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**CONDENSED MATTER PHYSICS**

***A part of the Special collection to the 100th anniversary of the birth of Ihor Yukhnovskii***

# Statistical theory of charged particle systems including triple bound states — and the Collaboration Lviv–Rostock

W. Ebeling *

Institute of Physics, Humboldt University, Berlin, Germany

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Honoring the hundredth anniversary of the birthday of Ihor R. Yuknovskii we analyze new developments in the statistical thermodynamics of Coulomb systems. The basic idea of this work is to demonstrate that the exponential potential used in the first papers of Yukhnovskii is an appropriate reference system for a description of classical and quantum charged particle systems. We briefly discuss the collaboration between the groups of Ihor R. Yuknovskii in Lviv and Günter Kelbg in Rostock and analyze several approaches based on pair correlation functions and cluster expansion in the classical as well as in the quantum case. Finally, we discuss the progress in the statistical description of bound states of three particles as in helium plasmas and in $MgCl_2$-solutions in the classical case and present new results regarding the influence of three-particle bound states. In particular, we give new expressions for the cluster integrals and the mass action functions of helium atoms and ionic triple associates as well as for the equation of state (EoS).

**Key words:** *correlation functions, fugacity expansions, mass action constants, atom formation*

Dedicated to the 100th birthday of Ihor R. Yukhnovskii (01.09.1925–26.03.2024)

## 1. Ihor Yukhnovskii and the statistical theory of systems of charged particles

The “Statistical theory of equilibrium systems of charged particles” is one of the main topics of the work of Ihor R. Yuknovskii and is also the title of his habilitation thesis, which he defended in 1965 at the Taras Shevchenko University in Kyiv [1]. We want to show here that besides his big influence on the development of science and society in Ukraine, Ihor Yukhnovskii had a large international impact, in particular on a scientific school at Rostock University. At this University near the coast of the Baltic Sea, the research on charged particles also had a high priority due to the pioneering work of Prof. Hans Falkenhagen (1895–1971) and Günter Kelbg (1922–1988). At this time the basic ideas in this field were developed in the school of Peter Debye, the teacher of Hans Falkenhagen. The “Debye–Hückel–Onsager–Falkenhagen theory” was quite successful in interpreting data. However, this theory was still very much based on intuitive methods [2–4]. Only in the 40–50th of the 20th century the statistical theory of many-particle effects in Coulombic systems was systematically developed using distribution functions by Nikolai N. Bogoliubov [5, 6] and in a different line based on a graph technique by Mayer, Haga, and Poirier, and, most systematically, by Harold Friedman [7]. The third line of systematic statistical approach to Coulomb systems was based on collective variables and is due to Ihor R. Yukhnovskii in Lviv and Günter Kelbg in Rostock.

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*Email: ebeling@physik.hu-berlin.de.

The idea to model ions in solution interacting as effective charged spheres was proposed by Peter Debye, Erich Hückel and Lars Onsager and since then is a standard tool of electrolyte theory [2–4, 7, 8]. The common idea of the works of Günter Kelbg and Ihor Yukhnovslii was to use potentials possessing a Fourier transform and describes this way the screening effects in a most elegant way. The method also allows one to introduce collective variables and to develop a quite effective mathematical technique following the methods by Bohm, Pines and Zubarev [9–18].

Günter Kelbg's and Ihor R. Yukhnovskii's students Norbert Albehrendt, Hartmut Hetzheim and Grigori Bigun continued this work [19–23]. In particular, the late Hartmut Krienke (1943–2023), developed their work for the classical case with many fruitful applications to electrolytes [24]. He also continued collaboration between the groups in Rostock and in Lviv and researched together with Myroslav Holovko, e.g., generalized virial expansions and solvation effects [25, 26]. Further, he developed and analyzed several more general models of effective interactions for electrolytes with non-additive radii [27, 28, 31–34]. In some common work with Hartmut Krienke we discussed several more general models of effective interactions for electrolytes. For example, we discussed in detail the model of charged spheres with non-additive radii [27, 28].

In their first approach to electrolytes, Kelbg and Yukhnovskii used the strict expansions regarding the plasma parameter which were developed in 1946 by Nikolai N. Bogoliubov, solving the so-called BBGKY hierarchy with systematic expansion methods [5, 6] and developed applications to the individual macroscopic properties of ionic species. Individual activity coefficients and individual electrical conductivities of ions are of high relevance for many problems connected with electrolytes. Some basic elements of an extension from Coulomb systems to the more general exponential potentials were given in [24]. A detailed description of the Glauberman–Yukhnovskii–Kelbg theory including an extensive representation of many successful applications to a comparison of the experimental data is given in special chapter in the monograph of Falkenhagen [2, 3]. Here one finds 20 pages of a comprehensive presentation of the Glauberman–Yukhnovskii–Kelbg theory. Despite much success in the description of data, the work on the exponential potential should still be continued [30]. In his heritage, Hartmut Krienke left some notes with the plans for proceeding with the exponential potential. The general idea was to consider a species-independent simple exponential potential as some reference system and treat the short range perturbation by some type of generalized cluster expansion, similar to the one devised in [22, 24, 25].

This work led, in particular, to a summary of the existing theoretical knowledge on the activity coefficients of electrolytes and extended also the theory to mean-spherical approximations and led to applications to transport properties. Special interest was devoted to the consequences of charge asymmetry and of higher charging for the individual ionic properties. This way new information was obtained about the hydration sphere which strongly depends on the charges. The unfinished plan of Hartmut Krienke was to proceed along the same line for species-dependent exponential interactions [30]. The collaboration between the groups of Kelbg in Rostock and Yukhnovskii in Lviv has also been continued in the field of quantum statistics of Coulomb systems [21, 35–39]. Some results of this collaboration, as well as recent developments, will be discussed here.

## 2. Classical systems with exponential interactions

### 2.1. Basic assumptions and model

In the 1950's, Ihor R. Yukhnovskii developed together with his adviser Glauberman [1, 8] a theory of electrolytes based on the method of Bogoliubov [5, 6]. This theory was later extended to the range of higher concentrations in many subsequent works, in particular by using collective coordinates [1, 11]. For the description of the forces between charged particles Yukhnovskii and Glauberman used the effective potential, that had already been proposed in 1927 by Kramers in quantum theory [40] and in 1934 by Hellman in quantum chemistry [41–43]. We refer to this class of potentials as exponential potentials and consider first the simplest form

$$V_{ij}(r) = \frac{Z_i Z_j e^2}{4\pi\epsilon_0\epsilon_r r}[1 - \exp(-\alpha r)], \tag{1}$$

where $Z_i$ are the charge numbers. The exponential potential introduced by Kramers and Hellmann has a finite height at $r = 0$. Glauberman and Yukhnovskii [8, 11] used this potential for solving equilibrium problems of electrolyte theory and Kelbg developed successful applications to transport problems, in particular, applications to conductance and viscosity of electrolytes [2, 3, 12, 13]. Kelbg extended the potential to the quantum-statistical case and studied the applications to plasmas.

**Figure 1.** Ihor Yukhnovskii was fond of nature and liked to walk or to jog in woods. Here we see him on a visit to University of Rostock in 1972 walking in the forest near the Baltic Sea and walking along the beach with his colleagues Günter Kelbg (left-hand) and Werner Ebeling (right-hand) (Fotos: Dorit Hagen).

These calculations were based on the general concepts of the Mc Millan–Mayer theory of solutions [7]. We used approximations of the nonlinear Debye–Hückel and Onsager–Fuoss type, then calculated pressure, osmotic coefficient, electrical and free energy [22]. By Debye-charging we obtained the Helmholtz free energy, and the individual activity coefficients of electrolytes with concentration $n_0$, the ion densities $n_i = \nu_i n_0$, the ion charges $e_i = Z_i e$, and the ionic strength $I = n_0 \sum_i \nu_i z_i^2/2$ . The potentials of the average force between the ions $i$ and $j$, $\psi_{ij}$, are usually separated into the long-range Coulomb potential and a short-range potential $V'_{ij}(r)$. Here we proceed by including an additional exponential part and a short-range part

$$\psi_{ab} = \frac{Z_a Z_b \ell}{r} k_\mathrm{B} T[1 - \exp(-\alpha r)] + V'_{ab}(r); \qquad \ell = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_\mathrm{B} T}. \tag{2}$$

Here, $\ell$ is the Coulomb length and $\epsilon_r(T, p)$ is the relative dielectric constant of pure water or solvent. The length $\ell$ is also called Landau length or (double) Bjerrum length and is a function of temperature and pressure. Here, most calculations are for the temperature $T = 298.15$ K (i.e., 25°C) and $\epsilon_r = 78.36$, the Coulomb length is then $\ell = 715.4$ pm. The simplest possibility in our framework is to identify the long range part $V_{ij}$ with the exact Coulomb potential and to model the short-range repulsion by hard spheres with adaptable constact distances [22, 27, 28]. In order to better describe the physical situation around an ion, in the older work square well and step potentials were introduced [2–4, 31–33]. The hard-core distances were fixed for this model as the sum of Pauling radii. The remaining free potential parameters for the square-well potential were fitted to thermodynamic data, and the parameters of the step potential $h_{ij}$ were fitted to both thermodynamic data and to the conductance data for $c \leqslant 0.3$ mol/l for alkali halides. The only fixed parameter was for iodid ions $d_{JJ} = 0$ which corresponds to $h_{JJ} = 1.28$ (in units $k_\mathrm{B}T$). Physically, this corresponds to the a priori assumption that the iodide-ion is not hydrated.

Replacing here the pure Coulomb potential by an exponential potential allows one to take into account several effects, such as strong deviations at small distances from Coulomb's law due the hydration in solutions and due to Heisenberg uncertainty effects in quantum plasmas. As shown in particular by Kelbg, the first order theory for the exponential potential is aso analytically solvable as for the pure Coulomb potential but leads already to an enormous improvement.

Note that more appropriate for the description of the situation in the solvation region and near it may be the more flexible versions of the exponential potential [24, 33]:

$$V_{ij}(r) = Z_i Z_j k_{\mathrm{B}} T (\ell/r)[1 - \exp(-\alpha_{ij} r)] \tag{3}$$

or the equivalent "ansatz"

$$V_{ij}(r) = Z_i Z_j k_{\mathrm{B}} T (\ell/r)[1 - B_{ij} \exp(-\alpha r)], \qquad B_{ij} = \exp[\alpha - \alpha_{ij}]. \tag{4}$$

An alternative reference system is the Debye–Hückel model [57]:

$$V_{ij}(r) = Z_i Z_j k_{\mathrm{B}} T \frac{\ell}{r} + V'_{ij}(r); \quad V'_{ij}(r) = \infty \quad \text{if} \quad r < R_{ij}, \quad \text{else} \quad V'_{ij}(r) = 0, \tag{5}$$

where $\ell$ is the Coulomb length and $R_{ij}$ is the contact distance. Nowadays, the Debye–Hückel model of charged hard spheres is a kind of standard model with many succesful applications [31–34]. On the other hand, in comparison with the Debye–Hückel model, the exponential potentials have several important advantages [24]:

(i) The exponential potentials are rather smooth and possess a simple Fourier-transform. Therefore, it seems to be also well-suited for the treatment of all screening and collective effects.

(ii) For systems with exponential potential, there exist strict Bogoliubov-type expansions with respect to the plasma parameter.

(iii) The existence of a simple screening equation permits cluster expansions around the first exponential-type approximation similar to those for Debye–Hückel-type systems [22].

(iv) As shown by Kelbg, the exponential potential is quite useful in applications to quantum plasmas [14–17].

In general, in what follows we prefer to use exponential potentials with just one $\alpha$. We want to show that this basic case is already very flexible and permits, if adapted in the best possible way to the system, to reach excellent descriptions of real systems already in the first approximation. The easiest way to map a binary system to an approriate $\alpha$-parameter is the following choice of the $\alpha$-parameter:

(i) $\alpha = \alpha_{+-}$. This choice is related to the so-called opposite charge approximation in plasma theory.

(ii) More appropriate may be the request that the exponential potential covers the first deviation of important thermodynamic and transport quantities from the limiting law, in an exact way. We show how we may go from a matrix system with many $\alpha$-parameters, to a reference system with just one parameter. The request in the case of thermodynamic functions leads to the choice

$$\frac{1}{\alpha} = \frac{\sum_i \sum_j e_i^2 e_j^2 (1/\alpha_{ij})}{\sum_i \sum_j e_i^2 e_j^2}. \tag{6}$$

A different, even more efficient way, which we introduce herein later, is averaging of the screening functions at the level of pairs similar to equation (6). The most important advantage of the exponential potential as a reference system is based on the fact that the Fourier transform is so simple:

$$\tilde{V}_{ij}(k) = Z_i Z_j V(k) = Z_i Z_j k_{\mathrm{B}} T \ell \Big[\frac{4\pi}{k^2} - \frac{4\pi}{k^2 + \alpha^2}\Big]. \tag{7}$$

We note that our potential includes a weak short-range repulsion having a Fourier-transform. In spite of the simplicity of an extension by matrix terms, the screening problem is then much more difficult. The question about the choice of a charge-independent $\alpha$-parameter is to decide from case to case that the leading aspect should be that the encounters of opposite charges are well described.

