

Article

Hydrogen-, Helium-, and Lithium-like Bound States in Classical and Quantum Plasmas [†]

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[†] Dedicated to the late Günter Kelbg (1922–1988) on the occasion of his 100th birthday.

Abstract: We study the effective interactions and the mass action constants for pair and triple associations in classical and quantum plasmas. Avoiding double counting, we derive new expressions for the mass action constants. The calculations resulted in values that were substantially smaller than the standard ones in relevant temperature ranges by up to 50 percent. On this basis, we determine the pressure of H, He and Li plasmas and the osmotic coefficient of electrolytes with higher charges such as, e.g., seawater. Classical and quantum Coulomb systems show strong similarities. The contributions in low orders with respect to the interaction e^2 are suppressed by thermal and screening effects. The contributions of weakly bound states, near the continuum edge, to the mass action constants are reduced, replacing the exponential functions with cropped exponentials. The new mass action constants are consistent with well-known extended limiting cases of screening effects. We analyze classical examples including the salts CaCl_2 and LaCl_3 , and a model of seawater including multiple associations. In the case of quantum systems, we follow the work of Planck–Brillouin–Larkin for H plasmas and study He and Li plasmas. The equation of state (EoS) for wide-density regions is obtained through the concatenation of the EoS for the low-density region of partial ionization with the EoS of degenerate plasmas, where all bound states are dissolved and Fermi, Hartree–Fock and Wigner contributions dominate.

Keywords: statistical thermodynamics; few-body bound states; mass action constants; equation of state; bound state valley



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1. Introduction: Effective Interactions

Charged-particle systems are interesting objects of statistical physics, which show special features because of the long-range characteristic of the Coulomb interaction. Important examples include plasmas and electrolytes. Bound states or associations may be formed, and the composition is described by mass action laws. The correct introduction of association or ionization constants in plasmas and electrolytes is the main topic of the present work. For pair associations in plasmas (atom formation), this problem has already been solved by Max Planck in 1924 [1] for H plasmas, as outlined below in this section. The calculation of bound states in dense He or Li plasmas and the corresponding mass action laws is a difficult task of quantum statistics. We discuss descriptions at the physical and chemical levels in Section 2. After considering the classical osmotic pressure and the chemical potential including associations in Section 3, mass action constants for He and Li plasmas including excited states are derived in Section 4. Thermodynamic functions, such as pressure, for quantum plasmas including the bound state formation are presented in Section 5.

Within a chemical picture where bound states of the elementary particles are considered as new species, our charged-particle systems consist of different constituents i with charge $Z_i e$ (e is the elementary charge) and particle density n_i . In plasmas, these are nuclei, electrons, and ions as bound states with different degrees of ionization; in electrolytes we

have ions and associations. At larger distances, the forces between charges in plasmas and in electrolytes are basically the same as Coulombic forces:

$$\beta V_{ij} = \frac{\ell_{ij}}{r}; \quad \ell_{ij} = Z_i Z_j \ell, \quad \beta = \frac{1}{k_B T}, \quad \ell = \frac{\beta e^2}{4\pi\epsilon}. \quad (1)$$

where ℓ_{ij} is the Coulomb length and $\epsilon = \epsilon_r \epsilon_0$ is the dielectric constant with the relative dielectric constant ϵ_r . There is a difference between standard chemical and Coulomb binding:

- (1) Chemical forces are short-range and show strict saturation. For example, a hydrogen atom may bind with second one by chemical binding forming the H_2 molecule, but there is no way to bind a third one with the same-strength force.
- (2) Coulomb forces are long-range and are strictly additive; this is limited only by the tendency to form neutral configurations.

Most attention is, in this work, devoted to electrolytes and plasmas [2–4]. Another interesting example for association and bound-state formation is the quark-gluon plasma. Hadrons, which are color-neutral bound states of quarks, become dissolved at high energy densities, forming a new state of matter, which can be found, for example, in ultrarelativistic heavy ion collisions [5] or in the cores of neutron stars [6].

The application of mass action laws is standard for chemical binding, but it also works with modifications for Coulomb associations, as already shown by Arrhenius, Ostwald, Planck and Bjerrum [2,7,8]. To explore the limits of mass action laws and the peculiarities of binding by Coulomb forces is the aim of the present work. We show that the essence of this is the transition from the traditional exponentials in the mass action constants for chemical binding to the cropped exponentials, which reduces the contributions from weakly bound states with binding energies smaller $k_B T$ and considerably weakens associations.

The Coulomb force may be positive or negative depending on the charges that meet. Since, on average, positive charges are surrounded by negative charges and negative charges by positive ones, the Coulomb forces are, on average, screened within the Debye distances $r_D = 1/\kappa$ with $\kappa^2 = 4\pi\ell \sum_i Z_i^2 n_i$, where the sum over i concerns all ion species and electrons.

Within statistical physics, screening effects are due to contributions of the so-called ring diagrams. Since screening is a primary effect, all other effects in Coulomb systems, in particular the association effects, have to be treated in a way which is compatible with screening. In particular, naive definitions of mass action constants and mass action laws for Coulombic associations and ionization lead to internal contradictions and possibly to errors. Here, we will discuss the problem based on strict principles of statistical physics, which are compatible with the findings of Planck and Onsager. We show, in particular, that one should not include terms in the mass action constant, which have already been taken into account to obtain Debye's limiting law. Double counting leads to errors and has to be strictly avoided. This problem will be solved in the present work for classical $MgSO_4^-$, $CaCl_2^-$, $LaCl_3^-$ -like systems and in the quantum case for H, He and Li-like associations/ionization. In fact, Planck was the first to show [1] that in the bound-state part of the atomic partition function of Hydrogen the following characteristic expressions should appear,

$$\exp[-(\beta E_s^H)] - 1 + (\beta E_s^H). \quad (2)$$

Here, this is denoted by cropped exponential function, instead of the simple exponential $\exp[-(\beta E_s^H)]$. E_s^H is the binding energy of the intrinsic quantum state denoted by the quantum number s , in the case of the H atom $E_s^H = -1/s^2$ Ry (1 Ry = 13.60568 eV).

The introduction of a cropped exponential, which starts only with the second-order Taylor expansion, leads to the so-called Planck–Brillouin–Larkin partition function (PBL)

$$\sigma_H(T) = 2 \sum_{s=1}^{\infty} s^2 \left[e^{-E_s^H/k_B T} - 1 + \frac{E_s^H}{k_B T} \right]. \quad (3)$$

The factor $2s^2$ is the well-known degeneracy of the energy level E_s^H for the H atom. In the case of classical ions, we obtain structurally similar expressions [9], which we discuss in detail later. The transition from exponential functions to cropped exponentials reduces the contributions from bound states with binding energies near to the series limit, which are smaller than the thermal energy $|E_s^H| < k_B T$ or the extension of the bound-state electron density is larger than the Debye radius. The main reasons for the suppression of these states are:

- (i) The discrete states near to the continuum edge are not stable due to thermal collisions and screening effects;
- (ii) the contribution of these states is compensated by contributions of nearby states in the continuum;
- (iii) the discrete states near to the continuum edge are also destroyed if the wave functions are larger than the Debye length.

and therefore the Debye potential leads to a gap of energy levels near to the continuum. While PBL-type partition functions are generally accepted nowadays, the corresponding partition function for classical ionic pairs is still under discussion and the relation to the quantum problem is mainly ignored [2–4,7–13]. So far, the association problem for triple and higher associations has not been solved completely either. Our main task here is to propose new compatible partition functions and mass action constants for triple and quadruple associations in Coulombic systems.

The forces at short distances of ions are mainly repulsive since determined by the internal electronic shells. We introduce a potential of mean forces between the ions i and j as ψ_{ij} . In electrolytes the average forces at zero concentrations are defined by means of the Mc Millan–Mayer theory [2,7,9,12]. In plasmas, i.e., for charges imbedded into a vacuum, we follow the pioneering work of Günter Kelbg [3,4,11,13] and find an effective average potential of pair interactions from the binary Slater sums [14–16]

$$\psi_{ij} = -k_B T \ln S_{ij}(r_1, r_2), \quad (4)$$

where S_{ij} are the diagonal elements of the density matrix of pairs. The concept of Slater sums had been introduced by Slater and Morita, and was further investigated and applied to Coulombic systems by Günter Kelbg and his school [3,4,11,14,15]. In the classical as well as in the quantum case, the potentials of statistical averaged forces consist of a Coulombic and a short-range part. The electronic part of electrolytes is given by Coulomb's law, Equation (1). Both $\epsilon_r(T, p)$, the relative dielectric constant of pure water, and ℓ , the so-called Landau length or with the pre-factor 0.5 the Bjerrum length, are functions of temperature and pressure. The short-range forces can be modeled to be of hard-core type, where R_{ij} are the contact distances. Here, we will stick to this rough approximation since the R_{ij} comprises the most important key information for ionic solutions. For plasmas, the short-range forces are weaker and do not have a hard core contribution. An approximate description is given by the so-called Kelbg–Deutsch potential [14,15,17]

$$\psi_{ij}^{K-D}(r) = \frac{Z_i Z_j e^2}{4\pi\epsilon r} \left[\left(1 - \exp\left(-\frac{r}{\lambda_{ij}}\right) \right) \pm \frac{\delta_{ij}}{2} \exp\left(-\frac{r}{\lambda_{ij}}\right)^2 \right]; \quad \lambda_{ij} = \frac{(h/2\pi)}{(2m_{ij}k_B T)^{1/2}} \quad (5)$$

where $m_{ij} = m_i m_j / (m_i + m_j)$ are the relative mass and λ_{ij} is the so-called thermal De Broglie wave lengths. The \pm sign refers to fermions and bosons, respectively. Note that in Kelbg's exact expression generalized hypergeometric functions appear instead of exponentials [3,4]. The quantum effective potential has a finite value at zero distance [15]. Some approximate values for the characteristic lengths R_{ij} , λ_{ij} for electrolytes and corresponding lengths λ_{ij} for quantum systems are given in Table 1, in the quantum case for a typical temperature of 10^4 K.

Table 1. Table of contact distances for several ion pairs including alkaline earth metal ions, sulfate ions and adapted “ideal” seawater ions according to [18]. Further we give for quantum plasmas some typical values of the De Broglie thermal wavelength at $T = 10^4$ K (all length given in pm).

$i - j$	R_{\pm}	R_{++}	R_{--}	$i - j$	λ_{\pm}	λ_{++}	λ_{--}
$Na - Cl$	350	470	360	$H^+ - e$	204	7.4	297
$K - Cl$	320	400	360	$He^{2+} - e$	203	5.3	297
$Mg - Cl$	400	280	360	$Li^{3+} - e$	202	4.3	297
$Ca - Cl$	500	320	360				
$K - SO_4$	340	400	300				
$Mg - SO_4$	290	400	300				
$La - Cl$	270	430	360				

We consider plasmas of the light elements hydrogen, helium and lithium, and note that the role of a smallest distance between electrons and positive charges is, at lower temperatures, determined by the temperature independent Bohr radii

$$a_B^H = 52.9 \text{ pm}; \quad a_B^{He} = 26.4 \text{ pm}; \quad a_B^{Li} = 13.2 \text{ pm}. \quad (6)$$

For H, He and Li the lowest-bound states, the hydrogen, helium and lithium atoms consist of 2–4 charged particles. The outer electrons are only loosely bound with ionization energies in the range of 10–100 eV. For the full thermal ionization of all helium or lithium electrons we need far more than 100 eV, i.e., more than 10^6 K. An alternative way to reach high ionization degrees is to increase the particle density to regions of $n > 10^{23} \text{ cm}^{-3}$ where all atomic and molecular bound states are dissolved by screening, Pauli blocking effects and pressure ionization [15,19–21]. Earlier work to describe high-density and high-pressure effects was often based on the chemical picture [19]. In contrast to the physical picture, which normally uses perturbation expansions, the chemical picture is using chemical mass action laws (MAL) and has the advantage that it is based on a variational principle [12,16].

