Highly Charged Ions in a Dilute Plasma:
An Exact Asymptotic Solution Involving Strong Coupling

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Abstract

The ion sphere model introduced long ago by Salpeter is placed in a rigorous theoretical setting. The leading corrections to this model for very highly charged but dilute ions in thermal equilibrium with a weakly coupled, one-component background plasma are explicitly computed, and the subleading corrections shown to be negligibly small. This is done using the effective field theory methods advocated by Brown and Yaffe. Thus, corrections to nuclear reaction rates that such highly charged ions may undergo can be computed precisely. Moreover, their contribution to the equation of state can also be computed with precision. Such analytic results for very strong coupling are rarely available, and they can serve as benchmarks for testing computer models in this limit.

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I. INTRODUCTION AND SUMMARY

Here we describe a plasma configuration whose exact asymptotic solution can be obtained in a strong coupling limit. The solution is given by the ion sphere result presented by Salpeter [1] plus a simple smaller correction. This is accomplished by using the effective plasma field theory methods advocated by Brown and Yaffe [2]. In this field-theory language, the old Salpeter result corresponds to the tree approximation and our new correction is the one-loop term. In usual perturbative expansions, the tree approximation provides the first, lowest-order term for weak coupling. Here, on the contrary, the tree approximation provides the leading term for strong coupling, with the corrections of higher order in the inverse coupling. This is the only example of which we are aware in which the tree approximation yields the strong coupling limit. This strongly coupled system is interesting from a theoretical point of view and our results can be used to check numerical methods.

The plasma consists of very dilute “impurity” ions of very high charge $Z_p e$, $Z_p \gg 1$, in thermal equilibrium with a classical, one-component “background” plasma of charge $ze$ and number density $n$, at temperature $T = 1/\beta$. The background plasma is neutralized in the usual way, and it is dilute. We use rationalized electrostatic units and measure temperature in energy units so that the background plasma Debye wave number appears as

$$\kappa^2 = \beta (ze)^2 n. \quad (1.1)$$

The internal coupling of the background plasma is described by the dimensionless coupling parameter

$$g = \beta \frac{(ze)^2}{4\pi} \kappa = \frac{(ze)^2}{4\pi T} \kappa. \quad (1.2)$$

The assumed weak coupling of the dilute background plasma is conveyed by

$$g \ll 1. \quad (1.3)$$

Although the internal coupling of the background plasma to itself is assumed to be very weak and the impurity ions are assumed to be so very dilute that their internal interactions are also very small, we shall require that the ionic charge $Z_p$ is so great that the coupling between the impurity ions and the background plasma is very large. To make this condition more precise, we define

$$\bar{Z}_p = \frac{Z_p}{z}, \quad (1.4)$$
which is the magnitude of the impurity charge measured in units of the dilute background ionic charge. Then the explicit condition that we require is that

\[ g\bar{Z}_p \gg 1. \]  

(1.5)

Since the limit that we use may appear to be obscure, we pause to clarify it. Even though \( g\bar{Z}_p \gg 1 \), we assume that \( g \) is sufficiently small that \( g^2\bar{Z}_p \ll 1 \). We may, for example, take \( g \to 0 \) with \( g^\alpha \bar{Z}_p = \text{const.} \), and \( \alpha \) in the interval \( 1 < \alpha < 2 \). Then \( g\bar{Z}_p = \text{const.} / g^{\alpha-1} \gg 1 \) while \( g^2\bar{Z}_p = \text{const.} g^{2-\alpha} \ll 1 \).

Standard methods express the grand canonical partition function in terms of functional integrals. Brown and Yaffe [2] do this, introduce an auxiliary electrostatic potential, and integrate out the charged particle degrees of freedom to obtain the effective theory. This technique will be described in more detail in Sec. II below. The saddle point expansion of this form for the grand partition function yields a perturbative expansion, with the tree approximation providing the lowest-order term. Here, on the contrary, we express the *impurity ion number* in terms of an effective field theory realized by a functional integral. The saddle point of this form of the functional integral involves a classical field solution driven by a strong point charge.

The result for the impurity ion number reads

\[ N_p = N_p^{(0)} \exp \left\{ \frac{3}{10} (3g)^{2/3} \bar{Z}_p^{5/3} \right\} \]

\[ + \left( \frac{9}{g} \right)^{1/3} \mathcal{C} \bar{Z}_p^{2/3} + \cdots - \frac{1}{3} g \bar{Z}_p + \mathcal{O}(g^2 \bar{Z}_p) \} \right\}. \]  

(1.6)

Here \( N_p^{(0)} \sim \exp\{\beta \mu_p\} \) is the number of impurity ions defined by the chemical potential \( \mu_p \) in the absence of the background plasma; keeping this chemical potential fixed, the background plasma alters this number to be \( N_p \). The added \( \cdots \) stand for corrections to the analytical evaluation of the classical action displayed in the \( \bar{Z}_p^{5/3} \) and \( \bar{Z}_p^{2/3} \) terms of Eq. (1.6). The sizes of these omitted corrections are compared to the exact numerical evaluation of the action in Fig. 2 below. This figure shows that the relative sizes of these terms are small \( (\ll 1) \) in the limit in which we work \( (gZ \gg 1) \). The constant \( \mathcal{C} = 0.8499 \cdots \). The final \( -g\bar{Z}_p/3 \) term in the exponent is the relatively small one-loop correction. As shown in detail in the discussion leading to Eq. (3.63) below, the error in the result (1.6) is of the indicated order \( g^2 \bar{Z}_p = g (g\bar{Z}_p) \) and is thus negligible in the limit \( g \ll 1 \) that concerns us.
The number correction (1.6) can be used to construct the grand canonical partition function \( Z \) for the combined system by integrating the generic relation

\[
N_a = \frac{\partial}{\partial \beta \mu_a} \ln Z
\]

for \( a = p \) and using the boundary condition that \( N_p \to 0 \) as \( \beta \mu_p \to -\infty \). Since \( N_p \) depends upon the chemical potential \( \mu_p \) only in the factor \( N_p^{(0)} \sim \exp\{\beta \mu_p\} \), this integration gives

\[
\ln Z = N_p + N^{(0)}.
\]

Here we have identified the constant of integration, the constant that remains when \( N_p \) vanishes, to be \( N^{(0)} \), the number of background plasma particles in the absence of the impurity ions. In our limit in which the background plasma is very weakly coupled, \( N^{(0)} \sim \exp\{\beta \mu\} \) is just the number of non-interacting particles of chemical potential \( \mu \).

