Integral-equation method for partially ionized plasmas

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(Received 2 May 1983)

A pseudoclassical integral-equation method for obtaining the equation of state, pair-distribution functions, and static structure factors for partially ionized plasmas is presented. The electron-ion charge distribution is separated into a localized, quantum-mechanical part and a delocalized, nearly classical part. The Planck-Larkin method is used to separate the electron distribution. Localized-electron distributions are obtained from solutions of the Schrödinger equation. Distribution functions for ions and free electrons, including weakly bound electrons, are obtained from solutions to the classical hypernetted-chain (HNC) integral equation. Pseudopotentials that have two-body quantum mechanics built in, but which preclude strong bound states, are used as input to the HNC. The results are applied to H and Ar plasmas.

I. INTRODUCTION

The equation of state of partially ionized plasmas has been calculated from an activity expansion of the grand-canonical partition function.[1-5] For multiply ionized plasmas, such that the ions are strongly coupled while the electrons are moderately coupled, further progress has been made by summing all orders of classical ion-ion correlations.[6] The resulting activity expressions have no restriction on ion-ion coupling and the strength of electron-ion coupling determines the range of validity. A shortcoming of the activity-expansion method is that it does not yield pair-distribution functions and partial structure factors which are required in electrical conductivity, line shape, and a number of other applications. In the present work we will use the results of the activity expansion to develop a classical integral-equation method for obtaining distribution functions. This is justified through the use of a weak pseudopotential that precludes strong bound states. In this approach, bound states appear as new composite particles. In so doing we take account of the nearly classical long-range, many-body divergencies and at the same time remove the short-range, few-body divergencies by inclusion of quantum mechanics. Differences arise between the two methods because we will (1) ignore density dependence of the pseudopotentials arising from multiparticle quantum-mechanical corrections, (2) consider only single-electron bound-state excitations, (3) assume that ion cores interact pairwise, and (4) use the hypernetted-chain integral-equation approximation.

Due to the reliance of the present work on the results of previous analysis,[3,4,6] a brief account of that work will be useful here. A more complete summary is given in Ref. 6 (hereafter referred to as I).

The procedure of I starts with the usual procedure of expanding the logarithm of the grand-canonical partition function in powers of the activity, such that each term $z^n b_n$, $n = 2, 3, \ldots$ sequentially turns on two-body interactions, three-body interactions, etc., where the z^n are activities and the b_n are cluster coefficients. The second step is

a formal elimination of the activity through the density constraint, yielding a density expansion whose nth term is $\rho^n B_n$, where the ρ_n are densities and the b_n are virial coefficients. The Lagrange inversion method for obtaining the virial series used by Kahn[7] for one-component systems is most relevant here, since a somewhat similar inversion procedure will be used in subsequent steps. Schematically the first two steps in the procedure expressed in terms of the pressure are steps (1) and (2):

$$V^{-1}\ln\Xi \to \beta P(\{z_i\}, \{b_n\}) \to \beta P(\{\rho_i\}, \{B_n\}) \ ,$$

where the index i ranges over electrons and nuclei. Steps (1) and (2) are appropriate for short-ranged potentials, but not for the Coulomb potential, since each of the b_n and B_n are individually divergent. For Coulomb systems, as is well known, it is necessary to switch on the full N-body problem at the outset while only partially turning on Coulomb coupling. Higher-order Coulomb terms are then switched on in a systematic way to obtain results for a fully coupled N-body system.

Specializing to Coulomb systems, the next step in the procedure of I is step (3):

$$\beta P(\{\rho_i\}, \{B_n\}) \to \beta P(\{\rho_i\}, \{S_n\}) \ ,$$

where the S_n/ρ^n are closely related to virial coefficients for a screened potential which approaches the Debye-Hückel potential when the Debye length is greater than the thermal de Broglie wavelength. The S_n were first derived by Abe[8] for the classical one-component plasma (OCP) and are generally referred to as "Abe nodal functions." The S_n are related to the nonideal free energy according to

$$(F - F_0)/kT = -VS = -V\left[S_R + \sum_n S_n\right] \ , \tag{1}$$

where S is the Mayer S function. In step (2) S is expressable as an infinite sum over virial coefficients for unscreened potentials. In step (3) S is completely resummed graphically and a screened potential is introduced. The leading density term comes from the ring diagrams and yields the Debye-Hückel free-energy term,

$$S_R = \frac{1}{12\pi\lambda_d^3} \,,$$

where

$$\lambda_d = \left[kT \bigg/ \left[4\pi e^2 \sum_i Z_i^2 \rho_i^2 \right] \right]^{1/2}$$

is the Debye length and Z_i is the ionic charge. Explicit expressions for the S_n are given in Ref. (4). The quantum-mechanical generalization of the S_n has been given by DeWitt.[9] They involve a dynamically screened potential and are not readily evaluated. In the limit $\gamma = \lambda/\lambda_D \to 0$, where $\lambda = \hbar/\sqrt{mkT}$ is the thermal de Broglie wavelength, the quantum result is equivalent to replacing the Boltzmann factors for the Debye potential, that appear in the classical theory, with Slater sums.[3]

When $\gamma \neq 0$ the classical Debye-Hückel term S_R is reduced by a factor $f(\gamma)$. The odd powers in the expansion of $f(\gamma)$ come from B_2, B_3, etc., for the Coulomb potential, while the even powers result from many-body quantum sums.[10] The replacement procedure just mentioned picks up the odd-power terms but misses the even-power terms, so that the error in this approach is $\propto S_R\gamma^2$. This is only a few percent at $\gamma = 0.5$.[3] Similar considerations apply to the virial-like terms. The even-power terms in $f(\gamma)$, for example, can be approximately evaluated from a properly chosen pseudopotential.[10]

When a substantial number of composite particles are formed, the density expansion is nonconvergent. The grand-canonical ensemble works with physical clusters and it is the natural ensemble to use in this case.[11] Classically it is now necessary to carry out an Abe-type nodal expansion which involves both irreducible and reducible diagrams. Since real multicomponent plasmas are being considered, quantum mechanics must be included. Due to the demonstrated success of replacing classical Boltzmann factors with Slater sums, that procedure is adopted here. The many-body problem has already been solved in step (3) and there is no need to actually carry out a diagrammatic resummation of $P(\{z_i\}, \{b_n\})$. Instead, this is accomplished by an inversion procedure similar to that developed by Kahn,[7] for the virial series but going in the opposite direction. As a result, the next step in the method of I is step (4):

$$\beta P(\{\rho_i\}, \{S_n(\{\rho_i\})\}) \to \beta P(\{z_i\}, \{\hat{O}_n S_n(\{z_i\})\}) \,,$$

where $\hat{O}_n$ is a differential operator acting on S_n.

The activity expression generated in step (4) involves the S_n which are in the form of screened virial coefficients that are appropriate for a density expansion or an activity expansion for a nonreacting gas.[3] Due to the exponential behavior of bound states when $|\beta E| > 1$ the terms in $\beta P(\{z_i\}, \{\hat{O}_n S_n(\{z_i\})\})$ are not properly ordered in powers of the activity. The fifth step in the procedure then is to properly reorganize the activity expansion into generalized cluster coefficients for the screened Coulomb potential: Step (5) is

$$\beta P(\{z_i\}, \{O_n S_n(\{z_i\})\}) \to \beta P(\{z_i\}), \{C_n\}) \,,$$

where the C_n are generalized cluster coefficients. For example,

$$C_3 = S_3 + \frac{1}{2!} \sum_i z_i \left[\frac{\partial S_2}{\partial z_i} \right]^2 \,, \qquad (2)$$

which is easily shown to have the property $C_3 \to z^3 b_3$ for ordinary potentials, such that[4] $S_3 \to -\rho^3 B_3/2$ and $S_2 \to -\rho^2 B_2$.