For electrolytes, the applicability of the physical and chemical picture has also been discussed in the literature [2,7–9,12,22,23]. The main task of the present work is to develop mass action constants for triple and higher associations, which are consistent with screening effects and avoid any double counting of Coulombic effects. Standard approaches to association effects in electrolytes, in particular with multiple charged ions, are usually based on the classical concepts of Bjerrum, Fuoss and Kraus [2,7]. While these authors define pairs and triplets as spatially defined special configurations, our concept of associations is not based on a spatial criteria but on the strength of the interaction. This is measured in powers of the Bjerrum interaction parameter $b = (Ze^2 / \epsilon k_B TR)$, and, in the quantum case, the corresponding $(Ze^2 / \epsilon k_B T \lambda)$ or $(Ze^2 / \epsilon k_B T a_B)$. This way we avoid any double counting of Coulombic effects. As Onsager pointed out in 1968 at a conference in Montpellier, one has to consider the correct balance between various effects like in a ledger, but having some freedom in the definition of associations and mass action constants. Using the freedom in the choice of the mass action constant, we assume that associations are formed by higher-order (negative) contributions of binary charge interactions b^n with $n \geq 4$ to the pressure and other thermodynamic functions. Triple or quadruple associations are generated by (negative) contributions of three or four opposite charges. by higher orders in the interaction e^2 , etc., to the pressure. Such a definition of associations may seem less transparent in comparison with spatial definitions; however, it allows one to integrate screening. Therefore, this concept is easier to introduce in the light of statistical thermodynamics, which has been working with expansions in e^2 since the pioneering work of Joseph Mayer. Our concepts were first developed for electrolytes in [2,9]. Alternative concepts of electrostatic associations have been considered in many works [24–26]. The basic concepts for the quantum case are due to Planck, Brillouin and Larkin [1,15] and

are connected with several quantum effects affecting the states with near to zero binding energy, which leads to the cropped partition functions introduced above.

The influence of an electrostatic pair and triple associations of ions is of high relevance for many real electrolytic systems with higher ionic charges as MgSO_4 , MgCl_2 or Na_2SO_4 , in particular in studies of seawater, which is the most relevant associating electrolyte in nature [18]. In the quantum case, it is the sun plasma, which plays a central role for life on earth and is connected with multiply charged ions, such as He^{2+} or Li^{3+} , forming bound states. Note that for systems with multiply charged ions the differences between the individual and the mean activities are larger than usual [7], which requires special attention to the influence of charge asymmetry on the individual ionic activities. Most of our studies are restricted to weakly associating systems, where less than about 1/3 of the charges are associated, and where a quasi-linear (semi-chemical) approach to the mass action law works.

2. Physical and Chemical Level of Descriptions

2.1. Virial Expansions and Mass Action Constants

Let us assume we have an associating system forming bound states. In the low-density limit, we consider the approximation of an ideal mixture of different components, neglecting all interactions with the exception of reactive collisions to establish chemical equilibrium. This chemical level is described by mass action laws which relate the free particle densities n_i^* of the different components in chemical equilibrium, introducing mass action constants $K_i(T)$ which depend only on temperature T .

As an example, we consider H, He and Li plasmas. For H plasmas with components e , H^+ , and H , the composition is given in the approximation of ideal systems by the mass action law

$$n_{\text{H}}^* = n_e^* n_{\text{H}^+}^* K_{\text{H}}(T). \quad (7)$$

For He plasmas, we have the components e , He^{++} , He^+ , and neutral He with two ideal mass action laws

$$n_{\text{He}^+}^* = n_e^* n_{\text{He}^{++}}^* K_{\text{He}^+}(T), \quad n_{\text{He}}^* = n_e^{*2} n_{\text{He}^{++}}^* K_{\text{He}}(T). \quad (8)$$

For Li plasmas with components e , Li^{3+} , Li^{++} , Li^+ , and Li , we have three ideal mass action laws

$$n_{\text{Li}^{++}}^* = n_e^* n_{\text{Li}^{3+}}^* K_{\text{Li}^{++}}(T), \quad n_{\text{Li}^+}^* = n_e^{*2} n_{\text{Li}^{3+}}^* K_{\text{Li}^+}(T), \quad n_{\text{Li}}^* = n_e^{*3} n_{\text{Li}^{3+}}^* K_{\text{Li}}(T). \quad (9)$$

Note that the asterisks denote the free particle densities. The total particle densities would contain also the contribution of the bound states; see Section 4.

The thermodynamic properties of these plasmas are easily obtained if we use the approximation of ideal associating plasmas within a chemical picture. The EoSs for the pressure are given approximately by [21]

$$\begin{aligned} \beta p^{\text{H}} &= n_e^* + n_{\text{H}^+}^* + n_{\text{H}}^*, \\ \beta p^{\text{He}} &= n_e^* + n_{\text{He}^{++}}^* + n_{\text{He}^+}^* + n_{\text{He}}^*, \\ \beta p^{\text{Li}} &= n_e^* + n_{\text{Li}^{3+}}^* + n_{\text{Li}^{++}}^* + n_{\text{Li}^+}^* + n_{\text{Li}}^*. \end{aligned} \quad (10)$$

For the pressure as function of density and temperature, virial expansions are known where virial coefficients are introduced. For interacting plasmas/electrolytes, we may expect that this virial expansion remains valid, except that now additional interaction terms will appear. Because of the long-range character of the Coulomb interaction, a series expansion in powers of densities is not possible, and additional terms with broken exponents and logarithmic terms appear; see [15]. Inserting the mass action laws (7)–(9) into Equation (10), we see that the mass action constants are connected with the coefficients in

the virial expansion. However, the virial coefficients for the interacting plasma contain also contributions from scattering states, in addition to the bound state contributions described by the mass action law.

We may conclude that any realistic virial expansion, which includes bound states will include important information about the association constants, which appear as essential parts of the virial coefficients. The terms corresponding to mass action constants should be positive and strongly increasing at low temperatures. For Coulombic systems, the statistical expressions for the pressure may be obtained from derivatives of the free energy which follows from statistical thermodynamics in the form of cluster contributions. The negative free excess energy of classical charged hard spheres and, quite similar, non-degenerate plasma reads in the quantum case [2,12,20]

$$F_{\text{ex}} = F_{\text{DH}} + F_2 + F_3 + \dots = -k_B T V \left[\frac{\kappa^3}{12\pi} \sum_{ij} \zeta_i^0 \zeta_j^0 R(\kappa \lambda_{ij}) + \sum_{i,k} S_i^{(k)} \right] \quad (11)$$

where R_{ij} in the classical case is now replaced by λ_{ij} . $R(x)$ is the so-called ring function in the Debye-Hückel-like approximation and ζ_i^0 are Onsager's relative screening factors defined according to [18,20] as

$$\text{quantum case : } R(x) = 1 - \frac{3}{16} \sqrt{\pi} x + \frac{1}{10} x^2 - \dots \quad (12)$$

$$\text{classical case : } R(x) = 1 - \frac{3}{4} x + \frac{3}{5} x^2 - \dots, \quad (13)$$

$$\zeta_i^0 = \frac{n_i e_i^2}{\sum_j n_j e_j^2}. \quad (14)$$

The sums are to be extended over the species of ions i and all orders of clusters k . The corresponding diagrams modelling screening are of ring-type, called Mayer's ring diagrams. Contributions, which are used for generating screening in Coulomb systems should not appear again in second, third and higher cluster integrals. This is the reason for subtracting certain terms in the cluster integrals. Therefore, the mass action constants for Coulombic systems have a specific structure, they exclude the lower powers in the interaction parameters.

Since we are mainly interested in association effects, we apply the following approximations [20] by introducing the so-called opposite charge approximation (some times called reduced mass approximation). We replace all reduced masses and distances with the plus-minus parameters

$$m_{ij} \rightarrow \mu = \frac{m_+ m_-}{m_+ + m_-}, \quad R_{ij} \rightarrow R = R_{\pm}; \quad \lambda_{ij} \rightarrow \lambda = \lambda_{\pm}. \quad (15)$$

This is physically justified by the fact, that in associating systems most encounters are of plus-minus type. Technically, this gives large simplifications [16,20]. We assume here that only one kind of \pm pairs exists. The strong coupling contributions to the cluster functions $S_i^{(k)}$ were derived in the framework of a quasi-classical cluster expansion for clusters of order $k = 2, 3, 4, \dots$, which are formed by ions of kind i , and are given as [2,12,16]

$$\begin{aligned} S_i^{(2)} &= \frac{1}{2} n_i \sum_j n_j \int d\mathbf{r}_j [\psi_{ij} - \frac{1}{2} G_{ij}^2], \\ S_i^{(3)} &= \frac{1}{2 \cdot 3} n_i \sum_{jk} n_j n_k \int d\mathbf{r}_j d\mathbf{r}_k [\psi_{ij} \psi_{ik} \psi_{jk} + G_{ij} \psi_{ik} \psi_{jk} + G_{ik} \psi_{ij} \psi_{jk} + G_{kj} \psi_{ik} \psi_{ij}], \\ S_i^{(4)} &= \frac{1}{2 \cdot 3 \cdot 4} n_i \sum_{jkl} n_j n_k n_l \int d\mathbf{r}_j d\mathbf{r}_k d\mathbf{r}_l [\psi_{ij} \psi_{jk} \psi_{kl} \psi_{il} + \dots]. \end{aligned} \quad (16)$$

with the definitions

$$\psi_{ij} = \exp[G_{ij} - \beta V'_{ij}] - 1 - G_{ij}; \quad G_{ij}(r) = -Z_i Z_j \ell \frac{\exp(-\kappa R_{ij} - \kappa r)}{(1 + \kappa R_{ij})}. \quad (17)$$

Here, the strong coupling function ψ_{ij} is of higher-order $O(e^4)$ in the interactions. V'_{ij} is the hard-core potential and the Kelbg potential in the classical and the quantum case, respectively. In the following, we are using the so-called nonlinear Debye-Hückel approximation for charged hard spheres [18,23]. In the quantum case, the exponential functions in ψ_{ij} are replaced by the Slater functions [15,16]. The density-dependent expression for the pressure derived from the free energy reads in the quantum case is [2,9,15,16]

$$\begin{aligned} \beta p(n_1, n_2, \dots, T) = \sum_i n_i \left[1 - \frac{Z_i^2}{6\kappa} \sum_j \zeta_j \bar{R}(\kappa \lambda_{ij}) - 2\pi \sum_j n_j \lambda_{ij}^3 \left(\bar{G}_{ij}(\kappa) + K_{20}(\zeta_{ij}) \right) \right. \\ \left. - 8\pi^2 \sum_{ik} n_j \lambda_{ij}^3 n_k \lambda_{ik}^3 \left(\bar{G}_{ijk}(\kappa) + K_{30}(\zeta_{ij}, \zeta_{ik}, \zeta_{jk}) \right) \right. \\ \left. - 4\pi^3 \sum_{ikl} n_j \lambda_{ij}^3 n_k \lambda_{ik}^3 n_l \lambda_{il}^3 \left(\bar{G}_{ijkl}(\kappa) + K_{40}(\zeta_{ij}, \zeta_{ik}, \zeta_{il}, \dots) \right) + \dots \right]. \end{aligned} \quad (18)$$

In the classical case, the λ_{ab} are replaced by R_{ab} . The temperature functions $K_{20}(\zeta)$, $K_{30}(\zeta)$ and $K_{40}(\zeta)$ describe in the classical and in the quantum case the two- and three- particle bound states [2,9,15,16]. Further we have $\bar{R}(x) = R(x) + xR'(x)$ with $R(x)$ defined above. The functions \bar{G} are weakly depending on κ and not relevant for binding. Now, the problem is to isolate the mass action contributions, i.e., the bound state parts, is to identify these terms in the general cluster expansion. According to our basic assumption, the mass action constants $K^{(2)}$, $K^{(3)}$ etc. are the positive definite even parts of the functions $K_{20}(\zeta)$, $K_{30}(\zeta)$, $K_{40}(\zeta)$, which are dominant for strong binding, e.g.,

$$4\pi^{3/2} \lambda_{\pm}^3 K_{20}(\zeta_{\pm}) = K_{+,-}^{(2)} + \delta; \quad 8\pi^2 \lambda_{\pm}^6 K_{30}(\zeta_{2+,-}, \zeta_{--}) = K_{-2+,-}^{(3)} + \delta. \quad (19)$$

with δ asymptotically small for strong binding. The lower orders in interaction up to e^4 automatically do not contribute to the mass action constant, due to our way of construction.