The equation of state can be found from the well-known relation for a grand canonical ensemble with partition function \( Z \),

\[
\beta p V = \ln Z.
\]

However, the grand canonical partition function \( Z \) is a function of the temperature and chemical potentials and, to obtain the equation of state, we must re-express it in terms of the observed, physical particle numbers rather than their chemical potentials.

To do this, we need to express \( N^{(0)} \sim \exp\{\beta \mu\} \) in terms of the true number of background particles \( N \), a number that differs from \( N^{(0)} \) because of the presence of the impurity ions. There is a significant difference because, although the impurity ions are few in number, they are assumed to be extremely highly charged. We again use the general formula (1.7), but this time to compute \( N \) using the solution (1.8):

\[
N = \frac{\partial N_p}{\partial \beta \mu} + N^{(0)}.
\]

The measured impurity number \( N_p \) does depend upon \( \beta \mu \) because it entails the dimensionless coupling parameter \( g \) defined in Eq. (1.2). For simplicity of exposition, in that definition we used a Debye wave number \( \kappa \) that was defined in terms of the true background density \( n \). Although the distinction is not important for the leading terms that concern us, we nevertheless note that the correct wave number that appears in our functional integral...
formalism involves the ‘bare’ number density \( n^{(0)} = N^{(0)}/V \), with \( g \sim \sqrt{n^{(0)}} \sim \exp\{\beta \mu/2\} \), and so
\[
\frac{\partial g}{\partial \beta \mu} = \frac{1}{2} g . \tag{1.11}
\]
Hence,
\[
N = N^{(0)} + \frac{1}{2} g \frac{\partial}{\partial g} N_p . \tag{1.12}
\]

Using this relation to determine \( N^{(0)} \) in terms of the physical quantities \( N \) and \( N_p \) places relationship (1.9) of the pressure to the partition function (1.8) in the proper form of an equation of state. To simply bring out the main point, we include here only the leading terms, to obtain
\[
pV \simeq \left\{ N - \bar{Z}_p \frac{(3g\bar{Z}_p)^{2/3}}{10} N_p \right\} T . \tag{1.13}
\]

Although the fraction of impurity ions in the plasma \( N_p/N \) may be quite small, there may be a significant pressure modification if \( \bar{Z}_p \) is very large. Note that the free particle contribution, an additional term of \( N_p \), is omitted here since it is not multiplied by the large factor in the term that we have retained.

The number result (1.6) also directly yields the plasma correction to a nuclear fusion rate, since
\[
\Gamma = \Gamma_C \frac{N_1^{(0)} N_2^{(0)}}{N_1 N_2} \frac{N_{1+2}^{(0)}}{N_{1+2}^{(0)}}, \tag{1.14}
\]
where \( \Gamma_C \) is the nuclear reaction rate for a thermal, Maxwell-Boltzmann distribution of the initial (1,2) particles in the absence of the background plasma. We use the notation 1 + 2 to denote an effective particle that carries the charge \((Z_1 + Z_2)e\). This formula was obtained in a different guise by DeWitt, Graboske, and Cooper [3]. The relation of the form (1.14) that we use to previous results is discussed in detail in the Appendix. The formula holds when the Coulomb barrier classical turning point of the nuclear reaction is small in comparison with the plasma Debye length. This is spelled out in detail in a recent work by Brown, Dooling, and Preston [4], who also show that the result (1.14) is valid even if the background plasma involves quantum corrections. The conditions needed for the formula (1.14) to hold are also discussed in the work of Brown and Sawyer [5], although sometimes in a rather implicit fashion. This work does show, however, that the result (1.14) is valid if \( \kappa r_{\text{max}} \ll 1 \), where \( \kappa = \beta e^2 \) is the Debye wave number and \( r_{\text{max}} \) is the turning point radius defined by \( r_{\text{max}} = 2(e^2/4\pi m\omega^2)^{1/3} \) where \( \omega = 2\pi T/\hbar \) is the imaginary time frequency associated
with the temperature $T$. It should be remarked that DeWitt, Grabske, and Cooper \[3\] assumed that the nuclear reaction rate formula (1.14) held only if the background plasma had a classical character, but that the work of Brown, Dooling, and Preston \[4\] shows that it is valid even if the plasma involves quantum effects.

Our result (1.6) for the number corrections presents the plasma correction to the fusion rate for our special case as

$$\Gamma = \Gamma_C \exp \left\{ \frac{3}{10} (3g)^{2/3} \left[ (\bar{Z}_1 + \bar{Z}_2)^{5/3} - \bar{Z}_1^{5/3} - \bar{Z}_2^{5/3} \right] \right\} \exp \left\{ \left( \frac{9}{g} \right)^{1/3} C \left[ (\bar{Z}_1 + \bar{Z}_2)^{2/3} - \bar{Z}_1^{2/3} - \bar{Z}_2^{2/3} \right] \right\}. \tag{1.15}$$

The first line agrees with Salpeter’s calculation \[1\]; the second is new. Again the correction can be large.

We turn now to describe the basis for these results in detail.

II. REMEMBERANCE OF THINGS PAST

To begin, we need to review a simple case of the general plasma effective field theory formulation presented by Brown and Yaffe \[2\]. First we note that the grand canonical partition function for a one-component classical plasma may be expressed as the functional integral (which are discussed in detail, for example, in the first chapter of the book by Brown \[6\]),

$$Z = \int [d\chi] \exp \left\{ -\int (d^3r) \left[ \frac{\beta}{2} \left( \nabla \chi(r) \right)^2 - g_S \lambda^{-3} e^{i\varepsilon e^2 \beta \chi(r)} \right] \right\}. \tag{2.1}$$

Here

$$\lambda^{-3} = \frac{(d^3p)}{(2\pi \hbar)^3} \exp \left\{ -\beta \frac{p^2}{2m} \right\} \tag{2.2}$$

defines the thermal wave length $\lambda$ of the plasma particles of mass $m$. These particles have a chemical potential $\mu$ and spin weight $g_S$ so that their density in the free-particle limit is given by

$$n^{(0)} = g_S \lambda^{-3} e^{\beta \mu}. \tag{2.3}$$
We use rationalized Gaussian units so that, for example, the Coulomb potential appears as \( \phi = e/4\pi r \). We shall be a little cavalier about the uniform, rigid neutralizing background that we tacitly assume to be present. We shall explicitly include its effects when needed.