The advantage of expressing βP in terms of the C_n is that they can be factored into terms that involve n-particle bound states, $(n-1)$-particle bound states, etc.,[11] which enter the activity expansion effectively as powers of $z, z^2, \ldots, z^n$. The sixth step in the method of I is to factor out strong bound states as new components and to renormalize βP such that it involves an augmented set of activities $\{z_{i'}\}$, which now includes the original set plus additional members corresponding to composite particles: Step (6) is

$$\beta P(\{z_i\}, \{C_n\}) \to \beta P(\{z_{i'}\}, \{C_{n'}\}) \,,$$

where the $C_{n'}$ are an augmented set of cluster coefficients corresponding to the $\{z_{i'}\}$. The $C_{n'}$ do not involve strong bound states since they have been used to define the augmented set of activities, $\{z_{i'}\}$. They include only continuum states and weakly bound states.

In the present work due to its relative simplicity, particularly with regard to obtaining distribution functions, we wish to develop a HNC integral-equation approximation to the results of I. In some respects the HNC procedure will have a greater range of validity than I. For potentials that do not have a $1/r$ singularity at $r = 0$, e.g., a system of charged hard spheres,[12] we could simply use the HNC approximation on step (2). Due to the presence of strong electron-ion interactions at small r, this is not possible for real plasmas. However, since the $C_{n'}$, exclude strong bound states, they can be calculated from weak pseudopotentials which approach a constant as $r \to 0$, but are proportional to $1/r$ when $r > \lambda$. All that needs to be done to apply the HNC procedure is to derive the renormalized, but unscreened, density expansion $\beta P(\{\rho_{i'}\}, \{B_{n'}\})$ consistent with $\beta P(\{z_{i'}\}, \{C_{n'}\})$. This is accomplished by working backward from step (6), skipping step (5), since we wish to keep strong bound states factored into new components. Step (7) is, therefore,

$$P(\{z_{i'}\}, \{C_{n'}\}) \to P(\{z_{i'}\}, \{\hat{O}_{n'} S_{n'}(\{z_{i'}\})\}) \,.$$

Step (8) corresponds to going from step (4) to step (3) and step (9) corresponds to going from step (3) to step (2): Step (8) can be written as

$$\beta P(\{z_{i'}\}, \{\hat{O}_{n'} S_{n'}(\{z_{i'}\})\}) \to \beta P(\{\rho_{i'}\}, \{S_{n'}(\{\rho_{i'}\})\}) \,,$$

step (9) as

$$\beta P(\{\rho_{i'}\}, \{S_{n'}(\{\rho_{i'}\})\}) \to \beta P(\{\rho_{i'}\}, \{B_{n'}\}) \,.$$

Now, since $\beta P(\{\rho_{i'}\}, \{B_{n'}\})$ involves weak, unscreened pseudopotentials, it can be immediately calculated in the HNC approximation, which is much easier than the Abe procedure given by step (8). A formal method for going

from step (2) to step (9) has been given by Vorob'ev and Gleizer.[13] Apparently only very limited calculations have been carried out with that method.

The justification of the calculations to be carried out in the present work was just described. Additional details will be provided when appropriate. Section II describes how the weak pseudopotentials are constructed. Section III describes the multicomponent HNC method and the equations used to obtain the equation of state. Section IV gives calculational results for hydrogen and argon plasmas.

II. PLASMA PSEUDOPOTENTIALS

The concept of using the Slater sum to obtain a pseudopotential that has quantum-mechanics built in appears to have started with Morita.[14] Kelb[15] and Ebeling[16] have derived analytic results for hydrogenic potentials. Klimontovich and Kraeft[17] have carried out similar work for screened hydrogenic potentials. Barker[18] has given an exact evaluation of the two-particle Slater sum for hydrogen. Dunn and Broyles[10] and Pokrant et al.[20] include N-particle density dependence in the pseudopotentials.

In the present work we will apply a method similar to that used by Barker[18] for hydrogen. The effective potentials given in Ref. 21, which represent the interaction between an electron and a composite particle, will be used. They have the form (in rydbergs)

$$rV_{ei}(r) = -2 \left[(Z-N) + \sum_{n=1}^{n^*} N_n e^{-\alpha_n r} \right] , \tag{3}$$

where N is the number of bound electrons in the composite particle, N_n the number of electrons in the shell having principle quantum number n, n^* is the principal quantum number of the valence shell, and the α_n are screening parameters. The α_n were obtained by iterating on the Dirac equation to obtain $Z-N$ dependent fits to experimental isoelectronic ground-state energy levels. The resulting analytic potentials are very similar to Hartree-Fock self-consistent-field potentials.

Following Barker the effective potentials of Eq. (1) are converted to pseudopotentials according to

$$\beta u_{ei}(r,\beta) = -\ln W_{ei} , \tag{4}$$

where W_{ei} is the two-particle Slater sum given by

$$W_{ei} = W_{ei}^b + W_{ei}^c , \tag{5}$$

$$W_{ei}^b = \left[\frac{2\pi\beta\hbar^2}{\mu_{ei}} \right]^{3/2} \sum_{n=n'}^{\infty} \sum_{l=l'}^{\infty} (2l+1) \Psi_{nl}^*(r) e^{-\beta E_{nl}} \Psi_{nl}(r) , \tag{6}$$

$$W_{ei}^c = \left[\frac{2\pi\beta\hbar^2}{\mu_{ei}} \right]^{3/2} \left[\sum_l (2l+1) \int_0^{\infty} \Psi_l^*(r,p) e^{-\beta p^2/\mu_{ei}} \right.$$
$$\left. \times \Psi_l(r,p) dp \right] , \tag{7}$$

where μ_{ei} is the reduced mass, the E_{nl} are the energy levels for quantum state (n,l), p is the relative momentum, and

(n',l') are the ground-state quantum numbers. The sum in Eq. (6) starts at (n',l'), since by definition core states are already occupied and no additional particles can become bound in these configurations. When $r > \lambdabar_{ei} = \hbar/\sqrt{2\mu_{ei}kT}$, $u_{ei} \rightarrow V_{ei}$. For $r \rightarrow 0$, $u_{ei} \rightarrow$ const, whereas $V_{ei} \rightarrow \infty$. In the present work we further decrease the u_{ei} interaction for small r by excluding highly occupied bound states from the definition of βu_{ei}. How this is done is now described.

In principle, it would seem that it should be possible to insert the pseudopotentials for point charges, given by Eq. (5), into the coupled HNC equation and allow composite particles to form out of the pseudopotential for pure Coulomb interactions. However, the calculation of the energy levels of two-electron composites requires a precise quantum treatment for the second electron, whereas the current method only treats this interaction as a classical interaction between particles that interact through the two-particle pseudopotential. Aside from inadequate physics this calculation cannot be pursued to low temperature since g_{ei}, the electron-ion pair distribution function, becomes strongly peaked and the iterative procedure required to solve the coupled HNC equations become unstable. The situation for both of these problems can be improved by treating composite particles as new components. In this approach the part of g_{ei} associated with bound electrons is separated out and defines the composite particle. As a result, the g_{ei} that is calculated in the HNC solution does not include occupation of strong bound states (i.e., states having $|E| > kT$). An additional reason for making this separation is that electrical conductivity calculations require partial structure factors for unbound and weakly bound electrons. It remains to produce a definite description of how the Slater sum is broken into a part describing localized electrons (composite particles) and a part describing the interaction between delocalized electrons and ions. An important question to answer is this; "what are the composite particle energy levels?" The results of Refs. 2–4, 6, and 10 provide guidance.