For pair associations, the most useful splitting for the classical as well as for the quantum case is given in [15,16]. It is based on exact relations valid for the K-functions for pairs with opposite charges as

$$[K_{20}(\zeta) + K_{20}(-\zeta)]/2 = m(\zeta); \quad [K_{20}(\zeta) + K_{20}(-\zeta)]/2 = \sqrt{\pi} \sigma(\zeta). \quad (20)$$

This means that the even part of the function $K_{20}(\zeta_{\pm})$ defines the bound state part m and σ of the pair partition functions in the classical and the quantum case, respectively.

$$m(x) = \sum_{k=2}^{\infty} \frac{\zeta^{2k}}{(2k)!(2k-3)}; \quad \sigma(\zeta) = \sum_{k=2}^{\infty} \frac{\zeta(2k-1)\zeta^{2k}}{(2k)!}. \quad (21)$$

The mass action constants for pair formation are

$$K_{\pm}^{(2)} = 8\pi R_{\pm}^3 m(\zeta_{\pm}); \quad K_{\pm}^{(2)} = 8\pi^{3/2} \lambda_{\pm}^3 \sigma(\zeta_{\pm}). \quad (22)$$

We see that in both cases the mass action constants are defined by the bound state parts of the virial function and have a quite characteristic similar structure. Along this line our hypothesis is, that the even parts of the K_{30} and K_{40} functions, are basically responsible for the formation of triples and quadruples.

For example, we assume that the mass action constant for He-like triple bound states is given by the trace over the states relative to the center of mass

$$K_{(2+),2-}^{(3)} \sim \text{Tr}_{rel}'' \exp[-\beta H_{(2+),2-}^{(3)}] \sim [K_{30}(\xi_{\pm}, \xi_{--}) + K_{30}(-\xi_{\pm}, \xi_{--})]/2 \quad (23)$$

Here, the double dash means that by performing the relative trace all divergent states have to be identified and omitted.

2.2. Mass Action Functions for Coulombic Pairs

No doubt, nature is unique and cannot be divided into physical or chemical systems. Nevertheless, physicists and chemists look at natural systems in a quite different way. Physicists like elementary units like electrons, nuclei or bare ions. Chemists like to speak about more complex chemical units like atoms and molecules. According to classical equilibrium thermodynamics, the mass action constant for chemical binding is

$$K(T) \sim \exp[-\Delta G/k_B T] \quad (24)$$

where ΔG is the change of the Gibbs potential in the reaction, which is approximately given by the effective bound state energy E_B of the associate. For all quantum bound states studied here, the binding energy is $E_B = C \text{ Ry}$ with $C = 1$ for hydrogen, i.e., the bound state energy is proportional to e^4 and the mass action constant proportional to $\exp(Ce^4/k_B T)$. However, as already mentioned, we may expect some peculiarities for Coulomb binding with respect to the dependence on e^2 .

For the hydrogen-like association, (24) leads to

$$K_H(T) = 8\pi^{3/2} \lambda_{\pm}^3 \sum_s s^2 \exp(-\beta E_s^H) = 8\pi^{3/2} \lambda_{\pm}^3 \sum_{s=1}^{\infty} s^2 \left[1 - \frac{\beta E_B}{s^2} + \frac{(\beta E_B)^2}{2!s^4} - \frac{(\beta E_B)^3}{3!s^6} + \dots \right]. \quad (25)$$

Max Planck showed in 1924 that the first two terms in this series are compensated for by contributions from the continuum of relative states and therefore should be omitted. So, we arrive at cropped exponentials and get the new mass action constant for the formation of H-atoms

$$K_H(T) = (2\sqrt{\pi} \lambda_{ei})^3 \sum_s s^2 [\exp(-\beta E_s^H) - 1 - \beta E_s^H] = (2\sqrt{\pi} \lambda_{ei})^3 \sum_s \left[\frac{(\beta E_B)^2}{2!s^2} - \frac{(\beta E_B)^3}{3!s^4} + \dots \right]. \quad (26)$$

The question is whether we have the freedom to go from the classical ansatz using the exponential function (25) to a different expression based on the cropped exponential (26) for Coulombic systems. Onsager's argument from 1968 that we have principally some freedom in the exact definition of mass action constants as far as we observe the balance of the total contributions to pressure, free energy, etc., was a comment on a famous historical controversy about the correctness of theoretical expressions for the mass-action constant of ion association in electrolytes, connected with names like Bjerrum, Fuoss, Kraus, Falkenhagen and others [2,7,8]. Lars Onsager made clear that some rigorous statements about correctness or erroriness of definitions of mass action constants do not have a precise meaning. In Onsager's words [9,23]: "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 side of the ledger would be entered elsewhere with the same effect." Note that the problem of defining mass action constants for electrolytic associations is equivalent to the problem of mass action constants for plasma reactions. Following Onsager's views, we assume that statements about correctness of regularized partition functions do not have a direct physical meaning, and the choice of Coulomb partition function is to some extent free to choose [9,15,16]. The terms *correct* or *wrong* should only be applied to observable quantities as pressure and free energy. Taking this view, our choice is based on the criterion of maximal simplicity.

Pair association: In earlier works, Falkenhagen and coworkers [2,9] proposed for the pair formation of charged hard spheres with diameter R and Bjerrum parameter $b = \ell/R$ the mass action constant [2,7,9]

$$K_{\pm}^{(2)}(T) = 8\pi R_{\pm}^3 \cdot m(\xi_{\pm}) = 8\pi \ell_{\pm}^3 \cdot n(\xi_{\pm}), \quad n(\xi) = m(\xi)/(\xi)^3. \quad (27)$$

Instead of the function $n(\xi_{\pm})$, Fuoss and Kraus [8] used the notation $Q(\xi_{\pm})$. The pair association functions $m(x)$ or $n(x)$ are related to the $E_1(x)$ functions and to the so-called Kirkwood function [2,9]. The values of the function $m(b)$ are tabulated in [2,9]. For higher b , they are in asymptotic agreement with the function $b^3 Q(b)$ used by Bjerrum, Fuoss and Kraus [7]. However, we observe considerable differences for intermediate and for smaller b -values. For practical calculations, we may use the approximations [27]

$$m(b) \simeq \frac{b^4}{24} \cdot \left(1 + \frac{b^2}{90} + \frac{b^4}{8400} + \frac{b^6}{530,000} \right) \quad \text{if } b < 10 \quad (28)$$

$$m(b) \simeq \frac{\sinh(b)}{b} \simeq \frac{\exp(b)}{(2b)} \quad \text{if } b > 20. \quad (29)$$

The last expression gives the asymptotic behavior for very large interaction parameters b . For a first estimate, one may take only the first term in Equation (29), which gives the so-called weak approximation to the mass action constant

$$K_{\pm}^{(2)}(T) \simeq (\pi/3) \frac{\ell_{\pm}^4}{R_{\pm}}. \quad (30)$$

The given functions show the typical structure of a cropped exponential and agree asymptotically with the Bjerrum theory. In the Bjerrum theory of associating electrolytes, which has been further developed by Fuoss and Kraus [8], the result for the mass action constant reads

$$K_{\pm}^{(2)}(T) = 8\pi \ell_{\pm}^3 Q(b), \quad (31)$$

where $Q(b)$ is a tabulated function [7,8]. Asymptotically, the function $Q(b)$ is identical to $n(b)$. However, in the whole region of finite b -values, it is larger than our expression. As an example, for $b = 10$ is $Q(10) = 4.519$, $n(10) = 2.155$ and for $b = 20$ is $Q(20) = 3890$, $n(20) = 1932$. This means, we predict a much smaller degree of association than the Bjerrum–Fuoss–Kraus theory [7,8]. For example, for the association constant of MgSO_4 with $R_{\pm} \sim 290$ pm and $b \sim 10$ we obtain a value of about $k_{2+,2-}^{(2)} \simeq 10$ [mol/liter], while the Bjerrum–Fuoss–Kraus theory would give about double the value. We will show later that our estimate for the association constant of MgSO_4 in seawater gives about the correct value of 10%, as observed in experiments [28].

The fact that our expression for the mass action constant is based on power expansions beginning with higher-order e^8 is connected to the peculiarity of Coulombic systems, namely that the Debye screening, which is present everywhere, needs and absorbs all lower powers of e^2 in the series.

Quantum theory of pair association: As first shown by Planck, Brillouin, Larkin and others [1,15,16], the quantum statistics of pair formation like in hydrogen plasmas leads to quite similar expressions, where the PBL partition function σ appears [15]. In quantum statistics the partition function is expressed by a power series in the interaction parameter [15] $\xi_{\pm} = -Z_i Z_j \ell / \lambda_{\pm}$. This series for $\sigma(\xi)$ -function is in full agreement with the early result by Max Planck [1]. There is also a structural analogy to the series $m(\xi)$ for the classical case. The only difference is that we have to use other coefficients and other definitions of the parameter ξ [15]. The virial function for the quantum case $Q_4(x)$ has more advanced coefficients expressed by Riemann's known Zeta and Euler's Gamma functions, well known from mathematical physics [15,16]. The hydrogenic partition function may

be written as a function of the interaction parameter including the electronic spin states $s_e = 1/2$ in the form

$$\sigma(\xi_{ie}, s_e) = (2s_e + 1) \sum_{s=1}^{\infty} s^2 \left[\exp\left(\frac{\xi_{ie}^2}{4s^2}\right) - 1 - \left(\frac{\xi_{ie}^2}{4s^2}\right) \right] = (2s_e + 1) \left[\frac{\zeta(2)}{32} \xi_{ie}^4 + \frac{\zeta(4)}{128} \xi_{ie}^8 + \dots \right] \quad (32)$$

This relation is often called Planck–Brillouin–Larkin function (PBL-function), since it was first used by Max Planck in 1924 and later rederived and more strictly founded by Brillouin in 1932, Larkin in 1960 and these authors [15,16]. In low binding approximations, this gives, for the hydrogenic mass action constant,

$$K_{\pm}^H \simeq \frac{\pi^2 \sqrt{\pi}}{24} \frac{\ell_{\pm}}{\lambda_{\pm}}. \quad (33)$$

The comparison with the classical Equation (30) provides the following recipe for the transition from classical to quantum statistical mass action constants

$$R_{\pm} \rightarrow \frac{8}{\pi \sqrt{\pi}} \lambda_{\pm}, \quad (34)$$

what is near to the estimates for corresponding transitions of the Debye–Hückel distance $a \rightarrow (\sqrt{\pi}/4) \lambda_{ie}$ given in [15,16,20].

