

On Saha's equation for partially ionised plasmas and Onsager's bookkeeping rule

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Abstract. In this work we study several definitions of free and bound states in plasmas and the consequences of Onsager's bookkeeping rule for the thermodynamic functions. In particular we investigate Onsager's rule of balance between the contributions of free and bound charges. We show that this rule guarantees at low densities the independence (stationarity) with respect to the fine details of the definition of bound states (chemical species). The Brillouin-Planck-Larkin atomic partition function which is the most natural choice is modified and the consequences of such changes are investigated. We study the free energy landscape in dependence on different choices of the mass action constant and formulate the condition of stationarity with respect to free parameters. We show that at high densities the condition of stationarity is violated (except in certain saddle points) so that in general the chemical description of plasmas can be applied only with great care.

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1 Introduction

The theory of ionisation processes in weakly ionised plasmas is based on Saha's equation which was formulated by Saha 1920-1921 during a stay at the Berlin University [1]. In Saha's theory the ionisation is treated as a chemical equilibrium between free electrons and ions on one hand and bound electron-ion pairs on the other hand. Nearly at the same time Bjerrum formulated in Denmark a theory of weak electrolytes which in fact is based on similar principles [2–4]. Modern versions of the mass action law of weakly ionised electrolytes were developed in recent work [5].

In the plasma theory as well as in the electrolyte theory the fundamental question arises which states are to be treated as “free” and which states are “bound”. Bjerrum assumed that ion pairs with electrostatic energy larger than $2k_B T$ corresponding to distances $r < q_0 = e^2/2D_0k_B T$ may be treated as new chemical entities called ion pairs (e — ionic charge, D_0 — dielectric constant, T — temperature). For plasmas this question was even more complicated and several proposals going back to Bohr, Herzfeld, Planck and others were available [6–12].

Onsager's book-keeping rule was formulated first at a conference on electrochemistry in Montpellier [13,14]. This rather general rule says, that in the chemical picture

bound and free state contributions correspond to different pages of a ledger. With proper bookkeeping the result of calculations is not influenced by the distribution on different pages. In other words, in a correct theory the finer details of the definition of an ion pair/a bound state do not matter [13]. We will show here that the key point of Onsager's bookkeeping rule is the stationarity (neutrality) of the thermodynamic properties with respect to finer details. Here we will consider several definitions of bound states in plasma theory and will generalize them in such a way that the bookkeeping rule is exactly fulfilled.

Furthermore we will analyze the problem of choosing “optimal” mass action constants. There are two criteria which will be discussed.

- Simplicity: as was shown already some time ago there are concrete choices for the mass action constant which guarantee maximal simplicity of the thermodynamic functions [11,17].
- Stationarity: another natural criterion for a “good” choice is to require that for the given choice the free energy is stationary (insensitive) with respect to changes.

Stationarity means here that the results are not sensitive with respect to small changes of free parameters in the mass action constant. In other words the results are not sensitive with respect to the details of the definition of the chemical species. This means that the free energy should

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correspond to extrema or saddle points with respect to the free parameters.

Here we will modify several proposals for the mass action constant in such a way that Onsager's bookkeeping rule is exactly fulfilled. This way we continue an earlier work in the field of ionic solution theory [15].

2 Different mass action constants and the bookkeeping rule

In quantum mechanics the term "bound state of pairs" is usually associated with discrete states of particle pairs with attractive interactions. For Coulomb systems this leads to difficulties due to the infinite number of discrete states of the $1/r$ -potential. Therefore a maximal main quantum number s_m was introduced. States with $s < s_m$ are considered as bound. This leads for hydrogen-like systems to a finite partition function (I -ionisation energy)

$$\sigma_m(T) = \sum_{s=1}^{s_m} s^2 \exp\left(\frac{I}{kTs^2}\right) \quad (1)$$

and to the mass action constant

$$K_m(T) = \Lambda^3 \sigma_m(T); \quad \Lambda = \left(\frac{\hbar^2}{2\pi m_{ie} kT}\right)^{1/2} \quad (2)$$

where m_{ie} is the reduced mass. The choice of the maximal quantum number s_m is still free. There are several proposals. For example Riewe and Rompe argue [10] that states with binding energies $|E_s| < kT$ should be considered as quasi-free due to their limited stability. This leads to

$$s_m \simeq \left\lceil \frac{I}{kT} \right\rceil. \quad (3)$$

We mention that the terms under the sum in equation (1) have a minimum just at the quantum number defined by equation (3). In other words the cutting defined by equation (3) corresponds to the standard procedure for asymptotic series. According to Brillouin and Planck a soft cutting is more appropriate [9,16]

$$K(T) = \Lambda^3 \sum_{s=1}^{\infty} w_s s^2 \exp\left(\frac{I}{kTs^2}\right) \quad (4)$$

where the weight function is defined by

$$w_s = 1 - \left(1 + \frac{I}{kTs^2}\right) \exp\left(-\frac{I}{kTs^2}\right). \quad (5)$$

In the decades after Planck and Brillouin several alternative possibilities were discussed [11,12].