The question whether two potential models A and B are equvalent is not trivial. Most often one uses the rule that the two 2nd virial coefficients for the two potentials are similar or even identical. This, however, does not work for Coulomb systems, since the 2nd virial coefficients do not exist. Therefore, we use the prescription that two potential models for the ionic interaction are equivalent, if the first deviations from Debyes limiting law are equal.

We start as in [24] from the case of no additional short-range corrections and use the Bogoliubov approximation $F_{ij}(1,2) = 1 + g_{ij}(1,2)$:

$$g_{ij}(1,2) + \beta V_{ij}(1,2) + \beta \sum_{k} n_k \int V_{ik}(1,3) g_{jk}(2,3)\,\mathrm{d}\mathbf{3} = 0. \tag{8}$$

This approximation may be considered as the first term of a Bogoliubov-type expansion with respect to the plasma parameter [2, 3]. In some sense, the Bogoliubov equation for the correlaton function $g_{ij}$ is related to the Ornstein-Zernike equation which is the basis of HNC and MSA-related theories [4]. We have to note, however, that the Bogliubov-type approach is historically the first systematic approach to Coulomb systems and is related too, but in detail it is quite different from MSA-type approximations [4].

In the general case that $\alpha$ is a matrix, the correlation function was obtained by solving the integral equations [2, 3, 57]. In the simplest case, that all $\alpha$ are equal, or that we use an averaged one, the solution is particularly easy and reads

$$g_{ij} = -Z_i Z_j \frac{\ell \alpha^2}{r(p^2 - s^2)} \big[\exp(-pr) - \exp(-sr)\big]. \tag{9}$$

The parameters $s$ and $p$ are solutions of a 4th order polynomial. At very small densities, the solutions are $s = \alpha$ and $p = \kappa = 1/r_D$. At intermediate densities we have [2, 3]

$$p = \frac{\alpha}{2}\left[\sqrt{1 + 2\frac{\kappa}{\alpha}} - \sqrt{1 - 2\frac{\kappa}{\alpha}}\right]; \qquad s = \frac{\alpha}{2}\left[\sqrt{1 + 2\frac{\kappa}{\alpha}} + \sqrt{1 - 2\frac{\kappa}{\alpha}}\right]. \tag{10}$$

We study now the thermodynamic functions for the case that we have only one $\alpha$. The Coulomb energy is

$$U^C = \frac{V}{2} k_{\mathrm{B}} T \sum_{ij} n_i n_j Z_i Z_j \int \frac{\ell}{r_{12}} g_{ij}(1,2)\mathrm{d}\mathbf{2} = -k_{\mathrm{B}} T \sum_{ij} n_i n_j Z_i^2 Z_j^2 \ell^2 \frac{\alpha^2}{(p^2 - s^2)} \left[\frac{1}{p} - \frac{1}{s}\right]. \tag{11}$$

The most easy way to extend this formula to mixtures with parameter $\alpha_{ij}$ avoiding a matrix calculation is the averaging at the level of the screening functions of pairs instead of averaging the $\alpha_{ij}^{-1}$ as in equation (6)

$$U^C = -k_{\mathrm{B}} T \sum_{ij} n_i n_j Z_i^2 Z_j^2 \ell^2 \frac{\alpha_{ij}^2}{(p_{ij}^2 - s_{ij}^2)} \left[\frac{1}{p_{ij}} - \frac{1}{s_{ij}}\right]. \tag{12}$$

Further results and applications will be given below. The success of the description by exponential potentials is based on the fact that an essential part of the short-range effects is included by an optimum choice of the exponential potential. According to Yukhnovskii and Kelbg, we get for the contribution of the Kramers–Hellmann potential [1, 12, 13]

$$\beta F_{KY} = \beta F_{\mathrm{id}} - \frac{\kappa^3}{12\pi} \tau\left(\frac{\kappa}{\alpha}\right); \qquad \beta p = n - \frac{\kappa^3}{24\pi} \varphi\left(\frac{\kappa}{\alpha}\right), \tag{13}$$

$$\varphi(x) = \frac{1}{x^3}\left(\frac{1}{4}X^3 - \frac{2}{3}X - \frac{3}{4X}\right); \qquad \tau(x) = \frac{3\alpha^3}{4\pi\kappa^3}\left(Y^2 - 2Y + \frac{2}{3}Y^3 - \frac{1}{2}Y^4 + \frac{5}{6}\right), \tag{14}$$

$$x = \frac{\kappa}{\alpha}; \qquad X = \sqrt{1 + 2\frac{\kappa}{\alpha}}; \qquad Y = 2 + X. \tag{15}$$

For the excess chemical potential of an ion and the mean activity coefficient there follows a simple form [8]

$$\mu_i^{\mathrm{ex}} = -\frac{e_i^2\alpha}{4\pi\epsilon_0\epsilon_r k_{\mathrm{B}}T\kappa}\left[1-\frac{1}{\sqrt{1+2(\kappa/\alpha)}}\right], \quad \log f_{\pm} = -\frac{|e_1e_2|\alpha}{4\pi\epsilon_0\epsilon_r k_{\mathrm{B}}T\kappa}\left(1-\frac{1}{X}\right). \tag{16}$$

Remember that we have for the Debye–Hückel model for the mean activity and the free energy function

$$\ln f_{\pm}^{\mathrm{DH}} = -\frac{|Z_1Z_2|\ell\kappa}{(1+\kappa a)}; \qquad \tau_{\mathrm{DH}}(\kappa a) = 1-\frac{3}{4}(\kappa a)+\frac{3}{5}(\kappa a)^2-\frac{3}{6}(\kappa a)^3+\ldots \tag{17}$$

For comparison of the Debye–Hückel reference system with the simple exponential system, we may define $a$-parameter conjugated to our $\alpha$-parameter by $a = (3/2\alpha)$ or in the case of mixtures by $a_{ij} = (3/2\alpha_{ij})$.

Further corrections by a short-range and a hard core part of the potential may be included by the second virial contribution [4]. This will be discussed below. The case of complex $\alpha$ which corresponds to oscillating potentials remains to be discussed.

## 2.2. Individual electrolytic conductivities

As known already to Nernst, the effect of nonideality on the conductivity is structurally closely related to the effect on the osmotic pressure. Including external electrical fields is an extra big chapter of the electrolyte theory [2–4] which we can only touch upon here, making use of the many parallels between individual osmotic coefficient and transport. As a matter of fact, not only historically but also systematically, the extension of the equilibrium theory of electrolytes to weak external field effects is based on quite similar tools of statistical physics. In our case, the relevant tools are the pair distribution functions and the tools of density and interaction. Here we haven't got enough space to repeat the transport theory [2, 3, 29], we give only the key ideas and present some extrapolations.

Under the influence of weak external electrical fields $E$, the pair distribution is split into an equilibrium and a non-equilibrium part which is a solution of differential equations formulated by Onsager. The perturbation is different from zero only for oppositely charged ions and is known in several approximations [33]: in order to get the effects of nonideality on conductivity we have to calculate by standard methods [2, 3] the relaxation force and the electrophoretic force and the corresponding contributions to the specific conductivity [27, 28]:

$$\frac{\sigma_i}{\sigma_{i0}} = \bar{\alpha}_i + S_i^{\mathrm{elp}} + S_i^{\mathrm{rel}}; \qquad \sigma_{i0} = \frac{n_ie_i^2}{\rho_i}, \tag{18}$$

where $\sigma_{i0}$ is the ideal conductivity and $\rho_i$ is the friction parameters of the ions. The first term reflects the decrease of conductivity due to association. This is the Arrhenius effect which is parallel to the effect of the osmotic coefficient. As far as the association is weak, we may just take over the earlier found expression. The next correction which is dominant is due to hydrodynamic interactions and is called electrophoretic effect. For the estimation of the electrophoretic force action on the ion $i$ may use the expression for the Coulombic energy per ion since ($\eta_0$ — viscosity) [2, 3]:

$$S_i^{\mathrm{elp}} = -k_{\mathrm{B}}T\frac{\rho_iZ_i^2}{3\pi\eta_0}\sum_j n_jZ_j^2\ell^2\left[\frac{1}{p}-\frac{1}{s}\right]. \tag{19}$$

Note that in the case that the the short-range components of the forces are species-dependent, the solution for the correlation function is more complicated and strictly speaking needs a matrix theory.

Our approach will be applied now to conductivities using, in particular, the fact that individual conductivities are structurally related to the individual energies and osmotic pressures. We show that we can proceed this way to concentrations of interest for the description of measured conductance data. Further we also include some applications of the exponential potential to quantum statistics which go back to Kelbg [14, 15]. We use as measures of concentration the molar concentration $c_i$ in mol/dm$^3$ in the solute as well as the density $n_i = N_i/V$ of the species $i$. The first term reflects the Arrhenius effect, i.e., a decrease of conductivity due to association. As far as field effects are weak, we may just take over the expression for the degree of ionization given above. The next correction is due to hydrodynamic interactions. Its contribution to the specific conductivity is negative and can be expressed by the electrical part of the electrical energy density. This way, two nonideality contributions are already known from equilibrium results. Expressions for the relaxation part of conductivity are known for ions with non-equal contact distances $a_{ij} = R_{ij}$:

$$S_i^{\mathrm{rel}} = -\frac{\ell \kappa q}{3(1-q)} \sum_j \zeta_j^0 \left(1 + \frac{|Z_i|}{|Z_j|}\right)\left(\frac{1}{1+\kappa a_{ij}} - \frac{\sqrt{q}}{1+\sqrt{q}\kappa a_{ij}}\right). \tag{20}$$

The free parameters are here the contact distances and the friction constants $\rho_i$, which are related to the Stokes radii and to the limiting molar conductivities $\sigma_{i0}$ by classical relations and $q = 1/2$ [2, 3]. We approximated here the relaxation part of the conductivity as a sum of binary contributions and refer to this as a partial fraction representation.

The corresponding expressions for the exponential potential are also known in part. Particularly easy is the electrophoretic part which is expressed by the known Coulomb $u_i^{\mathrm{el}}$ given above. In order to find the relaxation part of conductivity for more general exponential potentials, we have to calculate the perturbation of the correlation function in the external field (here in $x$-direction). For our exponential potential we find

$$g_{12}(r) \sim \frac{\partial}{\partial x}\left\{A_0\left[\frac{\exp(-pr)}{r} - \frac{\exp(-sr)}{r}\right] + A_1\left[\frac{\exp(-p'r)}{r} - \frac{\exp(-s'r)}{r}\right]\right\}. \tag{21}$$

The calculation of the relaxation term is easy for $B_{12} = 1$; the two relevant roots are [2, 3, 12, 13]:

$$p' = \frac{\alpha}{2}\left(\sqrt{1+2\sqrt{q}\frac{\kappa}{\alpha}} - \sqrt{1-2\sqrt{q}\frac{\kappa}{\alpha}}\right); \quad s' = \frac{\alpha}{2}\left(\sqrt{1+2\sqrt{q}\frac{\kappa}{\alpha}} + \sqrt{1-2\sqrt{q}\frac{\kappa}{\alpha}}\right).$$

Based on this result, we may obtain the conductivity for the exponential potential. An application to NaCl in aqueous solution is shown in figure 2 representing the results due to Kelbg. We see a very good agreement of theory with the data up to 1 mol/l [2, 3]. Kelbg found as adapted parameter $\alpha^{-1} = 370$ pm. One may be sure that the model with more than 1 adaptable $B_{ij}$-parameters describes for NaCl the data even up to 1.5 mol/l. In figure 2 we show the theory for charged spheres, corresponding to the parameters $R_{\mathrm{NaNa}} = 479$ pm, $R_{\mathrm{NaCl}} = 350$ pm, $R_{\mathrm{ClCl}} = 360$ pm found by fitting contact distances in [27, 28]. The model of charged hard cores is in reasonable agreement with the data only up to $c = 0.2$ mol/l. Beyond this concentration, the theoretical curve starts to deviate from the data for NaCl at $c > 0.3$ mol/l, although the exponential potentail model still fits well. We may conclude that the exponential potential describes the effective forces somewhat better. We note that the Pauling radii of the corresponding ions are $R_{\mathrm{Na}} = 95$ pm, $R_{\mathrm{Cl}} = 167$ pm, which means that the fitted contact distances substantially deviate from the sums of the Pauling radii. In conclusion, we may say that the exponential potential used by Kelbg and Yukhnovskii is well suited, and probably a combination of exponential potential and hard core potentials has best perspectives.

Our figure 2 which is due to Kelbg [2, 3], demonstrates an excellent description of the data up to 1 mol/l for the mean activity coefficients and for the conductivity. Anyhow, we see that the given theory for the exponential potential given above provides a most simple and useful first approximation which agrees well with more advanced theories of the ionic conductivities discussed above [27, 28]. A different successful strategy is to combine an exponential potential with one free parameter with a hard core potential. In all cases it is highly recommended to use for the fit not only one set of data for a specific property but much better several data series for different properties, e.g., activities and conductivities. Note that conductivities permit very precise measurements and are more sensitive to association and to anion-cation interactions.