In I a diagrammatic analysis was used to replace the bare Coulomb potential with an exponentially screened Coulomb interaction. The resulting electron-nucleus screened energy levels, appearing in the $C_{\underline{n}}$ of step (5), were expanded in a perturbation series of the form

$$E_{nl}(\lambda_d) = E_{nl}^0 + \frac{Ze^2}{\lambda_D} + \frac{A_{nl}e^4}{\lambda_D^2} + \cdots , \tag{8}$$

where the E_{nl}^0 are isolated ion energy levels, Z is the nuclear charge, the A_{nl} are state-dependent constants and λ_D is a screening length for an exponentially screened Coulomb potential given by

$$\lambda_D = \{kT / [4\pi e^2 (z_e + Z^2 z_\alpha)]\}^{1/2} . \tag{9}$$

z_e and z_α are electron and nucleus activities, respectively, defined by

$$z_i = (2s_i+1)\lambda_i^{-3} e^{\mu_i/kT} \tag{10}$$

and

$$\lambda_i = (2\pi\hbar^2/m_i kT)^{1/2} . \tag{11}$$

One-electron composite particle activities, obtained by decomposition of C_2 into effective one-body and two-body components, were then defined as the product of the electron and nucleus activities weighted by modified Boltzmann factors according to

$$z_{ea}^{nl} = 2^{5/2}(2l+1)\hbar_{ea}^3(e^{-\beta E_{nl}} - 1 + \beta E_{nl})z_e z_\alpha . \tag{12}$$

The subtraction of the two leading terms of the Boltzmann factor results from analytic compensation with scattering states. The corresponding sum over all bound states is referred to as the Planck-Larkin partition function.[22]

The first-order shift in the Coulomb energy levels given by Eq. (8) is the same for all states and in Ref. (4) Eq. (12) was rewritten in the form

$$z_{ea}^{nl} = e^{-Ze^2/kT\lambda_D} z_{ea}^{nl,s} \tag{13}$$

$$= \left[1 - \frac{Ze^2}{kT\lambda_d} + \frac{1}{2}\left[\frac{Ze^2}{kT\lambda_D}\right]^2 - \cdots \right] z_{ea}^{nl,s} , \tag{14}$$

where[23]

$$z_{ea}^{nl,s} = 2^{5/2}(2l+1)\hbar_{ea}^3$$

$$\times [e^{-E_{nl}^s/kT} + e^{Ze^2/kT\lambda_D}(-1 + E_{nl}/kT)]z_e z_\alpha \tag{15}$$

and

$$E_{nl}^s = E_{nl} - Ze^2/\lambda_D . \tag{16}$$

The Taylor-series expansion terms in the brackets of Eq. (14), which are due to electron-ion bound states, are the same order as terms due to electron-electron and ion-ion interactions. After all terms of the same size are collected together it was shown that all the terms in Eq. (14) are redistributed into the terms that insert a composite particle activity in each place that fundamental particle terms appear. The simplest example of this is the replacement of the screening length given, by Eq. (9), by

$$\lambda_D = \left[kT/4\pi e^2(z_e + Z^2 z_\alpha + (Z-1)^2 \sum_{n,l} z_{ea}^{nl,s}\right]^{1/2} .$$

Generalization to include multielectron composites was also carried out in Ref. (4). The resulting activity expansion resembles the fundamental particle expansion with the composite particles entering as additional components. However, since the activities used in that work were screened by the plasma, i.e., involve screened energy levels, composite particle terms appear that have no counterparts in the fundamental particle expansion. As a result, it is not clear how to write down a Helmholtz free-energy expression, treating composites as additional components, that does not mix up (double count) the screening corrections.

The expansion (14) is always valid for screened Coulomb energy levels, but is most useful when the first-order perturbation term in expansion (8) is the dominant correction. When this is the case the wave functions are only slightly modified, due to the second-order perturbation correction, from those for an isolated ion. When $\lambda_D \rightarrow \lambda_c^{nl}$, the critical screening value for state (n,l), then

$E_{nl} \rightarrow 0$ and the expansion (14) becomes artificial. In this case the level E_{nl} is more appropriately treated on the same basis as a continuum state. When $\lambda_D \leq \lambda_c^{1s}$ composites do not form at all and the expansion reverts back to the fundamental particle form. Since $z_\alpha \ll \rho_\alpha$ for strongly coupled systems, the density at which this occurs is somewhat higher than predicted by the disappearance of the $1s$ state in a Debye screened potential, i.e., the screened energy levels that appear in an activity expansion are different than those that appear in the density expansion at the same (ρ, T) point, suggesting that possibly neither are true energy levels of the many-body system. Since the activity series works with physical clusters, it seems that activity-dependent energy levels are more likely to be related to physical observables.

It was shown in I that the screened composite activity expression given in Ref. (4) can be renormalized such that the activities for composite particles involve the isolated ion energy levels. In this case the composite activities enter the activity expression analytically exactly the same as fundamental particles, i.e., the extra terms associated with screened composite particle activities have been absorbed in the renormalization. This result can be immediately inverted to obtain a multicomponent expression for the Helmholtz free energy in which the composite particles enter as new fundamental components. This free energy is thermodynamically related to $\beta P(\{\rho_i,\},\{S_{\underline{n}'}(\{\rho_{i'}\})\})$ appearing in step (8).

In general, each bound state could be treated as a separate component. This is a clear concept for composite states that are highly occupied, but states having binding energy large compared to kT should not need to be treated in a special way. The Planck-Larkin partition function gives an analytic way of separating the bound-state charge densities into a part associated with composites and a part which is treated as being delocalized. This result has already been used in Eq. (12) for screened charge densities. When the first-order perturbation term of Eq. (14) is dominant, use of the isolated ion energy levels in a Planck-Larkin partition function provides a proper way of defining the charge density of composite particles. In this case the interaction between unscreened composite particles in excited states is large at fairly low densities. When the free energy is minimized, as discussed in Sec. III, this repulsion will tend to depopulate excited states. The total pressure arising from particles in these states will nevertheless always exceed that which occurs when they are treated as ideal and having isolated ion energy levels. This is qualitatively similar to treating particles in these states as noninteracting but screened according to, for example, the confined atom model.

A physical interpretation of the results of I is as follows. At high temperature a heavy ion moving through a plasma will polarize the electron distribution such that unbound electrons moving in its vicinity will spend a little extra time passing by. This polarization screens the interaction of the ion with other plasma particles. When $kT < |E_b|$, the binding energy, there is a possibility that electrons will form stable bound states. In this case at large distances the electron-ion interaction will again be screened by the polarized free electrons which are within a
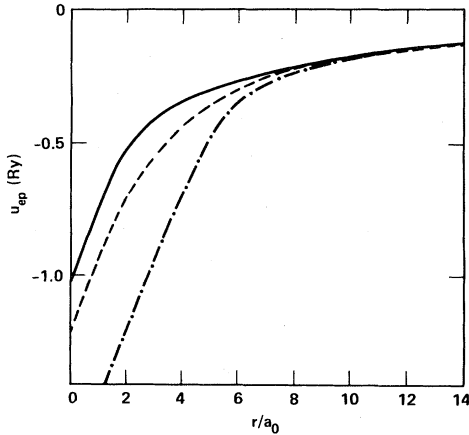
FIG. 1. Hydrogenic electron-ion pseudopotentials for $kT = 12.53$ eV. —·—, Barker potential given by Eq. (4); — — —, Dunn-Broyles potential given by Eq. (21); ———, Planck-Larkin potential given by Eq. (20).

FIG. 2. Pseudopotentials for e-Xe$^+$ interaction at $kT = 2$ eV. — — —, Barker-type pseudopotential with core states excluded; · · · , Planck-Larkin pseudopotential. Effective potential given by Eq. (3).

sphere of radius a_0/Z centered on the ion. After an electron enters a low-lying bound orbit the free electrons that were initially spending a little extra time in the vicinity of the ion move away but, now since the bound state is an extreme form of polarization, the tendency for them to be replaced by other free electrons is diminished. The result is that the binding energies of deep bound states are considerably less shifted than predicted by the static screened potential. The equilibrium distribution of electrons around ions is determined by free-energy minimization. This picture of the plasma is consistent with the results of I and also forms the basis for the present work.