The validity of the functional integral representation (2.1) is easy to establish. The second part in the exponential is written out in a series so as to produce the fugacity expansion

\[
Z = \sum_{n=0}^{\infty} \frac{1}{n!} (g_S \lambda^{-3})^n e^{n\beta\mu} \int (d^3r_1) \cdots (d^3r_n) \\
\int [d\chi] \exp \left\{ -\int (d^3r) \left[ \frac{\beta}{2} \left( \nabla \chi(r) \right)^2 + i e \beta \chi(r) \sum_{a=1}^{n} \delta (r - r_a) \right] \right\}. \tag{2.4}
\]

This Gaussian functional integral can be performed by the functional integration field variable translation

\[
\chi(r) = \chi'(r) - \sum_{a=1}^{n} \frac{i e}{4\pi |r - r_a|}. \tag{2.5}
\]

Since

\[
-\nabla^2 \frac{1}{4\pi |r - r_a|} = \delta (r - r_a), \tag{2.6}
\]

and the Laplacian \( \nabla^2 \) can be freely integrated by parts in the quadratic form \( \chi(-\nabla^2)\chi \), after the translation a Gaussian functional integration appears with quadratic form \( \chi'(-\nabla^2)\chi' \) with no coupling linear in \( \chi' \). The original measure \([d\chi] = [d\chi']\) is taken to include factors such that this remaining purely Gaussian function integral is simply unity. For pedagogical clarity, we make use of the definition (2.2) of the thermal wavelength to write the result of these manipulations as

\[
Z = \sum_{n=0}^{\infty} \frac{1}{n!} g_S^2 e^{n\beta\mu} \int \frac{(d^3r_1)(d^3p_1)}{(2\pi \hbar)^3} \cdots \frac{(d^3r_n)(d^3p_n)}{(2\pi \hbar)^3} \\
\exp \left\{ -\beta \left[ \sum_{a=1}^{n} \frac{P_a^2}{2m} + \frac{1}{2} \sum_{a,b=1}^{n} \frac{(ze)^2}{4\pi |r_a - r_b|} \right] \right\}. \tag{2.7}
\]

This is precisely the familiar fugacity expansion of the classical grand canonical partition function. The diagonal sum where \( a = b \) in the Coulomb potential must be deleted. This omission of the infinite self-energy terms is automatic if the dimensional regularization
scheme is employed as advocated by Brown and Yaffe [2]. Here we shall instead regulate the theory by (at first implicitly) replacing the point source $\delta(\mathbf{r} - \mathbf{r}_a)$ with a source $\delta_R(\mathbf{r} - \mathbf{r}_a)$ that has a small extent about $\mathbf{r}_a$ and (at first implicitly) removing the self energy terms, with the limit $\delta_R \rightarrow \delta$ finally taken in the subtracted theory.

The derivative of the logarithm of a grand canonical partition function with respect to a chemical potential (times $\beta$) gives the particle number conjugate to that chemical potential. Thus, if we temporarily add another particle species $p$ of charge $e_p = Z_p e$ to the previous functional integral, take the described derivative, and then take the limit in which this new species is very dilute, we get the desired functional integral representation for the background plasma correction to the new species free particle number relation in the presence of plasma interactions,

\[
N_p = \frac{N_p^{(0)}}{Z} \int [d\chi] e^{iZ_p e \beta \chi(0)} \exp \left\{ - \int (d^3r) \left[ \frac{\beta}{2} (\nabla \chi(r))^2 \right. \right. \\
\left. \left. - n \left( e^{i e_p \beta \chi(r)} - 1 - i e_p \beta \chi(r) \right) \right] \right\}.
\]

To express this more precisely, in Eq. (2.8) $N_p^{(0)} = g_{p} \lambda_p^{-3} V \exp\{\beta \mu_p\}$, where the subscript $p$ is used to indicate that these are the properties of the sparsely populated ‘impurity’ ions of charge $e_p = Z_p e$, with $V$ denoting the system volume. So Eq. (2.8) describes the background plasma correction to the free-particle chemical potential – number relationship for these $p$ ions immersed in the weakly-coupled, one-component plasma. The original chemical potential derivative that leads to this result entailed a volume integral. In virtue of the translational invariance of the background plasma, the result is independent of the particular value of the spatial coordinate in the electric potential $\chi(\mathbf{r})$ in the initial factor, and this coordinate may be placed at the origin (as we have done), giving the factor $e^{i e_p \beta \chi(0)}$ shown. The volume integral then combines to form the total free-particle number $N_p^{(0)}$ that appears as a prefactor. We have now subtracted terms from the second exponential, the exponential of the action functional of the background plasma, to remove an overall number contribution and to include the effect of the rigid neutralizing background. These same subtractions must now be made in the normalizing partition function $Z$ that appears in the denominator of Eq. (2.8). Thus $Z$ is defined by the functional integral of the second exponential that appears in Eq. (2.8). The effect of the uniform neutralizing rigid background
charge is contained in the term $\imath e\beta\chi$ that is subtracted from the exponential $\exp\{\imath e\beta\chi\}$. The additional 1 is subtracted from this exponential for convenience.

To simplify the notation, we write Eq. (2.8) as simply

$$N_p = \frac{N_p(0)}{Z} \int [d\chi] e^{-S[\chi]} ,$$

(2.9)

where the effective action $S[\chi]$ contains all the terms in both exponents in Eq. (2.8). The loop expansion is an expansion about the saddle point of the functional integral. At this point, the action $S[\chi]$ is stationary, and thus the field $\chi$ at this point obeys the classical field equation implied by the stationarity of the action.

The tree approximation is given by the evaluation of $S[\chi]$ at the classical solution

$$\chi(\mathbf{r}) \to i\phi_{cl}(\mathbf{r}) ,$$

(2.10)

namely

$$S[i\phi_{cl}] = -\int (d^3\mathbf{r}) \left\{ \frac{\beta}{2} \left( \nabla \phi_{cl}(\mathbf{r}) \right)^2 + n \left[ e^{-\beta z e \phi_{cl}(\mathbf{r})} - 1 + \beta z e \phi_{cl}(\mathbf{r}) \right] - \beta Z_p e \delta(\mathbf{r}) \phi_{cl}(\mathbf{r}) \right\} ,$$

(2.11)

whose stationary point defines the classical field equation

$$-\nabla^2 \phi_{cl}(\mathbf{r}) = zen \left[ e^{-\beta z e \phi_{cl}(\mathbf{r})} - 1 \right] + Z_p e \delta(\mathbf{r}) .$$

(2.12)

