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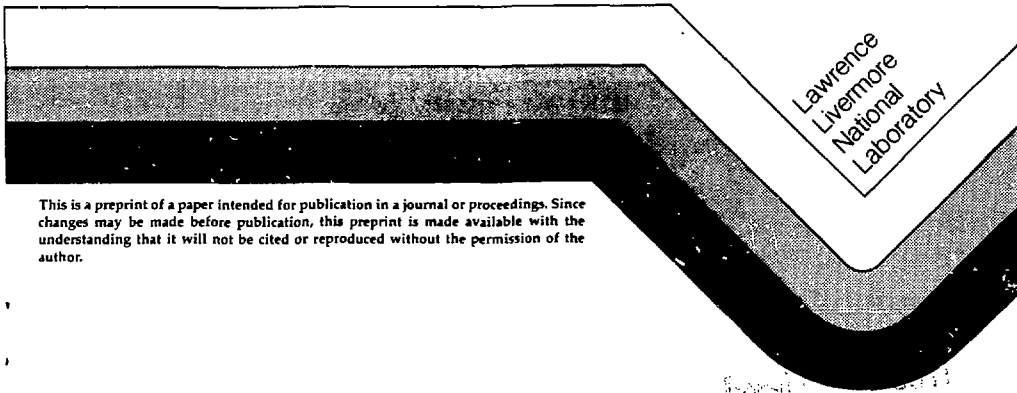
EQUATION OF STATE OF PARTIALLY-IONIZED DENSE PLASMAS

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I. Introduction

The present chapter describes methods for calculating the equation of state of partially-ionized dense plasmas. The term dense plasma is used rather than strongly coupled plasma, since it is possible that at plasma conditions such that only a few levels can be observed spectroscopically the plasma coupling parameters are not large. Due mainly to their importance in theoretical astrophysics, the properties of partially ionized plasmas have been of interest for a long while (E. Schatzman this volume). More recently, this interest has intensified due to the development of methods for producing partially ionized plasmas in the laboratory. This has opened up large programs of experimental investigation (V. Fortov this volume) and of practical application (S. Eliezer this volume).

The literature on the equation of state of partially ionized plasmas is extensive. Reviews are given in References [1-4]. Practical applications frequently use density functional, average atom-methods; particularly in the Thomas-Fermi approximation. Density functional approaches are discussed elsewhere in this volume (see chapters by Eliezer, Hansen, March and Senatore). In the current chapter we consider detailed statistical mechanical

methods that explicitly treat the distribution over ionic species and their energy level structure. These detailed approaches are generally characterized as being in the "chemical picture" when a free energy expression is minimized or in the "physical picture" when the starting point is the grand canonical ensemble.

The free energy minimization method has been the traditional approach. It is based on a number of intuitive assumptions involving the effect of the plasma environment on the internal states of ions and atoms and the separability of the free energy. *This is of course the appeal of the method,* since a computationally tractable procedure can be obtained relatively easily. On the other hand, the physical picture approach views the system in terms of its fundamental constituents, so that composite particles arise naturally in the formalism and intuitive assertions are not required. The meaning of these statements will become clear in the following discussion.

II. The Chemical Picture

Fontaine et al. [5] have discussed in detail the approximations used in the free energy minimization method. The most important of these is the assumed factorizability of the partition function into translational, Z_{TRANS} configurational, Z_{CONF} , and internal, Z_{INT} , parts according to

$$Z = Z_{\text{TRANS}} Z_{\text{CONF}} Z_{\text{INT}} \quad (2.1)$$

This has the result that the free energy is modular, since,

$$F = -kT \ln Z \quad (2.2)$$

$$= -kT \ln Z_{\text{TRANS}} Z_{\text{CONF}} Z_{\text{INT}} \quad (2.3)$$

$$= F_{\text{TRANS}} + F_{\text{CONF}} + F_{\text{INT}} \quad (2.4)$$

The modular form of Eq. (2.4) makes it possible to improve one part of the calculation without modifying the other parts. This has a great appeal from both a modelistic and a computational point of view and explains the great appeal of the chemical approach.

A. The Saha Equation

We now present some simple examples of partially ionized systems within the chemical picture. In most of the discussion the electrons are assumed to be non-degenerate. This is generally a very good assumption [6] and in any case the reader can consult the original papers. The purpose of these examples is: 1) to show that careless use of the free energy method can lead to physically incorrect results and that even the best approaches, so far proposed, involve intuitive reasoning; 2) To motivate use of the more cumbersome physical picture to treat partially-ionized plasmas. For practical calculations, the results of the activity expansion method can be used to construct a physically consistent free energy expression.

Partially-ionized plasmas by definition involve long-range Coulomb interactions, so that, F_{CONF} is not obviously negligible even at low density. Intuitively one expects that Eq. (2.4) approaches an ideal gas like limit at low density. Accordingly, in the earliest application of the free energy minimization method Saha [7] assumed that $F_{\text{CONF}} = 0$ and that F_{INT} could be approximated by the ground state Boltzmann factors of the atomic and ionic species. For example, in the case of hydrogen ionization [8]

$$F_{\text{TRANS}} = - N_e kT \left[\ln \left(\frac{g_e}{\rho_e \lambda_e^3} \right) + 1 \right] - N_p kT \left[\ln \left(\frac{g_p}{\rho_p \lambda_p^3} \right) + 1 \right] - N_H kT \left[\ln \left(\frac{g_H}{\rho_H \lambda_H^3} \right) + 1 \right] \quad (2.5)$$

where $\rho_i = N_i/V$ is the number density for ions of type i ,

$$\lambda_i = (2\pi \hbar^2 / m_i kT)^{1/2} \quad i = \{e, p, H\} \quad (2.6)$$

is the de Broglie wavelength, g_i is the statistical weight,

$$F_{\text{CONF}} = 0 \text{ and } F_{\text{INT}} = - N_H kT \ln \left(g_{1s} e^{-\beta E_{1s}} \right) \quad (2.7)$$

Using the fact that at equilibrium the free energy must be a minimum together with the stoichiometric constraints gives

$$\nu_e + \nu_p = \nu_H \quad (2.8)$$

$$\text{where } \nu_i \equiv \partial F / \partial N_i \quad (2.9)$$

is the chemical potential and H refers to hydrogen atoms in the 1s state. The solution of Eqs. (2.5-2.9) is

$$\frac{\rho_e \rho_p}{\rho_H} = \left(\frac{g_e g_p}{g_H} \right) \left(\frac{\lambda_H^3}{\lambda_e^3 \lambda_p^3} \right) e^{\beta E_{1s}} \quad (2.10)$$

Equation (2.10) is the well known Saha equation. More general equations in this form are usually also referred to as Saha equations. Equation (2.10) yields physically unacceptable results at high density, since the ionization state along an isotherm continuously decreases with increasing density, when in fact it should increase after some point, i.e., Eq. (2.10) does not produce

pressure ionization. Multi-electron atoms require the simultaneous solution of a set of relations similar to Eq. (2.10).