When second-order terms in Eq. (14) become important the results of Ref. (4) suggest that the composite particle wave functions are polarized by the plasma, whereas the expansion derived in I has redistributed these polarization terms into the interaction correction. In the present work a pseuodpotential constructed from two-body unscreened wave functions, but excluding strong bound states, is used in a many-body classical calculation. It is unlikely that this will reproduce short distance quantum corrections equivalent to a multielectron solution to the Schrödinger equation. It should, however, be adequate as long as the low-lying wave functions are not strongly modified. Using the Planck-Larkin partition function as a basis for separating the two-particle Slater sum into a localized part and a delocalized part yields

$$W_{ei} = W_{ei}^B + W_{ei}^I ,$$ (17)

where W_{ei}^B is the localized bound-state part given by

$$W_{ei}^B = \left[\frac{2\pi\beta\hbar^2}{\mu_{ei}} \right]^{3/2} \sum_{n,l} (2l+1)\Psi_{nl}^*(r)$$

$$\times (e^{-\beta E_{nl}} - 1 + \beta E_{nl})\Psi_{nl}(r) ,$$ (18)
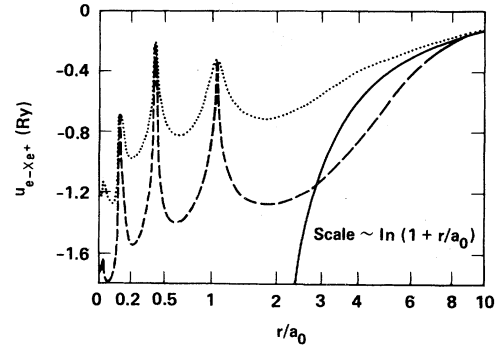
and W_{ei}^I is the delocalized part given by

$$W_{ei}^I = \left[\frac{2\pi\beta\hbar^2}{\mu_{ei}} \right]^{3/2}$$

$$\times \left[\sum_l (2l+1) \int_0^\infty \Psi_l^*(r,p)e^{-\beta p^2/\mu_{ei}}\Psi_l(r,p)dp \right.$$

$$\left. - \sum_{nl} (2l+1)\Psi_{nl}^*(r)(1-\beta E_{nl})\Psi_{nl}(r) \right] .$$ (19)

Each state that contributes appreciably to W_{ei} is treated as a new component. The charge distribution of high-lying bound states, a part of the charge distribution for low-lying states, and the continuum states are all treated on the same basis. They are used to define an electron-ion pseudopotential that precludes strong bound states according to

$$\beta u_{ei}(r,\beta) = -\ln W_{ei}^I .$$ (20)

Equation (20) will be referred to as the Planck-Larkin pseudopotential.

Figure 1 compares various pseudopotentials for electron-proton interactions having $kT = 12.53$ eV. The Planck-Larkin- and Barker-type pseudopotentials were obtained from numerical solutions of the Schrödinger equation. All the potentials approach $-e^2/r$ for large r. The Dunn and Broyles form is an approximate analytic form obtained from the high-temperature N-particle Slater sum, given by

$$u_{ij} = z_i z_j e^2 (1 - e^{-r/\lambda_{ij}})/r .$$ (21)

Equation (21) includes a high-temperature correction for bound states and thus lies between the Planck-Larkin and Barker potentials.

Figure 2 shows some results for e-Xe$^+$ at 2 eV. The peaks in the potential occur at the nodes of the $5p$ state. Higher states in the Slater sum keep the peaks in the pseudopotential bounded. Pseudopotentials for composite ions would be difficult to fit and consequently they are tabulated at precisely those discrete values of r that will be used to solve the coupled HNC equations. For $r > \lambda_{e\text{-Xe}^+}$ the pseudopotential approaches the input effective potentials given by Eq. (3), so that long-range, many-particle screen-

ing is nearly classical.

Another consideration is electron degeneracy and exchange. To account for this, W_{ee} can be split according to

$$W_{ee} = \tfrac{1}{2}(W_{e \uparrow e \downarrow} + W_{e \uparrow e \uparrow}) , \qquad (22)$$

where $W_{e \uparrow e \downarrow}$ is given by Eq. (5) and

$$W_{e \uparrow e \uparrow} = 2 \left[\frac{2\pi \beta \hbar^2}{\mu_{ee}} \right]^{3/2}$$

$$\times \sum_{l \text{ even}} (2l+1) \int_0^\infty \Psi_l^*(r,p) e^{-\beta p^2/\mu_{ee}} \Psi_l(r,p) dp . \qquad (23)$$

Like-spin and unlike-spin electrons are treated as separate components[19] having interaction potentials given by

$$\beta u_{e \uparrow e \downarrow} = -\ln W_{e \uparrow e \downarrow}, \qquad (24)$$
$$\beta u_{e \uparrow e \uparrow} = -\ln W_{e \uparrow e \uparrow} .$$

When a third electron is also within a de Broglie wavelength of the interacting pair, diffraction corrections between pairs of particles are accounted for but interference scattering between these diffraction patterns is ignored. By studying the N-particle ring diagrams it was shown in Ref. (10) that this makes the pseudopotential more repulsive at small distances. Three-electron and higher exchange terms are also not included. Due to the added complexity of treating the electrons as two separate components we will generally use an averaged potential given by $\beta u_{ee} = -\ln W_{ee}$, which is equivalent to using Eqs. (24) in the range where the two-particle exchange approximation is strictly valid.

III. THE INTEGRAL-EQUATION METHOD

The activity method of I, on which the current tegral-equation method is based, is restricted by several parameters:

(1) the electron-ion plasma parameter

$$\Lambda_{ei} = \beta \xi_i e^2 / \lambda_D < 1 ,$$

where ξ_i is the net charge $Z_i - N_i$;

(2) the diffraction parameter

$$\gamma_{ij} = \lambdabar_{ij} / \lambda_D < 1 ;$$

(3) the degeneracy parameter

$$\theta_e = (\lambda_e / a_e)^3 < 1 ,$$

where λ_e is the electron thermal de Broglie wavelength and $a_e = (3/4\pi\rho_e)^{1/3}$; and

(4) the screening overlap parameter

$$\tau = \bar{r}/\lambda_D < 1 ,$$

where $\bar{r}$ is the mean ionic core radius.

It is also limited such that there is no appreciable overlap of the charge density of electrons on neighboring ions. Since all orders of Coulomb coupling are included in the HNC equation, the present method removes the restriction on Λ_{ei}. The pseudopotential given by Eq. (20) approxi-

mates the many-body part of $f(\gamma)$, discussed in Sec. I, thus relaxing the restriction of γ_{ij}. Some relaxation of the restriction on core-core interactions is also obtained, but the other restrictions remain. As a result, the current work will be most useful for multiply ionized high-Z plasmas, such that the ions are strongly coupled while the electrons are only slightly degenerate and moderately coupled. However, most previous theoretical work has been applied to hydrogen and we will make some contact with this work in what follows.

Equation (42) of I gives an activity expression for βP, as a function of the renormalized Mayer S function, for reacting partially ionized Boltzmann plasmas [see step (7) of Sec. I]. Equation (61) in I is a similar result with Fermi statistics used for the electrons. In the present work we incorporate quantum diffraction and exchange corrections into pseudopotentials, which are to be used in classical expressions so that Eq. (42) of I is the correct form to use. As discussed in Sec. I, this was obtained by starting with an expression derived in Refs. 3 and 4, which obtains βP from a differential operator acting on $S(z_e, z_\alpha)$, and carrying out a renormalization to obtain βP from a differential operator acting on $S(z_e, z_\alpha, z_H, \ldots)$, where

$$S(z_e, z_\alpha, z_H, \ldots) = \frac{1}{12\pi\lambda_d^3} + z_e^2 s_{ee} + 2z_e z_\alpha s_{e\alpha}^c$$
$$+ 2z_e z_H s_{eH}^c + z_\alpha^2 s_{\alpha\alpha}$$
$$+ 2z_\alpha z_H s_{\alpha H}^c + z_H^2 s_{HH}^c + \cdots . \qquad (25)$$