Much later the so-called Brillouin-Planck-Larkin partition function could be derived by exact quantum-statistical methods [11,16,17]. In order to introduce this into the Saha equation the heuristic argument of maximal simplicity of the thermodynamic functions was exploited.

After all these findings the question arises: What is the best choice and what is here the meaning of any valuation? Evidently the choice of the mass action constant is not unique. There was a long discussion about the different possible choices up to a clarifying discussion remark given by Onsager at a conference in Montpellier [3,13,14]: "The distinction between free ions and associated pairs depends on an arbitrary convention. Bjerrum's choice is good, but we could vary it within reason. In a complete theory this would not matter; what we remove from one page of the ledger would be entered elsewhere with the same effect."

The really deep content of this phrase is not easy to understand and we will rephrase it several times and finally give it the form of a recipe which is easier to handle than the general rule contained in Onsager's phrase. What did Onsager mean with this metaphor? Evidently Onsager wanted to tell us that the correct formulation of the mass action law requires a careful bookkeeping of the free and bound state contributions.

3 Density expansions and bookkeeping

We start our analysis with the statistical thermodynamics of a hydrogen-like plasma consisting of electrons (denoted by index 1) and ions (denoted by index 2) at very small densities $n_1 = n_2 = n$. Then free energy density and osmotic pressure are given by [11,12,17]

$$f = f_{id} - k_B T \left(\frac{\kappa^3}{12\pi} + n^2 8\pi \Lambda^3 k_0(T) + \dots \right) \quad (6)$$

$$p = 2nk_B T - k_B T \left(\frac{\kappa^3}{24\pi} + n^2 4\pi \Lambda^3 k_0(T) + \dots \right). \quad (7)$$

Here Λ is the thermal de Broglie wavelength defined by equation (2) and κ is the reciprocal Debye length

$$\kappa^2 = \frac{8\pi n e^2}{k_B T}. \quad (8)$$

Further $k_0(T)$ is the so-called mean virial function for hydrogen-like plasmas:

$$k_0(T) = \frac{1}{4\Lambda^3} (\lambda_{11}^3 K_0(\xi_{11}) + 2\lambda_{12}^3 K_0(\xi_{12}) + \lambda_{22}^3 K_0(\xi_{22})) \quad (9)$$

where the interaction parameters for a pair ij is given by

$$\xi_{ij} = -\frac{e_i e_j (2m_{ij})^{1/2}}{\hbar (kT)^{1/2}}. \quad (10)$$

The virial functions themselves are given by

$$K_0(\xi) = Q(\xi) - \frac{1}{2}(1 - \Theta(\xi))E(\xi) \quad (11)$$

with the Heisenberg contribution

$$Q(\xi) = \sum_{m=1}^{\infty} q_m \xi^m \quad (12)$$

and the Pauli term $E(\xi)$ which contributes only for pairs of equal particles

$$E(\xi) = \sum_{m=0}^{\infty} e_m \xi^m. \quad (13)$$

The coefficients of these convergent series are explicitly known [11,17]. Here we do not need the explicit form but only the asymptotic representation for

$$\xi = \xi_{12} \gg 1. \quad (14)$$

According to

$$\xi^2 = \frac{4I}{kT} \quad (15)$$

we see that this corresponds to temperatures below 10^5 K.

The asymptotic representation is remarkably simple and reads

$$k_0(T) = -\frac{1}{64\pi}\xi^2 + \frac{1}{8\pi}\sigma_{\text{BPL}}(T) \quad (16)$$

with the Brillouin-Planck-Larkin partition function

$$\sigma_{\text{BPL}}(T) = \sum_{s=1}^{s_m} s^2 \left(\exp\left[\frac{I}{kTs^2}\right] - 1 - \frac{I}{kTs^2} \right). \quad (17)$$

Now we consider the process of the formation of hydrogen-like atoms at finite concentrations and formulate Saha's mass action law in connection with the Debye-Hückel law for the thermodynamic functions. Let α be the degree of ionisation. Then we have first the mass action law

$$\frac{1-\alpha}{\alpha^2} = nK(T). \quad (18)$$

The mass action constant is not yet specified, one may so far think about any of the expressions given above. Secondly we have to make a choice for the thermodynamic expressions. In a first approach we will make a Debye-Hückel ansatz for the pressure

$$\frac{p}{k_B T} = n(1+\alpha) - \frac{\kappa^3 \alpha^{3/2}}{24\pi} \Phi(a(T)\kappa\alpha^{1/2}) + \dots \quad (19)$$

Here the Debye-Hückel function is

$$\Phi(x) = \frac{3}{x^3} \left(1+x - \frac{1}{1+x} - 2\ln(1+x) \right) = 1 - \frac{3}{2}x + \dots \quad (20)$$

Here the Debye-Hückel diameter $a(T)$ is still free and we have a problem to derive this quantity in a consistent way from the quantum-statistical formulae given above.