This equation defining the classical potential $\phi_{cl}(\mathbf{r})$ is of the familiar Debye-Hückel form, and it could have been written down using simple physical reasoning. However, we have placed it in the context of a systematic perturbative expansion in which the error of omitted terms can be ascertained. In particular, we shall describe the one-loop correction that is automatically produced by our formalism. Moreover, we shall prove that higher-order corrections may be neglected. Our approach using controlled approximations in which the error is assessed, and making precise evaluations of a well defined perturbative expansions in terms of correctly identified coupling parameters, differs in spirit from much of the traditional work in plasma physics. For example, although previous work has been done by Vieillefosse on the solution of the non-linear Debye-Hückel equation, this work was not done in the context of a systematic, controlled approximation.
The one-loop correction to this first tree approximation is obtained by writing the functional integration variable as
\[ \chi(r) = i\phi_{cl}(r) + \chi'(r), \] (2.13)
and expanding the total action in Eq. (2.9) to quadratic order in the fluctuating field \( \chi' \). Since \( i\phi_{cl} \) obeys the classical field equation, there are no linear terms in \( \chi' \) and we have, to quadratic order,
\[ S[\chi] = S[i\phi_{cl}] + \frac{\beta}{2} \int (dr) \chi'(r) \left[ -\nabla^2 + \kappa^2 e^{-\beta ze \phi_{cl}(r)} \right] \chi'(r), \] (2.14)
where
\[ \kappa^2 = \beta (ze)^2 n \] (2.15)
is the squared Debye wave number of the mobile ions. The resulting Gaussian functional integral produces an infinite dimensional, Fredholm determinant. In this same one-loop order, the normalizing partition function \( Z \) is given by the same determinant except that it is evaluated at \( \phi_{cl} = 0 \). Hence, to tree plus one-loop order,
\[ N_p = N_p^{(0)} \frac{\text{Det}^{1/2} \left[ -\nabla^2 + \kappa^2 \right]}{\text{Det}^{1/2} \left[ -\nabla^2 + \kappa^2 e^{-\beta ze \phi_{cl}} \right]} \exp \left\{ -S[i\phi_{cl}] \right\} . \] (2.16)

III. COMPUTATION

A. Tree

To solve the classical field equation (2.12) in the large \( Z_p \) limit, we first note that the classical potential must vanish asymptotically so as to ensure that the resulting total charge density vanishes at large distances form the ‘external’ point charge \( e_p = Z_p e \),
\[ |r| \to \infty : \quad en \left[ 1 - e^{-\beta ze \phi_{cl}(r)} \right] \to 0 . \] (3.1)
Since \( \phi_{cl} \) vanishes asymptotically, its defining differential equation (2.12) reduces at large distances to
\[ -\nabla^2 \phi_{cl}(r) \simeq -\kappa^2 \phi_{cl}(r) , \] (3.2)
and thus, for $|\mathbf{r}|$ large,

$$\phi_{\text{cl}}(\mathbf{r}) \simeq (\text{const}) \frac{e^{-\kappa|\mathbf{r}|}}{|\mathbf{r}|}.$$  \hspace{1cm} (3.3)

Since this is exponentially damped, the coordinate integral of the left-hand side of Eq. (2.12) vanishes by Gauss’ theorem, and we obtain the integral constraint

$$z \, n \int (d\mathbf{r}) \left[ 1 - e^{-\beta z e \phi_{\text{cl}}(\mathbf{r})} \right] = Z_\nu.$$  \hspace{1cm} (3.4)

For small $r \equiv |\mathbf{r}|$, the point source driving term in the classical field equation dominates, giving the Coulomb potential solution

$$\phi_{\text{cl}}(\mathbf{r}) \simeq \frac{Z_\nu e}{4\pi r}.$$  \hspace{1cm} (3.5)

Thus we write

$$\phi_{\text{cl}}(\mathbf{r}) = \frac{Z_\nu e}{4\pi r} u(\xi),$$  \hspace{1cm} (3.6)

where

$$\xi = \kappa r,$$  \hspace{1cm} (3.7)

and the point driving charge $Z_\nu e$ is now conveyed in the boundary condition

$$u(0) = 1.$$  \hspace{1cm} (3.8)

The other boundary condition is the previously noted large $r$ limit (3.3) which now appears as

$$\xi \to \infty : \quad u(\xi) \sim e^{-\xi}.$$  \hspace{1cm} (3.9)

The action (2.11) corresponding to the classical solution is divergent since it includes the infinite self-energy of the point charge $e_\nu = Z_\nu e$ impurity. This self-energy must be subtracted to yield the finite, physical action. Following standard practice in quantum field theory, the divergent classical action (2.11) and the self-energy are first regularized — rendered finite — by replacing the point charge with a finite source. The self-energy is then subtracted, and finally the point source limit is taken. Regularization is achieved by the replacement $\delta(\mathbf{r}) \to \delta_R(\mathbf{r})$, where $\delta_R(\mathbf{r})$ is a smooth function of compact support. The regularized action obtained by making this substitution in the action $S[i\phi_{\text{cl}}]$ defined by Eq. (2.11) will be denoted as $S_{\text{reg}}$. The regularized self field $\phi_{\text{self}}(\mathbf{r})$ is the solution of

$$-\nabla^2 \phi_{\text{self}}(\mathbf{r}) = Z_\nu e \, \delta_R(\mathbf{r}),$$  \hspace{1cm} (3.10)
and it defines the self-action
\[ S_{\text{self}} = -\beta \int (d^3r) \left\{ \frac{1}{2} \left( \nabla \phi_{\text{self}}(r) \right)^2 - Z_p e \, \delta_R(r) \, \phi_{\text{self}}(r) \right\} . \] (3.11)

The identity
\[ \beta \int (d^3r) \left\{ \left( \nabla \phi_{\text{self}}(r) \right)^2 - Z_p e \, \delta_R(r) \, \phi_{\text{self}}(r) \right\} = 0 , \] (3.12)
which is easily verified through partial integration and use of the field equation obeyed by \( \phi_{\text{self}} \), can be used to write the self-energy action (3.11) as
\[ S_{\text{self}} = \beta \int (d^3r) \frac{1}{2} \left( \nabla \phi_{\text{self}}(r) \right)^2 \]
\[ = \beta \int (d^3r) \frac{1}{2} E_{\text{self}}^2(r) , \] (3.13)

which is just the impurity’s field energy divided by the temperature. It is convenient to use this form (3.13) in subtracting off the self-energy from \( S_{\text{reg}} \) and to also subtract the identity
\[ \beta \int (d^3r) \left\{ \nabla \phi_{\text{self}}(r) \cdot \nabla \phi_{\text{cl}}(r) - Z_p e \, \delta_R(r) \, \phi_{\text{cl}}(r) \right\} = 0 , \] (3.14)
proved in the same manner as Eq. (3.13). The point source limit \( \delta_R(r) \to \delta(r) \) can now be taken to secure the well-defined result
\[ S[i\phi_{\text{cl}}] \to S_{\text{sub}}[i\phi_{\text{cl}}] = \]
\[ = -\beta \int (d^3r) \left[ \nabla \left( \phi_{\text{cl}}(r) - \phi_{\text{self}}^P(r) \right) \right]^2 \]
\[ -n \int (d^3r) \left\{ e^{-\beta z e \phi_{\text{cl}}(r)} - 1 + \beta z e \, \phi_{\text{cl}}(r) \right\} , \] (3.15)

where
\[ \phi_{\text{self}}^P(r) = \frac{Z_p e}{4\pi r} \] (3.16)
is the point-source limit of the self-field.