In Eq. (25),

$$\lambda_D = \{ kT/4\pi e^2 [z_e + Z^2 z_\alpha + (Z-1)^2 z_H + \cdots] \}^{1/2} , \qquad (26)$$

$$s_{e\alpha}^c = \sqrt{2}\lambdabar_{e\alpha}^3 \left[\frac{1}{\pi} \int_0^\infty \sum_l (2l+1) dp \frac{\partial \delta_l}{\partial p} e^{-p^2/2\mu_{e\alpha}kT} \right.$$
$$\left. + (w_0 - w_1) \right]$$
$$+ 2\pi\lambda_D^2 \left[\frac{\xi_e \xi_\alpha}{kT} \right] - \frac{\pi}{2}\lambda_D \left[\frac{\xi_e \xi_\alpha}{kT} \right]^2 , \qquad (27)$$

where l is the angular momentum, p is the relative momentum, δ_l is the phase shift for the screened Coulomb potential,

$$w_0 = \sum_{n,l} (2l+1) ,$$

$$w_1 = \sum_{n,l} (2l+1) \frac{E_{nl}}{kT} ,$$

and ξ_i is the net change on species i. s_{ee} and s_{pp} are given by equations similar to Eq. (27) except, since there are no bound states $w_0 = w_1 = 0$. The last two terms in (27), corresponding to first- and second-order perturbation theory are subtracted from the scattering state term because they were used in constructing the screened potential. The two leading terms in the high-temperature expansion of the bound-state partition functions are included with the

scattering state contribution since they almost precisely compensate terms appearing in the scattering states.[22,10] The Planck-Larkin part of the two-particle trace has been factored out and used to define the augmented set of activity variables. In the Coulomb limit ($\lambda_D \to \infty$), the weak pseudopotential defined in Sec. II Eq. (19) corresponds pseudopotential defined in Sec. II Eq. (20) corresponds $s_{e\alpha}^c$ approaches the electron-nucleus component of B_2 appearing in step (9). In the present work screening is introduced via the HNC iteration procedure. Similar but slightly more complex considerations apply to s_{eH}^c, $s_{\alpha H}^c$, etc.[10] In complete generality these later contributions correspond to at least three-body interactions. In the present work, as described in Sec. II, we introduce two-body effective potentials to account for these terms. It is also assumed (definitely an approximation) that the interaction potential is not altered by the presence of additional particles.

Since composite activities enter Eq. (42) of I analytically exactly as fundamental particles it can immediately be inverted to obtain the corresponding Helmholtz free energy. Utilizing the connection between $S(\{\rho_{i'}\})$ and $S(\{z_{i'}\})$ derived in Refs. 3 and 4 the result is

$$F = F_e^0 + F_\alpha^0 + \sum_c F_c^0 - VkTS(\{\rho_{i'}\}) , \qquad (28)$$

where

$$F_e^0 = -N_e kT[\ln(g_e \rho_e^{-1} \lambda_e^{-3}) + 1] , \qquad (29)$$

$$F_\alpha^0 = -N_\alpha kT[\ln(g_\alpha \rho_\alpha^{-1} \lambda_\alpha^{-3}) + 1] , \qquad (30)$$

$$F_c^0 = -N_c kT\{\ln[g_c \rho_c^{-1} \lambda_c^{-3}(e^{-\beta E_c} - 1 + \beta E_c)] + 1\} , \qquad (31)$$

S is the interaction part of the Helmholtz free energy given by Eq. (23) of Ref. 4, the subscript α refers to bare nuclei, and the subscript c refers to composite particles. In this form S is explicitly divergence free. For the purpose of defining a set of coupled integral equations, having composites explicitly factored out and treated as new components, we decompose $S(\{\rho_{i'}\})$ into virial coefficients for the bare potentials [see step (9) of Sec. I]. It is now possible to apply the multicomponent hypernetted-chain integral-equation method to treat this many-component, many-body problem. In addition to the approximations implicit in the pseudopotentials, we have now also assumed the bridge diagram contribution to be zero. Numerical simulations have shown this to be a good approximation.[24] The HNC includes all orders of perturbation for both electrons and ions and should be better behaved outside the range of plasma parameters for which the approximations are appropriate. When better pseudopotentials are developed this approach will be useful over a large range of the plasma parameters.

The pair distribution functions in the HNC approximation are given by

$$g_{ij}(r) = \exp[-\beta u_{ij}(r) + h_{ij}(r) - c_{ij}(r)] , \qquad (32)$$

where the u_{ij} are the bare pseudopotentials discussed in Sec. II, the h_{ij} are the total correlation functions, and the c_{ij} are the direct correlation functions. The h_{ij} and c_{ij} are related through the Ornstein-Zernike relations which,

written in k space, for m components, are

$$\tilde{h}_{ij}(k) = \tilde{c}_{ij}(k) + \sum_{v=1}^{m} \rho_v \tilde{h}_{iv}(k) \tilde{c}_{vj}(k) . \qquad (33)$$

It is necessary to iterate to obtain self-consistent solutions to Eqs. (32) and (33). The methods used here are described in Ref. 12.

The excess energy per ion is given by

$$\frac{\beta E^{\text{ex}}}{N} = 2\pi\beta\rho \sum_{i,j} x_i x_j \int_0^\infty \frac{\partial(\beta u_{ij})}{\partial \beta} g_{ij}(r) r^2 dr , \qquad (34)$$

where $\rho = \sum_i \rho_i$ and $x_i = \rho_i/\rho$. The excess pressure is given by

$$\frac{\beta P^{\text{ex}}}{\rho} = -\frac{2}{3}\pi\beta\rho \sum_{i,j} x_i x_j \int_0^\infty g_{ij}(r) \frac{\partial u_{ij}}{\partial r} r^3 dr . \qquad (35)$$

The usual method to obtain the free energy is to integrate over a coupling constant which is equivalent to integrating the following thermodynamic relations from high temperature T' to T at constant composition and volume:

$$F = F(T') - T \int_{T'}^{T} \frac{E(\theta) d\theta}{\theta^2} . \qquad (36)$$

Hansen et al.[25] have derived a result for the Gibbs free energy in the HNC approximation which requires only an integration over the distribution functions. This method is much easier to apply than Eq. (36). In the present case the potential is temperature dependent and it is necessary to verify that the Hansen et al. result is still valid. In this case

$$U(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, \lambda) = \sum_{j=2}^{N} \lambda u(r_{1j}, \lambda) + \sum_{2 \le i < j \le N} u(r_{ij}) \qquad (37)$$

and it follows that

$$\beta\mu_i^{\text{ex}} = \rho \int_0^1 d\lambda \int d\vec{r} \sum_{j=1}^{j'} x_j \beta \frac{\partial u_{ij}(r, \lambda)}{\partial \lambda} h_{ij}(r, \lambda) . \qquad (38)$$

Now the derivation of Hansen et al. follows through without change except it involves $\beta(\partial u_{ij}/\partial \lambda)$ instead of βu_{ij} with the result

$$\beta\mu_i^{\text{ex}} = \sum_{j=1}^{j'} x_j \left[\frac{3}{2} \sum_0^\infty h_{ij}(r)\{h_{ij}(r)[h_{ij}(r) - c_{ij}(r)]r^2 dr \right.$$

$$\left. - \tilde{c}_{ij}^s(0)\} \right] , \qquad (39)$$

where $\tilde{c}_{ij}^s(0)$ is the transform of the direct correlation function with $-\beta \tilde{u}_{ij}(0)$ subtracted off. The total Helmholtz free energy is given by

$$F = F_e^0 + F_\alpha^0 + \sum_{c=1}^{c'} F_c^0 + \sum_{i'} N_{i'} \beta\mu_{i'}^{\text{ex}} + \beta P^{\text{ex}} V/N_0 , \qquad (40)$$

where F_e^0, F_α^0, and F_c^0 are the ideal free energies, the sum on c ranges over all composites, and P^{ex} is given by Eq. (35) with i,j now also ranging over composite particles. The charge densities that were subtracted off appear in F_c^0 as new ideal components. The total energy is obtained from
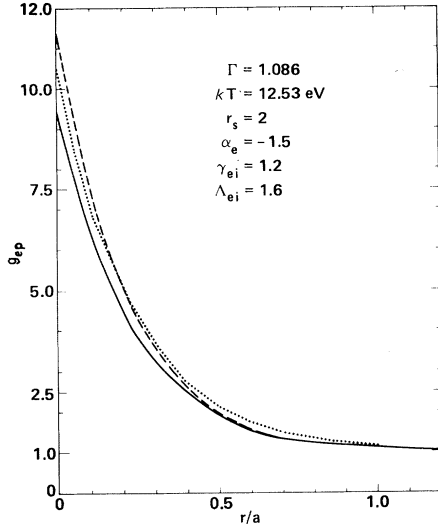
FIG. 3. Comparison g_{ep} of current work with the density-functional method (Ref. 27). — — —, density-functional method; $\cdots$, HNC method for fully ionized plasma reference system using the Barker pseudopotential; ——, HNC method for fully ionized plasma reference system using the Planck-Larkin pseudopotential.