2.3. Mass Action Functions for Coulombic Triples and Quadruples

The question how to define the association constant for triple associates is more difficult than the treatment of pairs. This is connected with the fact that the three-particle problem in classical and in the quantum case is not well-understood and correspondingly the statistical virial coefficients for three particles are not well-elaborated. We start with same general considerations. The main effect of pair and triple association is the decrease of effective ion numbers from n_i to αn_i . The task is to find α_i which is the degree of ionization. The following associates are of specific interest:

$$(\pm) \quad (-+) \quad (+, -, +) \quad (-, +, -) \quad (-, (2+), -) \quad (+, (2-), +). \quad (35)$$

As some classical examples, we may look at the Coulombic associates of Cl^- ions with Mg^{2+} -ions and with La^{3+} ions. In order to estimate triple associations, we study first the maximal binding energy of 3 ions in linear order, e.g. Cl-Na-Cl , Cl-Mg-Cl or $\text{Na-SO}_4\text{-Na}$ including that one ion is double charged. The biggest energy has the linear configuration $(-)(++)(-)$ or $(+)(--)(+)$ in the linear arrangement of the ions in contact. A simple estimate of the energy of 3 ions with the linear configurations $(-), (Z+), (-)$ or $(+)(Z+)(-)$ in contact gives the energy

$$E_{-, (Z+), -} = E_{+(Z-), +} = (2Z - 1/2)U_0 = 2\tilde{Z}U_0; \quad U_0 = \ell/a \quad (36)$$

which leads to $Z = 2$, $\tilde{Z} = 1.75$ the value $E = 2\tilde{Z}U_0$. These estimates show also that we should not expect the formation of triples in the case of univalent ions, since the formation of two separate pairs gives a lower energy than the formation of one triple. However, in the case of divalent ions, the formation of triples is of advantage and we may introduce an effective charge $\tilde{Z} = 1.75$. For the mass action constant of such triples, we expect the asymptote

$$K_{-(2+)-} = K_{+(2-)+} \sim \exp[2\tilde{Z}\beta U_0] = \exp[3.5\beta U_0]. \quad (37)$$

These results correspond to early estimates proposed by Kelbg, Friedman and these authors by using the results of mathematical studies of cluster integrals [12,13,27,29]. We consider now

the configurations of four classical ions like in LaCl_3 solutions. An estimate of the electrostatic energy of a LaCl_3 -quadruple with La in the center and three Cl-ions at the edges gives

$$E_{\text{LaCl}_3} \simeq (9 - \sqrt{3})U_0 = \tilde{Z}U_0 = 6.3U_0; \quad \tilde{Z} \simeq 2.1 \quad (38)$$

Evidently the formation of this quadruple is of some advantage in comparison to forming a pair with energy $3U_0$ or a triple with energy $6 - (1/2)U_0 = 5.5U_0$. The corresponding mass action constant is

$$K_{(2-)(2+)-} \simeq \exp[(3\tilde{Z}\beta U_0)] = \exp[6.3\beta U_0] \quad (39)$$

We consider a statistical approach to the mass action constants for the triple formation using the approximation of effective charges. In order to find effective approximations, we study the integrands of the triple integrals in more detail. We concentrate at the integrals with three ψ -factors assuming that they give the dominant contributions. These triple integrals contain in the integrands three factors with cropped exponentials

$$\exp[-\beta V_{ij} - \beta V'_{ij}] - 1 + \beta V_{ij}. \quad (40)$$

We observe the subtraction of first powers of the exponential, this is typical for all Coulomb forces which have to be screened. Some of these factors in the integrands of the relevant clusters for associating particles belong to attractive interactions and are rather big. However, in the case of repulsive charges, these factors ϕ_{ij} have negative exponents expressing the repulsion of two equally charged ions and are nearly constant. The essential point for the integration is that repulsive ions cannot come close to each other and further these factors expressing repulsion are rather slowly changing and converge at larger distances to $1/2$ (see Figure 1).

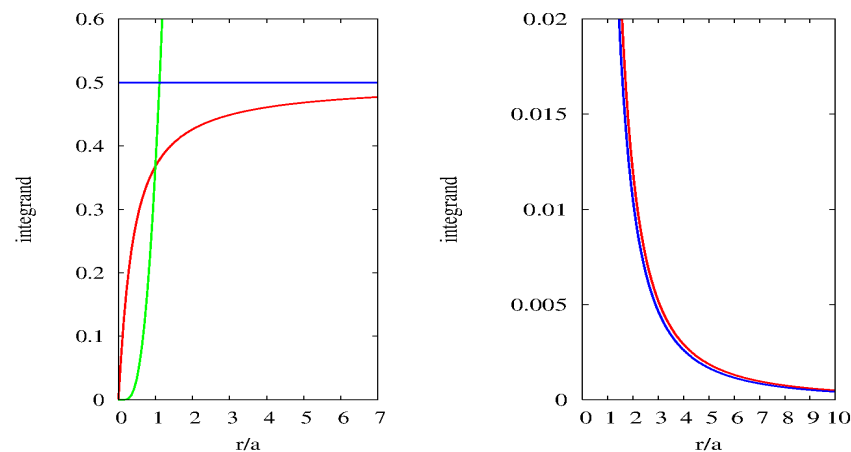


Figure 1. Typical factors in cluster integrals representing. **Left panel:** For repulsive ions exponential function (green), same function subtracting first two expansion terms (red), only second-order term (blue line). **Right panel:** exponential term subtracting the lowest power up to e^4 (in red) and the bare term of order ($O(\xi_{ij}^4)$) gives indeed a qualitatively correct overall shape. Note that all functions are multiplied with the spatial pre-factor x^2 .

We replace now in the integrals the repulsive factors by the constant $\xi_{--}^2/2$ what is due to the approximate distance $2R_{\pm}$ of the equal charges near to $\xi_{\pm}/8$ and calculate the first order integrals; further, we factorize the higher order parts of the integrals and arrive at

$$K_{2-, (2+)}^{(3)}(T) \simeq \pi^2 R_{\pm}^4 \ell_{--}^2 [C_{26} \xi_{\pm}^6 + m(\xi_{\pm}^2)^2]. \quad (41)$$

where $C_{26} \simeq 0.08$. Correspondingly we get e.g., by applications to the triple association of CaCl_2 we find approximately for the mass action constant about $6[\text{liter/mol}]^2$ [27,29].

For the quadruple formation we have to replace 3 repulsive factors by the constant $\tilde{\zeta}_{--}^2/2$. This way, with $C_{46} \simeq 0.022$ we obtain the estimate

$$K_{3-,3+}^{(4)}(T) \simeq \frac{\pi^3}{3456} R_{\pm}^3 \ell_{--}^6 [C_{46} \tilde{\zeta}_{\pm}^6 + m(\tilde{\zeta}_{\pm})^3]. \quad (42)$$

We find again that the mass action constants for Coulomb systems have a specific structure, excluding the lower powers in the interaction parameters. We repeat that these lower powers are unable to contribute to binding effects, since they are already absorbed in screening effects. Our method of approximating the mass action constants by the lowest diagrammatic contribution and for the higher contributions by products of pair factors is an assumption. We may, however, refer here to the Onsager freedom in the exact choice of the mass action constant as far as we observe the Onsager balances. We may refer further to the possibility to adapt our choice by means of the effective charges.

In the quantum case, we consider the quantum bound states of $k = 2$ or $k = 3$ electrons with one positively charged nucleus. In a first approach, we may assume a simple generalization of the known expression for hydrogen to helium by using cropped exponential functions instead of standard exponential functions. Here, the energy levels are to be collected from quantum calculations or from spectroscopic data. We subtracted here as for hydrogen the first two terms in the exponential series. Proceeding in a more systematic way, we have to sum up diagrams as in classical statistics, namely first all Feynman diagrams of ring type [15,16,30,31]. This means for Coulombic systems, starting with the Debye law the lower powers in the interaction strength ζ are already used for getting Debye's limiting law due to screening. Here again, Onsager's arguments come into play. If somebody insists, to use for plasmas partition functions a which contain the lowest orders in the ζ , then he should pay a price. Namely, if the lowest orders in ζ , means in e^2 are included in the mass action constants, they will be missing in the limiting law, which leads to deviations from Debye's coefficient in the root law. This is not necessarily incorrect. In order to complete then "Onsager's ledger" in a correct way we have to pay a price, a big complication of the theory. It is much better to leave the Debye-Hückel-terms intact and to define the mass action constants in a way, which does not touch the lower orders needed for providing the correct Debye Hückel-like terms. We will follow here this route and obtain mass action constants as asymptotic parts of the cluster integrals. Since the cluster integrals do not contain lower orders in e^2 , a procedure based on cluster expansions guarantees automatically our requests.

In quantum theory approximate methods to treat triple association of the type $(-, 2+, -)$ are known from the theory of Helium Quite effective is the method of effective charge. Formally, the problem is to treat the helium formation as bound state of two electrons and one two times positively charged alpha particle. The bound state energy of an electron-alpha pair is $Z^2 E_H$ where $Z = 2$ is the charge of the He-nucleus. For a pair of single charged ion and a Z -fold charged ion the quantum statistical theory [15,16,30] provides the expression for the mass action of a hydrogen-like pair [15]

$$K_{Z+,-}^{(2)}(T) = (2\sqrt{\pi}\lambda_{\pm})^3 \cdot \sigma(\xi_{Z=2}), \quad \xi_Z = Ze^2/k_B T \lambda_{\pm}. \quad (43)$$

In a first rough approximation of the bound states with two electrons, we may use the effective charge method of the variational quantum theory of He. The idea is to approximate the wave function as a product of two hydrogenic wave function. Each electron represents a cloud of negative charge which somehow shields the nucleus so that the other electron actually sees an effective nuclear charge $\tilde{Z} < 2$. The value of Z , which gives the minimal energy, is $\tilde{Z} = (Z - 5/16)$ and the minimal energy has the value 2.75 Ry with $\text{Ry} = |E_H|$. This is similar to the classical estimate Equation (36) with the difference that we find in the quantum case a factor 5/8 instead of the classical value 1/2. Looking for an analogy between classical and quantum distances, we find that for hydrogen the analog of the classical R_{\pm} is the double Bohr radius $2a_B$ and correspondingly for helium $2a_B/Z = a_B$. We may introduce for helium the effective charge $\tilde{Z} = (Z - 5/16) \simeq 1.69$ and, for the

effective distance, obtain $\tilde{R}_{\pm} \simeq 2a_B / \tilde{Z} \simeq 1.18a_B$. In a first approximation, we may compose the mass action constant of the He-atom by a contribution of the lowest-order binding with 4 + 2 attractive (\pm) interaction lines and two repulsive ($--$) interaction line what gives in first approximation the factor for the lowest diagram ($C_{26} \sim 0.18$). By adding the contributions of the ground state with cropped exponential function we get for the formation of an He-atom the following estimate of the mass action constant

$$K_{2-, (2+)}^{\text{He}}(T) \simeq (2\sqrt{\pi}\lambda_{\pm})^6 \left[C_{26}^{qu} \tilde{\tau}_{ee}^2 \tilde{\tau}_{ie}^6 + [\exp(5.8\beta\text{Ry}) - 1 - (5.8\beta\text{Ry})] \right]. \quad (44)$$

However, this and the previous estimates are only with respect to the ground state correct, the excited states are not correctly described. The needed inclusion of excited states is given in Section 4.