In order to solve this task we formulate Onsager's book-keeping rule explicitly. Going within the chemical picture to the limit of very small densities we find

$$\alpha = 1 - nK(T) + \dots \quad (21)$$

Comparing now equations (7) and (19) we get

$$n^2 8\pi \Lambda^3 k_0(b) = -\frac{1}{16\pi} \kappa^4 a(T) + K(T)n^2. \quad (22)$$

This leads to

$$K(T) = \Lambda^3 \sigma_{\text{BPL}}(T) + 4\pi l^2 (a(T) - a_0(T)) \quad (23)$$

with the Bjerrum-Landau length $l = e^2/kT$ and a new effective Debye-Hückel length a_0 which is defined by

$$a_0(T) = \frac{\Lambda}{8}. \quad (24)$$

The formula (23) is the explicit form of Onsager's book-keeping rule: we see that it assumes the form of a relation between the two free functions $K(T)$ and $a(T)$ in the chemical picture. Both are related to the BPL-mass action constant. There is one concrete choice of the Debye-Hückel diameter namely

$$a(T) = a_0(T) \quad (25)$$

where two terms on the r.h.s. cancel and we get the most simple expression for the mass action constant namely

$$K(T) = \Lambda^3 \sigma_{\text{BPL}}(T). \quad (26)$$

For any other choice of the mass action constant, the difference between the used effective diameter $a(T)$ and the expression $a_0(T)$ should be introduced. For example if we prefer to cut at a given maximal main quantum number s_m according the mass action constant $K_m(T)$ defined by equations (1, 2) then the effective diameter to be used in Debye-Hückel should have the value

$$a_m(T) = a_0(T) + \frac{1}{4\pi l^2} [K_m(T) - \Lambda^3 \sigma_{\text{BPL}}(T)]. \quad (27)$$

In other words, any other choice would violate Onsager's bookkeeping rule and in this way lead to inconsistency to exact quantum-statistical results.

There is still one complication which we have to mention: our calculations are so far based on the asymptotic representation (16) and not on the exact quantum-statistical expression (9). This however leads only to very small corrections at high temperatures $T > 10^5$ K. In the general case we find

$$\begin{aligned} a_0(T) &= \frac{\Lambda}{8} + \delta a_0 \\ \delta a_0 &= \frac{\Lambda^3}{8\pi\sqrt{\pi}l^2} \left[Q(-\xi) - \sqrt{2}K_0\left(-\frac{\xi}{\sqrt{2}}\right) \right] \\ &\quad - \frac{l}{12} \left[\ln(3\sqrt{2}\xi) + 2C - \frac{11}{6} \right]. \end{aligned} \quad (28)$$

The relative corrections to the first term are rather small and do not exceed 1% at 10^5 K. At high temperatures above $T \simeq 10^6$ K the deviations exceed 50% *i.e.* then the full expression for $a_0(T)$ must be used. At such high temperatures however we have always full ionisation and there is no need to study the Saha equation.

Let us summarize the two most interesting consistent choices of $a(T)$ and $K(T)$ which we have discussed so far:

- the Brillouin-Planck-Larkin mass action constant

$$K(T) = \lambda^3 \sigma_{\text{BPL}}(T) \quad (29)$$

in combination with a modified Debye Hückel diameter

$$a_{\text{BPL}}(T) = a_0(T) \simeq \frac{\Lambda}{8}; \quad (30)$$

- the traditional mass action constant based on a partition cut at the main quantum number $s = s_{\text{max}}$ in combination with the modified effective diameter $a_m(T)$ according to equation (28).

4 Statistical thermodynamics at finite densities

We formulate now approximate expressions for the free energy density in the chemical picture with a consistent choice of $a(T)$ and $\sigma(T)$. We denote the density of bound hydrogen atoms by n_0^* and the density of free electrons or ions by n^* . Then in the Debye-Hückel type approximation the free energy density is given by:

$$\beta f = n_0^* \left[\ln \left(\frac{n_0^* \Lambda_0^3}{\sigma(T)} \right) - 1 \right] + n^* \left[\ln \left((n^*)^2 \Lambda_1^3 \Lambda_2^3 \right) - 2 \right] - \frac{(\kappa^*)^3}{12\pi} \tau (\kappa^* a(T)) \quad (31)$$

where

$$\kappa^* = \left(\frac{8\pi n \times e^2}{kT} \right)^{1/2} \quad (32)$$

denotes the inverse Debye radius of the free charges and the Debye-Hückel function is defined by [3, 11]

$$\tau(x) = \frac{3}{x^3} \left[\ln(1+x) - x + \frac{x^2}{2} \right]. \quad (33)$$

The corresponding formula for the pressure is

$$\frac{p}{k_B T} = 2n^* + n_0^* - \frac{(\kappa^*)^3}{24\pi} \alpha^{3/2} \Phi(\kappa^* a(T)) + \dots \quad (34)$$

Here the Debye Hückel function Φ is defined as above.