$$E = \frac{\partial(\beta F)}{\partial \beta} = E_{kin} + E^{ex} + E_B \; , \tag{41}$$

where

$$E_{kin} = \frac{3}{2}\left[N_e + N_\alpha + \sum_{c=1}^{c'} N_c\right]kT \; , \tag{42}$$

E^{ex} is given by Eq. (34), and E_B is the energy of bound electrons

$$E_B = \sum_{c=1}^{c'} \frac{N_c E_c(e^{-\beta E_c} - 1)}{(e^{-\beta E_c} - 1 + \beta E_c)} \; . \tag{43}$$

The total pressure is correspondingly given by

$$P = \frac{2E_{kin}}{3V} + P^{ex} \; . \tag{44}$$

IV. RESULTS

A major goal of this work is to obtain the equation of state, pair-distribution functions, and structure factors for multiply ionized dense plasmas. It is desirable to compare the results with experiment and other theoretical calculations. However, most of the experiments[26] have achieved a relatively low-level of ionization and only a few first-principles calculations have been published. Recently Dharma-wardana and Perrot (DWP)[27] applied the density-functional method to nearly fully ionized hydrogen at $r_s = 1$ and 2 for a number of temperatures, where $r_s = a/a_0$, $a = [3(4\pi)^{-1}\sum_i \rho_i]^{1/3}$, and i ranges over all ions. The equation of state of partially ionized argon was studied in I. In the present work calculations for hydro-

gen and argon have been carried out under conditions similar to those studied in these two works.

The DWP hydrogen calculations for $r_s = 2$ and $kT = 12.53$ eV can be treated by both of the approaches considered here: (1) the fully ionized plasma reference system using pseudopotentials given by Eq. (4), and (2) the partially ionized plasma reference system using pseudopotentials given by Eq. (20). In view of the relatively small number of hydrogen atoms that form under these conditions it is most appropriate to work with a fully ionized plasma reference system. In order to work with a partially ionized reference system utilizing the Planck-Larkin pseudopotential, it would be necessary to factor out hydrogen atoms as a new component and carry out a free-energy minimization to obtain the number densities. At low temperature it would, in addition, be necessary to factor out H^-, H_2^+, and H_2 as new components. This requires a number of ion-atom, atom-atom, etc., interaction potentials and will not be undertaken in this work. Figure 3 is a comparison of g_{ep} obtained from the present work with that of DWP. The agreement is good. The Planck-Larkin result for fully ionized hydrogen is also shown. This calculation is incomplete since strong two-body bound states have been completely neglected but it should be a reasonable approximation when these states are not highly occupied. It is included in order to evaluate the importance of strong bound states at this temperature and density, indicated by the difference from the complete calculation. Calculations were also attempted at $r_s = 1$ and $kT = 12.53$ eV. The HNC procedure did not iterate to a convergent solution with the Barker-type pseudopotentials, while the fully ionized Planck-Larkin pseudopotentials gave distribution functions close to those tabulated in Table II of DWP. $r_s = 1$ is too dense to expect the two-body quantum corrections used in this work to be applicable and N-particle corrections similar to those obtained by Pokrant et al.[20] are required.

Figure 4 gives electron-electron pair distribution functions for the same conditions as Fig. 3. Electrons of opposite spin penetrate well inside the Landau length while Fermi repulsion helps prevent significant penetration by electrons of like spin. The total electron-electron distribution function is < 0.5 at $r = 0$ due to Coulomb repulsion. It is believed that the two-body diffraction approximation allows too much clustering of electrons at high density resulting in the HNC convergence problems at $r_s = 1$.

A quantity of considerable interest is the statically screened electron-ion interaction potential. This arises naturally in the density-functional method but is not part of the HNC method being developed here. However, since the pair-distribution functions are obtained, it is a simple matter to calculate the screened interaction between two free particles from Poisson's equation

$$\nabla^2 V_{ei}^s = -4\pi e^2\left[Z_i\delta(r) + \sum_{j(\neq i)} Z_j\rho_j h_{ij}\right] \; . \tag{45}$$

Taking the Fourier transforms of Eq. (45) yields

$$V_{ei}^s = -\frac{4\pi e^2 Z_i}{k^2 \epsilon} \; , \tag{46}$$
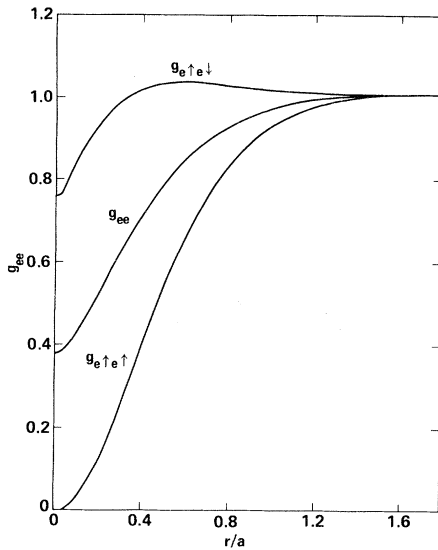
FIG. 4. Electron-electron distribution functions. Like-spin and unlike-spin distributions are indicated. g_{ee} is the average of these two distributions.

FIG. 5. ——, electron-proton static screening function $-rV^s_{ep}(r)$ given by the transform of Eq. (46); —·—, ratio of $V^s_{ep}(r)/V_{DH}$, where V_{DH} is the Debye-Hückel potential; — — —, Debye Hückel screening function that just supports a $1s$ state.

where ϵ is a screening function given by

$$\epsilon^{-1}=S_{ii}+\sum_{j(\neq i)}\frac{Z_j}{Z_i}\left[\frac{\rho_j}{\rho_i}\right]^{1/2}S_{ij} \tag{47}$$

and the S_{ij} are partial structure factors. When the Planck-Larkin pseudopotential is used to obtain S_{ij} the bound electronic charge density should be added to Eq. (45). This should have little effect on ϵ when there is no appreciable core overlap. In this case, to lowest order, the bound-state charge plus the neutralizing part of the nuclear charge acts like a neutral point as far as ϵ is concerned so that $Z_\alpha \rightarrow \xi_\alpha$ in Eq. (47). The transformed screened electron-ion potential for composite particles is given by

$$\widetilde{V}^s_{ei}=-\sum_{n=1}^{n^*}\frac{4\pi e^2 N_n}{k^2+\alpha_n^2}-\frac{4\pi e^2\xi_i}{k^2\epsilon} , \tag{48}$$

where the sum is over Fourier transforms of the short range parts of Eq. (3).

Figure 5 shows the screening function $-rV^s_{ep}(r)$ corresponding to the same conditions as in Figs. 3 and 4. As already discussed, in the current approach this is expected to apply to scattering states and weak bound states but not to strong bound states. The screened potential is stronger than a Debye potential for distances less than $0.7a_0$ but is weaker than a Debye potential for greater distances. For the purpose of comparing with DWP, the Debye potential that will just support a $1s$ state is also shown. It indicates that a potential having the strength of V^s_{ep} is close to being able to support a bound state. This is consistent with the results of DWP who obtain a static screened potential that just supports a $1s$ state.

