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APPLICATION OF A MODIFIED DEBYE-HÜCKEL
THEORY TO FULLY IONIZED GASES

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ABSTRACT

The equations of the Debye-Hückel theory, modified to include quantum statistics, are discussed. It is found that the nonlinear equations used by Cowan and Kirkwood are not unique, and that the nonlinear theory can be formulated in different ways to give different answers. The linearized equations of these alternative formulations are discussed, and the correct form of the linearized theory is established. From the linear theory, the Helmholtz free energy of a slightly degenerate plasma is derived, and from this result, useful formulae in the near-classical limit are obtained for the pressure and internal energy.

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I. INTRODUCTION

In its linearized form, the classical Debye-Hückel theory of ionic solu-
tions has been very useful in providing a quick derivation of the thermodynamic
properties of a fully ionized gas in the classical limit ($\hbar = 0$). The results of
this intuitive theory have been confirmed by a rigorous statistical-mechanical
derivation using the Mayer cluster expansion of the canonical partition func-
tion.[1] It has been shown that the linearized form of the Debye theory is equiva-
lent to the summation of the ring integrals of the classical cluster expansion.
The theory in its nonlinear form, however, is beset with insurmountable dif-
ficulties when applied to a classical multicomponent gas of point-charged par-
ticles. From the success of the Thomas-Fermi statistical theory of the atom,
it has been expected that by modifying the Debye-Hückel theory to the extent of
describing the electrons with Fermi statistics instead of Boltzmann statistics
the difficulties of the classical theory could be removed. Recently, Kirkwood
and Cowan have made detailed numerical calculations of the thermodynamic
functions of a dense plasma, using the nonlinear equations of a Debye-Hückel-
Thomas-Fermi theory.[2] Also, Landau and Lifshitz have indicated how the
linearized Debye theory may be amended to include the effects of quantum

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[1] E. W. Montroll and J. E. Mayer, J. Chem. Phys. 9, 626 (1941).

[2] R. D. Cowan and J. G. Kirkwood, J. Chem. Phys. 29, 264 (1958).

statistics.[3] Exact results for the thermodynamic functions of a slightly de-generate gas are now available.[4] In this note we examine the Kirkwood-Cowan theory in its linearized form. It is found that the logic used by them enables one to write two alternative sets of equations which give different answers for the same problem. Landau and Lifshitz use a slightly different set of equations and obtain results that disagree with the exact theory because of the violation of a symmetry requirement. We take the point of view that the Debye-Hückel theory, when modified with quantum statistics, should, in its linearized form, agree with the rigorous results obtained by summing the ring diagrams of the quantum-mechanical grand partition function. A form of the linearized theory that meets this requirement is given.

II. THE BASIC APPROXIMATIONS AND THE EQUATIONS OF THE DEBYE-HÜCKEL-THOMAS-FERMI THEORY

We consider a fully ionized gas composed of electrons with average density n_{-o} and ions of charge $z_i e$ and average density n_{+o}. Electrical neutrality requires that $z_i n_{+o}$ be equal to n_{-o}. Around each ion there is an average potential Ψ_+ due to the ion being a center surrounded by a statistical distribution of positive and negative charge; similarly, around each electron an average potential Ψ_- is defined. These average potentials satisfy Poisson's equation:

$$\nabla^2 \Psi_+ = - 4\pi \, z_i \, e\delta(r) - 4\pi \, \rho_+ \, ,$$

$$\nabla^2 \Psi_- = 4\pi \, e \, \delta(r) - 4\pi \, \rho_- \, . \tag{1}$$

[3] L. D. Landau and E. M. Lifshitz, Statistical Physics (Pergaman Press, 1958), pp 229 - 33.

[4] H. E. DeWitt, Thermodynamic Functions of a Partially Degenerate, Fully Ionized Gas, University of California Radiation Laboratory Report No. UCRL-5652, Aug. 1959.