## 2.3. Virial expansions for classical charged particles

More recently several thermodynamic and transport properties have been calculated for models of charged partcles. For simplicity, here we use charged spheres with adaptive non-additive contact

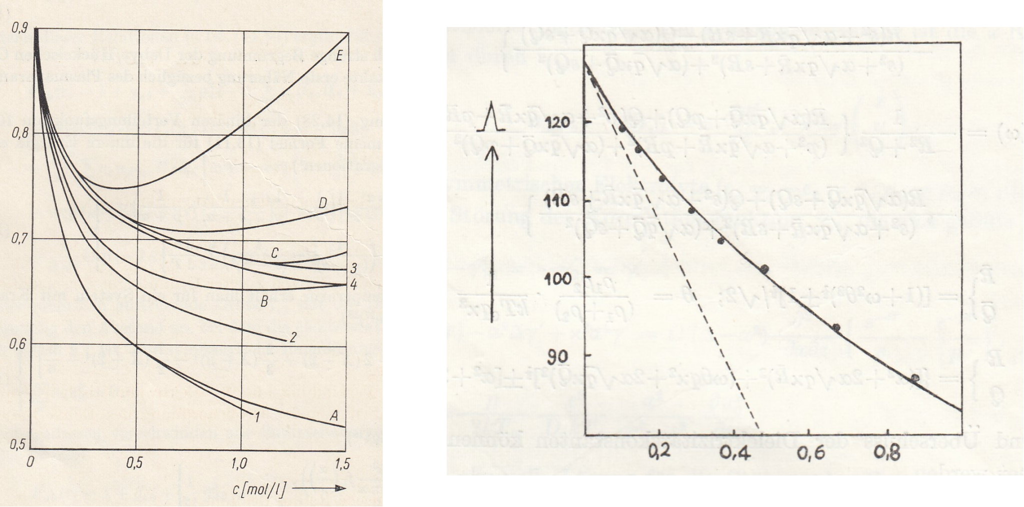


**Figure 2.** Left-hand: mean activity coeffiient according to Kelng [2, 3] for different parameters $\alpha^{-1} = 1.85, 2.50, 4.09, 4.50$ Å (from below) as well as several exprimental curves for LiOH–A, NaOH–B, NaBr–C HCl–D [2, 3]. Right-hand: the conductivity of NaCl with the Kelbg's theory for this potential with adapted $\alpha^{-1} = 3.1$ Å [2, 3].

distances $R_{ij}$ [27, 28]. The long-range part $V_{ij}$ is identified with the exponential potential of Kramers and Hellmann and consider the contact distance $R_{ij}$ as an adaptable parameter. This is the route we considered in the papers [27, 28, 34]. The statistical theory applied to our model potentials is based on the classical work of Mayer, extended by Friedman [7] and, in particular, by the collaboration Yukhnovskii–Kelbg [11, 19, 20]. This theory based on cluster expansions provided several exact results for the thermodynamic functions valid for small ionic densities. General expressions from statistical thermodynamics for the cluster contributions $S$ to the negative free excess energy of hard charged spheres read [2, 3, 7, 11, 19, 20]

$$F_{\text{ex}} = F_{DH} + F_2 + F_3 + \ldots = -k_{\text{B}} T V \left[ \frac{\kappa^3}{12\pi} \tau\left(\frac{\kappa}{\alpha}\right) + \sum_{i,k} S_i^{(k)} \right], \tag{22}$$

where $\tau(x)$ is the so-called ring function. The cluster integrals are expressed by the cluster pair functions $\psi$ which are in Kelbg–Yukhnovskii approximation

$$\psi_{ij} = \exp[g_{ij} - \beta V'_{ij}] - 1 - g_{ij}; \qquad \tau(x) = 1 - \frac{9}{8}x + \frac{3}{2}x^2 - \frac{21}{12}x^3 + \ldots \tag{23}$$

The sums should be extended over the species of ions $i$ and all orders of clusters $k$. The strong coupling contributions of ions $i$ read in the cluster order $k = 2, 3$ [2, 3, 7, 11, 19, 20]

$$S_i^{(2)} = \frac{1}{2} n_i \sum_j n_j \int \mathrm{d}\mathbf{r}_j \mathbf{g} \left[\psi_{ij} - \frac{1}{2} g_{ij}^2\right],$$

$$S_i^{(3)} = \frac{1}{2\cdot 3} n_i \sum_{jk} n_j n_k \int \mathrm{d}\mathbf{r}_j \, \mathrm{d}\mathbf{r}_k \left[\psi_{ij}\psi_{ik}\psi_{jk} + g_{ij}\psi_{ik}\psi_{jk} + g_{ik}\psi_{jk}\psi_{ij} + g_{jk}\psi_{ij}\psi_{ik}\right]. \tag{24}$$

The basic elements is the cluster function $\psi_{ij}$ which is of the order $O(e^4)$ in the interactions. We see here that the 2nd cluster integral starts with the order $e^4$ and the 3rd virial coefficient with the order $e^8$ [34].

Several values for the contact distance were fitted to the data [27, 28, 34]. We notice important deviations from additivity of individual radii.

**Calculation of triple integrals and mass action functions:** We come now to the derivation of mass action constants for the triple formation. Our basic assumption is that the convergent part of the cluster integrals is directly related to the mass action function of triple formation. More presicely, analyzing the triple cluster integral we have to select those parts which are non-negative, grow exponentially for $\epsilon k_{\mathrm{B}}T \longrightarrow \infty$ and depend only on the energy units, which are classically the Bjerrum energy $U_{Bj} = e^2/4\pi\epsilon\epsilon_0 R_{\pm}$ or the Rydberg energy Ry in the quantum case. In figure 3 we show several Mayer-like diagrams which are possible candidates for bound state contributions of 3 charged particles of type $(2+,-,-)$ since they contain at least one 4-fold $(+-)$-bound. From the 2-particle bound state problem, we know that a 4-fold $(+-)$-bound provides a tight $(+-)$-binding of two particles. The investigations of the diagrams with 3 or 4 nodes with only one 4-fold binding shows, however, that the integrals are, according to Friedmans estimates, evidently divergent. Including, however, two 4-fold $(+-)$-bounds, we arrive at the graphs (the lower diagrams) which are for sure convergent even without screening. This is the reason why we may include them in the classical and in the quantum case as the lowest order binding contributions of 3 or more particles. The basic assumption of the present paper is that the mass action constant is related to an asymptotic part of the 3rd virial coefficient, which should be convergent and non-negative and a exponentially growing function of the reciprocal Bjerrum temperature $\bar{\beta} = U_{Bj}/k_{\mathrm{B}}T$ or Rydberg temperature $\tilde{\beta} = Ry/k_{\mathrm{B}}T$. The technique of concrete evaluation of the virial coefficients is quite complicated [4, 7]. The method we used in [27, 28, 34] is based on expansions with respect to $e^2$. We provided in [34] only the coefficient of $e^{10} \sim \tilde{\beta}^5$. Here we generalize the approach and also obtain the coefficients of $e^8 \sim \tilde{\beta}^4$. In the fugacity series which is relevant for the determination of the mass action coefficients there appear reducible and irreducible terms (see [44] and figure 5), which both should be evaluated.

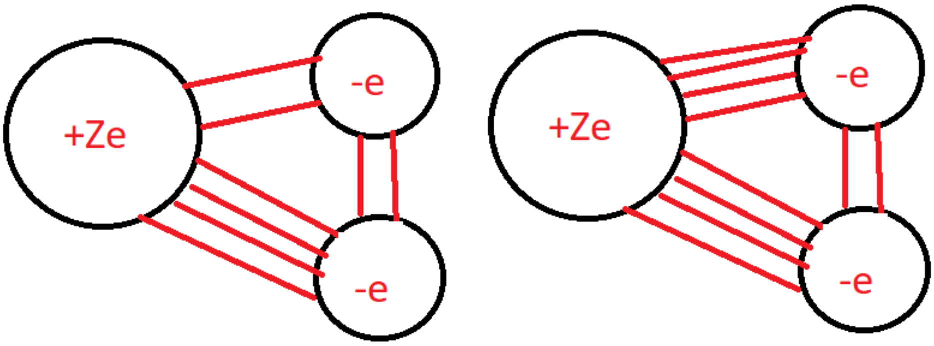


**Figure 3.** (Colour online) Typical 3-particle diagrams which we study here. The diagrams show one 2-fold charged positive ions as $\mathrm{Mg}^{++}$ or $\mathrm{He}^{++}$ and 2 negative single-charged ions as $\mathrm{Cl}^{-}$ or electrons connected by interaction bonds. The 2-fold and 4-fold lines stand for 2nd order and 4th orders of the expansions of the $\psi$-functions.

We may give this way the missing order $\bar{\beta}^4$ which is quite relevant. In the integrals there appear a strong coupling exponential function $\psi_{ij}$ analyzed in detail in [34] which is of a higher order $O(e^4)$ in the interactions. One of the reducible terms in the 3rd virial coefficient is just a square of the second virial coefficient. This provides a contribution $\delta K^{(3)}(T) \sim [S_i^{(2)}]^2$. With a correct normalization we get $\delta K^{(3)}(T) \sim 50\bar{\beta}^4$. For calculation of the irreducible graphs we have to solve 2-center integrals of the following type

$$\delta K^{(3)}(T) \sim \int_1^\infty \mathrm{d}r' \, (1/r')^{n-1} \int_1^\infty \mathrm{d}s' \, (1/s')^{m-1} \int_{|r'-t'|}^{r'+s'} \mathrm{d}t' \, (1/t') \,. \tag{25}$$

The case $m = n = 4$ was calculated in [34] leading to $a_5 = 3.1$. We add here the calculation for the case

$n = 2$, $m = 4$ finding the integral

$$C_{n=2,m=4} = \pi^2 \int\limits_1^\infty \mathrm{d}r' \; (1/r')^3 \int\limits_1^\infty \mathrm{d}s' \, (1/s')^2 \; \simeq \; \frac{\pi^2}{2} \simeq 4.93. \tag{26}$$

This provides the coefficients which are the sum of reducible and irreducible graph (48.92)

$$a_4 = (35.1 + 48.9) = 84; \qquad a_5 = 15.3. \tag{27}$$

Completing the previous paper we calculated the lowest order in the Taylor expansion of the triple mass action constant which permits to find a complete expression for the triple mass action constant

$$K^{(3)} = a_4 \bar{\beta}^8 + a_5 \bar{\beta}^{10} + \sum_{k=6} \frac{(7\bar{\beta})^{2k}}{2(2k)!} \tag{28}$$

for all (reduced) temperatures. Note that in comparison with reference [34], the new values for the triple association constant are larger than the results obtained earlier for $MgCl_2$ and for $Na_2SO_4$. Correspondingly, the new estimates give also larger values for the degree of triple association using the expressions

$$\delta^{(3)} = 2 n_+ n_-^2 f_\pm^2 K^{(3)}(T); \qquad \ln f_\pm = -\frac{z_+ z_-}{2} \frac{\kappa \ell}{(1+\gamma_\pm)}. \tag{29}$$

Here, $f_\pm$ are the activity coefficients in electrical oppositely charge approximation [27, 28].

## 3. Quantum statistics and cluster expansions

### 3.1. Kelbg potential and cluster expansions

At the end of the 60th and in particular after the first visit of Ihor Yuknovskii to Rostock University in 1968, quantum-statististical investigations were included into the collaboration beween the two schools. The collaboration led an exchange of students and aspirants and to many remarkable results [21, 25, 35–39, 45, 47]. One of the tasks was to extend the virial expansions in the canonical ensemble developed by Ihor Yukhnovskii [10, 11] and Günter Kelbg [14, 15]. In particular, the development of the method of fugacity virial expansions which we will present now, started in 1969 at a seminar in the Institute on the Dragomanov street in Lviv founded by Ihor R. Yukhnovskii. Since Prof. Yukhnovskii was of a high opinion about the prospects of this new "ansatz" based on fugacity virial expansions, he proposed to publish the 2 lectures in Lviv as Preprints of the Ukrainian Institute of Theoretical Physics [38, 39]. Here we summarize how the method presented for the first time in 1969 in a seminar at the Institute in Lviv, has developed over the years. In order to take into account the screening effects into statistical expansions we need to sum up an infinite number of ring-type diagrams in the grand-canonical ensemble.