The present method can readily be applied to multiply ionized plasmas such that the electrons are moderately coupled while the ions are strongly coupled. In this case
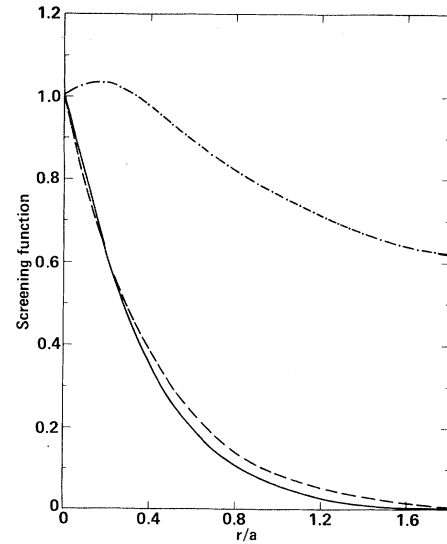
the ion-ion interactions are dominated by the Coulomb tail, so that $V_{ij}=\xi_i\xi_j e^2/r$. The corresponding electron-ion interactions are given by Eq. (4). Since the ion-ion interactions are classical the HNC equation treats this part of the calculation correctly, except for the neglect of the bridge functions. In order to make comparisons with the results of I, calculations have been carried out for Ar. Figure 6 compares the nonideal compressibility factors $\Delta PV/N_0 kT$ of the current work with those of I for $kT\geq 10$ eV and $\rho=1$ g/cm^3. The $\mathscr{P}_n$ functions are a series of approximations to $\beta P(\{z_{i'}\},\{\hat{O}_n\cdot S_n\})$ constructed
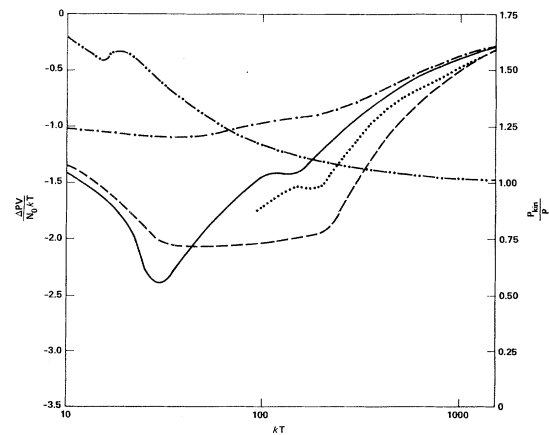

FIG. 6. Nonideal compressibility factors in various approximations for Ar at 10.2 eV and $\rho=1$ g/cm^3. —·—, ——, and $\cdots$ are the $\mathscr{P}_2,\mathscr{P}_3$, and $\mathscr{P}_4$ approximations of I, respectively; — — —, HNC result of present work; —··—, ratio of the kinetic pressure P_{kin} to the total pressure obtained in the $\mathscr{P}_3$ approximation of I (right-hand-side scale).
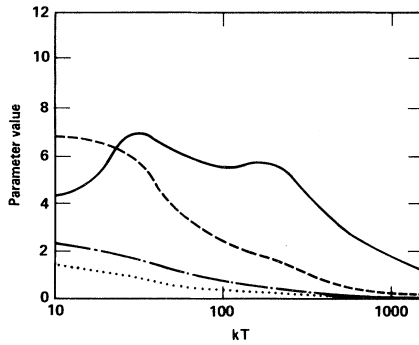
FIG. 7. Various plasma parameters as a function of temperature for the conditions of Fig. 6. ——, ion-ion Γ defined in text; — — —, Λ_{ei} in canonical ensemble defined with $\underline{Z} = \bar{Z}$; —·—, Λ_{ei} in grand-canonical ensemble also with $Z = \bar{Z}$; ···, γ_{ee}.

to converge rapidly when the heavy ions are strongly coupled. The nonideality correction of the current work was calculated from the ionization equilibrium obtained with the $\mathscr{P}_3$ approximation of I. At any given temperature only three ionic charge states are appreciably occupied. In the HNC calculations only these states are considered. This requires a straightforward contraction of the equations given in Sec. III. The $\mathscr{P}_4$ approximation of I is in somewhat better agreement with the current calculations, particularly at high temperature. It appears that inclusion of high $\mathscr{P}_n$ would further improve the agreement. The higher $\mathscr{P}_n$ present difficult numerically problems and were not calculated. This is also the reason results for $\mathscr{P}_4$ were not obtained at low temperature. The disagreement between the equation of state is not as large as indicated by Fig. 6. This is because the ionization equilibrium is affected by the degree of nonideality with the result that the total pressures and energies are in somewhat better agreement than are the partial contributions. It appears that inclusion of higher order $\mathscr{P}_n$ would further improve the agreement. Figure 6 also shows the ratio of P_{kin}/P for the $\mathscr{P}_3$ approximation.

Figure 7 shows various plasma parameters as a function of temperature for the conditions of Fig. 4. The derivation of I only applies when $\Lambda_{ei} \leq 1$ and $\gamma_{ee} \leq 1$ which occur for $kT < 70$ and 25 eV, respectively. Figure 4 shows that the $\mathscr{P}_4$ calculation and the HNC results are in moderate agreement for $kT < 90$ eV. Γ is the ion-ion strong-coupling parameter given by $\Gamma = \bar{Z}^2 e^2/kTa$. It has a maximum value of 7 at $kT = 29$ eV. This is the point of least accuracy for $\mathscr{P}_3$ (see Fig. 1 of I) and accounts for the abrupt minimum at this temperature. Using the $\mathscr{P}_3$ ionization equilibrium as initial input the free energy was minimized according to Eq. (40), at $kT = 10.2$ eV and $\rho = 1$ g/cm^3. The dominant species obtained by the activity-expansion methods were Ar^{4+}, Ar^{3+}, and Ar^{2+} with 57% of the ions being Ar^{3+} and $\bar{Z} = 2.83$. The corresponding HNC free-energy minimization gives $\bar{Z} = 2.90$. Some differences are to be expected since (1) the activity calculation considered multiply excited electronic states whereas the current work was limited to single-electron excitations, (2) only two-particle quantum effects were in-
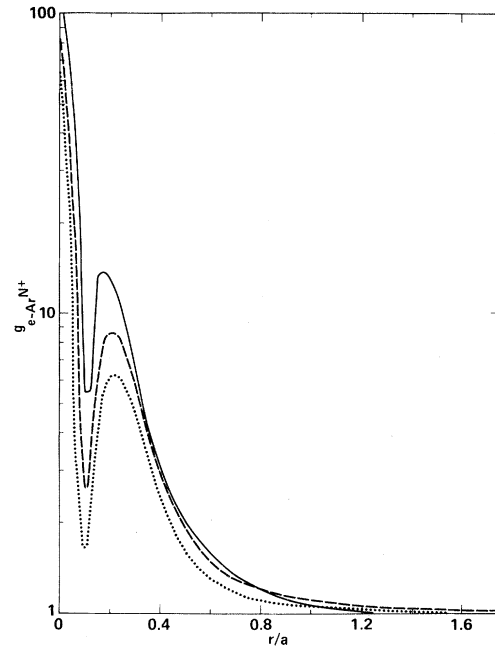

FIG. 8. Electron-ion distribution functions for the conditions of Fig. 6. ···, e-Ar^{2+} distribution; — — —, e-Ar^{3+} distribution; ——, e-Ar^{4+} distribution.

cluded in the pseudopotentials, (3) the HNC approximation does not include the bridge functions, and (4) the classical ion corrections were calculated in an approximate way in I.

