2006).
10. D. Beule, W. Ebeling, A. Förster, et al., *Phys. Rev. B* **59**, 14 (1999).
11. D. Beule, W. Ebeling, A. Förster, et al., *Contrib. Plasma Phys.* **39**, 21 (1999); *Phys. Rev. B* **63**, 060202R (2001).
12. W. Ebeling, H. Hache, H. Juranek, et al., *Contr. Plasma Phys.* **45**, 160 (2005).