For quantum-statistical Coulomb systems, the pair potential consists, the same as for the classical case, of a long-range part $V_{ab}$ which contains a Coulomb tail and has a Fourier transformable part and a short-range part. Following the work of Kelbg [14, 15, 18], the quantum form of the exponential potential is in the first approximation given by

$$V_{ij}^K(r) = \frac{e_i e_j}{4\pi\epsilon_0 r}\left[1 - \exp\left(-\alpha_{ij}^K r\right)\right]; \quad a_{ij}^K = \frac{2}{3\alpha_{ij}^K} = \frac{\sqrt{\pi}}{9}\lambda_{ij}; \qquad \lambda_{ij} = \frac{\hbar}{2 m_{ij} k_\mathrm{B} T}. \tag{30}$$

Here, we introduced, besides the $\alpha$-parameter, a corresponding distance parameter $a_{ij}^K$; which is a kind of effective hard core diameter for charges in a quantum plasma [35–37, 47, 57]. Note that in many applications instead of a manifold of $\alpha$ parameters, only one $\alpha_\pm$ is used. This is the simple opposite-charge approximation (OPA), which works well for two component plasmas in the region of partial ionization [57]. The quantum potential has a finite height in $r = 0$. A more precise quantum-statistical caculation leads Kelbg to the expression [18]

$$V_{ij}^{K}(r) = \frac{e_i e_j}{4\pi\epsilon_0 r}\left\{1 - \exp\left(\frac{r^2}{\lambda_{ij}^2}\right) + \sqrt{\pi}\frac{r}{\lambda_{ij}}\left[1 - \Phi\left(\frac{r}{\lambda_{ij}}\right)\right]\right\}. \tag{31}$$

We used here the standard definition of the error function $\Phi(x)$. For the Fourier transform, we get [14, 15, 38, 39]

$$V_{ab}^{K}(t) = \frac{e_a e_b}{\epsilon_0 t^2} M\left(1, \frac{3}{2}, -\frac{1}{4}\lambda_{ab}^2 t^2\right), \tag{32}$$

where $M = {}_1F_1$ is the well known confluent hypergeometric function, which is also called Kummer function. This first result by Kelbg which still neglects the exchange effects had been given already in 1963. The Kummer function may be represented in integral form or using a Taylor expansion or alternatively the asymptotics shows a decay like $x^{-2}$:

$$M\left(1, \frac{3}{2}, -x^2\right) = \frac{1}{2}\int_0^1 \mathrm{d}u\, \frac{\exp(-ux^2)}{\sqrt{1-u}} = 1 - \frac{1}{6}x^2 + \frac{1}{30}x^4 + \ldots \simeq \frac{1}{(1 + x^2/6)}. \tag{33}$$

We see that the Kummer function may be approximated by a simple rational function corresponding to equation (1), i.e., to an exponential form of the potential. This way the rational approximation leads us back to the previous exponential approximation with

$$\alpha_{ij}^{-1} = (\sqrt{\pi}/6)\lambda_{ij}.$$

This indeed shows a close relation between the full Kelbg quantum potential and the exponential potential, inspite of the quite different mathematical form. We have shown that the Fourier transforms of both potentials are quite similar and differ only for large Fourier vectors. Therefore, in applications, which are based on the Fourier transform as the screening procedure, we may replace the original Kelbg potential by the exponential potential and use the Kelbg–Yukhnovskii screening theory.

Besides we note that Kelbg also included the exchange effects and provided the Fourier transforms using hypergeometric functions, although the back transform to real space has not yet been found. A generalization to nondiagonal representations is the so-called Filinov approximation which is of much interest for numerical applications in path integral calculations [57, 58].

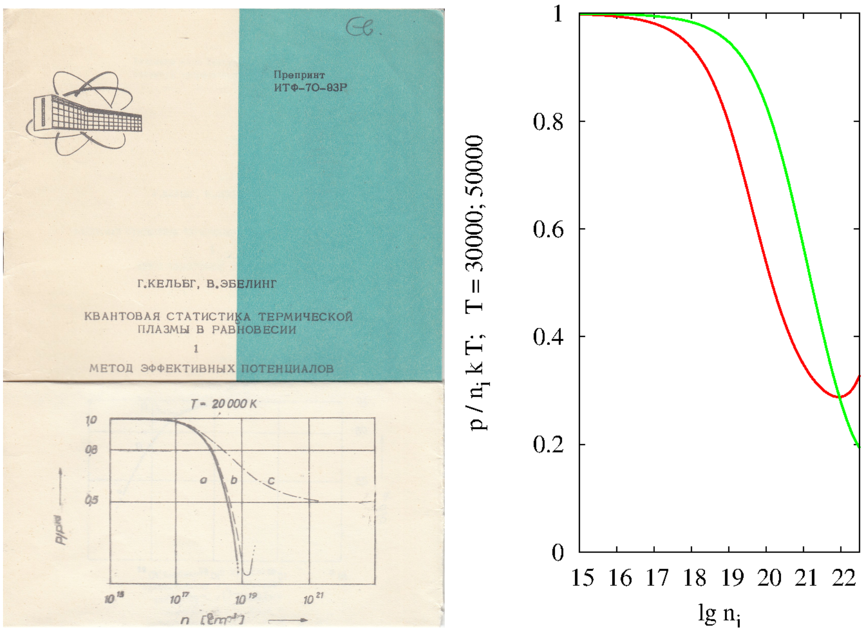
The fact that the main part of the potential $V_{ab}^{K}(\mathbf{r})$ has a Fourier transform

$$V_{ij}^{K}(\mathbf{r}) = \frac{1}{V}\sum_{k} \exp(-\mathrm{i}\mathbf{k}\mathbf{r})\, V_{ij}^{K}(\mathbf{k}) \tag{34}$$

suggests a special mathematical technique for the evaluation of the classical or quantum partition function which is based on the method of collective variables. This method was developed for Coulomb systems suggested first by Bohm, Pines and Zubarev and worked out then by Yukhnovskii and Kelbg. This method works in the classical as well as in the quantum case and typically leads to the following structure of the general partition function [10, 14, 15]:

$$\log Z(T, V, N) = \log[Z_{\mathrm{id}} Z_0] + \log Z_{\mathrm{ring}}(T, V, N) + \sum_{n=2}^{\infty} \log Z_n(T, V, N). \tag{35}$$

Here, $Z_0$ is the lowest order term which is of the order $e^2$ in the interaction and is connected with the contribution of the zero wave vector $\mathbf{k} = 0$ to the Fourier transform [11, 68]. This contribution is denoted as the self-energy of the long-range field [68]. It comprises the Hartree–Fock terms as well as possibly some ideal quantum terms (in dependence on the definition of the term $Z_{\mathrm{id}}$). The following ring term comprises a set of contributions typical of Coulomb systems which describe the screening effects and



Препринт
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Г.КЕЛЬБГ, В.ЭБЕЛИНГ

КВАНТОВАЯ СТАТИСТИКА ТЕРМИЧЕСКОЙ
ПЛАЗМЫ В РАВНОВЕСИИ
1
МЕТОД ЭФФЕКТИВНЫХ ПОТЕНЦИАЛОВ

**Figure 4.** (Colour online) Left-hand: equation of state (EoS) of hydrogen plasmas from a fugacity expansion (upper thin curve c) in comparison with the density expansion (lower fat curve a) and the cover of the Preprint ITF-7093P (Kiev, 1970) [38]. Right-hand: the EoS of hydrogen plasmas calculated by using Padé approximations [47, 56] for $T = 30\,000$ K (red curve) and for 50 000 K (green curve) as a function of $\log(n_i)$.

contain the Debye contribution and generalizations. The contributions $Z_0(T,V,N)$ and $Z_{\text{ring}}(T,V,N)$ are mainly determined by the Fourier transform of the long-range part of the effective potential and are essentially determined by contributions of order the $e^4$ in the interaction. This procedure traditonally performed in the canoncical ensemble. In connection with the task to treat the bound states in an effective way, in lively discussions in the Yukhnovslii seminars in 1969 in his Institute in the Uliza Dragomana the idea arose to transfer the whole procedure to the grand canonical ensemble [38, 39].

This way this fruitful new method was first demonstrated in the mentioned seminars in Lviv under the auspices of Ihor Yukhnovskii [38, 39, 44]. Extensive applications to real plasmas were given later by Rogers and DeWitt in the Livermore group [49–52, 54]. We explain here only the basic ideas and several analytical results. In order to have a closer relation between fugacities and densities, from now on we use the fugacities which are not dimenisonless as above but have a dimension of densities. For the definitions of new fugacities $z_i$ we use the relation with the chemical potentials $\mu_i$ by

$$z_i = \frac{(2s_i+1)}{\Lambda_i^3}\exp(\beta\mu_i); \qquad \Lambda_i = \frac{h}{\sqrt{2\pi m_i k_{\text{B}} T}}. \tag{36}$$

In terms of these new fugacities, we may derive a statistical expansion of the pressure [38, 39, 44, 47, 56] using as in [44] the Debye screening. However, much better is an approximation by screening the full exponential potential as in the classical case. For the ring contributions to the partition function, according to [14, 15] for one-component plasmas we find

$$\log Z_{\text{ring}}(T,V,N) = \frac{V}{4\pi^2}\int\limits_0^\infty \mathrm{d}t\, t^2\{w(t) - \ln[1+w(t)]\}; \quad w(t) = \frac{\kappa^2}{4\pi}\tilde{V}^K(\mathbf{t}). \tag{37}$$

The ring expression reduces in zeroth approximation to the Debye result. Here, we include the higher orders corresponding to the full exponential potential which leads to an substantial improvement. In a first approximation, we use the exponential approximation for the Kelbg potential and identify all elements of the matrix $\alpha_{ij}$ by just the one cooresponding to the pair of opposite charges $\alpha = \alpha_{ij} \rightarrow \alpha_{\pm}$. In this approximation, we avoid the matrix theory. A charging procedure in connection with the graph expansion leads to

$$p_{\text{ring}} = -\frac{K^3}{24\pi}\tilde{f}\left(\frac{K}{\alpha}\right); \qquad \tilde{f} = 1 - \frac{3\sqrt{\pi}}{16}(K\lambda_{\pm}) + \frac{1}{10}(K\lambda_{\pm})^2 + \dots \tag{38}$$

The ring function has been expressed here by an expansion [71, 72]. The full expression for the pressure consists, apart from the Fermi–Dirac part, of the ring term and the cluster series.

$$\beta p = \beta p_{\text{FD}} + \beta p_{\text{HF}} + \beta p_{\text{ring}} + \sum_{a,b} z_a z_b b_{ab}(K) + \sum_{a,b,c} z_a z_b z_c b_{abc}(K) + \dots \tag{39}$$

As the basic statistical quantity we consider the grand potential $\Omega = F - \sum N_i \mu_i$ which neglecting the fluctuations corresponds to the pressure $\Omega = -pV$. The grand potential $\Omega$ is a thermodynamic potential if the variables are $T, V$ and the chemical potential $\mu$ or the fugacity $z = \exp(\beta\mu)$. Note that the sums run here over all species. The ring function is of the same form as in the classical case equation (15). However, we have a grand-canonical screening quantity, instead of the canonical

$$K^2 = \sum_b K_b^2, \quad K_b^2 = 4\pi\ell Z_b^2 z_b. \tag{40}$$

Note that we may have a more complicated dependence on the masses. As already mentioned, we simplified here and have only a dependence on the relative mass $m_{\pm}$ of oppositeley charged pairs (OPA) [57, 71, 72].

Completing the earlier studies we are mostly interested in the bound state contributions which are contained in the virial coefficient. This was already demonstrated by Kelbg and this author in in the mentioned lecture in Lviv 1970 and is seen in figure 4. As shown in these figures, the relative pressure has characteristic shoulders which are signals of changes of the effective particles numbers in the system. In order to study these effects in detail, we first study a simple model system created by cutting all Coulomb forces at a finite distance $r_{\text{cut}}$, assuming $V_{ij}(r) = 0$ if $r > r_{\text{cut}}$. This way we avoid the divergences connected with the long range Coulomb interaction, which are regularized considering the screening effects but still keep the essence of the bound states. We introduce new fugacities $\tilde{z}$ which are normalized to converge at low densities to the densities at finite dilution [47]. As is well known, cluster expansions wihtin the grand ensemble lead to the series in terms of fugacities, which have a similar shape as the series in terms of densities but contain more terms stemming from reducible diagrams. We want to show here that expansions with respect to fugacities may be more appropriate for the description of the bound states than the well known virial expansions with respect to densities. We use here fugacities $\tilde{z}$ which are normalized in the way that they converge to densities at infinite dilution.

$$\begin{aligned} \beta p \;&=\; \sum_{j=1}^{\infty} b_j \tilde{z}^j = \frac{1}{V}\left(\tilde{Q}_1 \tilde{z} + \frac{1}{2!}\tilde{Q}_2 \tilde{z}^2 + \dots\right) \\ &-\; \frac{1}{2V}\left(\tilde{Q}_1 \tilde{z} + \frac{1}{2!}\tilde{Q}_2 \tilde{z}^2 \dots\right)^2 + \frac{1}{3V}\left(\tilde{Q}_1 \tilde{z} + \frac{1}{2!}\tilde{Q}_2 \tilde{z}^2 \dots\right)^3 . \end{aligned} \tag{41}$$

We see that the coefficients of the order $\tilde{z}^N$ are essentially given by $N$-particle traces. By comparison of equal powers $\tilde{z}^k$, we get

$$b_1 = \frac{1}{V}\tilde{Q}_1, \quad b_2 = \frac{1}{2V}\left(\tilde{Q}_2 - \tilde{Q}_1^2\right), \quad b_3 = \frac{1}{6V}\left(\tilde{Q}_3 - 3\tilde{Q}_1\tilde{Q}_2 + 2\tilde{Q}_1^3\right), \; \dots . \tag{42}$$

The general relations follow from Thiele's semi-invariants. The partition functions which are constituents of the virial coefficients are expressed by the $s$-particle traces

$$\tilde{Q}_s(T, V) = \text{Tr}_{1,2,..s}[\exp(-\beta H_s)] = \text{Tr}_{1,2,..,s}[\exp(-\beta\bar{h}^2\tau_s - \beta e^2\varphi_s)], \tag{43}$$

$$H_s = T_s + V_S, \qquad \tau_s = T_s/\bar{h}^2, \qquad \phi_s = V_s/e^2. \tag{44}$$

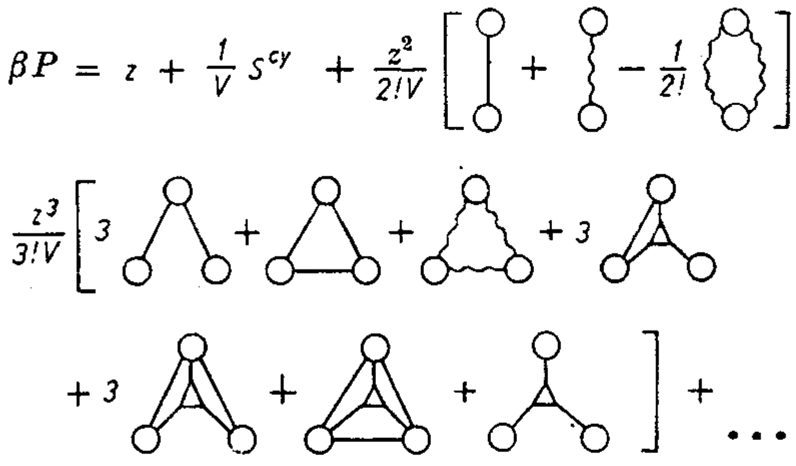

**Figure 5.** Graphs representating the fugacity expansion of the pressure in a Mayer-like Kelbg–Morita representation. The coefficient of $z^3$ corresponds to reducible and irreducible graphs which represent the 3rd virial coefficient. The convergent part of these diagrams provides the partition function of helium. The wavy lines represent Coulomb- (or Kelbg-) interactions and the normal lines stand for $\psi$-functions like in equations (23–24) [44].

