Degree of Ionization of a Plasma in Equilibrium *

G. ECKER and W. KRÖLL

Institut für Theoretische Physik der Universität Bochum **

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Previous investigations derived the SAHA equation for a plasma in equilibrium applying the free-bound concept valid for an isolated electron-ion pair. In our investigation of the "adapted free-bound model" (I) we have shown that due to the free-bound interaction the demarcation between free and bound states is shifted by $\Delta\chi = -e^2/r_0$. We study the influence of this shift of the ionization limit on the effective ionization energy in SAHA's equation. At the same time we account by interpolation for the contributions of the quasi-free highly correlated particles. The lowering of the free-bound limit causes an increase of the effective lowering of the ionization energy in SAHA's equation beyond the well-known e^2/D-term resulting from the free-free interaction. This additional term itself is of the order $O(e^2/D)$ and therewith much stronger than the correction found from higher order correlations of the free particles. On the other hand it is much smaller than the lowering of the free-bound limit.

SAHA's equation is used to describe the degree of ionization of a system in equilibrium. In writing down this equation it is common practice to treat the free and bound states of the electrons and ions as two different particle kinds, which do not interact with each other. Supposedly the whole phase space is accessible to each of these free and bound particles.

Under these conditions the degree of ionization is determined by the partition functions of the bound and free particle groups.

If one further neglects the interaction within these groups one arrives at the widely used simple form of the SAHA equation which depends only on the partition functions of the isolated free and bound particels and on the ionization energy of the isolated bound system. In this approximation one is confronted with the problem of the divergence of the partition function of the bound system.

To remove this divergence difficulty various models have been applied to account for the particle interaction. However, the interaction not only limited the partition function of the bound system, but also introduced additional terms which have been interpreted as an "effective lowering of the ionization energy". The introduction of such additional terms was not always strictly analytical deductive, but frequently intuitive on the basis of simple models.

Different results for this effective lowering of the ionization energy have been obtained so far:

The term $\Delta_1\chi = e^2/D$ (D – DEBYE length, e – elementary charge) for the lowering of the ionization energy in the SAHA equation has been calculated as the contribution of the free particle COULOMB interaction to the chemical potential [1–4].

If the influence of the nearest ionic neighbour on a neutral is assumed to dominate, then the lowering of the ionization energy is given by $\Delta_2\chi = 3\,e^2/r_0$ (r_0 – average interionic distance). This result was derived from the assumption that bound states do not exist if their energy exceeds the potential energy maximum between two ions in the average distance [5].

A stronger lowering of the ionization potential follows from the formula [6]

$$\Delta_3\chi = e^2/D + \bar{a}\, e^2/r_0$$

where the second term was added in analogy to metal theory to take into account the contributions of overlapping high energy bound states ($O(\bar{a}) = 1$). – The investigations [2, 3] restrict the term $\Delta_1\chi = e^2/D$ to the range below and the term $\Delta_2\chi \cong e^2/r_0$ to the range above the critical density

$$n_c \cong (3/4\,\pi) \cdot (k\,T/e^2)^3$$

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** Present address: 53 Bonn, Wegelerstr. 10.

1 R. ROMPE and M. STEENBECK, Ergebn. exakt. Naturw. **18**, 257 [1929].

2 P. DUCLOS and A. B. CAMBEL, Z. Naturforschg. **16 a**, 711 [1961].

3 G. ECKER and W. KRÖLL, Phys. Fluids **6**, 62 [1963].

4 A. SCHLÜTER, Proc. 5th Intern. Conf. Ionization Phenomena in Gases, Paris, Vol. **1**.

5 A. UNSÖLD, Z. Astrophys. **24**, 355 [1948].

6 G. ECKER and W. WEIZEL, Ann. Phys. Leipzig **17**, 126 [1956].

(k — BOLTZMANN's constant, T — temperature). Other investigations claim that the terms $\Delta_2\chi$ and $\Delta_3\chi$ should be added [7, 8].

It has been expected that the value of the lowering of the ionization energy depends on the thermodynamical potential used for the derivation of the SAHA equation [9].

Frequently the cut-off for the atomic partition function and the lowering of the ionization energy in the SAHA equation have been identified with each other [7–12]. However, the necessity to distinguish between these quantities was also pointed out [6].