Atoms of course have an infinite number of bound states. Including these states in the free energy minimization replaces Eq. (2.10), for hydrogen equilibrium, with

$$\frac{\rho_e \rho_p}{\rho_H} = \frac{g_e g_p}{Z_{INT}} \left(\frac{\lambda_H^3}{\lambda_e^3 \lambda_p^3} \right) \quad (2.11)$$

$$\text{where } Z_{INT} = \sum_j g_j e^{-\beta E_j} \quad (2.12)$$

The fact that the internal partition function appears in Eq. (2.11) is a result of the fact that the internal state of the atom must be in detailed balance.

The sum over j in Eq. (2.12) leads to a heavily studied difficulty [1]. In the specific case of hydrogen, the high temperature expansion of Eq. (2.12) gives (T in eV)

$$\begin{aligned} Z_{INT} &= 2 \sum_n n^2 e^{13.6/n^2 T} = 2 \sum n^2 + \frac{2}{T} \sum \frac{n^2}{n^2} + \frac{1}{2T^2} \sum \frac{n^2}{n^4} + \dots \\ &\approx 2 n^3 + \frac{2n}{T} + \frac{n^2}{6T^2} + \dots \end{aligned} \quad (2.13)$$

The first two terms in Eq. (2.13) diverge as $n \rightarrow \infty$, while the third and higher terms are dominated by the 1s term and converge rapidly.

In the chemical picture, until very recently [9-13], the divergence of the atomic partition function has been eliminated by asserting the effect of the plasma environment on the internal states of the atom, thus truncating the partition function. A frequently used model for bound states is the confined

atom model in which it is assumed that bound electrons are confined to a sphere determined by the average volume per ion. A convenient (but not unique) definition for the ionsphere radius is given by

$$a = \left[\frac{3}{4\pi \sum_j \rho_j} \right]^{1/3} \quad (2.14)$$

where j ranges over all heavy ions. Since $\sum_j \rho_j = \rho$, the total heavy ion number density, the ionsphere radius is not a function of the state of ionization. This is not true of some other definitions that appear in the literature, e.g. the sum on j in Eq. (2.14) is often taken over only the composite ions [14]. In the confined atom model the interaction potential has the form

$$\begin{aligned} V(r) &= -Z \frac{e^2}{r} & r \leq a \\ &= \infty & r > a \end{aligned} \quad (2.15)$$

Equation (2.15) of course also has a core electron contribution when applied to non-hydrogenic ions. The energy levels in this potential are nearly Coulombic unless $a \approx \bar{r}_j$ of the orbit of the bound electrons in state j , at which point they move rapidly toward positive energy (see Fig. 1 of Ref. (6)). Using the definition (2.14) the Saha equation is still given by Eq. (2.11) except the energy levels now depend on volume and only a finite number have negative energy.

B. Addition of Configurational Free Energy

Attempts to include the configurational free energy of the plasma are generally limited to weak coupling. The configurational free energy in this limit was first worked out by Debye and Hückel [15] in 1923 for electrolytic

solutions and is discussed in books on statistical mechanics [16]. It is valid when the plasma coupling parameters,

$$\Lambda_{ij} = \frac{Z_i Z_j e^2}{kT \lambda_D} \quad , \quad (2.16)$$

are all < 0.2 . In Eq. (2.16), Z_i and Z_j are the net charge factors and λ_D is the Debye screening length given by

$$\lambda_D = \left[\frac{kT}{4\pi e^2 \left(\sum_j Z_j^2 \rho_j \right)} \right]^{1/2} \quad . \quad (2.17)$$

In this approximation the configurational free energy is given by

$$F_{DH} = - \frac{kT V}{12 \pi \lambda_D^3} \quad . \quad (2.18)$$

Retracing our earlier steps with $F_{CONF} = F_{DH}$ replaces Z_{INT} in Eq. (2.12) with

$$Z_{INT} = \sum_j g_j e^{-\beta(E_j + Z e^2/\lambda_D)} \quad . \quad (2.19)$$

The effect of the Coulomb correlations appears in Eq. (2.19) as a lowering of the continuum by the amount Ze^2/λ_D and, consequently, the ionization balance is shifted toward increased ionization.

According to the Debye-Hückel theory the potential between an electron and a ion is given by

$$V_{ei}(r) = - Z_i e^2 \frac{e^{-r/\lambda_D}}{r} \quad . \quad (2.20)$$

The confined atom potential introduced via Eq. (2.15) is obviously a gross simplification of the actual potential and it has been proposed to instead use the Debye potential to account for the effect of the plasma environment on the

internal states [5,6,17]. The Debye energy levels are a function of both density and temperature through the screening length, λ_D [18]. Again working through the chemical equilibrium equations with both Debye energy levels and a Debye plasma correction replaces Eq. (2.12) with

$$Z_{INT} = \sum_j g_j e^{-\beta \left(E_j + \frac{Ze^2}{\lambda_D} - \frac{\rho_H Ze^2}{U \lambda_D} \right)} \quad (2.21)$$

where $U = \rho_e + \rho_p$.

At high temperature the number of atoms $\rightarrow 0$. Since to lowest order in the screening length $E_j = E_j^0 + Ze^2/\lambda_D$, the term in brackets in Eq. (2.21) becomes

$$E_j^0 + 2 Ze^2/\lambda_D \quad (2.22)$$

The continuum lowering term is thus twice what it was when isolated atom energy levels were used. This reveals that we have by intuitive reasoning introduced the same effect twice. Jackson and Klein [19] have shown that at least the linear shift Ze^2/λ_D cannot appear in the bound state energy levels. In fact recent experimental data reveals that hydrogenic spectra lines are hardly changed from their isolated atom values in dense plasmas [20].