The equilibrium composition is given by the non-ideal mass action law equation

$$\frac{n_0^*}{(n^*)^2} = \Lambda^3 \sigma(T) \exp \left(- \frac{l \kappa^*}{(1 + \kappa^* a(T))} \right) \quad (35)$$

where $l = \beta e^2 / \epsilon$ is the Bjerrum-Landau length.

The total number density of (positive/negative) charges is $n = n_0^* + n^*$ and the degree of ionisation is given by $\alpha = n^* / n$.

The general consistency relation between $\sigma(T)$ and $a(T)$ reads

$$\Lambda^3 \sigma(T) = \Lambda^3 \sigma_{\text{BPL}}(T) + 4\pi l^2 (a(T) - a_0(T)). \quad (36)$$

With the definition $y = a(T)/a_0(T)$ we may bring this balance relation into a more convenient form

$$\sigma(T) = \sigma_{\text{BPL}}(T) + \frac{1}{8} \xi^2 (y - 1). \quad (37)$$

This way we see, that in fact the parameter y is a free parameter in the definition of the partition function. The full partition function is linearly dependent on $y - 1$. In other words, $y - 1$ is a measure of the deviations of the used partition function from the BPL-partition function:

$$(y - 1) = 8\xi^{-2} (\sigma(T) - \sigma_{\text{BPL}}(T)). \quad (38)$$

So far we have assumed that the electrons, the ions and the atoms may be considered as ideal Boltzmann particles. Improving the model we will assume now that the electrons follow the Fermi statistics and that the atoms are spheres with radius R_H .

Introducing the degree of ionisation as the relation between number of free electrons and the total number of electrons

$$x = \frac{n^*}{n} \quad (39)$$

we find for the dimensionless free energy density in units of $k_B T$ as a function of the variables x and y the explicit form

$$\begin{aligned} \varphi(x, y) = & x k_e(x\nu) + x [\log x + \log \nu - 1] \\ & + (1-x) [\log(1-x) + \log \nu - 1 \\ & - \log(8\pi\sigma + 64\xi^2(y-1))] \\ & - \frac{2}{3} (8lx/\Lambda)^{3/2} (8\pi\nu)^{1/2} \tau \\ & \times \left(y(64\pi l\nu x/\Lambda)^{1/2} \right) + \varphi_{\text{vw}}. \end{aligned} \quad (40)$$

Here k_e denotes the standard Fermi function expressing the ideal electronic contribution to the free energy and $\nu = n\Lambda^3/2$ is the degree of degeneracy of the electrons. Furthermore we used the abbreviation φ_{vw} for the contribution of the short range van der Waals forces. We still have to specify this contribution due to the volume occupied by the atoms. As a first approximation we will assume here that the atoms are hard spheres with radius 0.82 Å and that electrons and ions have zero diameter; other values will not change the picture qualitatively. For our case we get

$$\varphi_{\text{vw}}(x, y; \nu) = \frac{16\pi R^3}{3\Lambda^3} \nu (x^2 - 3x + 2). \quad (41)$$

We see that from the point of view of the van der Waals repulsive interactions, full ionisation $x = 1$ is the most favourable state with respect to the free energy.

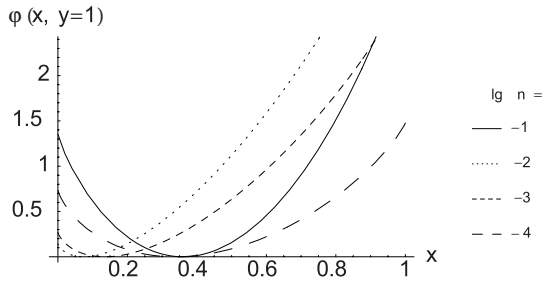


Fig. 1. Cross-section of the free energy landscape $\varphi(x, y)$ at $y = 1$ for $T = 50\,000$ K from $\nu = 10^{-4}$ to $\nu = 10^{-1}$. The minimum of the free energy with respect to x corresponds to the degree of ionisation. Increasing the density changes the degree of ionisation from medium to small values. The ionisation increases again at high densities as demonstrated here for $\nu = 10^{-1}$.