System

Subject of this investigation is a system of equal numbers of electrons and protons in thermodynamic equilibrium at a given temperature and volume. Both, electrons and protons are represented by point charges interacting according to COULOMB's law. The formation of hydrogen atoms is taken into account but not the effects of negative ions or molecules. No external influences and boundary effects are considered.

The model of a hydrogen plasma has been chosen for the sake of formal simplicity. For other plasmas the problems are similar and our procedure is readily applied.

Aim of this Investigation

It is our opinion that using the "naive free-bound approximation" described in the introduction and accounting only for weak pair interactions between the free particles one obtaines an effective lowering of the ionization energy given by $\Delta_1\chi = e^2/D$.

In a previous paper [13] we introduced the "adapted free-bound approximation" which differs from the "naive free-bound approximation" in two essential points:

First, it does not replace particle states by particle kinds and consequently avoids the incorrect double counting in the phase space. Second, it uses a different demarcation between free and bound states which accounts roughly for the free-bound interaction.

It must be expected that the shift in the free-bound demarcation affects the effective lowering of the ionization energy in SAHA's equation.

It is the aim of this investigation to study this influence accounting at the same time approximately for the higher order correlations and typical quantum-mechanical effects in the quasi-free subregion defined in I.

Saha's Equation for the Adapted Free-Bound Model

For the naive free-bound approximation one writes down the partition function of a system with a specific number of independent "free particles" and independent "bound particles". Minimalization with respect to the parameter of the free particle number provides the SAHA equation.

For the "adapted free-bound model" the problem is more complicated since we do not treat free and bound states as different particle kinds and moreover have three kinds of particle states: free states with weak pair correlation, quasi-free states and bound states (see Fig. 1). In considering a new

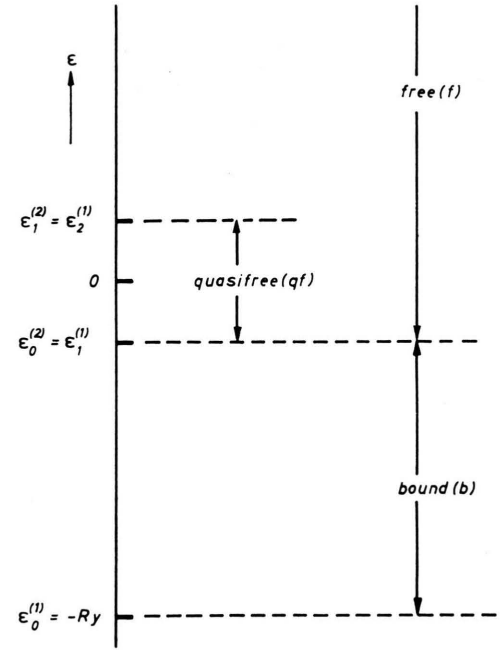

Fig. 1. Schematic representation of the terminology and definitions used in the text.

[7] H. BRUNNER, Z. Phys. **159**, 288 [1960].
[8] H. ROTHER, Ann. Phys. **2**, 326 [1958].
[9] H. R. GRIEM, Phys. Rev. **128**, 997 [1962].
[10] P. SCHULZ and W. WEIZEL, Z. Phys. **122**, 697 [1944].
[11] R. BORCHERT, Ann. Phys. Leipzig **6**, 332 [1950].
[12] H. N. OLSEN, Phys. Rev. **124**, 1703 [1961].
[13] G. ECKER and W. KRÖLL, Z. Naturforschg. **21 a**, 2012 [1966]; in the following called I.

approach to determine the degree of ionization for the adapted free-bound model one should bear in mind that there is no hope for an exact analytical description of the highly correlated quasi-free group. Consequently the approach should be such that it allows a reliable interpolation through this quasi-free region.