Using the form (3.6) for the classical solution we have, remembering that \( u(0) = 1 \),
\[ 4\pi r^2 \left[ \nabla \left( \phi_{\text{cl}}(r) - \phi_{\text{self}}^P(r) \right) \right]^2 \]
\[ = \frac{(Z_p e)^2}{4\pi} \left[ \frac{du(r)}{dr} - \frac{1}{r} \left( u(r) - u(0) \right) \right]^2 \]
\[ = \frac{(Z_p e)^2}{4\pi} \left\{ \left( \frac{du(r)}{dr} \right)^2 - \frac{d}{dr} \left[ \frac{1}{r} \left( u(r) - u(0) \right) \right]^2 \right\} . \] (3.17)
The final total derivative that appears here gives a null result since the end-point contributions vanish. Hence the subtracted action (3.15) now appears as

\[
S_{\text{sub}}[i\phi_{\text{cl}}] = - \int_0^\infty dr \left\{ \frac{\beta Z_p^2 e^2}{4\pi} \left( \frac{du}{dr} \right)^2 + 4\pi r^2 n \right\} \exp \left\{ \frac{-\beta Z_p^2 e^2}{4\pi r} u \right\} - 1 + \frac{\beta Z_p^2 e^2}{4\pi r} u \right\}.
\]

(3.18)

Changing variables to \( \xi = \kappa r \) and using the previously defined plasma coupling constant \( g = \beta (ze)^2 \kappa / (4\pi) \) gives

\[
S_{\text{sub}}[i\phi_{\text{cl}}] = - \int_0^\infty d\xi \left\{ \frac{\bar{Z}_p g}{2} \left( \frac{du(\xi)}{d\xi} \right)^2 + \frac{\xi^2}{g} \left[ \exp \left\{ -\bar{Z}_p g u(\xi) / \xi \right\} - 1 + \frac{\bar{Z}_p g}{\xi} u(\xi) \right] \right\}.
\]

(3.19)

Requiring that this new form of the action be stationary produces the classical field equation

\[
-Z_p g \frac{d^2u(\xi)}{d\xi^2} = \xi \left[ \exp \left\{ -\bar{Z}_p g u(\xi) / \xi \right\} - 1 \right].
\]

(3.20)

Note that the integral constraint (3.4) now reads

\[
\int_0^\infty d\xi \frac{\xi^2}{g} \left[ 1 - \exp \left\{ -\bar{Z}_p g u(\xi) / \xi \right\} \right] = \bar{Z}_p.
\]

(3.21)

**B. Ion Sphere Model**

In the large \( \bar{Z}_p \) limit which concerns us, the short distance form \( (3.5) \) (multiplied by \( \beta ze \)) is large (compared to one) over a wide range of \( |r| \), and the Boltzmann factor \( \exp\left\{ -\beta ze\phi_{\text{cl}}(r) \right\} \) is quite small in this range. We are thus led to the “ion sphere model” brought forth some time ago by Salpeter [1]. This model makes the step-function approximation

\[
1 - \exp \left\{ -\bar{Z}_p g u(\xi) / \xi \right\} \simeq \theta (\xi_0 - \xi).
\]

(3.22)

Placing this in the integral constraint (3.21) determines the ion sphere radius \( \xi_0 = \kappa r_0 \) to be given by

\[
\xi_0^3 = 3g \bar{Z}_p.
\]

(3.23)
FIG. 1: Numerical solution for $u(\xi)$ (solid line), ion sphere model $u_0(\xi)$ (short-dashed line), and the first correction $v_1$ (long-dashed line). For $\xi > \xi_0$, $u_0 = 0$; here $\xi_0 = 6.694$.

In the ion sphere model, the classical field equation \( (3.20) \) becomes

$$
\bar{Z}_p g \frac{d^2 u_0(\xi)}{d\xi^2} = \xi \theta (\xi_0 - \xi),
$$

and this has the solution, obeying the initial condition $u_0(0) = 1$,

$$
u_0(\xi) = \begin{cases} 
1 - \frac{(\xi/2\bar{Z}_p g)}{[\xi_0^2 - \frac{1}{3}\xi^2]}, & \xi < \xi_0, \\
0, & \xi > \xi_0.
\end{cases}
$$

Here the term linear in $\xi$, a solution of the homogeneous equation, has been determined by the continuity at the ion sphere surface, the condition that $u_0(\xi_0) = 0$. [Without this constrain an additional $\delta(\xi - \xi_0)$ would appear on the right-hand side of Eq. \( (3.24) \).] The nature of this “ion-sphere” solution $u_0(\xi)$ together with the exact solution $u(\xi)$ obtained by the numerical integration of Eq. \( (3.20) \), as well as the first correction described below, are displayed in Fig. 1.

We have appended the subscript 0 to indicate that this is the solution for the ion sphere model. Placing this solution in the new version \( (3.19) \) of the action gives

$$
-S_0 [i\phi_{cl}] = \frac{3\bar{Z}_p}{10} (3g\bar{Z}_p)^{2/3} - \bar{Z}_p.
$$

The final $-\bar{Z}_p$ that appears here comes from the $\exp \left\{ -\frac{\bar{Z}_p g}{\xi} u(\xi) \right\} - 1$ term in the action \( (3.19) \) along with the integral constraint \( (3.21) \). This additional $-\bar{Z}_p$ simply adds a constant to the chemical potential. Since a constant has no dependence on the thermodynamic parameters, this addition has no effect on the equation of state, the internal energy density, or any other measurable thermodynamic quantity. Moreover, the contributions of such constants clearly cancels in the ratio \( (1.14) \) that yields the background plasma correction to the nuclear reaction rate.
C. Ion Sphere Model Corrected

To find the leading correction to the ion sphere model result, we first cast the exact equations in a different form. We start by writing the full solution \( u(\xi) \) as

\[
u(\xi) = u_0(\xi) + \frac{\xi_0}{Z_p g} v(\xi), \tag{3.27}\]

where \( u_0(\xi) \) is the solution to the ion sphere model. The exact differential equation now reads

\[
\frac{d^2 v(\xi)}{d\xi^2} = \frac{\xi}{\xi_0} \left[ e^{-Z_p g u_0(\xi)/\xi} \exp \left\{ -\frac{\xi_0}{\xi} v(\xi) \right\} - \theta(\xi - \xi_0) \right]. \tag{3.28}\]