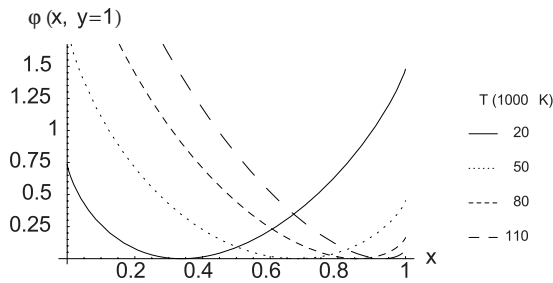


Fig. 2. Cross-section of the free energy landscape for $\nu = 10^{-4}$ from $T = 20\,000$ K to $T = 110\,000$ K. The minimum of the free energy with respect to x corresponds to the degree of ionisation. Increasing the temperature increases the degree of ionisation.

5 The free energy landscape and stationary partition functions

In the formulae given in the previous section, the choice of $K(T)$ and $a(T)$ (or correspondingly $\sigma(T)$ and y in the dimensionless writing) is still free within limits, as far as Onsager's bookkeeping rule is observed. The latter is expressed in equations (23, 37).

The standard choice is $a(T) = a_0(T)$ which corresponds to $y = 1$ [11, 17]. Fixing $a(T) = a_0(T)$ *i.e.* $y = 1$ the only free parameter in the free energy is the degree of ionisation. The minimum of the free energy with respect to variations of n^*

$$\frac{\partial(\beta f)}{\partial n^*} = 0 \quad (42)$$

or in dimensionless units with respect to x corresponds to the degree of ionisation

$$\alpha = x_{\min}. \quad (43)$$

For the choice $y = 1$ the minimum with respect to x is illustrated in Figures 1 and 2 for different values of the temperature and several densities. We may consider $\nu = n\Lambda^3/2$ as a measure of the dimensionless density.

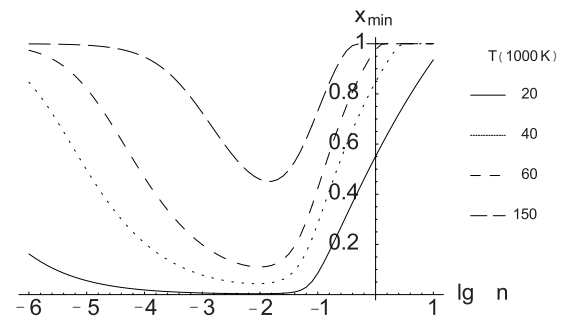


Fig. 3. Dependence of the degree of ionisation $\alpha = x_{\min}$ corresponding to the minimum of the free energy as a function of the dimensionless density. We see the valley of ionisation at medium densities which becomes flatter at higher temperatures. At very high densities $\nu > 1$ (in dimensionless units) the Fermi pressure of the electrons destroys the atoms and we observe full ionisation.

Figure 1 shows a cross-section of the free energy landscape $\varphi(x, y)$ with coordinate x as degree of ionisation and a fixed atomic radius $y = 1$ for a temperature of $T = 50\,000$ K and several densities from $\nu = 10^{-4}$ to $\nu = 10^{-1}$. By increasing the density from low values, *i.e.* $\nu = 10^{-4}$, to medium values, *i.e.* $\nu = 10^{-2}$, the minimum of the function $\varphi(x, y = 1)$ with respect to x , which in our model corresponds to the actual value of the degree of ionisation $\alpha = x_{\min}$, wanders from medium to low values of ionisation. That behaviour of the degree of ionisation is in agreement to studied real systems. For very high densities, *i.e.* $\nu = 10^{-1}$ and higher, the volume exclusion effect dominates and the large atoms become energetically unfavourable, which explains the jump of the minimum of φ from low to high values of x .

Figure 2 shows a cross-section of the free energy landscape $\varphi(x, y)$ with variable degree of ionisation x and a fixed effective radius $y = 1$ for a density of $\nu = 10^{-2}$ and different temperatures from $T = 20\,000$ K up to $T = 110\,000$ K. One can see the motion of the minimum of the free energy with respect to the ionisation degree to higher values when temperature is increasing. So the actual degree of ionisation $\alpha = x_{\min}$ increases with increasing temperature.

Figure 3 gives a compact overview over the behaviour of the model for a fixed effective radius $y = 1$ with regard to the external parameters temperature and density. It shows the positions of the minima of the free energy $\varphi(x, y = 1)$ for a fixed effective radius $y = 1$ with respect to the degree of ionisation x subject to the density ν in a range from $\nu = 10^{-6}$ to $\nu = 10$ for different temperatures. Thus the picture shows the dependency of the actual degree of ionisation α on the density for certain temperatures. The higher the temperature, the higher the ionisation is in general. For low densities the degree of ionisation is on a relatively high level, whereas for medium densities it drops down to quite small values, the so-called valley of ionisation, and rises rapidly to values close to unity for higher densities, where the volume exclusion