For the study of Li, where the situation is even more difficult, the method described above for the He-atom gives a first estimate for the Li-atom. We include in this estimate the contribution of the lowest-order binding diagram which is a ring with 4 + 2 attractive \pm interaction lines and four repulsive ($--$) interaction line, which gives

$$K_{3-, (3+)}^{\text{Li}}(T) \simeq (2\sqrt{\pi}\lambda_{\pm})^9 \left[C_{46}^{qu} \tilde{\tau}_{ee}^4 \tilde{\tau}_{ie}^6 + [\exp(19\beta\text{Ry}) - 1 - (19\beta\text{Ry})] \right]. \quad (45)$$

The quantum-statistical constants C_{26}^{qu}, C_{46}^{qu} are not yet known, a first estimate may be obtained by using the relation (33). For more precise calculations of the mass action constants for He and Li including excited states we refer to Section 4. Here, we restricted our study to the ground state contribution and an estimate of the free binding contributions. For a quantum-statistical calculation of the weak binding contributions which are of the order e^8 for 3 and e^{10} for 4 particles we need an extension of the tedious calculations of the density matrix which Kelbg and Hoffmann performed for the orders e^2, e^4, e^6 [4,11,13,14] to the next orders e^8 and e^{10} .

Concluding this section about mass action constants we have to note, that the chemical approach on the basis of mass action laws has certain limits. Only at lower densities, when chemical species are well-defined and distinguished from free particles, the approach by mass action laws works. As shown in particular by the modern theory of nonideal plasmas, a new effective Schrödinger equation replaces the standard wave equation [15,16,32]. The new theory shows the bound state levels and the continuum edge approach each other in dense systems and merge finally [32]. Beyond these densities, the distinction between bound and free relative states becomes questionable and one needs new concepts. We will come back to these problems in Sections 5 and 6.

3. Classical Osmotic Pressure and Chemical Potential Including Association

3.1. Semi-Chemical Description of Associating Systems

For practical calculations, in order to avoid heavy nonlinear mathematics, we develop now a semi-chemical or semi-physical approach that is half way between a full physical and a full chemical description [16,18,20]. In order to explain this, let us start with the case of pair association between a positive charge i and a negative charge e . Introducing the densities of free particles, e.g., of free electrons and free ions $n_e^* = \alpha n_e$, $n_i^* = \alpha n_i$, $n_{ie}^* = (1 - \alpha)n_i$ we get the nonideal mass action law (MAL) with the activity coefficients f_{\pm} :

$$\frac{1 - \alpha}{\alpha^2} = n_i f_{\pm}^2 K_2(T). \quad (46)$$

Rewriting this equation for the degree of ionization α in a form, which is appropriate for iterative solutions and starting with the zeroth approximation $\alpha^{(0)} = 1$ we get the first approximation (called semi-chemical approach)

$$\alpha^{(1)} = \frac{1}{1 + c(f_{\pm}(1))^2 K_2(T)}. \quad (47)$$

The range of validity of this simple quasi-linear approximation ends if more than about 1/3 of the ions are associated. This is a strict assumption which however leads to a great simplification of the mathematics and is justified for many interesting systems as e.g., for seawater-like mixtures [18]. For the activity coefficients f_{\pm} which appear in the mass action law we use in the classical case the standard expressions for the electrical parts

$$\ln f_{\pm} = \ln f_{\pm}^{\text{el}} = -\frac{z_{+}z_{-}}{2} \frac{\kappa \ell}{(1 + \gamma_{\pm})}. \quad (48)$$

In Debye-Hückel-, or mean-spherical approximations, respectively, we have [18,29]

$$\gamma_{\pm} = \kappa R_{\pm}; \quad \text{or} \quad \gamma_{\pm} = \frac{1}{2} \cdot \left(\kappa R_{\pm} + \sqrt{1 + 2\kappa R_{\pm}} - 1 \right). \quad (49)$$

We are using here the so-called opposite-charge approximation (OCA) or sometimes called reduced mass approximation (RMA), which is a specific property of Coulombic systems, based on the fact, that in the region of stronger interactions (larger Bjerrum parameters), the meeting of opposite charges dominates [16,21]. The main effect of pair and triple association is the decrease of effective particle numbers which leads to a decrease of the osmotic coefficients and the conductivities. Our first rational approximation to the MAL, which works only for regions where $\alpha > 2/3$, i.e., we are near to full ionization, is equivalent to a semi-physical approximation. This means, that physical and chemical expressions meet here at half way. In the general case, the degree of free ions of kind i is defined as that part of the ions which are not associated in pairs, triples, quadruples etc. We find this way

$$\alpha_i = \frac{N_i^{\text{free}}}{N_i^{\text{free}} + N_i^{\text{asso}}} = \frac{1}{1 + \delta_i^{(2)} + \delta_i^{(3)} + \delta_i^{(4)} + \dots}. \quad (50)$$

This is the typical mathematical structure in the semi-physical, semi-chemical approach suggested first by Justice. The terms $\delta_i^{(2)}$, $\delta_i^{(3)}$ and $\delta_i^{(4)}$ are in our approach calculated as the asymptotically big negative definite contributions from the 3rd and 4th virial coefficients etc. providing the relevant contributions to association. According to our estimates, the pair contribution is of order ζ^4 , the triple contribution is of order ζ^{10} , and the quadruple contribution is of order ζ^{14} [27].

More explicit is the degree of ionization of the charge i in semi-chemical approximation expressed by the mass action constants found above and the activities (fugacities) z_k by [29]

$$\alpha_i = \frac{1}{1 + \sum_{j \neq i} z_j K_{ij}^{(2)}(T) + 2 \sum_{j,k \neq i} z_j z_k K_{i,j,k}^{(3)}(T)} \quad (51)$$

where the $z_k = n_k f_k^{\text{el}}$ are the electrical contributions to the activities/fugacities (note that here short-range terms are omitted). The activity coefficients f_i^{el} are defined by the electrical parts of the chemical excess potentials which we approximate for charged hard cores by [18,33]

$$z_i = n_i f_i^{\text{el}}, \quad k_B T \ln f_i^{\text{el}} = -\frac{Z_i^2 \ell \kappa}{2} \sum_j \zeta_j^0 G_0(\kappa R_{ij}) + \dots; \quad G_0(x) = \frac{1}{1+x}. \quad (52)$$

Onsagers relative screening factor ζ_i^0 which have been used already above, are for a binary electrolyte ζ_1, ζ_2 in particular simple. We have for example for $\text{MgCl}_2, \text{CdCl}_2$ the pair $(1/2, 2/3)$ and for LaCl_3 the pair $(1/4, 3/4)$.

For the partial osmotic pressure, the osmotic coefficient, contributed by the ionic species i we obtain by using the virial formula and reinterpreting the strong coupling terms as contributions due to the association [18,27,29]

$$g_i = \beta P_i / (n_i k_B T) = \alpha_i - \frac{1}{6} Z_i^2 \kappa \ell \cdot \sum_j \zeta_j^0 \cdot [\tilde{G}_0]. \quad (53)$$

The first term in Equation (53) is interpreted as the effective degree of ionization or association, and may be found from Equation (51). We note that the expressions for the degree of ionization obtained this way are very near but not identical; to the α_i derived above, both expressions are identical only for small densities. Examples for the relative osmotic pressure are shown in Figure 2 for NaCl and for comparison also for a model of sea water.

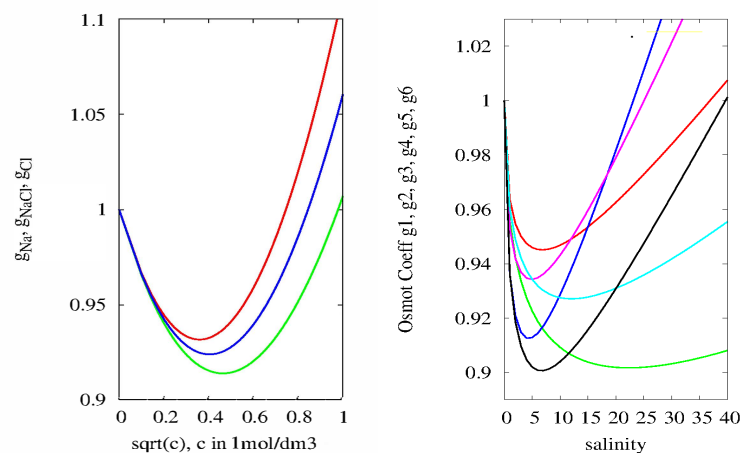


Figure 2. Left panel: Relative pressure for the ions Na^+ (above) and Cl^- (below) as well as the mean for a NaCl-solution. Right panel: Relative (individual) osmotic pressures for a mixture of six ions mimicking seawater including association in dependence on salinity S (gram salt per liter). We are sorting from below looking at the values at salinity $S = 5$. The lowest curve represents the ion SO_4^{2-} , then follow the curves for Mg^{2+} , K^+ , Ca^{2+} , Cl^- , Na^+ .

The small differences which we observe in the degrees of association obtained from the osmotic pressure or from calculations based on free energy is not a real inconsistency. The differences between calculation based on virial formula for the pressure and those based on cluster expansions for the free energy are known for decades. They cannot be avoided since they are of principal nature, the smallness of these differences is even often used as quality criterion of the both approaches. We remember here again Onsagers statement, that mass action constants are not uniquely defined. Essentially is that in the pressure approach the first term in Equation (53) may be interpreted as an ideal chemical contribution. Note that we are using here in simplest approximation for the zeroth order G_0 the Debye-Hückel-approximation; more advanced is the Mean Spherical Approximation (MSA) and the related Henderson-Smith approximation (HSA). The more advanced nonlinear Debye-Hückel-approximations (DHX) take into account the first- and second-order terms $G_1(x)$, $G_2(x)$.

3.2. Applications to CaCl_2 , LaCl_3 and a Seawater-Model

Relevant for pair and triple association are large negative contributions from the 2nd and 3rd virial coefficients. Following general results from statistical thermodynamics [2,12] we have shown that the key quantities for association are the asymptotically dominant parts of the strong coupling terms in the cluster integrals. We mention that there are different ways to estimate the triple association constant, the constant factor approximation which we prefer here but there exist also an effective charge approximation [29]. According to [29], both methods are in reasonable agreement for $\xi_{\pm} < 6$, then they start to disagree. In the constant

factor approximation, which we developed in Section 2, neglecting the weak binding term, the triple association constants for salts like CaCl_2 and ions like $(\text{LaCl}_2)^+$ have been estimated as

$$\begin{aligned} k_{\text{ClCaCl}} &= \pi^2 \ell^2 R_{\text{CaCl}}^4 \cdot m(\ell_{\text{CaCl}}/R_{\text{CaCl}})^2, \\ k_{\text{ClLa+Cl}} &= \pi^2 \ell^2 R_{\text{LaCl}}^4 \cdot m(\ell_{\text{LaCl}}/R_{\text{LaCl}})^2. \end{aligned} \quad (54)$$

Several numerical values of mass action constants for pair and triple formation estimated this way have been given also in [29]. A comparison of results for the activity coefficients using these formulae in comparison with results of Wilczek-Vera et al. [34] is shown in Figure 3. Our results are also in reasonable agreement with the Molecular Dynamics calculations of Valisko and Boda [24]. For the salt CaCl_2 we may compare directly with data points by Wilczek-Vera et al. [34]. The agreement of our results with these data and those of other workers for CaCl_2 is not quantitative but at least sufficient. For LaCl_3 our theory is not able to reproduce the pronounced minimum around $\sqrt{c} \sim 0.4(\text{mole/liter})^{0.5}$ predicted in [24]. The reason is possibly that we did not include so far the fourth virial coefficient.