We first consider electrons and ions as distinguishable and grouped in pairs. Neglecting all interactions except within the bound states we have the partition function of our system given by

$$Q = \sigma_t^N (\sigma_0 + \sigma_1 + \sigma_2)^N \tag{1}$$

with

$$\sigma_\mu = \int_{\varepsilon_\mu^{(1)}}^{\varepsilon_\mu^{(2)}} g_\mu(\varepsilon)\, e^{-\varepsilon}\, d\varepsilon\,, \qquad \mu = 0, 1, 2\,, \tag{2}$$

$$g_0 = \sum_\nu Ry\, \delta(\varepsilon - \varepsilon_\nu)\, \frac{1}{\varepsilon_\nu}\,, \qquad g_2 = \frac{V\, 4\pi (2m)^{3/2}}{h^3} \cdot \varepsilon^{1/2} \tag{3}$$

$g_1 = g_0$ for $\varepsilon_1^{(1)} < \varepsilon < 0$, $g_1 = g_2$ for $0 < \varepsilon < \varepsilon_1^{(2)}$

and

$$\varepsilon_0^{(1)} = -Ry\,, \qquad \varepsilon_0^{(2)} = \varepsilon_1^{(1)} = -\frac{e^2}{r_0}\,,$$
$$\varepsilon_1^{(2)} = \varepsilon_2^{(1)} = \frac{e^2}{r_0}\,, \qquad \varepsilon_2^{(2)} = \infty\,. \tag{4}$$

Here Q is the total partition function of the system, $\sigma_{0,1,2}$ are the contributions to the pair-partition functions and g the weight functions for the ranges 0, 1 and 2 specified in Fig. 1. σ_t is the partition function for the translational degrees of freedom of the center of gravity. ε indicates the energy of an isolated pair in its center of gravity system. N is the total number of electron-ion pairs, Ry the RYDBERG constant, m the electron mass, h PLANCK's constant.

Applying the trinominal formula to Eq. (1) we arrive at

$$Q = \sum_\nu \sum_\mu \binom{N}{\nu} \binom{\nu}{\mu} \sigma_t^N\, \sigma_0^{N-\nu}\, \sigma_1^{\nu-\mu}\, \sigma_2^{\mu}. \tag{5}$$

Each term of this sum gives the probability for the realization of a certain subdivision of our system into $(N-\nu)$ bound, $(\nu-\mu)$ quasi-free and (μ) free states.

We now account for the tıanslational exchange degeneracy within the bound group and within the group of free electrons and free ions. To do this we multiply each term of the sum in Eq. (5) belonging to the same ν with the factor $[(N-\nu)!\cdot\nu!]^{-1}$. The most probable term of the partition function – corresponding to the SAHA equation – is found by minimization with respect to ν and μ. This results in

$$\nu(\nu-\mu)/(N-\nu) = \sigma_1/\sigma_0\,,$$
$$\mu/(\nu-\mu) = \sigma_2/\sigma_1\,. \tag{6}$$

We now take the free-bound and the free-free interaction into account.

According to the ideas developed in I this does not affect the weight function g_0 below $\varepsilon_1^{(1)}$.

Within the free group we know from diagram techniques and other methods that the effect in σ_2 can be taken into account by using the new weight function $g_2(\varepsilon + e^2/D)$.

As a consequence of the free-bound interaction the particles in the group (1) can no longer be described by the weight function g_1 given in Eq. (3), since strong correlation effects become important. We now determine this weight function by interpolation between $\varepsilon_0^{(2)}$ and $\varepsilon_1^{(2)}$. Of course, this interpolation has to be carried out within the frame of our model assumption taking into account the translational degeneracy effects. That means we have to interpolate not between $g_0(\varepsilon)$ and $g_2(\varepsilon + e^2/D)$ as given in Eq. (3) but between g_0 and g_2/n_f, where n_f is the free electron density. The uncertainty of this interpolation procedure is minor since the interpolation interval is small and the weight function steady and monotonous. We find

$$g_1(\varepsilon) = \frac{1}{2}\left\{ c_2\left(\frac{e^2}{r_0} + E_D\right)^{1/2} - c_1\left(\frac{e^2}{r_0}\right)^{-5/2} \right\} \frac{\varepsilon}{e^2/r_0} + \frac{1}{2}\left\{ c_2\left(\frac{e^2}{r_0} + E_D\right)^{1/2} + c_1\left(\frac{e^2}{r_0}\right)^{-5/2} \right\} \tag{7}$$

with

$$c_1 = (Ry)^{3/2}, \qquad c_2 = 4\pi (2m)^{3/2}/h^3\, n_f\,. \tag{8}$$

Applying the results of Eqs. (1 – 4, 7, 8) in Eq. (6) and solving for $\nu = N_f$, $N - \nu = N_b$ we find the SAHA equation

$$\frac{N_f^2}{N_b} = 2\left(\frac{2\pi M k T}{h^2}\right)^{3/2} \frac{\exp\left\{-\beta\left(\chi - \frac{e^2}{D} - 0{,}4\,\frac{e^2}{D}\right)\right\}}{\sum\limits_{\varepsilon_0 = -Ry}^{\varepsilon_0^{(2)} \cong -e^2/r_0} \exp\{-\beta\,\varepsilon_n\}} \tag{9}$$

N_f gives the total number of free electrons, N_b the total number of bound pairs.