Low temperature plasmas have a neutral component for which Eq. (2.18) gives $F_{COMF} = 0$. The correlation of neutral particles is dominated by short range forces which are typically treated by a model potential such as Lennard-Jones. However, even this is too complicated for practical applications and results for hard spheres are usually utilized to account for neutral particles correlations in the more elaborate implementations of the chemical approach [5,6,14,21-22]. The easiest way to achieve this is to

replace V in the translational partition function (Eq. 2.5) by $V - V_0$ where V_0 is the volume excluded due to the hard sphere repulsion. If we identify the change in free energy as F_{CONF} then we find [6]

$$F_{CONF} = -kT \sum_i N_i \ln \left[1 - \frac{2\pi}{3V} \sum_j N_j (R_i + R_j)^3 \right] \quad (2.23)$$

where R_i and R_j are the hard sphere radii of particles i and j . Choosing the hard sphere diameters is of course the critical factor in the success of the method. An improved estimate of the free energy is given by the Carnahan-Starling [23] formula and it's multi-component generalization by Mansoori et al. [24].

C. Occupation Number Formalism

Before discussing the most recent work in the chemical picture. Two observations are useful. The first is that using the confined atom potential to obtain bound state energy levels together with hard sphere approximations to F_{CONF} is at least partly including the same effect twice; similar to using the Debye-energy levels together with the Debye-Hückel Coulomb interaction term. The second is that when the density passes through a critical value, such that a given bound state is screened into the continuum, then the partition function changes discontinuously by an amount equal to the statistical weight. This is clearly unphysical and leads to discontinuous derivatives of the free energy as well as computational problems in locating the minimum in the free energy. A practical method for dealing with this problem is to fit a smooth curve through the partition function that passes through the mid-points of the discontinuities. However, a theory that fundamentally avoids the problem is clearly required. The recent work of

Mihalas, Hummer and Däppen [9-12] and the related work of Sevastyanenko [13] does just that.

Mihalas, Hummer, and Däppen argue, by appealing to experiment [20,26] that the internal states of atoms and ions are to good approximation unshifted by the plasma environment. They introduce what they call an "occupation number formalism." They note that, if a configurational free energy, $f(V, T, \{n_i\})$, that depends explicitly on the occupation numbers of the individual states is added to the other free energy terms, then the ratio of the occupation of a state i of a given ion to the total occupation is given by

$$\frac{n_i}{n} = \frac{e^{-\beta(E_i + \partial f/\partial n_i)}}{\tilde{z}_{INT}} \equiv \frac{w_i e^{-\beta E_i}}{\tilde{z}_{INT}} \quad (2.24)$$

where

$$\tilde{z}_{INT} = \sum_i e^{-\beta(E_i + \partial f/\partial n_i)} \quad (2.25)$$

plays the role of the partition function and

$$w_i \equiv e^{-\beta \partial f/\partial n_i} \quad (2.26)$$

is the occupation probability. When $f = 0$ Eq. (2.24) reduces to the usual Boltzmann result. However, when f increases with increasing state index i , due to increasing hard sphere diameter for example, the ratio of n_i/n falls off rapidly compared to Boltzmann weight factors. This effectively cuts off the sum over states at some finite value of i . In this approach, screening of the energy levels is not required and the states are cut-off in a continuous manner.

For neutral particles Mihalas, Hummer, and Däppen use a hard sphere model similar to that discussed above with each state in principle having its own diameter. In the case of charged particles they do not in fact write down a term $f(V, T, \{n_i\})$ to obtain the w_i , instead they appeal to Stark ionization theory to define the w_i , i.e., that argue that the presence of a plasma microfield introduces a perturbation that depopulates high lying states. A detailed description is given in the referenced literature. This method produces physically acceptable answers but the quantitative values are to some degree dependent on the method of choosing hard sphere diameters and on the interpretation of Stark ionization theory. A method to systematically account for quasi-bound states and scattering states in high density application has not yet been presented.

III. The Physical Picture

The starting point in the physical picture of partially-ionized plasmas is the grand-canonical ensemble. Analogous to atomic and molecular gases one works from an activity expansion [8,16,26-30]. However, due to the long range of the Coulomb potential all cluster coefficients are divergent. This simply reflects the fact that Coulomb systems always display collective motion and do not approach a binary collision limit as the density is decreased. Nevertheless an activity expansion exists and can be obtained by accounting for the collective motion through diagrammatic resummation of the cluster coefficients. The collective motion is highly classical and it is advantageous to first work out a global solution to the many-body problem using classical theory and in the final result replace classical expressions with their quantum mechanical analogues. This limits the theory to regions where the ratio of the de Broglie wavelength to the plasma screening length is

less than unity. It is, however, possible without carrying out a full quantum mechanical calculation, to use pseudopotentials to treat the region where the de Broglie wavelength is greater than the plasma screening length [25-27,31-32].

The actual details of carrying out the steps described in the previous paragraph are somewhat tedious and it is easy to lose track of what is being attempted. A simple example for an ordinary gas will help demonstrate how reactions are naturally accounted for in the activity series. In particular, it will show clearly why it is convenient to introduce new variables to account for dimers, trimers, etc., that form at low temperature.

A. Atomic and Molecular Gases

Consider a hydrogen gas which is subject to two particle interactions, e.g., the Morse potential, but not three or higher particle interactions. The activity series for the pressure in this situation is given by [8]

$$\frac{P}{kT} = z_H + z_H^2 b_{HH} \quad (3.1)$$

subject to the usual density constraint

$$\rho_H = z_H \frac{\partial(P/kT)}{\partial z_H} = z_H + z_H^2 b_{HH} \quad (3.2)$$

where b_{HH} is the two-particle cluster coefficient, z_H is the activity of hydrogen atoms, given by

$$z_H = (2s + 1) \lambda_H^{-3} e^{\mu/kT} \quad (3.3)$$

and μ is the chemical potential defined by Eq. (2.9). The solution to Eqs. (3.1-3.2) that expresses z_H in terms of ρ_H is

$$z_H = [-1 + (1 + 8 \rho_H b_{HH})^{1/2}] / 4 b_{HH} \quad (3.4)$$

At high temperature $b_{HH} \rightarrow 0$, so that, to quadratic terms in the density the pressure is given by

$$\frac{P}{kT} = \rho_H - \rho_H^2 b_{HH} = \rho_H + \rho_H^2 B_{HH} \quad (3.4)$$

The second form of Eq. (3.4) uses the fact that the second virial coefficient is just the negative of the cluster coefficient and shows that we get the expected virial expansion at high T; provided the density is low enough that terms in ρ_H^3 are negligible. At low T on the other hand the cluster coefficient is a product of rotational, vibrational, and electronic terms according to

$$b_{HH} = 2 \lambda_H^3 \left(\frac{T}{2\theta_r} \right) \left(\frac{e^{-\theta_v/2T}}{1 - e^{-\theta_v/T}} \right) e^{4.7/T}, \quad (T \text{ in eV}) \quad (3.5)$$

At very low T $z_H \rightarrow (\rho_H/2b_{HH})^{1/2}$ and is $\ll \rho_H$, so that, $P/kT \rightarrow \rho_H/2$. This is just the pressure expected for an ideal gas of H_2 molecules.