Since \( u_0(0) = 1 \) is fixed (reflecting the presence of the large, ‘impurity’ point charge \( Z_p e \)), and since the solution must vanish at infinity, the proper solution to the non-linear differential equation is defined by the boundary conditions

\[
v(0) = 0, \quad \xi \to \infty: \quad v(\xi) \to 0. \tag{3.29}\]

On substituting the decomposition into the action, the cross term may be integrated by parts with no end-point contributions in virtue of the boundary conditions on \( v(\xi) \). We take advantage of this to move the derivative of \( v(\xi) \) over to act upon \( u_0(\xi) \) so that we now have \( d^2 u_0(\xi)/d\xi^2 \). Using Eq. (3.24) for this second derivative and identifying the ion sphere part then gives

\[
S_{\text{sub}}[i\phi_{\text{cl}}] = S_0[i\phi_{\text{cl}}] - \frac{\xi_0}{g} \int_{\xi_0}^{\infty} d\xi \xi v(\xi)
- \frac{\xi_0^2}{2g} \int_{0}^{\infty} d\xi \left( \frac{d v(\xi)}{d\xi} \right)^2. \tag{3.30}\]

Thus far we have made no approximations. To obtain the leading correction to the ion sphere result, we note, as we have remarked before, that the factor \( \exp \left\{ -\frac{Z_p g}{\xi} u_0(\xi) \right\} \) is very small for \( \xi < \xi_0 \), and so it may be evaluated by expanding \( u_0(\xi) \) about \( \xi = \xi_0 \). Using the result, we find that the leading terms yield

\[
\exp \left\{ -\frac{Z_p g}{\xi} u_0(\xi) \right\} \simeq \exp \left\{ -\frac{1}{2} \frac{(\xi_0 - \xi)^2}{(\xi_0 - \xi)} \right\}. \tag{3.31}\]
This approximation is valid for all $\xi$ because when $\xi$ is somewhat smaller than $\xi_0$ and our expansion near the end point breaks down, the argument in the exponent is so large that the exponential function essentially vanishes. Indeed, since we consider the limit in which $\xi_0$ is taken to be very large and the Gaussian contribution is very narrow on the scale set by $\xi_0$, we may approximate
\[
\exp \left\{ -\frac{\bar{Z}_p g}{\xi} u_0(\xi) \right\} \simeq \sqrt{\frac{\pi}{2}} \delta (\xi - \xi_0) + \theta (\xi - \xi_0) .
\]
(3.32)

Here the delta function accounts for the little piece of area that the Gaussian provides near the ion sphere radius since
\[
\int_{0}^{\infty} dx e^{-x^2/2} = \sqrt{\frac{\pi}{2}} .
\]
(3.33)

With this approximation, an approximation that gives the leading correction for the large $\bar{Z}_p g$ limit in which we work, Eq. (3.28) becomes
\[
- \frac{d^2 v_1(\xi)}{d\xi^2} = \sqrt{\frac{\pi}{2}} e^{-v_1(\xi_0)} \delta (\xi - \xi_0) + \theta (\xi - \xi_0) \frac{\xi}{\xi_0} \left[ \exp \left\{ -\frac{\xi_0}{\xi} v_1(\xi) \right\} - 1 \right] .
\]
(3.34)

It is easy to see that the first correction $v_1(\xi)$ does not alter the integral constraint (3.21). Placing the decomposition (3.27) in the constraint (3.21) and using the leading-order form (3.32) together with $v(\xi)$ replaced by $v_1(\xi)$ can be used to express the putative change in the constraint (3.21) in the form
\[
\Delta \bar{Z}_p = -\frac{\xi_0}{g} \int_{0}^{\infty} d\xi \xi \left\{ \sqrt{\frac{\pi}{2}} e^{-v_1(\xi_0)} \delta (\xi - \xi_0) + \theta (\xi - \xi_0) \frac{\xi}{\xi_0} \left[ \exp \left\{ -\frac{\xi_0}{\xi} v_1(\xi) \right\} - 1 \right] \right\} .
\]
(3.35)

But Eq. (3.34) and partial integration together with the boundary conditions (3.29) now show that
\[
\Delta \bar{Z}_p = \frac{\xi_0}{g} \int_{0}^{\infty} d\xi \xi \frac{d^2 v_1(\xi)}{d\xi^2} = 0 .
\]
(3.36)

The $\delta(\xi - \xi_0)$ in Eq. (3.34) requires that
\[
\left. \frac{d v_1(\xi)}{d\xi} \right|_{\xi=\xi_0+0} - \left. \frac{d v_1(\xi)}{d\xi} \right|_{\xi=\xi_0-0} = -\sqrt{\frac{\pi}{2}} e^{-v_1(\xi_0)} ,
\]
(3.37)
\[ v_1(\xi_0 + 0) - v_1(\xi_0 - 0) = 0. \] (3.38)

Since
\[ \xi < \xi_0 : \quad \frac{d^2 v_1(\xi)}{d\xi^2} = 0, \] (3.39)
and since \( v(0) = 0 \), we have
\[ \xi < \xi_0 : \quad v_1(\xi) = c_1 \xi, \] (3.40)
where \( c_1 \) is a constant that is yet to be determined. For large \( \xi \), \( v_1(\xi) \) is small and thus obeys the linearized version of Eq. (3.34),
\[ \xi \gg \xi_0 : \quad v_1(\xi) \sim e^{-\xi}. \] (3.41)

Since this damps rapidly on the scale set by \( \xi_0 = (3\bar{z}_0^g)^{1/3} \gg 1 \), the leading correction \( v_1(\xi) \) that we seek is given by the solution to
\[ \xi > \xi_0 : \quad \frac{d^2 v_1(\xi)}{d\xi^2} = 1 - e^{-v_1(\xi)}, \] (3.43)
which is the previous differential equation (3.34) in this region, but with the explicit factors of \( \xi/\xi_0 \) and \( \xi_0/\xi \) replaced by 1. This new approximate second-order, non-linear differential equation is akin to a one-dimensional equation of motion of a particle in a potential with \( \xi \) playing the role of time, and \( v_1(\xi) \) playing the role of position. Thus there is an "energy constant of the motion". Namely, if we multiply Eq. (3.43) by \( dv_1/d\xi \), we obtain a total derivative with respect to \( \xi \) whose integral gives
\[ \frac{1}{2} \left( \frac{dv_1(\xi)}{d\xi} \right)^2 - v_1(\xi) - e^{-v_1(\xi)} = -1, \] (3.44)
where the constant \(-1\) that appears on the right-hand side follows from the limiting form as \( \xi \to \infty \). It is easy to show that
\[ e^{-v} + v - 1 \geq 0. \] (3.45)