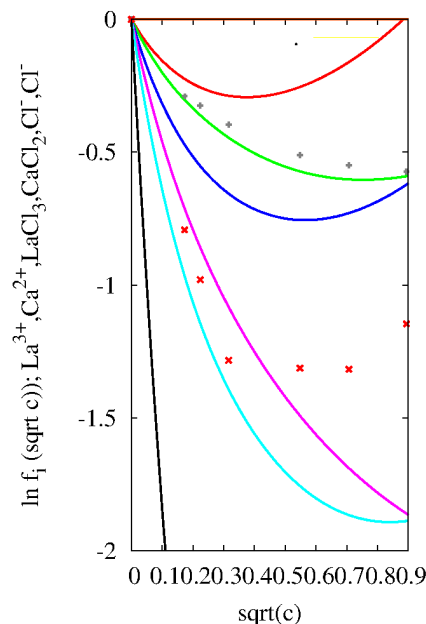


Figure 3. We show the activity coefficients of several ions and electrolytes. From above: Cl in CaCl_2 (red) and Cl in LaCl_3 (green), CaCl_2 (blue), LaCl_3 (magenta), Ca^{2+} (turquoise), La^{3+} (black). The activities were calculated in the semi-chemical approach neglecting so far quadruples, what could be the reason for too low values for the activities of CaCl_2 and LaCl_3 , Ca^{2+} and La^{3+} . The points denote data measured by Wilczek-Vera et al. [34] for Cl^- and La^{3+} in LaCl_3 .

For the fourth cluster integral and the corresponding association constants, a consequent statistical analysis is still missing. Therefore, we restrict ourselves here to an estimate following the lines valid for the third virial coefficient. In order to estimate the quadruple association constant for a salt like LaCl_3 we fix the Cl-Cl-distances at some energetically favorite distance like $\sqrt{3}R_{\text{LaCl}}$, which we guess from a symmetric configuration of the Cl-ions. Then the factors for the repulsive terms may be taken out, what leads to factorization of the remaining terms in the integral. Approximating again the repulsive term by the quadratic order and neglecting the weak binding term we get the estimate

$$k_{\text{LaCl}_3} = \frac{\pi^3}{3456} R_{\text{LaCl}}^3 \ell^6 \cdot [m(\ell_{\text{LaCl}}/R_{\text{LaCl}})]^3. \quad (55)$$

For the calculation of concrete values of the quadruple association constant we used data from MC simulations by Valisko and Boda [24], in particular the contact distances $R_{\text{LaLa}} = 430$ pm and $R_{\text{LaCl}} = 270$ pm corresponding to a relative large Bjerrum parameter

$\xi_{\pm} = 7.95$. The agreement of our results with available data (see Figure 3 [24,34]) is so far not sufficient. Note that we have to differ between association constants in the density scale of statistical mechanics particle number/cm³, and in the usual chemical concentration scale mol/liter. In order to switch to the chemical scale the standard recalculation is needed [29].

For MgSO₄ in standard seawater, the degree of association has been measured based on the attenuation of sound by Fisher [35]. Based on these data, Fisher concluded that about 9.2 percent of the total Mg in seawater exists as MgSO₄. Kester and Pytkowicz estimated the mass action constants for Mg and Ca and found a degree of association of about 10 percent [28]. Our calculation gives for normal ocean salinity for Mg a degree of association of about 12 percent, for SO₄ about 9 percent and for Ca about 4 percent. Looking at the uncertainties of the experiment and the theory, the agreement seems to be satisfactory.

We estimated the degree of triple association in seawater for the triples MgCl₂ and Na₂SO₄. We find according to our estimates that the formation of triples in seawater is rather seldom.

The predicted degrees of association to MgCl₂ and Na₂SO₄ obtained from our estimate are in the range of 10^{−4}. Qualitatively, this estimate and the shape of the curves seems to be reasonable (Figure 4).

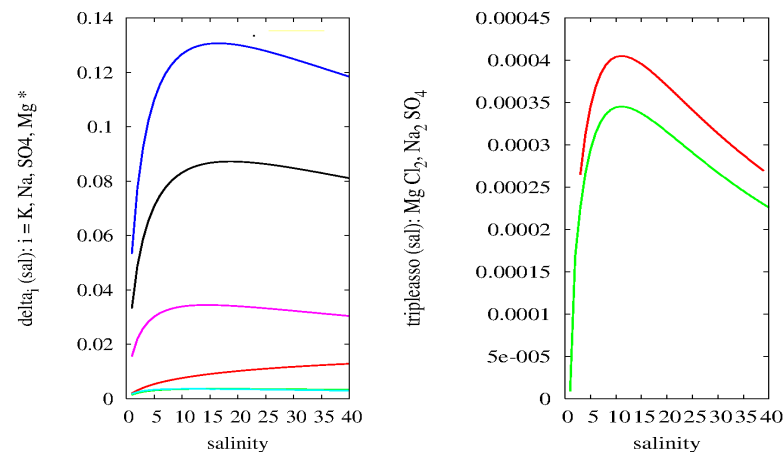


Figure 4. Left panel: Degrees association for ions in seawater. The curves describe (looking at mean salinities from above): Mg²⁺, SO₄^{2−}, Ca²⁺, Na⁺, K⁺, Cl[−], as a function of salinity. Right panel: Degree of triple association in seawater for the triples MgCl₂ (red) and Na₂SO₄ (green) which is according to our estimates rather low. Typical is the maximum at finite concentrations/salinities.

4. Quantum Bound States of He and Li Plasmas Including Excited States

The calculation of bound states in dense He or Li plasmas and the corresponding mass actions laws is a difficult problem in quantum statistics. We can use the approach for the H plasma [15] where we have to solve a two-particle problem to account for the formation of bound states, and where the solution in the low-density limit is well known [15].

In the case of He plasma, we have the doubly charged α particle as ion ($Z = 2$), total density n_i , and electrons, total density $n_e = 2n_i$ for charge neutral plasmas. The intrinsic factors for electrons are $\sigma_e = 2$ (spin 1/2), for the He⁺⁺ ion $\sigma_{\text{He}^{++}} = 1$. In the framework of the chemical picture, where bound states are considered as new species, in the low-density limit case we have free electrons, density n_e^* , free ions, density n_i^* , singly charged He⁺ ions, density n_{He^+} , and neutral He atoms, density n_{He} . A more detailed description takes into account not only the ground state of the few-particle system, but also all excited states and, in the general case, the scattering states in the continuum. For He⁺, the intrinsic partition function is calculated in analogy to the H atom, except that for the Z -fold charged ion, the Hydrogen-like energy spectrum $E_n^Z = Z^2 E_n^{\text{H}}$ occurs and the bound state system has charge

$+|e|$. As discussed above, the intrinsic partition function of the He^+ channel is (factor 2 from spin; note that we use n here as principal quantum number)

$$\sigma_{\text{He}^+}(T) = 2 \sum_{n=1}^{\infty} n^2 \left[e^{-4E_n^{\text{H}}/k_B T} - 1 + \frac{4E_n^{\text{H}}}{k_B T} \right]. \quad (56)$$

We do not want to repeat the discussion that the subdivision into the bound state part and the continuum part is arbitrary [15]. The definition of the bound state part, proposed in Equation (56), avoids artificial divergencies.

As discussed for the case of the H atom, the third term of the PBL partition function is related to the long-range character of the Coulomb interaction, so that scattering phase shifts cannot be introduced in the usual way. As is well known, this problem is solved by a partial summation of ring diagrams so that a screened potential can be introduced, and new terms appear in the virial expansion containing the square root of the density [15]. In the case considered here, the contribution to the polarization function describing screening is provided by the free electrons, the free ions, charge $Z = 2$, and the free singly charged He^+ ions, described below.

The calculation of the contribution of the charge-neutral He excited states is more complicated. We have to solve the three-body system, the α particle as a doubly charged ion, and two additional electrons. As known from spectroscopy, we have two different channels, spin-triplet ortho-helium and spin-singlet para-helium. Excitation energies and multiplicities are obtained, for example, from the NIST tables [36]. Bound states occur when the $1s$ state is occupied by one electron, the other electron occupies states in a center-symmetric potential that becomes Coulomb-like for highly excited states, with effective charge $Z = 1$ of the He^+ core ion. These Rydberg states behave like states of the H atom near the continuum limit at 1.80714 Ry ($1 \text{ Ry} = 13.60568 \text{ eV}$) so that the same divergences appear in the intrinsic partition function. There are other two-electron states where both electrons are excited, but the lowest, $2s2p$, has an excitation energy of 4.2858 Ry and is far in the continuum, so that it decays.

The intrinsic partition function for spin-singlet helium is (units: Ry)

$$\sigma_{\text{HePara}}(T) = e^{4\beta} [e^{1.80714\beta} - 1 - 1.80714\beta + e^{0.291908\beta} - 1 - 0.291908\beta + 3(e^{0.247644\beta} - 1 - 0.247644\beta) + \dots]. \quad (57)$$

The intrinsic partition function for spin-triplet helium is (units: Ry)

$$\sigma_{\text{Heortho}}(T) = e^{4\beta} \left[3(e^{0.350425\beta} - 1 - 0.350425\beta) + 5(e^{0.266308\beta} - 1 - 0.266308\beta) + 3(e^{0.266307\beta} - 1 - 0.266307\beta) + e^{0.266298/k_B T} - 1 - 0.266298\beta + \dots \right]. \quad (58)$$

The values for further excitation energies and multiplicities are obtained from the tables [36]. In both cases, to obtain convergent results, the second-order term in the $e\text{-He}^+$ interaction is subtracted because the Coulomb interaction requires the introduction of screening. The cluster decomposition of the polarization function describing the screening also includes a contribution from the singly charged He^+ ions as monopole contribution. A more sophisticated approach also provides contributions from a multipole expansion [37] but this cluster decomposition is not discussed here, see [15].

Now, we discuss the composition of ideal He plasmas and the mass action constants. Within our approximation, we obtain for the total densities

$$\begin{aligned} n_e &= n_e^* + n_{\text{He}^+}^* + 2n_{\text{He}}^* \\ n_i &= n_{\text{He}^{++}}^* + n_{\text{He}^+}^* + n_{\text{He}}^* \end{aligned} \quad (59)$$

with

$$\begin{aligned} n_{\text{He}^+}^* &= n_e^* n_{\text{He}^{++}}^* \frac{\Lambda_e^3 \Lambda_{\text{He}^{++}}^3}{\Lambda_{\text{He}^+}^3} \frac{\sigma_{\text{He}^+}}{\sigma_e \sigma_{\text{He}^{++}}} = n_e^* n_{\text{He}^{++}}^* K_{\text{He}^+}(T), \\ n_{\text{He}}^* &= n_e^{*2} n_{\text{He}^{++}}^* \frac{\Lambda_e^6 \Lambda_{\text{He}^{++}}^3}{\Lambda_{\text{He}}^3} \frac{\sigma_{\text{He}^{\text{ortho}}} + \sigma_{\text{He}^{\text{para}}}}{\sigma_e^2 \sigma_{\text{He}^{++}}} = n_e^{*2} n_{\text{He}^{++}}^* K_{\text{He}}(T). \end{aligned} \quad (60)$$

Charge neutrality means $n_e = 2n_i$ so that the properties of the He plasma are determined only by T and n_i . The ionization degree may be introduced as n_e^*/n_i .

Often, only the lowest term of the intrinsic partition function is considered when calculating the mass action constants. We refer to this reduction to the contribution of the ground state as the reduced intrinsic partition function. To show the influence of the excited states, the ratio of the chemical constants with all bound states to the cropped chemical constants with only the lowest bound state is shown as a function of T in Figure 5.

A more advanced treatment based on a Green function approach would introduce quasiparticle energies depending on T, n_i . For all charged particles, a Debye shift arises giving the Debye limiting behavior for the pressure and other thermodynamic functions. The medium modification of the bound state energies [32,38] leads to the so-called Mott effect, i.e., bound states are dissolved when the bound state energy approaches the continuum edge, see [15]. One problem, however, is that shifted energy levels cannot be introduced directly into our chemical approach, since this requires a new approach via the grand canonical ensemble [21], which will be briefly discussed in the next section.