This example shows that Eqs. (3.1-3.2) include the formation of hydrogen molecules without explicitly evaluating the occupation numbers, as required in a free energy minimization procedure. It also shows that we have an inconsistent expansion, in that we obtain second virial corrections due to hydrogen atom scattering at high T, while at low T, we obtain only the ideal gas contribution from the H_2 molecules. This is corrected by recognizing that, depending on bound state structure, the terms $z_H^n b_n$ are potentially composed of terms that range in order 1 to n in the activity. For example in the above example the term $z_H^2 b_{HH}$ can be decomposed as follows

$$z_H^2 b_{HH} = z_{H_2} + z_H^2 b_{HH}^S \quad (3.6)$$

$$\text{where } z_H \equiv z_H^2 b_{HH}^b \quad (3.7)$$

b_{HH}^b and b_{HH}^S are the bound and scattering state parts of b_{HH} . In other words the bound state term acts first order in the activity at low T. Similarly the term $z_H^3 b_{HHH}$ can be decomposed as follows

$$z_H^3 b_{HHH} = z_{H_3} + 2 z_H z_{H_2} b_{HH_2}^S + z_H^3 b_{HHH}^S \quad (3.8)$$

This procedure is self limiting in that, for example; 1) z_{H_3} will never be present in appreciable amounts and can be ignored; 2) if only a two-body collision approximation is sought the term in z_H^3 can also be dropped, since it represents true three body scattering.

Equation (3.2) still governs the elimination of the activity in terms of density, but if occupation numbers are desired one can decompose Eq. (3.2) as follows

$$\rho_H^* = z_H \frac{\partial(P/KT)}{\partial z_H} \quad , \quad \rho_{H_2} = z_{H_2} \frac{\partial(P/KT)}{\partial z_{H_2}} \quad (3.9)$$

where ρ_H^* is the explicit number of unbound atoms and ρ_{H_2} is the number of molecules. The differentiation in Eq. (3.9) is only on those terms that explicitly involve z_H or z_{H_2} in the reorganized activity series. The stoichiometric constraint requires that the total number of H atoms is given by

$$\rho_H = \rho_H^* + 2\rho_{H_2} \quad (3.10)$$

We note that as long as the number densities defined in Eq. (3.9) satisfy Eq. (3.10) we could vary the definition of z_{H_2} , provided nothing is dropped from the original activity series, i.e., it is possible to work with effective

occupation numbers rather than actual occupation numbers. The reason for this remark will become clear in the later discussion involving the Planck-Larkin partition [29] function.

B. Plasma Density Expansion

We now turn to plasmas. They are more complicated than ordinary gases since, as mentioned earlier, simple virial or cluster expansions do not exist. It is nevertheless possible to obtain a global classical many-body activity expression. To do this it is convenient to start from the canonical ensemble and develop a systematic expansion of the Mayer S function [34], given by

$$S = - \sum_{j=2}^{\infty} \bar{B}_j \frac{\rho^j}{j-1} \quad (3.11)$$

where the bar indicates multi-component structure. The function S is just the negative excess free energy so that

$$(F - \bar{F}_0)/V kT = - S \quad (3.12)$$

$$\frac{P}{kT} = \sum_{\nu} \rho_{\nu} + S - \sum_{\nu} \rho_{\nu} \frac{\partial S}{\partial \rho_{\nu}} \quad (3.13)$$

where ν is the species type.

Mayer [34] was the first to show that the sum over the most divergent diagrams in the expansion of each \bar{B}_n , i.e., the so-called ring diagrams, yields the Debye-Hückel free energy given by Eq. (2.18). ABE [35] showed how to systematically collect higher order diagrams, to obtain an expansion which closely resembles the virial expansion for the Debye potential given by Eq.

(2.20). The analogy is not complete since each ABE function is related to the B_n according to

$$S_n(\lambda_D) = \rho^n [-B_n(\lambda_D) + \phi_n(\lambda_D)] \quad (3.14)$$

where the $\phi_n(\lambda_D)$ are parts missing from B_n because they were used to create the screening in lower order terms. The ABE expansion of S for a multi-component system take the form

$$S = S_{ring} + \sum_{ij} S_{ij} + \sum_{ijk} S_{ijk} + \dots \quad (3.15)$$

where i, j, k, etc., range over all species,

$$S_{ring} = -F_{DH}/(VkT = 1/12 \pi \lambda_D^3) \quad (3.16)$$

$$S_{ij} = \rho_i \rho_j [-B_{ij}(T, \lambda_D) + \phi_{ij}] \quad (3.17)$$

and

$$\phi_{ij} = 2\pi \int_0^\infty r^2 dr \left(\beta v_{ij} - \frac{(\beta v_{ij})^2}{2} \right) .$$

Expressions for higher order S_n can be found in the cited literature. In the following discussion it will be convenient to define

$$s_{ijk} \dots = S_{ijk} \dots / \rho_i \rho_j \rho_k \dots \quad (3.18)$$

The ABE functions work from the weak coupling limit, while many interesting applications, especially for fully ionized plasmas, involve very strong coupling. Heavily studied in this regard are the one-component plasma model (OCP) of classical ions in a uniform neutralizing background of degenerate electrons and the screened OCP in which the electrons are allowed to respond to the heavy ions. The coupling in these cases is generally characterized by the parameter Γ given by

$$\Gamma = \frac{Z^2 e^2}{kT a} \quad (3.19)$$

where a is the ionsphere radius defined for an arbitrary number of components by Eq. (2.14). When $\Gamma > 1$ it would be very difficult to systematically calculate terms in the ABE series to achieve convergence. However, it is relatively easy to calculate the first few S_n and they turn out to be very gentle functions of the parameter Λ , defined in Eq. (2.16) (see Fig. 4 of Ref. (27)). In fact, it has been observed that to a good approximation, that the higher S_n can be systematically generated from S_2 according to

$$S_n/\rho \equiv S_n' = -c_n \Lambda \left(-\frac{S_{n-1}'}{c_{n-1} \Lambda} \right)^f \quad (3.20)$$

$$\text{where } f = (2.6 + 0.063 \ln \Lambda)^{1/(n-2)^{11/12}} \quad (3.21)$$

$$c_n = \frac{1}{4n} \frac{(2n-5)(2n-7) \dots 1}{(2n-4)(2n-6) \dots 2} \quad (3.22)$$