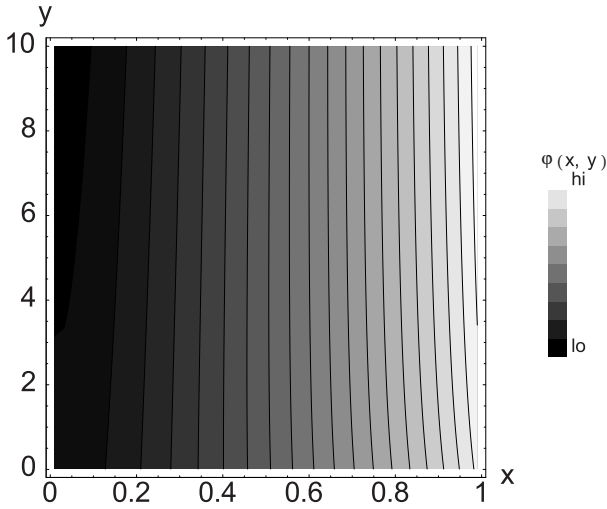


Fig. 4. Contour plot of the free energy $\varphi(x, y)$ for a small density $\nu = 10^{-4}$ and the temperature $T = 20000$ K. We observe a very long valley in the y -direction, which shows that the choice of y actually is of no importance for the ionisation equilibrium.

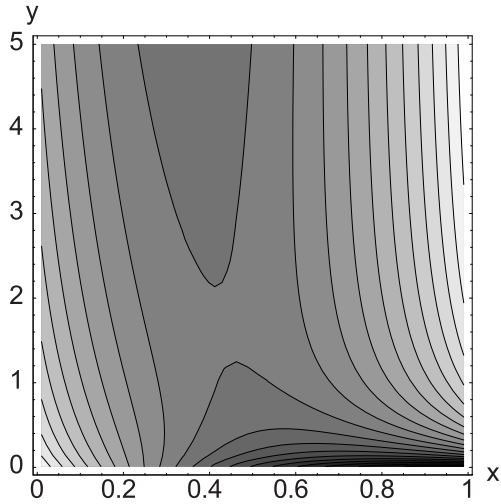


Fig. 5. Contour plot of the free energy $\varphi(x, y)$ for the density $\nu = 0.2$ and the temperature $T = 40000$ K. We see that at higher density a saddle point is formed which corresponds to points of stationarity with respect to the choice of y .

effect is the driving force for breaking the atoms to ions and free electrons.

As seen in Figures 4 and 5 changing the choice of the mass action constant and correspondingly the effective radius $a(T)$ or the parameter $y = a(T)/a_0(T)$ (both are connected by Eq. (37)) changes the location of the minimum of the free energy with respect to x . In other words the location of the minimum with respect to x (which gives the degree of ionisation) depends on the parameter y . By construction of our consistency condition equation (37) Onsager's condition is fulfilled in the limit of very small concentrations but already at moderate concentrations we

observe some sensitivity with respect to the choice of the mass action constant and the corresponding y -parameter. The sensitivity is small only near to the saddle points of the free energy surface which are the stationary values of the free energy density with respect to the degree of ionisation and with respect to the choice of the mass action constant. In the points of stationarity the variation with respect to the density of free ions equation (42) is zero and at the same time the variation with respect to the choice of the partition function disappears. This leads to the equation

$$\frac{\partial(\beta f)}{\partial \sigma} = 0. \quad (44)$$

Instead of varying σ we may also vary y since both quantities are linearly connected by Onsager's bookkeeping rule (37).

The variation with respect to n^* defined by equation (42) and applied to equation (31) leads back to our mass action law (35). The variation with respect to σ (44) leads to stationary values of σ or y respectively. In the limit of very small concentrations we find under the condition that Onsager's rule (37) is observed

$$\frac{\partial(\beta f)}{\partial \sigma} = O(n^3). \quad (45)$$

This relation guarantees that in the limit of small densities the condition of stationarity (44) is automatically fulfilled. In other words, due to the bookkeeping rule the linear variation disappears. Without observing the bookkeeping rule the stationarity is violated even in the limit of disappearing densities. In other words: bookkeeping at the level of the second virial coefficient guarantees the stationarity in the limit of small densities.

At moderate and at high densities the stationarity is not automatically given and we find some sensitivity with respect to the concrete choice of the mass action constant and the corresponding effective ion diameter. In order to come to a deeper understanding of this sensitivity we have to investigate systematically the free energy landscape as a function of the two variational parameters n^* and σ (or the corresponding y). It is useful to study the free energy landscape in the dimensionless form given above. The free energy per ion in units of kT is denoted by $\varphi(x, y; \xi, \nu)$. Here x, y are the variational parameters and the Born parameter ξ and dimensionless density $\nu = 0.5n\lambda^3$ serve as the (given) physical units for temperature and density. We remind again that the first variable x denotes the relation of free ion density to the total ion density the second variable denotes the choice of the partition function which is related to the parameter $y = a(T)/a_0(T)$ by our form of Onsager's balance relation (37).