Clearly the effect of the particle interaction on the SAHA equation is reflected in two changes:

1. The influence on the single particle function σ_0 through the upper limit $\varepsilon_0^{(2)} = -e^2/r_0$.
2. The additional terms in the exponent.

According to the results obtained in I the single particle partition function can be represented by the eigenvalues of the hydrogen atom in the whole range $\varepsilon_0^{(1)} - \varepsilon_0^{(2)}$.

The effective lowering of the ionization potential $\Delta\chi_{\text{SAHA}}$ in the SAHA equation is therefore

$$\Delta\chi_{\text{SAHA}} = e^2/D + 0{,}4 \cdot e^2/D \,. \tag{10}$$

Remembering that the classical value $\Delta_1\chi$ calculated with weak pair correlations neglecting free-bound interaction is

$$\Delta_1\chi = e^2/D \tag{11}$$

we find a "correction term"

$$\tilde{\Delta}\chi = 0{,}4 \cdot e^2/D \,. \tag{12}$$

Discussion

If one defines the ionization energy of an atom in a plasma as the energy difference between the lowest bound and the lowest free state, then this ionization energy is smaller than the ionization energy of the isolated system by

$$\Delta\chi \approx e^2/r_0 + e^2/D \tag{13}$$

according to our derivation in I. The physical background for this lowering of the ionization energy $\Delta\chi$ is the shift in the free-bound demarcation accounting crudely for the free-bound interaction. Except for the uncertain numerical factor this formula agrees with the result derived from UNSÖLD's concept [5] accounting at the same time for the effect of weak pair interactions.

The effective lowering of the ionization energy in SAHA's equation as described by formula (10) is not identical with $\Delta\chi$. Neither does it agree with the DEBYE term $\Delta_1\chi$.

The difference between $\Delta\chi$ and $\Delta\chi_{\text{SAHA}}$ may be elucidated in the following way. All free particle states are affected by free-bound and free-free interaction. In the lowest free state – to which $\Delta\chi$ refers – the free-bound interaction dominates through the term e^2/r_0. With increasing energy, however, the free-bound interaction becomes negligible in comparison to the DEBYE term of the free-free interaction. Since all free states contribute to the SAHA equation it is evident that

$$\Delta_1\chi = \frac{e^2}{D} < \Delta\chi_{\text{SAHA}} < \Delta\chi \approx \frac{e^2}{r_0} + \frac{e^2}{D} \tag{14}$$

holds.

This situation is demonstrated in Fig. 2, which shows the probability density of the pair representation. The light curve describes the case without interaction, whereas the heavy curve gives the probability density with free-free and free-bound interaction as approximated in this paper. The dotted line is based on the false assumption that the contribution of the free-bound interaction is independent of the free particle state; this assumption would produce $\Delta\chi_{\text{SAHA}} \cong \Delta\chi$.