In this way all our partition functions ($Q$-functions) have the structure of the basic trace function equations (46–48) and may be represented graphically as in figure 5. We remember the relation

$$(-1)\beta e^2\varphi_s = \sum_{1<i<j<s}\frac{\xi_{ij}}{|\mathbf{r}'_{ij}|};\qquad \mathbf{r}'_{ij} = \frac{(\mathbf{r_i}-\mathbf{r_j})}{\lambda_{ij}},;\qquad \xi_{ij} = -Z_iZ_j\frac{\ell}{\lambda_{ij}}, \tag{45}$$

and see that the contributions to equations (44–45) after resolvent expansion have the following structure

$$\tilde{Q}_s(T,V) = \sum_{1\leqslant i\leqslant j\leqslant s}\sum_n(-1)^n\xi^n_{ij}\frac{1}{2\pi\mathrm{i}}\int_C \mathrm{d}z\exp(-\beta z)\mathrm{Tr}_{1,2,\dots s}\left(\frac{1}{|\mathbf{r}'_{ij}|}\cdot\frac{1}{(\bar{h}^2\tau_s-z)}\right)^n. \tag{46}$$

The present structure consists of the sums of particle pairs connected by $\xi_{ij}$ interaction factors and should be considered as a series with respect to the powers $\xi^n_{ij}$. We may graphically represent all expressions by a sum of Mayer-like graphs consisting of points or bubbles (traces) and lines (interactions) which is quite similar to the $\lambda$-expansions analyzed in detail by Balescu [48]. The basic topological structure corrsponds to Mayers graph technique. However, the circles and lines we use do not have exactly the same meaning as we speak regarding the Kelbg–Morita diagram technique [14, 15]. Examples for the simplest Morita–Kelbg graphs are given in figure 5. The terminus Mayer-like means here that the diagrams are structurally similar to the Mayer diagrams for the classical case. However, the wavy lines represent Kelbg interactions instead of Coulomb interactions and the lines representing $\psi$-functions contain Slater functions instead of classical Boltzmann factors [57, 58]. The triangles in the center of a graph stand for proper 3-particle non-additive interactions, which we approximate here by pair products. We already see in the graph structure the roots of the cropping methods developed later. Cropping means formally that in bond state configurations, low order contributions in terms of $e^2$ should not be included into partition functions. The other coefficients are defined by cluster integrals, e.g., [23, 35–37, 44, 47, 56]. The coefficients in terms of fugacity and density expansions are up to a certain order exactly known [7, 23, 53, 54, 56]. In this quite complicated expansion, the coefficients $A_2$, $A_6$, $A_{10}$, ... represent the unscreened second and third virial coefficients which we need to extract the mass action constants for the formation of pair and triple bound states. Since all higher orders $A_k$ with $k > 5$ are only approximately known, we already have to find for helium and lithium, the appropriated approximations describing the binding effects.

### 3.2. Identifying the free and the bound state contributions

Assuming in the lowest order a Kelbg-like screening, we may write the statistical thermodynamics in the form of cluster expansions in the canonical ensemble which also had already been discussed in the preprint [38, 39] and was worked out later [56–58]. The negative free excess energy of classical and quasi-classical systems reads in the canonical ensemble [7, 56–58, 68]

$$F = F_{\mathrm{FD}} + F_{\mathrm{HF}} + F_{\mathrm{ring}} + \sum_{i} \mathrm{S}_{i}^{(k)}, \tag{47}$$

where the first 3 terms are the Fermi–Dirac, Hartree–Fock and Montroll–Ward contribution, which collects the contributions of ring diagrams [71, 72]. These contribitons are studied more in detail elsewhere [56, 57]. The sums should be extended over the species of ions $i$ and also to all orders of clusters $k$. The cluster integral of 3rd order may be expressed by screened 2- and 3-particle Slater functions

$$\tilde{S}_{ij} = S_{ij} \exp(g_{ij} - \beta V_{ij}); \quad \tilde{S}_{ijk} = S_{ijk} \exp[(g_{ij} - \beta V_{ij}) + (g_{ik} - \beta V_{ik}) + (g_{kj} - \beta V_{kj})]. \tag{48}$$

The final form of the 3-particle cluster integral including 3-particle quantum interactions is in the quantum case given by

$$S_{i}^{(3)} = \frac{1}{2 \cdot 3} n_i \sum_{jk} n_j n_k \int \mathrm{d}\mathbf{r}_j \, \mathrm{d}\mathbf{r}_k \big( \tilde{S}_{ijk} + \tilde{S}_{ij} g_{jk} g_{kj} + g_{ij} \tilde{S}_{jk} g_{kj} + g_{ij} g_{jk} \tilde{S}_{ki} - 2 g_{ij} g_{jk} g_{ki} \big). \tag{49}$$

Here, the first term which also includes proper 3-particle interactions gives the largest terms at a strong binding and provides the asymptotics. Evaluating the integrals, the cluster series have the following structure in the grand-canonical density representation

$$\begin{aligned} \beta p(z_i, T) = \beta p_{\mathrm{FD}} + \beta p_{\mathrm{FD}} + \sum_{i} z_i Z_i^2 \Bigg\{ & \sum_{j} \frac{2\pi \ell^2}{3} z_j Z_j^2 \tilde{f}_i(K \lambda_{ie}) + 2\pi \sum_{j} z_j \lambda_{ij}^3 \big[ G_{ij}(\kappa) + K_{20}(\xi_{ij}) \big] \\ & + 8\pi^2 \sum_{jk} z_j \lambda_{ij}^3 z_k \lambda_{ik}^3 \big[ \tilde{G}_{ijk}(\kappa) + \tilde{K}_{30}(\xi_{ij}, \xi_{ik}, \xi_{jk}) \big] + \ldots \Bigg\}. \end{aligned} \tag{50}$$

In a different form, we may represent the cluster expansion of the pressure within the canonical ensemble in terms of densities [56, 59–61]

$$\begin{aligned} \beta p(n_i, T) = \beta p_{\mathrm{FD}} + \beta p_{\mathrm{HF}} - \sum_{i} n_i \Bigg\{ & \frac{2\pi \ell^2}{3\kappa} Z_i^2 \sum_{j} n_j Z_j^2 \varphi_i(\kappa \lambda_{ij}) + 2\pi \sum_{j} n_j \lambda_{ij}^3 \big[ G_{ij}(\kappa) + K_{20}(\xi_{ij}) \big] \\ & + 8\pi^2 \sum_{ik} n_j \lambda_{ij}^3 n_k \lambda_{ik}^3 \big[ G_{ijk}(\kappa) + K_{30}(\xi_{ij}, \xi_{ik}, \xi_{jk}) \big] + \ldots \Bigg\}. \end{aligned}$$

Here, $\varphi(x)$ is in Debye–Hückel-like approximation $\varphi(x) = 1 - 3\sqrt{\pi}/8 + (3/10)x^2 + \ldots$. We do not specify the screening functions $G$, and $\tilde{G}$, which depend on the screening parameters $\kappa$ (canonical) and $K$ (grand canonical ) which are irrelevant in the present context of bound states and refer to [56]. We note that the graphs of Feynman-type like in figure 3 representating the terms in the pressure expansion for hydrogen plasmas and for helium plasmas which we should calculate contain at least one 4-ring ladder [76]. Figure 4 shows, as demonstrated already in 1970 at a seminar in Lviv, that fugacity cluster expansions are an appropriate instrument for the description of bound states without using any chemical tools such as mass action laws. A few years later this approach was taken up by the school of De Witt and Rogers in Livermore for the development of big astrophysical program packets ACTEX. Note that in his approach Rogers used numerical estimates of the cluster integrals equations (26) and (41) in the fugacity expansion [49–54]. The program packet ACTEX (activity expansions) developed by Rogers has been used as one of the fundaments for the big project OPAL used for astrophysical calculations of the composition and opacity of stars and in particular for the NASA Astrophysics Data Systems (ADS) [49–52, 54]. However, the OPAL equation of state is limited with respect to two aspects. Firstly, it is only available in the form of pre-computed tables that are provided by the Lawrence Livermore National Laboratory. However, these numerical applications require interpolations, which always lead to a loss of accuracy. Secondly, the OPAL equation of state is proprietary and is not freely available. Our method is with respect to the theoretical tools comparable to OPAL. It is, however, completely analytical and freely available [73, 74]. Further we notice in this context that it was developed first in Lviv under the auspices of Ihor R. Yukhnovskii [38, 39]. Here, we use only analytical estimates in order to proceed to a better understanding and also give a comparison with the method of mass action laws on the basis of the canonical ensemble.

### 3.3. The partition functions

We define here the partition functions and the corresponding mass action functions as the convergent part of the virial coefficients in the fugacity expansion. Following this idea in a recent work [76] we developed a new method for calculating partition functions of atoms which is an alternative to the traditional chemical approach. Our basic assumption is that the partition function of the atoms of hydrogen, helium and lithium can be represented by a convergent series with respect to the dimensionless reciprocal temperature

$$\tilde{\beta} = \mathrm{Ry}/k_{\mathrm{B}}T, \tag{51}$$

resulting from the quantum statistical expressions for virial coefficients:

$$\sigma_{\mathrm{atom}}(T) = \sum_{s_0}^{\infty} A_{s_0}\tilde{\beta}^{s_0}, \tag{52}$$

with $s_0 = 2, 4, 6$ for hydrogen, helium, and lithium plasmas.

**Hydrogen**: The information about two-particle bound states is contained in the virial function $K_{20}(\xi)$, which can be split in a contribution of free and bound states. Note that in the present definition of the 2nd virial function, the linear and the quadratic terms are missing since they are already included into the Hartree–Fock and the Debye–Hückel term. Formally we get the bound state part first by splitting into the negative contributions of lower orders which are influenced by the screening effects and the positive contributions of the bound states [56]

$$K_{20}(\xi) = -\frac{C_p}{12}\xi^3 + \sqrt{\pi}\sum_{m\geqslant 4}\frac{\zeta(m-2)}{2^m\Gamma(m/2+1)}\xi^m. \tag{53}$$

The bound state part of the 2nd virial function $K_{2b}$ is given by the even part of the virial function

$$K_{2b} = \frac{1}{2}[K_{20}(\xi) + K_{20}(-\xi)] = \sqrt{\pi}\sum_{m=4,6,..}\frac{\zeta(m-2)\xi_{ij}^m}{2^m(m/2)!} = 2\sqrt{\pi}\sum_{s=1}^{\infty}\left[\exp\left(\frac{\xi^2}{4s^2}\right) - 1 - \frac{\xi^2}{4s^2}\right].$$

The full function $K_{20}(\xi)$ may be decomposed into a bound and a free state part, alternatively we may split it into a direct and an exchange part [56]. The point where these aymptotic representations are non-analytic is $\xi_{ij} = 0$, since here the forces change from positive to negative values and at the same time the character of the symmetry changes. The quantum virial functions $Q(\xi)$ and $E(\xi)$ are discussed in detail in [56–58]. The Taylor series for the quantum virial functions are convergent for any physical meaningful value of the interaction parameter $\xi$. This is ensured, since for large powers the terms show the same behaviour as the series of the well-known exponential function. This way the coefficients of our series are known and have the values

$$A_0 = A_1 = 0, \quad A_2 = 1.0967, \quad A_3 = 0.1078, \quad A_4 = 0.0056, \ \ldots, \quad A_s = 4^s[\zeta(2s-2)/(2s)!]. \tag{54}$$

The series are convergent since the $\zeta$ functions converge to one. This means that the coefficients converge to those of an exponential series. We use the approximation

$$\sigma_H = 1.097\tilde{\beta}^2 + 0.108\tilde{\beta}^3 + \left[\exp(\tilde{\beta}) - 1 - \tilde{\beta} - 0.5\tilde{\beta}^2 - 0.166\tilde{\beta}^3\right]. \tag{55}$$

The basic assumption of this work is that the partition functions of He and higher atoms follow the same scheme. We evaluate the lowest coefficients as the binding parts of the cluster coefficients in quantum-statistical fugacity expansions of the pressure, by evaluating the convergent graphs. Based on the analysis of these virial coefficients, we identified the atomic partition functions and mass action constants as convergent higher-order contributions to the unscreened virial coefficients. The most important selection criterion among the large number of graphs is that the contributions are strictly positive and increase strongly with $\beta = 1/k_{\mathrm{B}}T$. The problem with this method is that the corresponding higher order diagrams are difficult to calculate since they include unknown three- and four-body quantum problems and further since the number of relevant diagrams increases with the particle number.