Above we considered in some detail the special case $y = 1$ which occurs now as a special cross-section. This choice corresponds physically as shown above to the Brillouin-Planck-Larkin expression for the atomic partition function. At low densities this choice satisfies the condition of stationarity and leads to a maximum of simplicity

$$\sigma(T) = \sigma_{\text{BPL}}(T); \quad y = 1. \quad (46)$$

This choice is now more or less standard in plasma physics. However we should not forget that this is not the only choice and that we always should check the sensitivity with respect to the choice of the partition function which corresponds to the free parameter y in the definition of the partition function equation (37). This question is directly connected to the properties of the free energy landscape.

Therefore we will study now the 2-dimensional representations of ϕ which include the y -dependence. Figure 4 shows contour plots of the free energy on the x - y -plane for small densities ν and for different temperatures. We see at $T = 20\,000$ K a very long valley in the y -direction. In this case the free energy is nearly independent of y , what this means is that the exact choice of y is actually of no importance. At very high temperatures a strong minimum at rather high y values is observed which seems to be unphysical. Here the chemical picture fails since small changes of the partition function might have big effects. From this follows that at high temperatures the use of the Saha equation leads to intrinsic difficulties. In this temperature region one should better use the physical picture.

However at lower temperatures $T < 50\,000$ K and low densities the free energy surface is so flat (see Fig. 4), that it is practically stationary. Here there are no problems with the formulations of the Saha equation or with the choice of the mass action constant. The concrete choice of the mass action constant is practically of no influence. This of course is due to the fact that we observed Onsager's bookkeeping rule which is a guarantee for stationarity at low densities (see Eq. (44)). At higher densities the situation is much more complicated. Our numerical investigation shows that at high densities and $T > 50\,000$ K it is difficult to reach stationarity except for special values of ν . The conclusion might be that it is not meaningful to use a chemical picture at high densities and high temperatures. For $T < 50\,000$ K the picture is simpler. We find points of stationarity which are saddle points on the free energy surface. Figure 5 shows that for $T = 40\,000$ K with increasing density a saddle point is formed which corresponds to points of stationarity with respect to the choice of y and the corresponding σ . By using mass action constants in the region of the saddle points we can guarantee that the thermodynamic functions are not sensitive with respect to the concrete choice. In regions far from the saddle point the stationarity with respect to the choice of y or the corresponding mass action constant is not guaranteed. This means that the use of a Saha equation may generate artefacts here.

Figures 6 and 7 show the dependence of free energy saddle point location on the dimensionless density ν for temperatures $T = 20\,000$ K and $T = 40\,000$ K. In dependence on the dimensionless density ν . In Figure 6 we represented the found saddle points and their position in the x - y -plane for a temperature of $T = 20\,000$ K and densities in a range of $\lg(\nu) = -1.4$ to $\nu = 1$. At a density of approx. $\lg(\nu) = -1.4$ a saddle point occurs in the free energy landscape on the left hand side of the lower edge of the region, *i.e.* $y = 0$, and then moves with increasing density in a curved line to higher values of y and x .

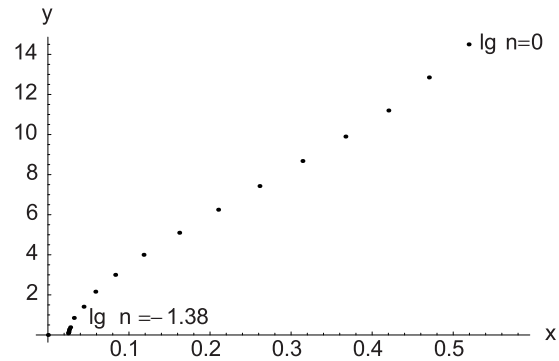


Fig. 6. Dependence of free energy saddle point location on the dimensionless density ν for temperature $T = 20\,000$ K.

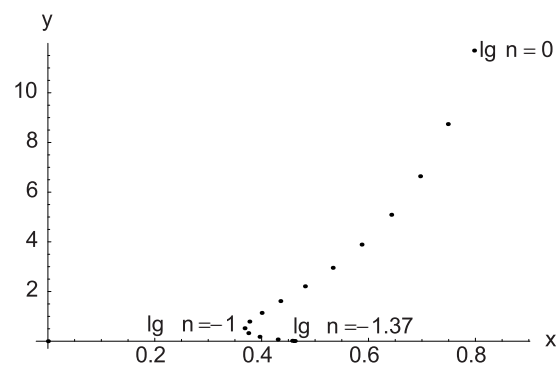


Fig. 7. Dependence of free energy saddle point location on the dimensionless density ν for temperature $T = 40\,000$ K.