To a good approximation (~2%) it is also possible to give an analytic expression for S_2 according to

$$S_2/\rho \equiv S_2' = -c_2 \Lambda (1 - e^{-0.628\sqrt{\Lambda}}) + 0.5 e^{-23.75/\Lambda} \quad (3.23)$$

Table I compares the ABE series result obtained from Eqs. (3.20-3.23) with the DeWitt fit [37] to Monte Carlo data, the Debye-Hückel result is also included. The approximate ABE result agrees with the Monte Carlo fit to within 2%, whereas the low density Debye-Hückel approximation is a factor of five too large at the highest value of Γ . Note that, even though all the ABE terms explicitly involve the Debye potential, the high density expansion involves a rather than λ_D . DeWitt has shown that at high density terms occurring in the S_n exactly cancel $S_{n \text{ ring}}$ [38].

TABLE I. ABE series fit to $-S/\rho$ compared to Monte Carlo data.

A	Γ	ABE	MC	D - H
1	0.693	0.268	0.265	0.333
3	1.443	0.694	0.704	1.000
10	3.218	1.877	1.900	3.333
50	9.410	6.761	6.631	16.667
500	43.679	35.074	35.381	166.667

An improvement on the OCP is to allow the electrons to respond to the classical ions, so that the electronic charge density builds up around them, effectively reducing the plasma coupling. Correspondingly the ABE series can be extended to include electrons, but not without introducing quantum mechanics into the electron-ion interactions to avoid the well known classical collapse. It was shown above that bound states must be treated in a special way, but for the present purposes it is sufficient to assume that, for example, $s_{e\alpha}$ involves mainly scattering states and can be approximated by the three rung ladder term; a good approximation when kT is sufficiently high. The ABE series is thus

$$(F - F_0) / V kT = - [S_{ring} + (\rho_e^2 s_{ee} + 2\rho_e \rho_\alpha s_{e\alpha} + \rho_\alpha^2 s_{\alpha\alpha}) + (\rho_e^3 s_{eee} + 3\rho_e^2 \rho_\alpha s_{ee\alpha} + 3\rho_e \rho_\alpha^2 s_{e\alpha\alpha} + \rho_\alpha^3 s_{\alpha\alpha\alpha}) + \dots] \quad (3.24)$$

If $z > 1$ it is easy to show for each set of terms corresponding to n^{th} order in the density that the terms $\rho_\alpha^n s_{\alpha\alpha\alpha\dots n}$ is the largest [36]. When ion-ion coupling is strong but electron-ion coupling is moderate Eq. (3.24) can be written in the form

$$(F - F_0)/VKT = - \left[S_{\text{socp}} + \frac{\rho_e \Lambda_{ee}}{3} + \rho_e^2 s_{ee} + 2 \rho_e \rho_\alpha s_{e\alpha} \right] \quad (3.25)$$

where

$$S_{\text{socp}} = \rho_\alpha \frac{\Lambda}{3} + \rho_\alpha^2 s_{\alpha\alpha} + \rho_\alpha^3 s_{\alpha\alpha\alpha} + \dots \quad (3.26)$$

is the electron screened OCP with the Debye length now given by

$$\lambda_D = \left[\frac{kT}{4\pi e^2 (\rho_e + Z^2 \rho_\alpha)} \right]^{1/2} \quad (3.27)$$

and the generating functions for S_n replaced by [36]

$$\frac{S_n}{\rho_\alpha W^{n-1}} \equiv S_n' = - C_n \Lambda \left(- \frac{S_{n-1}'}{C_{n-1} \Lambda} \right)^f \quad (3.28)$$

$$W = \frac{Z^2 \rho_\alpha}{\rho_e + Z^2 \rho_\alpha} \quad (3.29)$$

In a real plasma the electrons can be partially degenerate. Cooper and DeWitt [39] have shown how to introduce electron degeneracy in the Thomas-Fermi approximation. Following their procedure Eq. (3.25) becomes

$$(F - F_0)/VKT = - \left[S_{\text{socp}} + \frac{I_{-1/2} \Lambda_{ee}}{3} + I_{-3/2}^2 s_{ee} + 2 I_{-3/2} \rho_\alpha s_{e\alpha} + \dots \right] \quad (3.30)$$

where now

$$\lambda_D = \left[\frac{kT}{4\pi e^2 (I_{-1/2}(\alpha_e) + Z^2 \rho_\alpha)} \right]^{1/2} \quad (3.31)$$

$$W = \frac{Z^2 \rho_\alpha}{I_{-1/2}(\alpha_e) + Z^2 \rho_\alpha} \quad (3.32)$$

and

$$I_{-n/2} = \frac{(2s+1)}{\lambda_e^3} F_{-n/2} \quad (3.33)$$

is the Fermi function defined so that $I_{-1/2} \rightarrow \rho_e$ in the non-degenerate limit.

We now compare results for the Thomas-Fermi screened OCP [40] obtained with the two-component ABE series, using Eqs. (3.31-3.32) in Eq. (3.28), with the dielectrically screened one component hypernetted chain approximation (HNC). To obtain the ABE series result we note that in the degenerate limit

$$I_{-1/2}(\alpha_e) \rightarrow \frac{3}{2} \frac{kT \rho_e}{\epsilon_f}, \quad \epsilon_f = \frac{\hbar^2}{2m} (3\pi^2 \rho_e)^{2/3} \quad (3.34)$$

$$\Lambda = \Lambda_{\text{OCP}} \sqrt{W}, \quad \Lambda_{\text{OCP}} = (4\pi \rho_\alpha)^{1/2} (\beta Z^2 e^2)^{3/2} \quad (3.35)$$

$$W = 1 / \left[1 + 3 Z^{1/3} \left(\frac{4}{9\pi} \right)^{2/3} \frac{r_s}{\Gamma} \right] \quad (3.36)$$

$$r_s = a_e/a_0, \quad a_e = [3/4\pi \rho_e]^{1/3} \quad (3.37)$$

A comparison of excess free energies is given in Table II for $r_s = 0$ and $r_s = 0.1$. At each coupling the upper line is for the ABE series and the lower line is for the hypernetted chain. The overall agreement is good, although differences in $\Delta E/NkT$ range as high as 10%, indicating mostly errors in the generating procedure for the S_n and probably some smaller errors related to the HNC approximation. The Thomas-Fermi dielectric function is known to be quite good for high Z but poor for $Z = 1$ so that, the method given by Eqs. (3.30-3.37) is not adequate for dense low temperature hydrogen.