The treatment of the Li plasma follows the same approach. We have triply charged Lithium ions with the free ion density $n_{\text{Li}^{3+}}$ and degeneracy $\sigma_{\text{Li}^{3+}}$ (which is determined by the isotope, which should be considered as different species, but is not of relevance for our approach). We also have doubly ionized Li^{++} ions with density $n_{\text{Li}^{++}}$, singly ionized Li^+ ions with density n_{Li^+} , and neutral Li atoms with density n_{Li} . Higher clusters such as Li dimers are not considered here. As before, the intrinsic partition function for Li^{++} is Hydrogen-like with $Z = 3$, so that

$$\sigma_{\text{Li}^{++}}(T) = \sigma_{\text{Li}^{3+}} 2 \sum_{n=1}^{\infty} n^2 \left[e^{-9E_n^{\text{H}}/k_B T} - 1 + \frac{9E_n^{\text{H}}}{k_B T} \right]. \quad (61)$$

As for He, the singly charged Li^+ ion has two bound electrons that are in the singlet or triplet spin state. According to the data tables [36], the continuum limit is 5.55944 Ry, and the intrinsic partition function for spin-singlet Li^+ is (units: Ry)

$$\begin{aligned} \sigma_{\text{Li}^+, \text{para}}(T) &= \sigma_{\text{Li}^{3+}} e^{9\beta} [e^{5.5594\beta} - 1 - 5.5594\beta + e^{1.08171\beta} - 1 - 1.08171\beta \\ &+ 3(e^{0.98663\beta} - 1 - 0.98663\beta) + \dots]. \end{aligned} \quad (62)$$

The intrinsic partition function for spin-triplet Li^+ is (units: Ry)

$$\begin{aligned} \sigma_{\text{Li}^+, \text{ortho}}(T) &= \sigma_{\text{Li}^{3+}} e^{9\beta} [3(e^{1.22149\beta} - 1 - 1.22149\beta) \\ &+ 3(e^{1.05541\beta} - 1 - 1.05541\beta) + 5(e^{1.05538\beta} - 1 - 1.05538\beta) \\ &+ e^{1.05536\beta} - 1 - 1.05536\beta + \dots]. \end{aligned} \quad (63)$$

For the contribution of the neutral Li atoms, we consider three bound electrons, two of which occupy the 1s core state, and the third one can be excited. The energy spectrum is similar to that of hydrogen, where the modification of the Coulomb potential near the 1s core can be described by the quantum defect method. We use the empirical values of the excitation spectrum and have for the intrinsic partition function (continuum limit at 0.396284 Ry)

$$\begin{aligned} \sigma_{\text{Li}}(T) &= \sigma_{\text{Li}^{3+}} e^{14.5594\beta} [2(e^{0.396284\beta} - 1 - 0.396284\beta) \\ &+ 2(e^{0.260472\beta} - 1 - 0.260472\beta) + 4(e^{0.260469\beta} - 1 - 0.260469\beta) + \dots]. \end{aligned} \quad (64)$$

As for the He plasma, the composition of the Li plasma is described by

$$\begin{aligned} n_e &= n_e^* + n_{\text{Li}^{++}}^* + 2n_{\text{Li}^+}^* + 3n_{\text{Li}}^*, \\ n_i &= n_{\text{Li}^{3+}}^* + n_{\text{Li}^{++}}^* + n_{\text{Li}^+}^* + n_{\text{Li}}^* \end{aligned} \quad (65)$$

with

$$\begin{aligned} n_{\text{Li}^{++}}^* &= n_e^* n_{\text{Li}^{3+}}^* \frac{\Lambda_e^3 \Lambda_{\text{Li}^{3+}}^3}{\Lambda_{\text{Li}^{++}}^3} \frac{\sigma_{\text{Li}^{++}}}{\sigma_e \sigma_{\text{Li}^{3+}}}, = n_e^* n_{\text{Li}^{3+}}^* K_{\text{Li}^{++}}(T), \\ n_{\text{Li}^+}^* &= n_e^{*2} n_{\text{Li}^{3+}}^* \frac{\Lambda_e^6 \Lambda_{\text{Li}^{3+}}^3}{\Lambda_{\text{Li}^+}^3} \frac{\sigma_{\text{Li}^+, \text{ortho}} + \sigma_{\text{Li}^+, \text{para}}}{\sigma_e^2 \sigma_{\text{Li}^{3+}}} = n_e^{*2} n_{\text{Li}^{3+}}^* K_{\text{Li}^+}(T), \\ n_{\text{Li}}^* &= n_e^{*3} n_{\text{Li}^{3+}}^* \frac{\Lambda_e^9 \Lambda_{\text{Li}^{3+}}^3}{\Lambda_{\text{Li}}^3} \frac{\sigma_{\text{Li}}}{\sigma_e^3 \sigma_{\text{Li}^{3+}}} = n_e^{*3} n_{\text{Li}^{3+}}^* K_{\text{Li}}(T). \end{aligned} \quad (66)$$

Charge neutrality means $n_e = 3n_i$ so that the properties of the Li plasma are determined only by T and n_i . The ionization degree may be introduced as n_e^*/n_i .

We discuss different versions of the mass action constants $K(T)$,

- (i) in simplest case the reduced uncropped $K^0(T)$ where only the ground state $e^{-E_0/k_B T}$ is taken for the intrinsic partition function, all excited states and the low-order terms with respect to the interaction, $-1 + E_0/k_B T$, are neglected;
- (ii) the reduced cropped mass action constant $K^{\text{cropped}}(T)$ where only the ground state contribution $e^{-E_0/k_B T} - 1 + E_0/k_B T$ to the intrinsic partition function is taken and the summation over all excited states is neglected;
- (iii) the full cropped expression $K(T)$ given above, which contains the summation over all excited states.

We consider the ratios $K^{\text{cropped}}(T)/K^0(T)$ to see the effect of the subtraction of the low-order terms with respect to the interaction, and $K(T)/K^{\text{cropped}}(T)$ to see the effect of excited states. Calculations for $K_{\text{He}^+}(T)$, Equation (60), of both ratios as function of T are shown in Figure 5. The ratio $K^{\text{cropped}}(T)/K^0(T)$ is 1 for low T , but approaches zero for high T , where the subtraction of the low-order terms with respect to the interaction is important. This reduction is shown for the ground state contribution to the intrinsic partition function, but the reduction is even larger for the contribution of excited states.

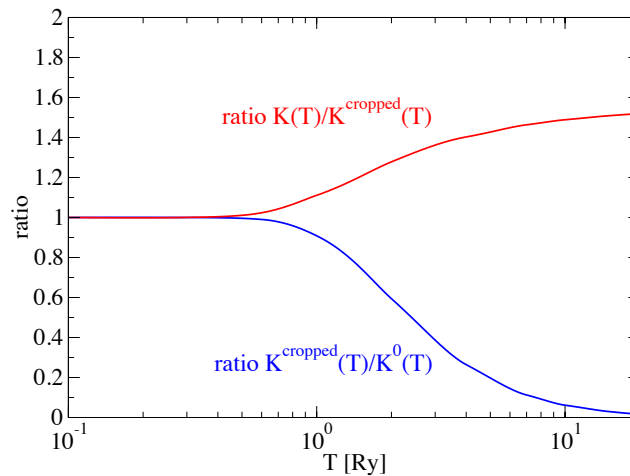


Figure 5. Mass action constants for the He^+ ion. The ratio $K^{\text{cropped}}(T)/K^0(T)$ shows the effect of subtracting the low-order terms with respect to the interaction, $-1 + E_0/k_B T$, for the reduced intrinsic partition function where only the ground state is considered. The ratio $K(T)/K^{\text{cropped}}(T)$ compares the fully cropped intrinsic partition function with the reduced cropped partition function to show the effect of including excited states.

The inclusion of all excited states in the full cropped expression $K(T)$ is interesting when compared with the ground-state contribution in the reduced cropped mass action constant $K^{\text{cropped}}(T)$, as shown in Figure 5 as a function of T for the He^+ ion. The ratio $K(T)/K^{\text{cropped}}(T)$ is also 1 for low T where excited states are not important, but increases with increasing T as thermal excitation is possible. Interestingly, this ratio saturates in the high T limit at $\pi^2/6 = 1.64493$ so the error in using the reduced cropped mass action constant does not become very large even at high temperatures. A similar behavior follows for the other mass action constants, including the saturation $\lim_{T \rightarrow \infty} K(T)/K^{\text{cropped}}(T) = \pi^2/6$.

5. Pressure of Quantum Plasmas Including Bound State Effects

5.1. The Valley of Bound States in the Relative Pressure and the Concatenation Method

For quantum systems the calculations of the EoS are more complicated, details are given in [21]. The low- and high-density regions are treated in different ways. For the low density region the cluster expansions given above work with a few modifications [15]. For low-density plasmas, we proceed with the calculations using the mass action law method as explained above. For the treatment of the ionization equilibrium in the low-density region we begin as before with the expressions given below for the mass action constants K_{H} , K_{He^+} , K_{He} , K_{Li^+} , $K_{\text{Li}^{++}}$, K_{Li} and fugacities in ring approximation, Equations (6) and (7) [20,21]. In this approximation, for example, for hydrogen plasmas for the relative pressure p/p_{id} the curve follows as shown in Figure 6 on the left. Beyond the minimum of the relative pressure, the approximations given above break down, since completely new effects appear such as Fermi–Dirac-, Hartree–Fock and Wigner effects, as explained in previous work [20,21].

For the calculation of the pressure at high densities, in contrast to the cluster expansions used so far, we use the more general quantum statistical formalism of Green’s functions and Feynman diagrams

$$p = p^{\text{FD}} + p^{\text{HF}} + p^{\text{ring}} - \frac{1}{2V} \int_0^1 \frac{d\lambda}{\lambda} \int d1 d2 V(1,2) [G_2(1,2,1',2';\lambda) - G_2^{\text{FD}} - G_2^{\text{HF}} - G_2^{\text{ring}}], \quad (67)$$

where $G_2(1,2,1',2')$ is the full two-particle Green’s function, which can be represented by Feynman diagrams. Note that, again, the first diagrams have to be calculated separately [21]. The essential part of the remaining diagrams, which represent the contributions of bound states, are of the ladder type and correspond to the diagrams for bound states that we calculated in Section 2. Note that for the treatment of the light elements up to Lithium, we have to include all Feynman diagrams, including one heavy ion and two to three electrons. In addition, the contribution of scattering states to the thermodynamic functions, not yet included in the approximation (59), can be obtained from the Green function approach, see [15,37,38]. This leads to expressions for the pressure in the grand canonical ensemble which extend the cluster expansions used above to higher density.

At very high densities, i.e., at high degeneracy, we assume that the effects of bound state are attenuated by high-density effects and are only a perturbation. Beyond densities of about 10^{23} electrons per cm^3 the bound state effects may be neglected in a first approximation. This is the idea behind the method of concatenation used here: We first calculated separately the EoS for small and for high densities using different methods, looked for crossing points, and concatenated the curves in a smooth way as shown in Figure 6 for Hydrogen plasmas. In the region where the relative pressure valley ends, the bound states are destroyed due to various high-density effects. The Schrödinger equation for bound states is now replaced by the Nambu–Bethe–Salpeter equations [15,21]. The main contributions to the EoS come in the high density region from Pauli and Hartree–Fock effects. In fact, we now have an EoS which is completely different from the low-density EoS. To explain how to proceed, we first consider Hydrogen plasmas and explain our method of concatenation which provides a smooth connection between the low density branch and the high-density branch. As our picture Figure 6 shows, the high density EoS and the corresponding result for low density p_{low} are crossing in the region of about $n_i = 10^{23} \text{ cm}^{-3}$. We construct a

convenient analytic interpolation as known from the theory of the electron gas [16] by using the interpolating function $w(x) = \tanh(x/2)/2$ which connects the two pieces in a smooth way at the crossing point $y_0 \simeq 18$ where $y = n_e \Lambda_e^3/2$. This way we get in our case with $a \simeq 0.1$

$$p_{\text{concat}} = p_{\text{low}} / (1 + \exp(a(y - y_0))) + p_{\text{high}} / (1 + \exp(-a(y - y_0))). \quad (68)$$

The present method of smooth concatenation at the crossing point provides a simple extension of the above two approaches to the whole range of densities. We demonstrate how the method of smooth concatenation works in Figure 6. In fact our way of interpolation between the low-density branch and the high-density branch is using $\tanh(x/2)$ – functions as is well known from electron gas theory [15,16,21].