Since asymptotically \( v_1(\xi) \) decreases when \( \xi \) increases, we must choose the root
\[ \frac{dv_1(\xi)}{d\xi} = -\sqrt{2 \left[ e^{-v_1(\xi)} + v_1(\xi) - 1 \right]} . \] (3.46)
The different functional forms for $v_1(\xi)$ in the two regions $\xi < \xi_0$ and $\xi > \xi_0$ are joined by the continuity constraint (3.38), which we write simply as

$$c_1 \xi_0 = v_1(\xi_0),$$

(3.47)

together with the slope jump (3.37) which, using Eq. (3.46), now requires that

$$\sqrt{2} \left[ e^{-v_1(\xi_0)} + v_1(\xi_0) - 1 \right] = \sqrt{\pi} \frac{e^{-v_1(\xi_0)} - v_1(\xi_0)}{\xi_0}. \quad (3.48)$$

Since we require that $\xi_0 \gg 1$, the second term on the right-hand side of this constraint may be neglected, which results in a transcendental equation defining $v_1(\xi_0)$, whose solution is

$$v_1(\xi_0) = 0.6967 \cdots . \quad (3.49)$$

We are now in a position to evaluate the leading contribution to the action (3.30). Since $v_1(\xi)$ damps rapidly on the scale set by $\xi_0$, in computing the leading term we can set $\xi = \xi_0$ in the integral that is linear in $v_1(\xi)$. The leading correction is given by

$$S_{\text{reg}}[i\phi_{\text{cl}}] \simeq S_0[i\phi_{\text{cl}}] + S_1, \quad (3.50)$$

in which

$$S_1 = -\frac{\xi_0^2}{g} C, \quad (3.51)$$

where

$$C = \int_{\xi_0}^{\infty} d\xi \left\{ v_1(\xi) + \frac{1}{2} \left( \frac{dv_1(\xi)}{d\xi} \right)^2 \right\}. \quad (3.52)$$

Here we have omitted the portion

$$\int_{0}^{\xi_0} d\xi \frac{1}{2} \left( \frac{dv_1(\xi)}{d\xi} \right)^2 = \int_{0}^{\xi_0} d\xi \frac{1}{2} \left( \frac{v_1(\xi_0)}{\xi_0} \right)^2 = \frac{1}{2} \frac{v_1^2(\xi_0)}{\xi_0} \quad (3.53)$$

because it is parametrically smaller — it is of relative order $1/\xi_0$ to the leading terms that we retain. We change variables from $\xi$ to $v_1$ via

$$d\xi = \left( \frac{dv_1}{d\xi} \right)^{-1} d\xi, \quad (3.54)$$

and use the result (3.46) for the derivative. Hence

$$C = \int_{0}^{v_1(\xi_0)} \frac{v_1 dv_1}{\sqrt{2} [e^{-v_1} + v_1 - 1]} + \frac{1}{2} \int_{0}^{v_1(\xi_0)} dv_1 \sqrt{2} [e^{-v_1} + v_1 - 1] \quad (3.55)$$
FIG. 2: Ratios of $S[i\phi_{cl}] - \bar{Z}_p$ for the ion sphere model result \ref{eq:3.26} [short-dashed line] and the corrected ion sphere model \ref{eq:3.57} [long-dashed line] to corresponding difference with the action \ref{eq:3.19} for the exact numerical solution $u(\xi)$ as functions of $g\bar{Z}_p$.

is a pure number,

$$C = 0.8499 \cdots.$$ \hfill (3.56)

In summary, recalling that $\xi_0 = (3g\bar{Z}_p)^{1/3}$, we now find that

$$- [S_0 + S_1] + \bar{Z}_p = \frac{3\bar{Z}_p}{10} (3g\bar{Z}_p)^{2/3} \left\{ 1 + \frac{10C}{3g\bar{Z}_p} \right\},$$ \hfill (3.57)

with the leading correction to the ion sphere model exhibited as being of relative order $1/(g\bar{Z}_p)$. Fig. 2 displays the exact numerical evaluation of the action compared with the ion sphere approximation [the leading term in Eq. \ref{eq:3.57}] and the corrected ion sphere model [the entire Eq. \ref{eq:3.57}].

D. One Loop

The one-loop correction for the background plasma with no “impurity” ions present is given by \[8\]

$$\det^{-1/2} [-\nabla^2 + \kappa^2] = \exp \left\{ \int (d^3r) \frac{\kappa^3}{12\pi} \right\}.$$ \hfill (3.58)

Since we assume that the charge $Z_p$ of the “impurity” ions is so large that not only $Z_p \gg 1$, but also $\bar{Z}_pg \gg 1$ as well, $\kappa r_0 \gg 1$, and the ion sphere radius $r_0$ is large in comparison to the characteristic distance scale for spatial variation in the background plasma, the Debye length $\kappa^{-1}$. In this case, the term

$$\kappa^2 \exp \{-\beta z e \phi(r)\}$$ \hfill (3.59)
in the one-loop determinant that enters into the background plasma correction to the “impurity” number,

$$\text{Det}^{-1/2} \left[ -\nabla^2 + \kappa^2 e^{-\beta z e \phi_{cl}} \right]$$  \hspace{1cm} (3.60)

can be treated as being very slowly varying — essentially a constant — except when it appears in a final volume integral. We conclude that in this case of very strong coupling,

$$\frac{\text{Det}^{1/2} \left[ -\nabla^2 + \kappa^2 \right]}{\text{Det}^{1/2} \left[ -\nabla^2 + \kappa^2 e^{-\beta z e \phi_{cl}} \right]}$$

$$= \exp \left\{ -\frac{\kappa^3}{12\pi} \int (d^3r) \left[ 1 - \exp \left\{ -\frac{3}{2} \beta z e \phi(r) \right\} \right] \right\}$$

$$= \exp \left\{ -\frac{\kappa^3}{12\pi} \frac{4\pi}{3} r_0^3 \right\} = \exp \left\{ -\frac{1}{3} g \bar{Z}_p \right\} ,$$ \hspace{1cm} (3.61)

where in the second equality we have used the ion sphere model that gives the leading term for large $\bar{Z}_p$.

This result is physically obvious. The impurity ion of very high $\bar{Z}_p$ carves out a hole of radius $r_0$ in the original, background plasma, a hole that is a vacuum as far as the original ions are concerned. The original, background plasma is unchanged outside this hole. This ion sphere picture gives the leading terms for very large impurity charge $\bar{Z}_p$. The corrections that smooth out the sharp boundaries in this picture only produce higher-order terms. The original, background plasma had a vanishing electrostatic potential everywhere, and the potential in the ion sphere picture now vanishes outside the sphere of radius $r_0$. Thus the grand potential of the background plasma is now reduced by the amount that was originally contained within the sphere of radius $r_0$, and this is exactly what is stated to one-loop order in Eq. (3.61).