TABLE II. Screening corrections to the energy of the OCP. The upper value at each Γ_{OCP} is from ABE series, and the lower value is from linear-response theory for a Thomas-Fermi dielectric function in HNC approximation.

Λ_{OCP}	Γ_{OCP}	$-\frac{(E - E_0)}{NKT}$		$-\frac{\Delta E}{NKT}$
		$r_s = 0$	$r_s = 0.1$	
0.5		0.1980	0.2224	0.0244
		0.1976	0.2215	0.0239
1	0.6934	0.3610	0.3940	0.0330
		0.3600	0.3923	0.0323
3	1.4423	0.8637	0.9216	0.0579
		0.8920	0.9458	0.0538
10	3.2183	2.3865	2.4999	0.1134
		2.2777	2.3784	0.1007
50	9.4101	7.4029	7.6938	0.2909
		7.4345	7.6916	0.2571
100	14.9380	11.9560	12.4010	0.445
		12.1640	12.5580	0.394
500	43.6790	37.2350	38.4150	1.180
		37.2290	38.3250	1.096

C. Plasma Activity Expansion

It was just shown how to treat fully ionized plasmas in the range of weak to strong ion coupling provided the electron-ion coupling is not too strong. Strong electron-ion coupling could be approximated by the use of pseudopotentials [31-32]. Classical Coulomb divergencies have thus been eliminated through many body diagrammatic resummations. The next step is to introduce the formation of composite particles into the formalism. As described earlier this involves switching from the canonical ensemble to the

grand canonical ensemble. For a one component system the pressure in the activity series can be expressed in terms of the function S through an infinite series of differential operations, according to

$$\frac{P}{kT} = z + S + \sum_{m=2}^{\infty} \frac{z}{m!} \left(\frac{\partial}{\partial z} z\right)^{m-2} \left(\frac{\partial S}{\partial z}\right)^m \quad (3.38)$$

subject to the constraint

$$\rho = z + \sum_{m=1}^{\infty} \frac{z}{m!} \left(\frac{\partial}{\partial z} z\right)^{m-2} \left(\frac{\partial S}{\partial z}\right)^m \quad (3.39)$$

where the Mayer S function defined by Eq. (3.11) is replaced by

$$S = - \sum_{j=2}^{\infty} \frac{B_j z^j}{\rho - 1} \quad (3.40)$$

and is no longer the negative excess free energy. Equation (3.38) is of course very complicated compared to the canonical pressure expression given by Eq. (3.13). Several questions arise: 1) Are Eqs. (3.13) and (3.38-3.39) equivalent and if so, 2) why use the much more complicated version given by Eqs. (3.38-3.39).

A very simple example can answer the first question. Compare the solution to Eqs. (3.13) and to (3.38-3.39) for the Debye-Hückel potential. In this case from Eqs. (2.16) and (2.18) we have

$$S(\rho) = \frac{\rho \Lambda}{3} \text{ and similarly } S(z) = \frac{z \Lambda_z}{3} \quad (3.41)$$

where Λ_z is Λ with ρ replaced by z . The solution to Eq. (3.13) is trivial,

$$\frac{P}{kT} = \rho(1 - \Lambda/6) \quad (3.42)$$

while Eqs. (3.38-3.39) requires the use of a computer to find a solution of

$$\frac{p}{kT} = z \sum_{m=0}^{\infty} \frac{(1 + \frac{m}{z})^{m-2}}{m!} \left(\frac{\Lambda_2}{z}\right)^m \quad (3.43)$$

$$\rho = z \sum_{m=0}^{\infty} \frac{(1 + \frac{m}{z})^{m-1}}{m!} \left(\frac{\Lambda_2}{z}\right)^m \quad (3.44)$$

The pressure from the canonical ensemble and the grand-canonical ensemble are found to agree up to $\Lambda = 4$, but not beyond (see Fig. 2 of Ref. (27)). This is just the point where the density fluctuations become infinite, since [27]

$$\frac{\langle n^2 \rangle - \langle n \rangle^2}{\langle n \rangle^2} = \frac{1}{1 - \rho \frac{\partial^2 S}{\partial \rho^2}} = \frac{1}{1 - \Lambda/4} \quad (3.45)$$

From which we conclude that the two expansions are the same in the fluid phase. No actual physical significance should be attached to the result (3.45) using the Debye-Hückel theory since it is inadequate when $\Lambda > 0.2$.

The answer to the second question is two-fold: first we have shown that the activity expansion is the natural expansion to account for reactions; second, the Coulomb divergencies present in the activity series are far more complicated than those that appear in the density series and the expressions (3.38-3.39) automatically eliminates them, i.e., we already worked out a method for resumming the divergencies in the S function. The main complication at this point concerns the fact that S is defined in terms of virial coefficients in the case of short-ranged interaction and by the ABE nodal functions in the case of long range interactions; whereas the activity expansion works in terms of cluster coefficients that have direct physical meaning, i.e., b_n represents the total effect of turning on n particle interactions. After first sequentially turning on all possible interactions involving up to $n - 1$ particles.

It has been shown how to systematically regroup the terms in Eq. (3.38) such that a generalized cluster expansion is obtained [42]. The resulting expansion is generalized in the sense that the usual cluster expansion is obtained for short ranged interactions while temperature and activity dependent coefficients involving the ABE nodal functions, S_n , are obtained for long-range interactions. To illustrate the procedure consider the first few terms in Eq. (3.38)

$$\frac{P}{kT} = z + S + \frac{z}{2} \left(\frac{\partial S}{\partial z} \right)^2 + \frac{z}{3!} \frac{\partial}{\partial z} z \left(\frac{\partial S}{\partial z} \right)^3 + \dots \quad (3.46)$$

$$= z + S_{ring} + S_2 + S_3 + S_4 \dots + \frac{z}{2} \left(\frac{\partial S_{ring}}{\partial z} + \frac{\partial S_2}{\partial z} + \frac{\partial S_3}{\partial z} + \dots \right)^2 + \frac{z}{3!} \frac{\partial}{\partial z} z \left(\frac{\partial S_{ring}}{\partial z} + \frac{\partial S_2}{\partial z} + \dots \right)^3 + \dots \quad (3.47)$$