The δ functions express the boundary conditions, which are:

$$\lim_{r \to 0} r \Psi_+ = z_i e ,$$

$$\lim_{r \to 0} r \Psi_- = - e .$$ (2)

The average charge densities are given by:

$$\rho_+ = e(z_i n_{++}(r) - n_{-+}(r)) ,$$

$$\rho_- = e(z_i n_{+-}(r) - n_{--}(r)) ,$$ (3)

where $n_{++}(r)$ and $n_{-+}(r)$ are the average particle-number densities of ions and electrons, respectively, at a distance r from a given ion. Similarly, n_{+-} and n_{--} are the densities of ions and electrons about a given electron. The average distribution of negative charge about an ion must be the same as the average distribution of positive charge about an electron; hence, we have the basic symmetry requirement:

$$n_{-+}(r) = z_i n_{+-}(r) .$$ (4)

Since the electrons obey Fermi statistics, the average density of electrons about ions may be written as:

$$n_{-+}(r) = \left\langle \sum_{p_i} [1 + \exp(-a_e + \beta p_i^2/2m + \beta w_{-+}(r,a))]^{-1} \right\rangle_a ,$$ (5)

where $w_{-+}(r,a)$ denotes the energy of an electron at a distance r from an ion, in the presence of all the remaining ions and electrons in a particular configuration denoted by a. The averaging in (5) is taken over all configurations, with the distance r held fixed. An initial basic assumption of the Debye-Hückel approach is that Eq. (5) is approximated by:

$$n_{-+}(r) \cong \sum_{p_i} \left[1 + \exp\left(-a_e + \beta p_i^2/2m + \beta \left\langle w_{-+}(r,a) \right\rangle_a \right) \right]^{-1} .$$ (6)

This assumption is rigorously true only to first order in $w_{-+}(r, a)$, since there is no reason to expect that $\langle w_{-+}^n \rangle_a$ is equal to $\langle w_{-+} \rangle_a^n$ for n greater than 1. Henceforth, the average electron-ion energy, $\langle w_{-+}(r, a) \rangle_a$, will be denoted by $\bar{w}_{-+}(r)$. If the summation of (6) over momentum states p_i is converted to an integration, the following equation, in the notation of the previous paper is obtained:

$$n_{-+}(r) = n_{-o} \zeta_e^{-1} \mathcal{J}_{1/2}\left(a_e - \beta \bar{w}_{-+}(r)\right) , \tag{7}$$

where

$$\zeta_e = \frac{(2\pi\hbar)^3 n_{-o}}{(2 s_e + 1) \pi^{3/2} (2mkT)^{3/2}} \tag{8}$$

$$\mathcal{J}_{1/2}(a) = \frac{4}{\sqrt{\pi}} \int_o^\infty \frac{dx\, x^2}{1 + \exp(-a + x^2)} .$$

Similarly, for the ions, we find:

$$n_{++}(r) = n_{+o} \zeta_i^{-1} \begin{cases} \mathcal{J}_{1/2}\left(a_i - \beta w_{++}(r)\right) & \text{F.D.} \\ \mathcal{G}_{1/2}\left(a_i - \beta w_{++}(r)\right) & \text{B.E.} \end{cases} \tag{9}$$

depending on whether the ions are fermions or bosons. The charge density must vanish as r approaches ∞, since the system is electrically neutral; this requirement determines the chemical potentials a_e and a_i in (7) and (9) from the equations:

$$\zeta_e = \mathcal{J}_{1/2}(a_e)$$
$$\zeta_i = \mathcal{J}_{1/2}(a_i) \quad \text{or} \quad \mathcal{G}_{1/2}(a_i) . \tag{10}$$

In the classical limit, $\hbar \to 0$, (7) and (9) reduce to Boltzmann statistics:

$$n_{-+}(r) = n_{-o} \exp\left(-\beta \bar{w}_{-+}(r)\right)$$
$$n_{++}(r) = n_{+o} \exp\left(-\beta w_{++}(r)\right) . \tag{11}$$

Classically, the average energies go to $w_{-+}(r) \rightarrow -z_i e^2/r$ and $w_{++}(r) \rightarrow +z_i^2 e^2/r$ as r approaches 0. Consequently, $n_{++}(r)$ vanishes as r approaches 0, but $n_{-+}(r)$ has an essential singularity. This catastrophic divergence renders the classical nonlinear Debye-Hückel equations inapplicable to a gas of point charges. The Fermi form (7) of $n_{-+}(r)$ is well behaved at $r = 0$, since the repulsions due to the Pauli principle prevent the classical piling-up of negative charge around the ion.