This argument carries on to the higher loop terms as well, but we shall now also sketch the application of the previous formal manipulations to them as well.

**E. Higher Loops**

As shown in detail in the paper of Brown and Yaffe [2], $n$-loop terms in the expansion of the background plasma partition function with no impurities present involve a factor of $\kappa^n$ which combines with other charge and temperature factors to give dimensionless terms of the form

$$g^{n-1} \int (d^3r) \kappa^3.$$  \hspace{1cm} (3.62)
With the very high \( Z_p \) impurity ions present, each factor of \( \kappa \) is accompanied by 
\[
\exp\{-\frac{1}{2} \beta e \phi_{\text{cl}}(r)\}
\]
whose spatial variation can be neglected except in the final, overall volume integral. Thus, in the strong coupling limit of the type that we have set, we have the order estimate
\[
 n - \text{loop} : \\
g^{n-1} \kappa^3 \int (d^3 r) \left[ 1 - \exp\left\{ -\frac{n + 2}{2} \beta z e \phi_{\text{cl}}(r) \right\} \right] \\
\sim g^{n-1} \kappa^3 r^3 \sim \bar{g}^n Z_p. \tag{3.63}
\]

Again, since we assume that \( g \) is sufficiently small so that although \( gZ_p \gg 1, g^2 Z_p \ll 1 \), all the higher loop terms may be neglected.

In this discussion, we have glossed over the powers of \( \ln g \) that enter into the higher-order terms as well as the quantum corrections that can occur in higher orders. They vanish in our strong coupling limit.

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APPENDIX: RATE RELATED TO PREVIOUS WORK

We write the result (1.14) in the form used by Brown, Dooling, and Preston [4] (BDP) which is not the notation of DeWitt, Graboske, and Cooper [3] (DGC). In the grand canonical methods employed by BDP, the temperature and chemical potentials are the basic, fundamental parameters. Thus, in this grand canonical description, the effect of the background plasma on nuclear reaction rates appears in terms of number changes with the chemical potentials held fixed. On the other hand, in the canonical ensemble description employed by DGC, the temperature and particle numbers are the basic, fundamental parameters.

To connect the two approaches, for the relevant case in which “impurity” ions \( p \) are dilutely mixed in a background plasma, we first note the general structure in the grand canonical method. Since the impurities are very dilute, the effect of the background plasma on their number is entirely contained in the first term of the fugacity expansion, the linear...
term in \( z_p = \exp\{\beta \mu_p\} \). In the free-particle limit where there is no coupling of the impurities to the background plasma, the impurity number density – chemical potential connection reads

\[
n_p^{(0)} = g_{sp} \lambda_p^{-3} e^{\beta \mu_p},
\]

where \( g_{sp} \) and \( \lambda_p \) are the impurities’ spin weight and thermal wavelength, respectively. Thus the effect of the background plasma appears as

\[
n_p = n_p^{(0)} e^{\Delta_p} = g_{sp} \lambda_p^{-3} e^{\beta \mu_p} e^{\Delta_p},
\]

where we have chosen to write the plasma correction in terms of an exponential. The only feature of the correction \( \Delta_p \) that we need note is that it is independent of the impurity fugacity \( z_p \) since we are working in the \( z_p \to 0 \) limit. In summary, the correction in the grand canonical description appears as

\[
\frac{n_p}{n_p^{(0)}} = e^{\Delta_p},
\]

with the total number \( N_P = n_p V \), where \( V \) is the volume of the system.

The grand canonical partition function \( Z \) for the complete system including the various impurity ions defines the thermodynamic potential \( \Omega(\beta, \mu) \) via

\[
Z = e^{-\beta \Omega},
\]

and the particle number \( N_a \) of species \( a \) with chemical potential \( \mu_a \) is given by

\[
N_a = -\frac{\partial \Omega}{\partial \mu_a}.
\]

Hence, since generically \( \partial N^{(0)}/\partial \mu = \beta N^{(0)} \), this can be integrated to produce

\[
\Omega = \Omega_B - \frac{1}{\beta} \sum_p N_p^{(0)} e^{\Delta_p},
\]

where \( \Omega_B \) is the thermodynamic potential of the background plasma in the absence of the extra impurity ions and where, as we have just shown,

\[
N_p^{(0)} = N_p \exp\{-\Delta_p\}.
\]

The canonical partition function \( Z_N \) defines the Helmholtz free energy \( F(\beta, N) \) via

\[
Z_N = e^{-\beta F},
\]

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with the connection
\[ F = \Omega + \sum a \mu_a N_a. \] (A.9)

Since
\[ \beta \mu_p = \ln \left( n_p^{(0)} \lambda_p^3 g_{sp}^{-1} \right), \] (A.10)

the Helmholtz free energy for a free gas of impurities is thus given by
\[ \beta F_p^{(0)}(\beta, N_p^{(0)}) = N_p^{(0)} \left[ \ln \left( n_p^{(0)} \lambda_p^3 g_{sp}^{-1} \right) - 1 \right]. \] (A.11)

The additional ionic impurities change the background plasma free energy from
\[ F_B = \Omega_B + \sum_{a \neq p} \mu_a N_a, \] (A.12)

where the sum runs over all the particles in the plasma except for the impurity ions, to
\[ F = F_B + \sum_p F_p^{(0)}(\beta, N_p) + \sum_p \Delta F_p. \] (A.13)

Using Eq’s. (A.12), (A.9), and (A.6) produces
\[ \beta \Delta F_p = \beta \mu_p N_p - N_p^{(0)} e^{\Delta_p} - \beta F_p^{(0)}(\beta, N_p), \] (A.14)

and, since \( \mu_p \) is fixed in terms of the free gas number densities \( n_p^{(0)} = n_p \exp\{-\Delta_p\} \), we find that
\[ \beta \Delta F_p = -N_p \Delta_p. \] (A.15)

Thus, in the canonical ensemble approach employed by DGC [3], the previous number ratio is expressed in terms of a Helmholtz free energy change,
\[ \frac{n_p}{n_p^{(0)}} = \exp \left\{ -\beta \frac{\Delta F_p}{N_p} \right\}. \] (A.16)

These authors sometimes write this in terms of a ‘chemical potential’. However, within the grand canonical description that we always employ, a chemical potential is an independent variable that is not changed as interactions are altered, and so in the context that we use this nomenclature is not suitable.

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