Now if we collect terms such the occurrence of each S_n is considered to increase the order by the amount $n - 1$, we obtain

$$C_2 \equiv S_2 \quad (3.48)$$

$$C_3 \equiv S_3 + \frac{z}{2} \left(\frac{\partial S_3}{\partial z} \right)^2 \quad (3.49)$$

$$C_4 \equiv S_4 + z \left(\frac{\partial S_2}{\partial z} \right) \left(\frac{\partial S_3}{\partial z} \right) + \frac{z}{3!} \frac{\partial}{\partial z} z \left(\frac{\partial S_2}{\partial z} \right)^3 \quad (3.50)$$

⋮
⋮

The sum of the indexes $n - 1$ in Eq. (3.48) is of course just unity. In Eq. (3.49) the sum in each term is equal to 2, etc. As already mentioned the S_n for short ranged potentials are given directly from the definition (see Eq. 3.11) and it is easy to verify that

$$C_j = z^j b_j \quad , \quad (3.51)$$

i.e., the C_j offer an alternative route to those generally presented in text books for generating the b_j in terms of the B_j . For a Coulomb potential, however, the ratio C_j/z^j , which is normally only a function of temperature, depends on both temperature and activity through the ABE nodal functions, s_j . For short-ranged potentials the C_j given by Eq. (3.51) produce the usual result for the pressure,

$$\frac{p}{kT} = z + \sum_{j=2}^{\infty} C_j = z + \sum_{j=2}^{\infty} z^j b_j \quad . \quad (3.52)$$

However, due to the activity dependence for long-ranged potentials the pressure equation takes a much more complicated form. The first terms for a two-component plasma of electrons and ions of type α , is given by

$$\frac{p}{kT} = z_e + z_\alpha + x_R + \sum_{j=2}^{\infty} C_j + z_e \frac{\partial x_R}{\partial z_e} \frac{\partial C_j}{\partial z_e} + z_\alpha \frac{\partial x_R}{\partial z_\alpha} \frac{\partial C_j}{\partial z_\alpha} + \dots \quad (3.53)$$

where to lowest order $x_R = S_{ring}$ and in general

$$x_R = \left. \frac{P(S)}{kT} \right|_{S = S_R} = z_e + z_\alpha \quad , \quad (3.54)$$

i.e., a multi-component generalization of Eq. (3.38) in which S is everywhere replaced with S_{ring} , and the C_j are a multi-component generalization of Eqs. (3.48-3.50). A more complete version of Eq. (3.53) is given in Ref. (42).

The complete multi-component version of Eq. (3.53) gives a classical activity expression for the pressure that is formally valid for all plasma couplings. However, it cannot avoid the collapse due to electron-ion interactions. To avoid this problem requires the introduction of quantum mechanics. This is mainly a few particle phenomena which has little effect on

the collective motion when $\kappa < \lambda_z$. Consequently for most applications it is sufficient to simply replace the classical cluster coefficients for the screened potential appearing in the C_j with their quantum mechanical counterparts involving the appropriate traces over the few particle Hamiltonian operator. A quantum mechanical treatment that accounts for quantum effects on collective motion has been given by DeWitt [43].

As a simple example of the proposed approximation consider the classical version of the electron-ion cluster coefficient, $C_{e\alpha}$, arising in C_2 , where

$$C_2 \equiv C_{ee} + 2C_{e\alpha} + C_{\alpha\alpha} \quad (3.55)$$

From Eq. (3.48) we have $C_{e\alpha} = S_{e\alpha}$, so that, with $i = e, j = \alpha$, Eq. (3.17) gives a classical result for $C_{e\alpha}$. We now replace $b_{e\alpha} \equiv -B_{e\alpha}$ with

$$b_{e\alpha} = 4\pi\kappa_{e\alpha}^3 \text{Tr} \left(e^{-\beta H_2} - e^{-\beta H_0} \right) \quad (3.56)$$

but leave $\phi_{e\alpha}$ completely classical. The two particle trace in Eq. (3.56) is over a Debye-like potential in which ρ is replaced by z in Eq. (2.17). Quantum corrections to $\phi_{e\alpha}$ are given by DeWitt [43]. The first order correction in powers of κ/λ_z is recovered by the described procedure.⁴⁷ The coefficient $b_{e\alpha}$ gives the correction to thermodynamic quantities due to the redistribution of states resulting from switching on two-body interactions, relative to that already included in the ideal gas distribution. No states are created in this process but some states may enter the negative energy domain. Even so $b_{e\alpha}$ is a continuous function of interaction strength [3]. Replacements similar to Eq. (3.56) are carried out for all the b_j occurring in higher C_j . Consequently Eq. (3.53) is a continuous function of temperature and activity (density) and does not suffer from the discontinuous behavior present in some versions of the chemical picture. It is important that this property be preserved in the

subsequent analysis. Also since the $b_j(\lambda_z)$ have no bound states when λ_z (see Eq. (3.64)) is less than some critical value (0.84 a_0 for H), pressure ionization is naturally included in Eq. (3.53).

Beth and Uhlenbeck [44] long ago showed that $b_{e\alpha}$ can be evaluated in terms of bound states and scattering phase shifts according to

$$b_{e\alpha} = b_{e\alpha}^b + b_{e\alpha}^s \quad (3.57)$$

$$b_{e\alpha}^b = \sqrt{2} \lambda_{e\alpha}^3 \sum_{n\ell} (2\ell + 1) e^{-BE_{n\ell}} \quad (3.58)$$

$$b_{e\alpha}^s = \frac{\sqrt{2}}{\pi} \lambda_{e\alpha}^3 \sum_{\ell} (2\ell + 1) \int_0^{\infty} dp \frac{d\delta_{\ell}(p)}{dp} e^{-\beta p^2/2\mu_{e\alpha}} \quad (3.59)$$

where $\delta_{\ell}(p)$ is the phase shift for the ℓ^{th} partial wave, p is the relative momentum and $\mu_{e\alpha}$ is the reduced mass. A connection of Eq. (3.57) with the high temperature expansion for a Coulomb potential, given by Eq. (2.13) can readily be established. Integrate Eq. (3.59) by parts and use the Levinson theorem [45] result that the scattering phase shift at zero energy is equal to $n\pi$. This gives

$$b_{e\alpha}^s = \frac{\sqrt{2}}{\pi\mu_{e\alpha}} \beta \lambda_{e\alpha}^3 \sum_{n\ell} (2\ell + 1) \int_0^{\infty} dp p \delta_{\ell} e^{-\beta p^2/2\mu_{e\alpha}} - n\pi \quad (3.60)$$