Comparing the new partition function with the traditional approach of chemical physics to define the partition functions as sums of terms $\exp(-\beta\epsilon_n)$ where the $\epsilon_n$ are expressed by the known energy levels of the atom, we find that the new partition functions are modified in the spirit of Planck–Brillouin–Larkin (PBL) by introducing the elements of cropping. In other words, the exponential functions are replaced by functions without the lowest powers in $\tilde{\beta} = \mathrm{Ry}/k_{\mathrm{B}}T$. In this way, we retain the basic features and the low-temperature behavior of the traditional approach. However, on the other hand, we avoid any double counting of terms of lower order in $e^2$, which in Coulomb systems are used for purposes of screening and electroneutrality and are no more free for the purposes of binding.

As already shown above, considering [75, 76], we have nowadays a complete understanding of the problem for hydrogen based on the exact results from the quantum statistics of hydrogen [47]. The complete series for the partition function of H are known, and we see that a low-order Rydberg expansion obtained from quantum statistics works for $\tilde{\beta} \leqslant 2$ and agrees well with the correct PBL partition function. A representation by two Taylor terms works already well at high temperatures with $\tilde{\beta} < 2$. On the other hand, the naive exponential approach agrees with the Planck partition for $\tilde{\beta} \geqslant 3$. We find that the transition occurs in a rather interesting region covering for hydrogen temperatures around 75 000 K where the binding effects are weak. The first orders in the Taylor expansion with respect to Ry correspond to the so-called ladder diagrams of quantum statistical graph expansions (see figures 3 and 5). The quantum statistical analysis confirmed Planck's results from 1924 [56] as well as the findings of Klimontovich for weak deviations from equilibrium [55].

We consider now the partition functions for **helium**: Here, the calculations are not yet fully finished. The results given in [75, 76] based on diagrammatic calculations of the lowest binding diagrams including ireducible diagrams (shown in figures 3 and 5) as well as reducible diagrams (shown in figure 5) provided the estimate [75, 76]

$$\sigma_{\mathrm{He}} \simeq 14.90\tilde{\beta}^4 + 373\tilde{\beta}^5. \tag{56}$$

On the other hand, the asymptotics are determined by the ground state of the helium atoms $\tilde{\epsilon}_{\mathrm{He}} \simeq 5.087$ and we find:

$$\sigma_{\mathrm{He}} \sim \exp(\tilde{\beta}\tilde{\epsilon}_{\mathrm{He}}). \tag{57}$$

We combine both results and propose to take the lower order terms from the evaluation of the graphs and the higher order terms from the asymptotics to find [75, 76]

$$\sigma_{\mathrm{He}} = 14.90\tilde{\beta}^4 + 373\tilde{\beta}^5 + \left[\exp(\tilde{\beta}\tilde{\epsilon}_{\mathrm{He}})\right]' = 14.90\tilde{\beta}^4 + 373\tilde{\beta}^5 + \sum_{k=6}^{\infty}\frac{(\tilde{\epsilon}_{\mathrm{He}}\tilde{\beta})^k}{k!}. \tag{58}$$

On the other hand, we have a different estimate based on the tables of the excitation energies of helium taken from [63, 75] as well as on the theoretical insight, that cropping should be applied to each of the electrons extra. These representations suggest that Taylor expansion in the dimensionless $\tilde{\beta}$-parameter as well as the asymptotics start for helium with the terms [75]:

$$\left[\exp(4\tilde{\beta}) - 1 - 4\tilde{\beta}\right] \cdot \left[\exp(1.807\tilde{\beta}) - 1 - 1.807\tilde{\beta}\right]. \tag{59}$$

Avoiding any overlap of the lower orders, we find another estimate

$$\sigma_{\mathrm{He}}(T) \simeq 14.90\tilde{\beta}^4 + 373\tilde{\beta}^5 + \left[\exp(4\tilde{\beta}) - 1 - 4\tilde{\beta} - 8\tilde{\beta}^2\right] \times\left[\exp(1.807\tilde{\beta}) - 1 - 1.807\tilde{\beta} - 1.622\tilde{\beta}^2\right]. \qquad (60)$$

This gives, e.g., $\sigma_{\mathrm{He}}(100\,000\ \mathrm{K}) \simeq 20464$. We have applied here extra cropping steps to the exponent of each of the electrons to obtain the terms of the order $\tilde{\beta}^n$ with $n \geqslant 6$ which complement our diagrammatic calculations. To obtain better results, we need to calculate more diagrams of the order $\tilde{\beta}^n$ with $n = 5, 6, \ldots$. In figure 6, we compare the low order expansions for hydrogen and for helium with approximations, that interpolate between a power law and exponential functions. Note that the corresponding mass action function is

$$K_{\mathrm{He}}(T) = (2\sqrt{\pi}\lambda_{ie}^3)^2\Big\{14.90\tilde{\beta}^4 + 373\tilde{\beta}^5 + \left[\exp(4\tilde{\beta}) - 1 - \tilde{\beta} - 8\tilde{\beta}^2\right]\left[\exp(1.807\tilde{\beta}) - 1 - 1.807\tilde{\beta} - 1.622\tilde{\beta}^2\right]\Big\}. \qquad (61)$$

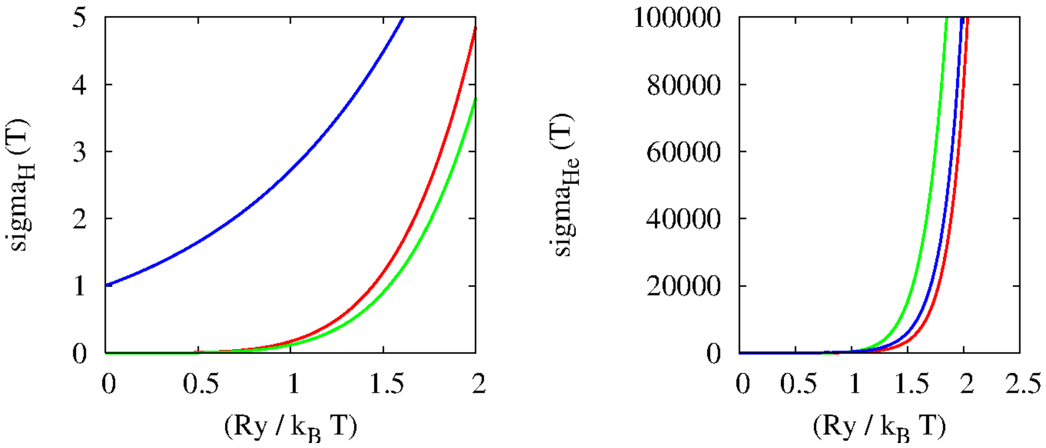

**Figure 6.** (Colour online) Partition function of H (left-hand) and He (right-hand). The green curves show the first terms of a Taylor expansion, the blue curves show the exponential approximation and the red curves interpolate between the Taylor series and the asymptotic exponential representation.

The new results are generally much lower than the naive exponential approach without cropping. Due to these differences, we recommend for further applications the formulae which interpolate between the Taylor expansions and the asymptotics, i.e., between higher and lower temperatures. The interpolating formulae are shown as red curves. For lower temperatures, the new formulae are practically identical to the asymptotics and for higher temperatures to the estimates calculated from the diagram expansions. We can see for hydrogen that the low-order diagrams are only first approximations and should be supplemented by calculating further diagrams. We show later that the at high temperatures the concentrations, predicted for the atom formation, are lower than in previous calculations. This can be important for estimating ionization in stars and the fusion devices, for example.

From the point of view of our cluster analysis, the consideration of bound states requires the following steps:

(i) Identify the convergent contributions of two-, and three- particle clusters to the coefficients of the fugacity or density expansions.

(ii) Identify the positive definite and, at low $T$, asymptotically large contributions that define the mass action constants. Note that the candidates for the contributions of bound states are diagrams with an even number of lines. They should contain at least one 4-fold (+−) interaction line like in figure 3.

(iii) Most important: quantum statistics of Coulomb systems teaches us that a class of diagrams which are, e.g., of linear order in $e^2$ or are of ring type are consumed by processes of screening or cancelled out by electro-neutrality. Such diagrams should not be included into the binding expressions like mass action functions. This is the origin of the cropping steps, which we applied. Following Onsager's postulates, any double-counting of contributions should be strictly avoided. A graph can either provide a contribution of free states or of the bound states.

## 4. The equation of state for hydrogen plasmas

Analyzing equation (50) we find the structure

$$\beta p(n_i, T) = \beta p_{\mathrm{FD}} + \beta p_{\mathrm{HF}} + \beta p_{\mathrm{sc}} + \beta p_{\mathrm{bo}}, \tag{62}$$

with a bound state (discrete state) contribution

$$\beta p_{\mathrm{bo}} = +2\pi \sum_j n_j \left\{ \lambda_{ij}^3 \left[ K_{2b}(\xi_{ij}) \right] + 8\pi^2 \sum_{ik} n_j \lambda_{ij}^3 n_k \lambda_{ik}^3 \left[ K_{3b}(\xi_{ij}, \xi_{ik}, \xi_{jk}) \right] + \dots \right\},$$

and a contribution of scattering states (free states)

$$\beta p_{\mathrm{sc}} = -\sum_i n_i \left\{ \frac{2\pi\ell^2}{3\kappa} \sum_j n_j Z_i^2 Z_j^2 \varphi_i(\kappa\lambda_{ij}) + 2\pi \sum_j n_j \lambda_{ij}^3 \left[ \tilde{G}_{ij}(\kappa) + K_{2f}(\xi_{ij}) \right] \right.$$
$$\left. + 8\pi^2 \sum_{ik} n_j \lambda_{ij}^3 n_k \lambda_{ik}^3 \left[ \tilde{G}_{ijk}(\kappa) + K_{3f}(\xi_{ij}, \xi_{ik}, \xi_{jk}) \right] + \dots \right\}.$$

Let us now consider the simplest case of low-density hydrogen plasmas. Based on th present analysis, the EoS for hydrogen plasmas reads in the lowest order in the density, i.e., including only quadratic terms in the density [47, 56] ($n_i$-density of the nuclei):

$$\beta p = 2n_i - A_0(T) n_i^{3/2} - n_i^2 B_2(T) + \dots\,, \tag{63}$$

$$A_0(T) = (\sqrt{8\pi}/3)\ell^{3/2}; \quad B_2(T) = \left[ 8\pi\sqrt{\pi}\lambda_{ie}^3 \sigma_{PBL}(T) + K^*(T) \right]. \tag{64}$$

Here, the bound state contribitons are the PBL-partition function and the contributions of scattering states in the correction function $K^*(T)$ which is numerically relatively small. Larkin has shown that in the classical case $K^*(T) = 0$. A simple low-temperature approximation is

$$K^*(T) \simeq -\sqrt{\pi}\lambda_{ie}^3 \xi_{ie}^2. \tag{65}$$

We may use this expression to define a quantum length (Kelbg length) by

$$K^*(T) = -4\pi\ell^2 a^K(T). \tag{66}$$

The Kelbg length $a^K(T)$ is a kind of quantum Debye–Hückel distance between the charges. The full quantum function $K^*(T)$ is exactly known; it can be expressed by the quantum virial functions defined above [47, 56]. The functions are also tabulated [47]. This way, the quantum statistical analysis confirms Planck's results from 1924 [47] as well as the findings of Klimontovich [55]. Evidently there are no open problems left for hydrogen.

For a more convenient way of calculating the free densities of electrons, ions (protons) and atoms $n_e^*$, $n_i^*$, $n_0^*$, we go to the chemical picture introducing free and bound particles.

$$\beta p = n_i^* + n_e^* + n_0^* - \frac{\kappa^{*3}}{24\pi} \left[ 1 - \frac{3}{2}\kappa^* a^K(T) + \dots \right], \qquad n_0^* = n_e^* n_i^* 8\pi\sqrt{\pi}\lambda_{ie}^3 \sigma_{PBL}(T). \tag{67}$$

Here, $\kappa^{*2} = 4\pi\ell(n_e^* + n_i^*)$ defines the Debye quantity of the free particles, and the conservation relations are $n_e = n_e^* + n_H^*$, $n_i = n_i^* + n_H^*$.