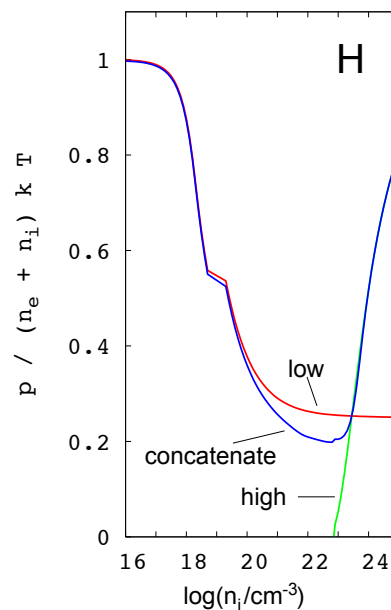


Figure 6. Hydrogen plasmas: We demonstrate the method of smooth concatenation for a hydrogen plasma at $T = 20,000$ K. After identifying a crossing point near to $n_i \simeq 10^{23} \text{ cm}^{-3}$ we construct a smooth concatenation of the branches on the left (red) and right (green) sides of the intersection of the low-density branch (red) with the high-density branch (green). The blue curve shows the result of the concatenation using complementary \tanh -functions ($a \simeq 1$; $y = n_e \Lambda_e^3/2$).

5.2. Applications to Hydrogen, Helium and Lithium Plasmas

In the high-density regions, the fugacities and the contributions of the ideal pressure must take into account the Fermi, Hartree–Fock and Wigner effects.

Hydrogen plasmas: For simplicity, we have treated only approximately the formation of H_2 -molecules, which dominate at temperatures below $10,000$ K [19]. The shoulder in Figure 6 reflects the formation of atoms and the minimum reflects the formation of atomic and molecular bound states. In the temperature range studied here ($10,000$ – $50,000$ K), no first order phase transitions were observed in our approximation.

Helium and lithium plasmas: Except for the need to include higher bound states, the details of the calculations for these plasmas are analogous to hydrogen [21]. Explicitly, for helium and lithium plasmas, we obtain expressions of the form (note that the z_e, z_i are fugacities [15,20,21])

$$p = p_e^{\text{FD}} + p_i^{\text{B}} + p_e^{\text{HF}} + p_i^{\text{Wi}} + 2z_e^{\text{HF}} z_i^{\text{Wi}} K_{ei} + 3(z_e^{\text{HF}})^2 (z_i^{\text{Wi}}) K_{iee}, \quad (69)$$

$$p = p_e^{\text{FD}} + p_i^{\text{B}} + p_e^{\text{HF}} + p_i^{\text{Wi}} + 2z_e^{\text{HF}} z_i^{\text{Wi}} K_{ie} + 3(z_e^{\text{HF}})^2 z_i^{\text{Wi}} K_{iee} + 4(z_e^{\text{HF}})^3 z_i^{\text{Wi}} K_{ieee}. \quad (70)$$

The abbreviations are FD: Fermi-Dirac effects; HF: Hartree-Fock effects; Wi: Wigner effects. These provide the main corrections to the ideal pressure in the quantum case. The pre-factors z_k denote the fugacities of the plasma species, these terms are completely different for low and for high densities. The expressions we use for low densities are similar to those used for electrolytes in Chapter 3. Here the fugacities have to be calculated in Hartree-Fock or Wigner approximations [15,16]. Furthermore, in the high density case, the bound states must be estimated including so-called Pauli blocking and other high density effects [32,37,38]. These effects model, for example, the rule that states occupied by atomic electrons cannot be occupied by free electrons with the same spin state. At high electron densities, this leads to the destruction of atomic states, which require a relatively large phase space [20,21]. We also need to account for energy shifts due to Pauli effects. What is new in contrast to our previous work [20,21] is that here we use the new expressions for the mass action constants at lower densities.

We perform a composition of all relevant contributions at low and high densities as Fermi-Dirac, ring, and ladder contributions as well as high-density Hartree-Fock contributions to the electronic pressure and the Wigner-De Witt contributions to the ionic pressure. We show in Figure 7 (left) results for Helium plasmas in the range 50,000–80,000 K and in Figure 7 (right) for lithium plasmas in the range 80,000–200,000 K.

In this way, we have now found closed-form expressions for the pressure of Hydrogen and other light plasmas expressed by our estimates of the mass action constants. Essentially, we use an inversion of the fugacity series, applying different formulas for the range of low densities, including bound states, on one side and large densities on the other side where bound states are destroyed. Both limits are connected by interpolation, so that some uncertainties in the transition region are still to be discussed. In Li plasmas, the fourfold association is relevant and we can again use our estimates for the mass action constant. We mention the similar situation in hydrogen molecular plasmas, which were studied in a previous work [19,21]. Our relatively simple formulas allow the calculation of a density series at a given temperature in only a few minutes on a standard personal computer and can be extended to other light elements. As in the classical case, complex mixtures, as they occur in nature, are also within the range of possible calculations, for example, to calculate the isentropic EoS for solar plasmas [21].

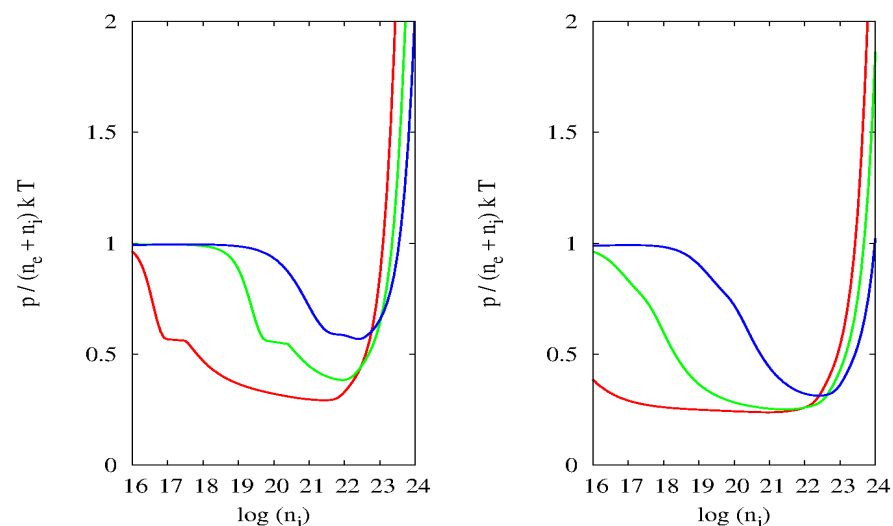


Figure 7. Helium and Lithium plasmas: Low and high-density approximations are concatenated by complementary $\tanh(x)$ functions at the crossing point. Left panel: Helium plasmas at 30,000 K (red), 50,000 K (green) and 80,000 K (blue curve) as functions of the total ion density. Right panel: Lithium plasmas at temperatures 80,000 K (red), 120,000 K (green), 200,000 K (blue). The minima are due to the formation of bound states.

6. Conclusions

In the present review, ion association and ion-electron bonding are discussed in the classical and quantum cases for electrolytes and for quantum plasmas. Pair, triple, and quadruple association are considered systematically and on same footing, and the mass action constants are calculated. To a large extent, we follow Onsager's idea that physics/chemistry are like a ledger book in which free and bound-state contributions are on different pages and must be treated differently. However, we have some freedom to move between the pages of the ledger, provided we respect the general balance. This approach is not restricted to electrolytes and plasmas; it can be applied to other systems with bound states, such as quark-gluon plasmas with quarkonium states [6,39,40]. Because of confinement and color saturation, the forces between quarks are not as simple as in the Coulomb systems discussed above and will not be discussed in the present work. However, it should be mentioned that a main issue of our work, compensating for the contributions of bound states and scattering states and the correct formulation of the mass action law is also an important issue in the hadron-quark plasma transition region and the consideration of correlations in the quarkonium state of matter; see also [39–41]. From our methods of statistical cluster expansion, it follows as a strict consequence that the low-order contributions in e^2 should be excluded from the definition of the mass action constants, what technically means that instead of the standard exponential functions known from classical chemical physics, cropped exponential functions appear for Coulombic systems. In this way the double counting of diagrams is avoided. The configuration integral or the corresponding quantum statistical trace over the operator $\exp(-\beta H_s)$ of the s -particle bonding group is expanded with respect to the interaction parameter e^2 , and all divergent terms in the expansion are identified and omitted. The resulting convergent temperature function yields the regularized partition function, in the simplest case in the form of a cropped exponential function, and the mass action constant of the bound cluster. In fact, the new mass action constants for electrolytes and quantum plasmas are substantially smaller, often by a factor of two, than the standard values, and accordingly the association and atom formation is strongly reduced. Furthermore, we show that the Coulomb association is typically transient in classical and in quantum systems, reaching a maximum at finite concentrations/densities.

We calculate activity coefficients and relative pressure in 1-1, 1-2, 2-2, and 1-3 electrolytes and, in parallel, the corresponding association effects in Hydrogen, Helium, and Lithium plasmas. We consider the specific properties of systems with Coulomb forces, such as electro-neutrality and screening effects, which lead to a constraint that avoids double counting of diagrams. This point has been overlooked in many previous studies. We show that these effects lead to quite typical specific structures of the Coulombic mass action constants derived for examples of binary, triple and quadruple association in classical and quantum examples. As relevant applications, we have studied a seawater-like ionic mixture and a Helium quantum plasma. We apply semi-chemical methods corresponding to an approximation of the law of mass action by rational polynomials. These approximations do not require a high numerical effort, but are restricted to weak degrees of association.

Our results are first summarized for the classical case: Based on the results of statistical physics, we recommend, in addition to the standard methods for calculating the degrees of association of ions and for individual activities and osmotic coefficients, new statistical tools that work from low to moderate concentrations. In the classical case, we use as a basic model charged hard spheres with individual non-additive contact distances in combination with the nonlinear Debye-Hückel approximations for screening. Association effects are included by allowing us to use cropped exponentials and rational polynomials instead of exponentials and full nonlinear mass action laws. The new cropped mass-action constants are generally smaller than the standard expressions based on exponential functions. For the seawater example, our results for the association are in agreement with available experimental results. Our semi-chemical approximations are restricted to lower degrees of association, but allow the treatment of interesting real systems, such as seawater [18] and solar plasmas [21], without much numerical effort.

In the quantum case, for example, for Hydrogen, Helium, and Lithium plasmas, we distinguish, using calculations, between the cases of low-, non- and higher-degenerate densities. In between, where the strongest bound state-association effects are observed, the relative pressure develops a minimum, the valley of bound states. Beyond this valley, all bound states are subsequently destroyed in connection with Fermi, Pauli blocking, Hartree–Fock, and Wigner effects. Despite the completely different physical nature, we see that the transient nature of association/bound state effects is the same for classical and for quantum systems: association or binding to atomic states has a clear maximum degree in a range of finite concentrations/densities.

For quantum plasmas, we concatenate the curves obtained for the regions to the left and right of the valley of bound states, near the crossings by smooth concatenation with tanh functions.

In both the classical and quantum cases, the proposed formulas are analytical. Therefore, results can be obtained on home computers even for complex mixtures, as shown here for the example of seawater and in other work for solar plasmas [21]. In this way, our methods can be offered for semi-quantitative estimates for quite complex mixtures containing ions with higher charges.

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