The last term in Eq. (3.60) is equal and opposite to the first term in the high temperature expansion of Eq. (3.58). Higher order Levinson theorems exist [46] that allow an additional integration by parts so that the second term in the high temperature expansion of Eq. (3.58) is also cancelled, i.e. After this analysis the two terms that cause the internal partition function to diverge at high T (see Eq. (2.13)) are found to be analytically missing from $b_{e\alpha}$. These terms are classical and their contribution to the pressure

was already included in the ideal gas term. A detailed description of this point has been given in the WKB approximation [47,48]. Similar cancellations were also shown to occur in the higher b_j . Note that the b_j are still all divergent, but the types of divergences occurring in the so called internal partition function are fictitious and do not occur in the complete result. It should also be noted that part of the confusion results from labeling the sum over states in $b_{e\alpha}^b$ as a partition function. The relevant physical quantity that corrects thermodynamic functions is the full $b_{e\alpha}$.

The form of $b_{e\alpha}^b$ that results after the analytic compensation with the continuum is

$$b_{e\alpha}^b = \sqrt{2} \kappa_{e\alpha}^3 \sum_{n\ell} (2\ell + 1) (e^{-\beta E_{n\ell}} - 1 + \beta E_{n\ell}) \quad (3.61)$$

This is known as the Planck-Larkin partition function. For short range forces no problem arises in splitting the cluster coefficient according to Eqs. (3.6 or 3.8), so that, one can work directly from the Boltzmann factor to define composite particle activities. For a potential such as the Debye potential the number of bound states can be large and also the number varies with density in principle requiring the introduction of a large set of new activity variables with accompanying interaction potentials and ABE functions. However, use of Planck-Larkin weight factors to define composite particle activities effectively cuts the sum off when the binding energy is less than kT , so that generally only a few new activity variables are required. Everything else is simply treated as part of a redefined continuum. The occupation numbers given by equations similar to Eq. (3.9) are thus effective occupation numbers and not the actual occupation numbers, which explains the earlier remark. If the total occupation of a state is required, as for

example in opacity calculations, it can be obtained from a complimentary calculation after the equation of state is obtained [49-50].

Two additional steps are required before the Coulomb cluster expansion can be applied to partially ionized plasmas. The first is to introduce an augmented set of activity variables [42] to account for reactions taking place in the plasma, similar to those introduced for molecular hydrogen in Eq. (3.6). The second is to account for the fact that in multiply ionized plasmas the heavy ions can be strongly coupled while the electrons are only moderately coupled to ions. This requires a step similar to Eq. (3.26) occurring in the canonical ensemble, which accounts for heavy ion interactions through a complete sum over classical ABE functions.

After the first step a multi-component version of Eq. (3.53) is obtained in which composite particles whose binding energy is $> kT$ act analytically exactly like fundamental particles (see Eq. (42) of Ref. (34)). As the density is changed, such that the binding energy becomes less than kT , states smoothly switch over to being weak and are treated along with continuum states. An important result of the analysis is that strong states, having binding energy $> kT$, are unscreened by the plasma. The screening that was present in Eq. (3.53) has been used to create the new activity variables. The total number of bound states is still, however, determined by the Debye-like potential. The best way to handle the states having binding energy less than kT seems to be a procedure similar to Eqs. (2.24-2.26), where these levels are also unscreened but their occupation numbers are greatly diminished due to interaction with neighbors. The occupation numbers are effectively zero for bound states not allowed by the screened potential [51]. An alternative procedure has also been proposed [52].

A numerically tractable procedure for calculating the equations of state after recollecting terms to account for strong ion coupling is given by

$$\frac{P}{kT} = I_{3/2} + \sum_j z_j + S + p_3 + p_4 + \dots \quad (3.62)$$

where j ranges over all heavy nuclei and all composite particles having binding energy $> kT$,

$$S = S_{\text{socp}} + I_{-1/2} e^2 / kT \lambda_z + I_{-3/2}^2 s_{ee} + 2 I_{-3/2} \sum_j z_j s_{e\alpha}^L \quad (3.63)$$

S_{socp} has the same functional form as Eq. (3.26), but with the screening length given by

$$\lambda_z = [kT / (4\pi e^2 \{ I_{-1/2} + \sum_j z_j^2 z_j \})]^{1/2} \quad (3.64)$$

and the lowest order p_n is given by

$$p_3 = \sum_j z_j (e^{\partial S / \partial z_j} - 1 - \partial S / \partial z_j) \quad (3.65)$$

subject to the usual density constraints similar to Eqs. (3.9-3.10).

Applications of Eq. (3.62) to an argon plasma was given in Ref. (36). The equation of state results obtained for very dense plasmas are found to agree quite well on the average with the Thomas-Fermi-Kirzknits [51] equation when the ion correlations are treated in the OCP approximation. Thomas-Fermi theory, however, does not give very accurate derivatives of the equation of state.

For lowly ionized plasmas using the procedure described thus far, the interactions involving neutral particles must be calculated from few particle cluster expansions, i.e., similar to the hydrogen example described earlier. This of course would be unwieldy for dense systems such as those recently

considered by Saumon and Chabier [52]. What is needed is a procedure that in some approximation includes all orders of interaction. This is accomplished for multiply ionized ions through S_{socp} given by Eq. (3.26). For an idealized neutral hard sphere gas it can be obtained from the Carnahan-Starling formula and its multi-component generalization [23-24]. For realistic interaction potentials a good method of carrying out this calculation is to use the HNC equation [31]. In this approach one uses effective potentials to account for ion-ion interaction but, since the HNC equation is classical, it is necessary to use pseudopotentials to account for the electron-ion interaction. A free energy minimization is used to obtain the ionization balance.

What we want to do is to find a solution to the generalized form of Eq. (3.53) that includes all coupling orders for both electrons and ions. Since it is proposed to work in the chemical picture we need to convert Eq. (3.53) to a free energy form similar to Eq. (3.12). Due to the renormalization that was carried out to create composite particle activities the Planck-Larkin part of the free energy for strong bound states appears in quasi-ideal gas terms. Pseudopotentials are constructed from the remaining part of the trace [31] that appears in the renormalized S function.

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