For the temperature $T = 40\,000$ K the saddle points in the free energy landscape occur at a density of approximately $\lg(\nu) = -1.4$ in the middle of the lower edge of the region and then they move with increasing density in a curved line. We may use these results as a kind of recipe: for a given density we find the y -value corresponding to a saddle point. Then using this we find the stationary values of the partition function and the mass action constant (corresponding to the given saddle point) from equation (37) and $K(T) = \Lambda^3 \sigma(T)$. Finally we get the stationary value of the effective radius $a(T) = a_0(T)y$. With these choices the stationarity of the free energy and other thermodynamic functions are guaranteed. By using any other choice for the mass action constant we take the risk that the thermodynamic functions might strongly change with any variation of the mass action constant. Following Onsager, this is an unphysical effect, an artefact which should be avoided. Strictly speaking the chemical picture of plasmas makes no sense if the condition of stationarity with respect to the choice of the mass action constant is violated.

6 Discussion and conclusions

At first several remarks about the character of the approximations used here seem to be necessary. All results given in this work are exact up to the second order in the

density. This is the approximation of the second virial coefficient which is the next step beyond the simple Debye law. The bookkeeping according to Onsager is indeed heavily based on the available expressions for the virial functions. The terms beyond the second virial functions are based on Debye-Hückel-type approximations for the high-density behavior. Therefore a few remarks about the Debye-Hückel approximation may be appropriate:

- the old Debye-Hückel cannot be considered as old-fashioned, it is still a powerful instrument and found recently interesting applications and developments (see [5, 18, 19]);
- the variant of the Debye-Hückel theory used here is in fact not a classical theory. We use exact quantum-statistical results up to the second order in the density;
- the Debye-Hückel functions serve only for an approximate guess of the higher orders in the density which are not known from quantum-statistical calculations. They provide us with expressions for the higher-order density dependence which are relatively simple and allow analytical calculations.

A consequent extension to higher order terms in the density may be based on Padé approximations in combination with numerical results obtained by Quantum Monte-Carlo and Quantum Molecular Dynamics (see [12, 19–21]). This method allows, in principle, access to different thermodynamic properties in wide ranges of density and temperature. A disadvantage is however, that the Padé approximations are – as a rule – quite complicated, so that analytical calculations require big efforts. Furthermore in order to give a proper description of thermodynamic equilibrium within the Padé approximation in the chemical picture (PACH) for given temperature and density one has to minimize the free energy with respect to the abundances of the various free and composite particles. We may achieve this only numerically by a simulated annealing procedure [19] that finds the optimal numbers of free and composite particles within a certain ensemble. We plan to go this way in future work but here we are more interested in qualitative and semi-quantitative results which are relatively easily obtained within the Debye-Hückel formalism.

Now let us draw several conclusions: we have shown that the chemical description of partially ionized plasmas may be generalized in a systematic way by using the available information from quantum statistics. An important role is played here by Onsager's bookkeeping rule, which provides us the tools for a correct formulation of the chemical picture. The key idea of Onsager is that in a correct theory, the details of the distinction between free and bound states have only a minor influence on the results. We have shown here that this condition is fulfilled automatically at small densities, if Onsager's book-keeping rule is observed. At higher densities the situation is quite complicated as we have shown here by an extensive numerical study of the free energy landscape. Here the only way to reach independence of the free energy with respect to the free parameters in the chemical picture is to search for stationary points on the free energy surface. As we have demonstrated here (see Figs. 5–7) the stationary points

are in general saddle points. Operating on these saddle points, *i.e.* using a corresponding choice of the mass action constant, we may expect that the resulting physical thermodynamic quantities do not depend on the concrete choice of the mass action constant. For any other choice the results may depend on the definition of the mass action constant. Of course, this cannot be accepted in the framework of a good theory. Therefore we come to the conclusion that at high density the chemical picture has to be treated with much care. The recipe that we propose here, is to make sure that the results are stationary with respect to the concrete choice of the mass action constant. We have demonstrated here that this is indeed possible, since the free energy surface possesses saddle points which correspond to stationarity. Summarizing we may say that the chemical picture which is so successful at low densities comes to limits of applicability at high densities. Working with the chemical picture at high densities requires much care, needing always comparison with existing numerical data [19, 21] and in all cases, we have to make sure that the results are stationary with respect to the concrete choice of the constants of chemical equilibrium. Our critical analysis of the chemical picture for plasmas has shown that Onsager's condition of insensitivity (stationarity) with respect to the concrete choice of the mass action constant plays an important role. At low density this stationarity is automatically fulfilled if the bookkeeping between bound and free state contributions is observed (Onsager's book-keeping rule). At high densities however, bookkeeping is not sufficient to provide the required insensitivity. We have to search for the stationary points (saddle points) and this is, in general, not a trivial task. We repeat again, that the use of the chemical picture of plasmas, which is so useful for many applications of practical interest, requires much care to guarantee that the thermodynamics is physically meaningful.

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