The Kelbg length is an aggregated quantity which includes several contributions from the scattering states. Using the analogies between the classical Debye–Hückel theory and this quantum approach to plasmas we get as in [47, 57] the so-called quantum Debye–Hückel approximation QDHA which was obtained in [47, 57] by summing up further higher order terms in the density

$$p = n_i^* + n_e^* + n_0^* - \frac{\kappa^{*3}\varphi(\kappa^* a(T))}{24\pi}; \quad \kappa^{*2} = 4\pi\ell(n_e^* + n_i^*); \tag{68}$$

$$\frac{n_0^*}{n_e^* n_i^*} = 8\pi\sqrt{\pi}\lambda_{ie}^3 \sigma_{PBL}(T) \exp\left[ - \kappa^* \ell G(\kappa^* a(T))\right]; \tag{69}$$

$$G_{\mathrm{DH}} = \frac{1}{1+x}; \qquad \varphi_{\mathrm{DH}}(x) = 1 - \frac{3}{2}x + \frac{9}{5}x^2 - 2x^3 + \ldots \tag{70}$$

Note that this convenient approximation which is often used for hydrogen calculations of free densities [47, 57] is at low densities equivalent to the exact equations (63–66) and differs only in the approximative higher orders. An essential insight is that the correction to the PBL-expression $K^*(T)$ is not a contribution to binding but stems from the scattering states and should be treated together with the Debye term [47, 62]. This is possible, since the contributions depend only on $\kappa^*$, the Debye parameter of the free plasma. The QDHA is based on the analogies and an exptrapolation [71, 72]. Now we derive a better founded approximation within the schema of the exponential potential. This way we proceed from the DH-approximation to the new KY (Kelbg–Yukhnovskii) approximation. Following Kelbg, we define the quantities

$$\frac{1}{\alpha^K(T)} = \frac{2}{3}a^K(T) = -\frac{2K^*(T)}{12\pi\ell^2} \simeq \frac{\sqrt{\pi}}{6}\lambda_{ie} \tag{71}$$

and a dimensionless quantum Kelbg parameter and a quantum Kelbg distance

$$x = q_K = \kappa a^K(T) = (\sqrt{\pi}/4)\kappa\lambda_{\pm}; \qquad a_{ij}^K = (\sqrt{\pi}/4)\lambda_{ij}. \tag{72}$$

We define further the Kelbg–Yukhnovskii functions with $X = \sqrt{1 + 2\kappa/\alpha^K} = \sqrt{1 + (4/3)\kappa a^K(T)}$ in analogy to the Debye–Hückel functions:

$$G_{\mathrm{KY}}(x) = \frac{6}{\sqrt{\pi}x}\left[1 - \frac{1}{\sqrt{1 + (\sqrt{\pi}/3)x}}\right] = 1 - \frac{\sqrt{\pi}}{4}x + \ldots, \tag{73}$$

$$\tau_{\mathrm{KY}}(x) = \frac{1}{x^3}\left(\frac{1}{4}X^3 - \frac{3}{2}X + 2 - \frac{3}{4X}\right) = 1 - \frac{3\sqrt{\pi}}{8}x + \ldots. \tag{74}$$

This way we get the new formulae for the EoS of hydrogen plasmas denoted as Kelbg–Yukhnovskii approximation:

$$p = n_i^* + n_e^* + n_0^* - \frac{\kappa^{*3}}{24\pi}\varphi_{\mathrm{KY}}(\kappa^* a^K(T)); \qquad \kappa^{*2} = 4\pi\ell(n_e^* + n_i^*), \tag{75}$$

with the mass action law

$$\frac{n_0^*}{n_e^* n_i^*} = 8\pi\sqrt{\pi}\lambda_{ie}^3 \sigma_{PBL}(T) \exp\left[ - Z_i \ell \kappa^* G_{\mathrm{KY}}(\kappa^* a^K(T))\right]. \tag{76}$$

Graphical representations show that the QDHA and the QKYA are similar in shape, although the QKYA is characterized by a longer range of the correlations as the QDHA and as the ring functions derived in [71, 72]. The transition from the earlier ring functions QDHA [71, 72] to the present QKYA is in our view an improvement, since the Kelbg–Yuknovskii functions are stemming from a systematical evaluation of ring diagrams and are better founded. We calculated with the new KY approximations the pressure of an hydrogen plasmas and show the results for the two temperatures $T = 31250$ K and $T = 63500$ K in comparison with the recent results from Path Integral Monte Carlo (PIMC) calculations. We see in figure 7 that the agreement is rather good up to $n_i = 10^{21}$ cm$^{-3}$.

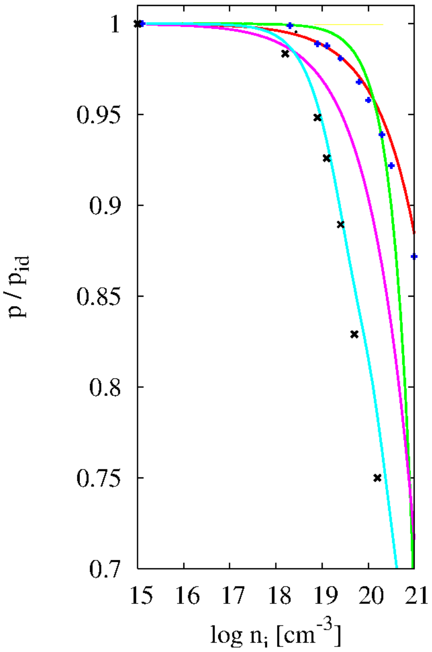

**Figure 7.** (Colour online) The EoS of hydrogen calculated within the Kelbg–Yukhnovskii approximation (QKYA) for the temperatures $T = 31250$ K (turquoise line) and 62500 K (red line), and a comparison with data from recent Monte Carlo PIMC calculations [64, 65]. The two additional lines (magenta and green) show the density expansion including only the terms up to the quadratic order after equations (64–65).

We worked so far with just one quantum parameter, namely $\kappa^* a^K(T)$. This gives already quite satisfactory results. We show now that the method of averaging at the level of screening functions for pairs leads to better approxinations. Let us start with the excess part of the chemical potential which is determined by the ring contributions. In extended QDHA, we have

$$G_{ij} = \frac{e_i^2 e_j^2}{\left(\sum_i \sum_j e_i^2 e_j^2\right)} \frac{1}{1 + \kappa^* a_{ij}^K}. \tag{77}$$

The KY-theory gives the mass action law

$$\frac{n_0^*}{n_e^* n_i^*} = 8\pi\sqrt{\pi}\lambda_{ie}^3 \sigma_{PBL}(T) \exp\left[-Z_e Z_i \ell \kappa^* G(\kappa^* a_{\pm}^K)\right]. \tag{78}$$

A graphical representation shows that the approximations QDHA and QKYA are similar in shape, although the QKYA based on the true ring functions for the Kelbg potential is characterized by a longer range of correlations as the QDHA which was based on the ring functions derived in [71, 72]. We may represent the new expressions for $\tau$ and $G$ as functions of the quantum length $a^K = 3/2\alpha^K$ and find

$$G_{\mathrm{KY}}(\kappa a) = \frac{3}{2a}\left(1 - \frac{1}{\sqrt{1 + 4a/3}}\right) = 1 - (\kappa a) + \frac{10}{9}(\kappa a)^2 - \frac{35}{27}(\kappa a)^3 + \dots, \tag{79}$$

$$\varphi_{\mathrm{KY}}(\kappa a) = 1 - \frac{3}{2}(\kappa a) + 2(\kappa a)^2 - \frac{70}{27}(\kappa a)^3 - \dots . \tag{80}$$

Note that the DH and the KY theories are similar in shape but have different asymptotics

$$G_{\mathrm{KY}} \sim \frac{3}{2\kappa a}; \quad G_{\mathrm{DH}} \sim \frac{1}{\kappa a}; \quad \varphi_{\mathrm{KY}} \sim \frac{2}{3\sqrt{3}(\kappa a)^{3/2}}; \quad \varphi_{\mathrm{DH}} \sim \frac{3}{(\kappa a)^2}. \tag{81}$$

The excess part of the chemical potentials which determines the Saha equation is now given by

$$\mu_i^{\mathrm{ex}} = \mu_i^{\mathrm{ring}} = -k_{\mathrm{B}} T Z_i \ell \kappa^* \sum_j G_{ij}(\kappa^* a_{ij}^K; n_i). \tag{82}$$

An explicite form is

$$\mu_i^{\mathrm{ex}} = -\frac{3e_i^2 \alpha}{4\pi\epsilon_0 \epsilon_r k_{\mathrm{B}} T 2 a^K \kappa^2} \left[ 1 - \frac{1}{\sqrt{1 + (4/3)(\kappa a^K)}} \right]. \tag{83}$$

In the same way we may calculate the Coulomb energy.

## 5. The equation of state for helium plasmas

We consider the example of hydrogen as a good plan how to proceed for helium and begin with the virial expansion in the density. An extension of the virial series for $Z > 1$ elements reads with the notation $n = n_e + n_i = (1 + Z)n_i$, where $n_i$ is the density of the nuclei [56]:

$$\begin{aligned} \beta p = n - A_0(T) n^{3/2} - n^2 B_2(T) - \frac{3}{2} A_3(T) n^{3/2} \ln n - A_4(T) n^{5/2} \\ - 2A_5(T) n^3 \ln n - B_3(T) n^3 + \ldots \end{aligned} \tag{84}$$

The concrete values of the temperature functions $A_i(T)$, $B_k(T)$ follow by a comparison with the cluster expansion and are given for $i = 1, 2, 3, \ldots$, $k = 2, 3$, e.g., in [23, 56]. Our basic idea is that the basic convergent part of the 3rd virial coefficient $B_3(T)$ can be identified with the partition function and the mass action function of the helium formation. The problem is that the coefficients $B_3(T)$ and the coefficients beyond are not well studied yet. Therefore, the partition functions are often approximated by elementary expressions based on the known energy levels [63]. Often these calculations neglect so far the compensation effects between the high discrete and the low scattering states except, e.g., in [76]. We know from the studies for hydrogen, that for $T > I/k_{\mathrm{B}}$, which is the ionization temperature, the way of cropping is essential and the compensation effects determine the value of the partition functions. We should expect that for helium the compensation effects between high discrete and low scattering effects play an essential role, too. We must expect that these compensation effects dominate beyond the ionization temperatures, i.e., for helium about $I/k_{\mathrm{B}} \simeq 630000$ K. Let us consider first a representation for high temperatures where the bound states are irrelevant. Note that the contributions of bound states start with the power $\xi_{ie}^4$. The first terms of the pressure read

$$\begin{aligned} \beta p(n_i, T) = \sum_i n_i - \frac{2\pi\ell^2}{3\kappa} \sum_{ij} n_i n_j Z_i^2 Z_j^2 \varphi_i(\kappa\lambda_{ij}) - \sum_{ij} n_i n_j Z_i^3 Z_j^3 \ln\left[\frac{\kappa}{\alpha_{ij}}\right] \\ - 2\pi \sum_j n_j \lambda_{ij}^3 K_{20}''(\xi_{ij}) + \ldots \end{aligned} \tag{85}$$

The bound state contributions are defined only for $\xi_{ij} > 0$. We assume that the 3rd virial functions have the same structure as the 2nd virial coefficients, having a bound state and a free state contribution

$$K_{30}(\xi) = K_{3b}(\xi) + K_{3f}(\xi). \tag{86}$$

We identify the contribution of the bound states to the 3rd virial function following the lines developed above for the partition function of hydrogen.

We calculate now the EoS of helium plasmas and start with an ideal approximation. For He-plasmas we have the following relations between the species including mass action laws:

$$\begin{aligned} n_e &= n_e^* + n_{\mathrm{He}^+}^* + 2n_{\mathrm{He}}^*, \quad n_i = n_{\mathrm{He}^{++}}^* + n_{\mathrm{He}^+}^* + n_{\mathrm{He}}^*, \\ n_{\mathrm{He}^+}^* &= n_e^* n_{\mathrm{He}^{++}}^* K_{\mathrm{He}^+}(T), \qquad n_{\mathrm{He}}^* = n_e^{*2} n_{\mathrm{He}^{++}}^* K_{\mathrm{He}}(T). \end{aligned} \tag{87}$$

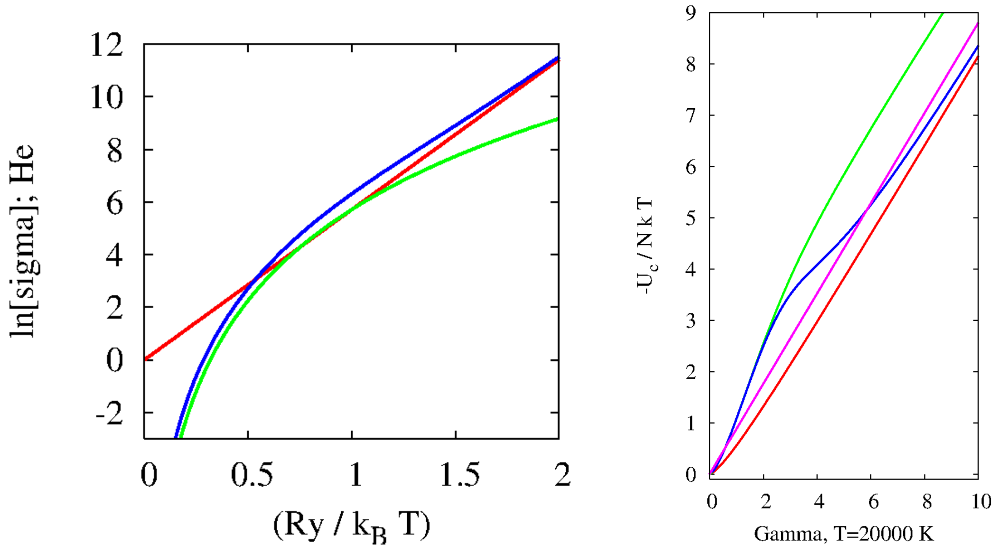

**Figure 8.** (Colour online) Left-hand: comparison of several estimates for the partition functions of helium. The relevant new results are for high temperatures in the left-hand lower corners, where the new results (blue curves) deviate from the traditional exponential partition functions (red curves). The new (blue) curves were obtained by interpolations between a low order polynomial (green line) and the high order exponential term (red line). Right-hand: comparison of the present new approximation for the Coulomb energy (blue line) with the Unsöld aymptotics (magenta line), the estimate by Brilliantov (red line) and the Debye energy (green line) which is correct mainly for small densities.