Figure 8 is a plot of free-electron—ion distribution functions as a function of r/a for the calculation just described. The minimum around $r = 0.18a = 0.86a_0$ is due to exclusion of electrons from the region of the filled L shell. The three distributions have very similar shapes except $g_{e\text{-Ar}^{3+}}$ crosses $g_{e\text{-Ar}^{4+}}$ around $r = a$ and tails off to unity much slower than $g_{e\text{-Ar}^{4+}}$ or $g_{e\text{-Ar}^{2+}}$. This crossing has a pronounced effect on the small-k behavior of the partial structure factors as shown in Fig. 9. Figure 10 gives the corresponding ion-ion distribution functions for ions of like charge. The behavior of $g_{\text{Ar}^{3+}\text{-Ar}^{3+}}$ is different than for the other two ions. It goes above one for $r > a$ which is apparently due to the long-range tail on $g_{e\text{-Ar}^{3+}}$.

Figure 11 gives g_{ee} for the same conditions as in Figs. 6—10. The HNC calculations were carried out for two different models of free-electron interactions: (1) classical electrons and (2) the pseudopotential given by the averaged version of Eq. (24). The classical electron distribution function has a peak well above unity for r in the vicinity of $0.4a$. This results from a compromise between the long-range attraction of several electrons toward the multiply ionized ions and the mutual repulsion between the same electrons. The electron distribution obtained from the pseudopotential, including the net effect of quantum diffraction and quantum statistics, is somewhat different than the classical distribution. The quantum effects reduce the Coulomb repulsion at short distances and also allow electrons of opposite spin to both be near $r = 0$, thus
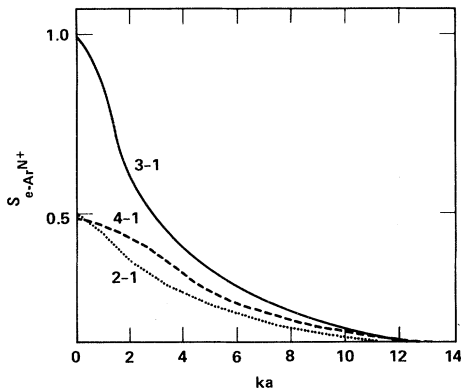
FIG. 9. Electron-ion static structure factors corresponding to the conditions of Fig. 6. $\cdots$, e-Ar^{2+} structure factor; $- - -$, e-Ar^{4+} structure factor; ———, e-Ar^{3+} structure factor.

accounting for $g_{ee}\neq 0$ at $r=0$ and the higher maximum in g_{ee} near $r=0.35a$.

Figure 12 gives the screened Coulomb part of Eq. (48) for e-Ar^{4+} and e-Ar^{3+} interactions. The corresponding Debye potential and the screened potential obtained using the activity method of I are also shown. Results for e-Ar^{2+} interactions are not shown but they lie close to the e-Ar^{3+} curve. Since few positive ions approach each other within $0.5a$, the screened potentials are somewhat stronger than the Debye-Hückel potential. The functional forms of the various electron-ion potentials are different, which is another difference with simple Debye theory. It is also noted that the ion of largest net charge is preferentially screened by the electrons, especially for $r>a$. Small oscillations in the screened potentials (not shown) set in for $r>2.3a$. These oscillations are due to long-range ionic order and become more pronounced as the coupling is increased. The corresponding ion-ion potentials have attractive wells. The screening function obtained in the grand-canonical formalism is much longer ranged than those obtained by the current method. This results from the fact that the strongly coupled particles contribute very little to the screening in the grand-canonical formalism so that, for the particular conditions being considered here, the re-
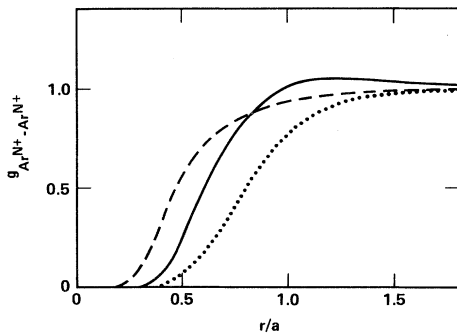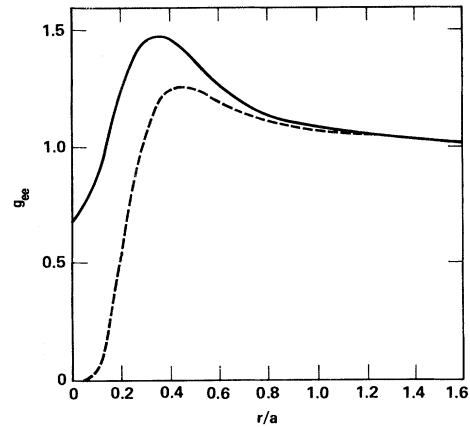

FIG. 11. Electron-electron distribution functions for the conditions of Fig. 6; $- - -$, assumes free-electron interactions are classical; ———, electrons are assumed to interact through two-body pseudopotentials discussed in Sec. II.

sulting screening parameter is close to the electron Debye length.

V. DISCUSSION

It has been shown that pseudopotentials obtained from the two-particle Slater sum give good results for partially ionized plasmas when inserted in classical integral equations. In order to apply classical equations in regions where composite particles form, the charge density of localized electrons was factored out and treated as new components. In so doing the charge distributions of bound electrons within the composite particles were obtained from solutions to the Schrödinger equation. The charge distribution of weakly bound electrons and unbound electrons was obtained from the HNC equation. Screening of the composite energy levels does not occur explicitly in this formulation; contrary to Debye-Hückel-like formulations. Instead we have used the results of I, which showed that bound-state screening terms are the same size as terms appearing in the electron-electron and ion-ion per-
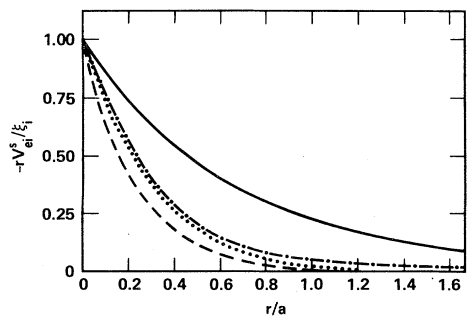

FIG. 10. Ion-ion distribution function for ions of like charge. $- - -$, Ar^{2+}-Ar^{2+} distribution; ———, Ar^{3+}-Ar^{3+} distribution; $\cdots$, Ar^{4+}-Ar^{4+} distribution.

FIG. 12. Static electron-ion screening functions for the conditions of Fig. 6; $- - -$, Debye-Hückel; $\cdots$, e-Ar^{4+} screening function; $-\cdot-$, e-Ar^{3+} screening function; ———, screening function that occurs in the grand-canonical ensemble method of I.

turbation expansions in the activity, and have treated this screening on the same basis as interaction terms. As a result, the energy levels for composite particles that enter the theory are unshifted by the plasma. The results of Ref. 4 show that at some high densities there are no bound states, so that it is not reasonable to use the current method at high density. A complete formulation of the problem would allow the composite particle energy levels to shift, but by a much smaller amount than predicted by the Debye potential.

The method developed here gives the equation of state, pair distribution functions, and their transforms. A number of approximations were made. The most serious is probably the neglect of several-particle diffraction and exchange effects when several free electrons are within a sphere of size λ_e. Approximations similar to those discussed here work reasonably well for the zero-temperature electron gas.[28] The pseudoclassical problem itself was solved only approximately, due to the neglect of the bridge functions. Multielectron bound-state excitations do not present conceptual difficulty, but were neglected due to numerical expedience.

In future work we plan to study the effect of several-particle quantum corrections to the pseudopotential.[20] The quantitative accuracy of the calculations can be improved by including the bridge functions. Several methods for doing this are available. The Rosenfeld-Ashcroft method[29] is based on parametrized hard-sphere bridge functions. It works well for monotonic repulsive potentials, but some modifications will be required to apply it to electron-ion bridge functions. The work of Iyetomi and Ichimaru[30] calculates the lowest-order bridge function for any potential that does not diverge at $r = 0$. These authors apply a "stretching function" to obtain higher bridge functions.

ACKNOWLEDGMENTS

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