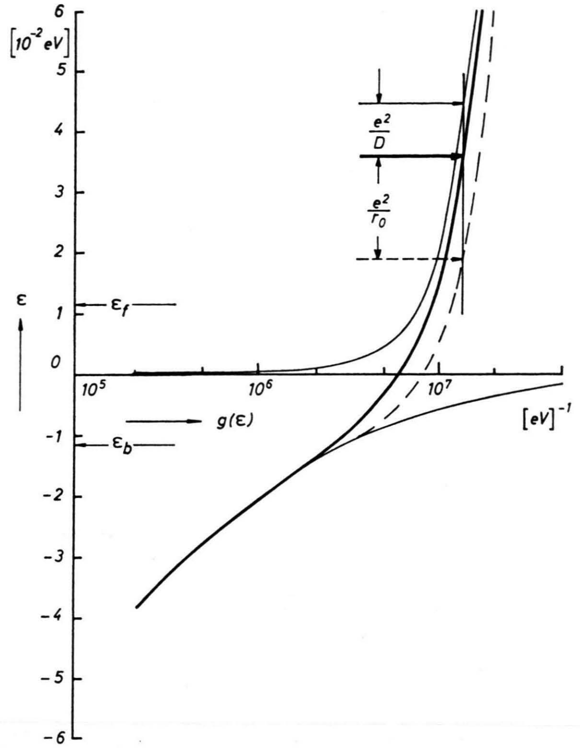

Fig. 2. Weight function $g(\varepsilon)$ used in the calculation of the partition function: Light curve—$g(\varepsilon)$ as calculated for an isolated atom and a free electron-ion pair without interaction. Dotted curve—$g(\varepsilon)$ as derived under the false assumption of a free-bound interaction independent of the free particle state. Heavy line—correct $g(\varepsilon)$ curve.

The correction to the DEBYE term as calculated here is much stronger than the correction found from classical cluster expansions. The reasons are the new free-bound definition accounting for the free-bound interaction, quantum-mechanical effects and strong correlations below $\varepsilon = \varepsilon_2^{(1)}$Here it is quite obvious that a claim of accuracy of one per cent [9] cannot be substantiated.

Different values of the lowering of the ionization potential calculated with the use of different thermodynamic potentials are caused by errors in the analysis.

The plasma interaction also affects the SAHA equation through the limitation of the single particle partition function. For temperatures low enough, so that the higher terms in the partition function do not contribute this effect is of course negligible. As it becomes important with increasing temperatures the limitation is determined by e^2/r_0 and not by e^2/D as suggested in Ref. [9].

The above formalism requires extension where the neutral-neural interactions are important. This is the case for the interpretation of the surprising results found from experiments under extreme pressures [14].

[14] Y. N. RYABININ, Gases at High Densities and Temperatures, Pergamon Press, London 1961.

Uniform Description of Core and Sheath of a Plasma Column

G. ECKER

Institut für theoretische Physik, Universität Bochum

and H. KANNE

Institut für theoretische Physik, Universität Bonn

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Weakly ionized plasmas bounded by insulated walls have been studied for the limiting cases of very low and very high pressure in numerous papers. These investigations base the particle kinetics either on the model of "collision dominated motion" or on the model of "inertia dominated motion". Corresponding model regions are matched neglecting the transition region.

We consider a weakly ionized plasma bounded by insulated walls. Its particle production is due to electron collisions and its particle destruction due to wall recombination. Describing the electrons as in quasiequilibrium and ion-neutral interaction by constant mean free time collisions it is possible to derive for arbitrary plasma pressure an integrodifferential equation valid throughout the plasma core, the transition region and the sheath. No matching of model regions is required. The well-known LANGMUIR and SCHOTTKY theories are shown to be asymptotic solutions of this general treatment.

Aim of the Investigation

Until now a uniform description of core and sheath of a plasma column exists only for the case of very low pressure, where the mean free path of the ions is much larger than the radius of the column. Since under these circumstances the ions fall freely from their point of production towards the wall the model of "inertia limited motion" is applicable throughout the whole column [1, 2].

However, with increasing pressure the ions suffer collisions within the plasma column, which affect the applicability of the inertia limited model. To overcome this difficulty it is common practice to subdivide the whole column into two model regions, the "core" and the "sheath". These two model regions are matched at their interface. The core is described by the limiting kinetic model of "collision-dominated motion" [3]. Within the sheath the inertia limited model of the low pressure case is applied.

It is true that for sufficiently high pressure the collision dominated approximation holds in the center of the column and the inertia limited approximation close to the walls. It is also true that both kinetic models break down in the transition region between core and sheath. The errors introduced by the core-sheath-matching which neglects the transition region are unknown.

In this investigations we aim to give for arbitrary pressures a uniform wall to wall treatment of the plasma column without invoking and matching model regions. This is done for a special case which allows the desired accuracy and is still close to reality. The theories of LANGMUIR and SCHOTTKY valid in the low and high pressure limits respectively are shown to be asymptotic solutions of this general theory.

[1] J. LANGMUIR and L. TONKS, Phys. Rev. 34, 876 [1929].

[2] S. A. SELF, Phys. Fluids 6, 1762 [1963].

[3] W. SCHOTTKY, Phys. Z. 25, 635 [1924].