Charge neutrality means $n_e = Zn_i = 2n_i$ so that the properties of the He plasma are determined only by $T$ and the total density of nuclei $n_i$. The ionization degree may be introduced as the relation between free electron density and total electron density $\alpha_e = n_e^*/Zn_i$. For the pressure, we have within the approximation of ideal particles

$$\beta p = n_i^*(1+Z) + n^*_{\mathrm{He}^+} + n^*_{\mathrm{He}}. \tag{88}$$

Here, the density $n_i$ and the temperatute $T$ are the relevant independent variables and $n_j^*$, $n^*_{\mathrm{He}^+}$, $n^*_{\mathrm{He}}$ are dependent variables. We go now to a chemical description including nonideality effects, which follows the lines of our fugacity expansion. Using this analogy we get the new formulae for the EoS of helium plasmas $Z = 2$ with $n_i = n^*_{\mathrm{He}^{++}}$:

$$p = n_i^* + n_e^* + n^*_{\mathrm{He}^+} + n^*_{\mathrm{He}} - \frac{2\pi\ell^2}{3\kappa^*}\big[Z_i^4 n_i^* \varphi(\kappa^*\lambda_{ii}) + n_e^{*2}\varphi(\kappa^*\lambda_{ee}) \tag{89}$$

$$+n_e^* n^*_{\mathrm{He}^+}\varphi(\kappa^*\lambda_{e,\mathrm{He}^+}) + Z_i^2 n_i^* n_{\mathrm{He}^+}\varphi(\kappa^*\lambda_{i,\mathrm{He}^+}) + Z_i^2 n_i^* n_e^* \varphi(\kappa^*\lambda_{ie})\big] \tag{90}$$

with the sccreening parameter defined by the concentrations of all charged species

$$(\kappa^*)^2 = 4\pi\ell(n_e^* + n^*_{\mathrm{He}^+} + 4n^*_{\mathrm{He}^{++}}). \tag{91}$$

Following the line of our fugacity expansion, we get now two mass action laws

$$\frac{n^*_{\mathrm{He}^+}}{n_e^* n_i^*} = 8\pi\sqrt{\pi}\lambda_{ie}^3 \sigma^{\mathrm{PBL}}_{\mathrm{He}^+}(T)\exp\big[-\ell\kappa^* G_{\mathrm{KY}}(\kappa^* a^K_{e,i+}(T))\big], \tag{92}$$

and

$$\frac{n^*_{\mathrm{He}}}{(n_e^*)^2 n_i^*} = 8\pi\sqrt{\pi}\lambda_{ie}^3 \sigma_{\mathrm{He}}(T)\exp\big[-2\ell\kappa^* G_{\mathrm{KY}}(\kappa^* a^K_{ie}(T))\big]. \tag{93}$$

Here, the $a_{ij}^{K}(T)$ are appropriately chosen Kelbg lengths. We underline that the main source for this derivation is the comparision with the exact fugacity cluster expansion. We have ensured that the chemical representation using the species $n_i^*$, $n_e^*$, $n_{\mathrm{He}^+}^*$, $n_{\mathrm{He}}^*$ is at low densities fully equivalent to the exact fugacity expansion and this way also to the exact density expansion. A direct comparison of the partition functions and the EoS for He with other sources is difficult since in most applications, e.g., to stellar athmospheres (see, e.g., [77]) a different normalization is used. The mentioned authors follow in most cases the traditional definitions of Eggert, Saha and Unsöld. Relative partition functions are defined for each ionization step $k$ and are denoted by $U_k(T, n_e)$. The relative partition functions depend on temperature and on densities, corresponding to density-dependent cutting of the summations over atomic states. Therefore, it may be easier to compare the particle densities predicted by different methods. Due to our predicion of lower values of our mass action constants, we find at high $T$ smaller densities of free charged particles as in standard calculations. In other words, corresponding to figures 6 and 8, we predict at higher temperatures smaller atom densities than in the standard approaches [77]. This provides us with the basic part of the EoS of helium.

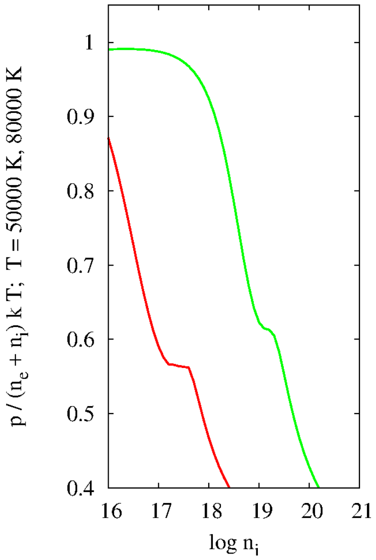

**Figure 9.** (Colour online) EoS of helium plasmas from the chemical approximation given above represented in the form of the relation of total pressure to the ideal Boltzmann pressure at densities $n_i < 10^{21}\,\mathrm{cm}^{-3}$. We show the relative pressure $\beta p/(n_e + n_i)$ for $T = 50000, 80000$ K (red, green curves) as a function of $\log(n_i)$. The shoulders correspond to the formation of helium ions.

In the last part of this chapter we want to show how our theory can be made compatible with Unsöld's work on astrophysical plasmas. As shown in [67–70], we find for $Z \gg 1$ and strong ion-ion correlations for the Coulomb energy and the corresponding lowering of ionization energy the asymptotics:

$$U_{i,C} = -a(Nk_{\mathrm{B}}T)\Gamma; \qquad p_{i,C} = -\frac{a}{3}(n_i k_{\mathrm{B}}T)\Gamma_i. \tag{94}$$

There exist several estimates for the coefficient [67]. The theory of Berlin and Montroll provides $a = (3/2)^{4/3} = 1.7171$, Unsöld finds $a = 1.7861$ and Brilliantov $a = 0.881$ [57, 66, 67]. We see that the slopes predicted by Berlin, Montroll and Unsöld are in resonable agreement. On the other hand, the estimate by Brilliantov agrees well with a numerical fit of simulation data for classical plasmas by De Witt which provide $a = 0.899$ and what may be even more convincing, with the bound given by Onsager in 1937 $a = 0.9$ [57]. Sinnce the differences are not well understood, we use here the analytically obtained slope by Brilliantov [68]. We compare in figure 8 r.h.s. different analytical approximations for the Coulombic energy of a plama with the asymptotic by Brilliantov [57] and the Debye energy.

We need a generalization of the KY theory which is appropriate for multi-charged ions as has been developed in [57, 68]. Let us consider a plasma with multi-charged ions denoted by indices $i$. According to Brilliantov, we do not permit the realization of high $k$-modes $k > k_i = (9\pi^2 n_i)^{1/3}$, since the corresponding plasma modes cannot ne realized. Then, the integration should be restricted to lower modes and we get for the contribution of these species to the Coulomb energy and to the chemical potentials [58, 68]

$$U_i^C = -k_\mathrm{B} T n_i Z_i^2 \sum_j Z_i^2 \frac{\kappa^2}{p_{ij}^2 - s_{ij}^2} m_{ij}. \tag{95}$$

Here, the matrix $m_{ij}$ is defined by

$$m_{ii} = \left[\frac{1}{p_{ii}} \arctan\left(\frac{k_i}{p_{ii}}\right) - \frac{1}{s_{ii}} \arctan\left(\frac{k_i}{s_{ii}}\right)\right], \tag{96}$$

$$m_{ij} = \left[\frac{1}{p_{ii}} - \frac{1}{s_{ii}}\right] \quad \text{if} \quad i \neq j, \qquad k_i = (9\pi^2 n_i)^{1/3}. \tag{97}$$

Note that this variant of the theory contains the free parameters $\alpha_{ij}$ and $k_i$ and may be adapted this way to specific tasks. The $p_{ij}$ and $s_{ij}$ are given by

$$p_{ij} = \frac{\alpha_{ij}}{2}\left(\sqrt{1 - 2\frac{\kappa}{\alpha_{ij}}} - \sqrt{1 + 2\frac{\kappa}{\alpha_{ij}}}\right); \quad s = \frac{\alpha_{ij}}{2}\left(\sqrt{1 + 2\frac{\kappa}{\alpha_{ij}}} + \sqrt{1 - 2\frac{\kappa}{\alpha_{ij}}}\right). \tag{98}$$

We remember the relations [2, 3]

$$s_{ij} p_{ij} = \kappa^2; \qquad (s_{ij} + p_{ij})(s_{ij} - p_{ij}) = \alpha_{ij}\sqrt{1 - 4\kappa^2/\alpha_{ij}^2}. \tag{99}$$

We mention that the method of mode restriction is of particular interest for the treatment of heavy ions in plasmas, since ions behave in plasmas in a completely different way than electrons and tend to form lattice-like structures, which leads to a dependence on $n_i^{1/3}$. However, we will not discuss this problem here in detail and refer to [57, 58, 67–70]. Note, that in general, the transition to restricted modes, i.e., to including arctan-functions, may be relevant only in case of strong ion-ion correlations

## 6. Conclusions

In this work we discuss the collaboration between the groups of Ihor R. Yukhnovskii in Lviv and Günter Kelbg in Rostock and analyze several approaches based on pair correlation functions and cluster expansion in the classical as well as in the quantum case. An essential role in this collaboration played the exponential potential which has an easy Fourier transform and is in the quantum case equivalent to the Kelbg potential. Finally, we discuss the progress in the statistical description of bound states of three particles as in $\mathrm{MgCl_2}$-solutions in the classical case and in quantum helium plasmas. We presented new results about the effects of three-particle bound states, in particlular new expressions for the cluster integrals and the mass action functions of ionic triple associates and helium atoms.

We use here a chemical description derived from the fugacity expansion, having in mind Onsager's view that we have some freedom in defining the chemical species. Like in writing the ledger for a company, we may write some effects on a left-hand page of the lecture and some on a right-hand page. This has the same effect as far as a correct summation is observed. A chemical description is some kind of optimum arrangement between left-hand and right-hand (free and bound), since a minimization of the free energy is considered, which, however, like in the case of a ledger, is strictly forbidden, and is any double counting of the terms. In the case of a ledger, this is against the law, while in the case of nature, it violates the laws of nature! Our cropping procedure is a direct consequence of avoiding the double counting of terms. Not observing this, means to admit errors.

Our new results for the equation of state of hydrogen and helium plasmas are essential based on the lectures given by Günter Kelbg and this author on a seminar directed by Ihor R. Yukhnovskii in 1970 in the Institute on the Dragomanov street in Lviv. This way we demonstrate here the key results of about 60 years of collaboration between two groups working in Lviv and in Rostock, which was full of hard work connected as well as with many unforgettable warm personal meetings with Ihor Rafailovich and his colleagues.

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# Статистична теорія систем заряджених частинок, включаючи потрійні зв’язані стани, та співпраця Львів–Росток

В. Ебелінг

Інститут фізики, Університет Гумбольдта, Берлін, Німеччина

Вшановуючи сторічний ювілей від дня народження Ігоря Р. Юхновського, ми аналізуємо нові досягнення в статистичній термодинаміці кулонівських систем. Основна ідея цієї роботи полягає в демонстрації того, що експоненціальний потенціал, використаний у перших статтях І. Р. Юхновського, є адекватною системою відліку для опису класичних та квантових систем заряджених частинок. Ми коротко обговорюємо співпрацю між групами Ігоря Юхновського у Львові та Гюнтера Кельба в Ростоку та аналізуємо деякі підходи, що грунтуються на парних кореляційних функціях та кластерних розвиненнях як у класичному, так і в квантовому випадку. Насамкінець, ми розповідаємо про прогрес у статистичному описі зв’язаних станів трьох частинок, таких як у плазмі гелію та в розчинах $MgCl_2$ у класичному випадку, та представляємо нові результати щодо впливу тричастинкових зв’язаних станів. Зокрема, ми наводимо нові вирази для кластерних інтегралів та констант рівноваги. у випадку атомів гелію та іонних потрійних асоціатів, а також для рівняння стану.

**Ключові слова:** *кореляційні функції, розклади за фугітивністю, константи хімічної рівноваги, утворення атомів*