By the same reasoning, the density of positive charge around an electron is given by:

$$n_{+-}(r) = n_{+o} \zeta_i^{-1} \cdot \begin{cases} \mathscr{I}_{1/2}(\alpha_i - \beta w_{+-}) & \text{F.D.} \\ \mathscr{G}_{1/2}(\alpha_i - \beta w_{+-}) & \text{B.E.}, \end{cases} \tag{12}$$

and, similarly, for negative charge around the electron we have:

$$n_{--}(r) = n_{-o} \zeta_e^{-1} \mathscr{I}_{1/2}(\alpha_e - \beta w_{--}). \tag{13}$$

In order to obtain usable equations, it is next assumed that the various average energies are related to the average potentials as follows:

$$\begin{aligned} w_{++} &= z_i e \Psi_+ \\[4pt] w_{-+} &= -e \Psi_+ \\[4pt] w_{+-} &= z_i e \Psi_- \\[4pt] w_{--} &= -e \Psi_- \end{aligned} \tag{14}$$

The justification of this basic assumption and the other approximations of the Debye-Hückel theory are discussed in detail by Fowler.[5]

Kirkwood and Cowan form a nonlinear equation for Ψ_+ by using (7) for $n_{-+}(r)$ and the Boltzmann form for $n_{++}(r)$. The equation for Ψ_- is coupled

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[5] R. H. Fowler, _Statistical Mechanics_ (Cambridge University Press, 1955), second edition, pp. 269 - 74.

to Ψ_+ by the use of the symmetry requirement (4). These equations are:

$$\nabla^2 \Psi_+ = -4\pi z_i e \delta(r) - 4\pi e[z_i n_{+o} \zeta_i^{-1} \mathcal{J}_{1/2}(\alpha_i - \beta z_i e \Psi_+)$$
$$- n_{-o} \zeta_e^{-1} \mathcal{J}_{1/2}(\alpha_e + \beta e \Psi_+)]$$

$$\nabla^2 \Psi_- = 4\pi e \delta(r) - 4\pi e[n_{-o} \zeta_e^{-1} \mathcal{J}_{1/2}(\alpha_e + \beta e \Psi_+)$$
$$- n_{-o} \zeta_e^{-1} \mathcal{J}_{1/2}(\alpha_e + \beta e \Psi_-)] .$$

(15)

(For generality, we have retained quantum statistics for the ions as well as electrons.) Using the same logic, however, one arrives at an alternative set of equations by first writing an equation for Ψ_-, and then coupling the equation for Ψ_+ to that for Ψ_- with the symmetry requirement. This alternative set is:

$$\nabla^2 \Psi_- = 4\pi e \delta(r) - 4\pi e[z_i n_{+o} \zeta_i^{-1} \mathcal{J}_{1/2}(\alpha_i - \beta z_i e \Psi_-)$$
$$- n_{-o} \zeta_e^{-1} \mathcal{J}_{1/2}(\alpha_e + \beta e \Psi_-)]$$

(16)

$$\nabla^2 \Psi_+ = -4\pi z_i e \delta(r) - 4\pi e[z_i n_{+o} \zeta_i^{-1} \mathcal{J}_{1/2}(\alpha_i - \beta z_i e \Psi_+)$$
$$- z_i n_{+o} \zeta_i^{-1} \mathcal{J}_{1/2}(\alpha_i - \beta z_i e \Psi_-)] .$$

Both sets of equations, (15) and (16), reduce to the classical nonlinear equations of the Debye-Hückel theory in the classical limit, $\hbar \to 0$. For positively and negatively charged particles of comparable mass, there is no reason to prefer one set over the other. However, for real electrons and nuclei with their tremendous mass difference, the set (15) used by Kirkwood and Cowan seems more reasonable for approximate numerical computation of the thermodynamic functions of a dense plasma.

To examine the consequences of the two alternative sets of equations, we look at the solutions of their linearized forms. The linearized equations

are valid for r sufficiently large so that $\beta z_i e^{\Psi_\pm}$ and $\beta e^{\Psi_\pm}$ are much greater than 1. The $\mathscr{L}_{1/2}$ (or $\mathscr{G}_{1/2}$) functions may be expanded in Taylor series to give:

$$\zeta_e^{-1} \mathscr{L}_{1/2}(a_e + \beta e \Psi_+) = 1 + \beta e \theta_e^2 \Psi_+ + \ldots$$

$$\zeta_i^{-1} \mathscr{L}_{1/2}(a_i - \beta z_i e \Psi_+) = 1 - \beta z_i e \theta_i^2 \Psi_+ + \ldots, \tag{17}$$

where

$$\theta_e^2 = \zeta_e^{-1} \mathscr{L}_{1/2}'(a_e) = \mathscr{L}_{-1/2}(a_e)/\mathscr{L}_{1/2}(a_e)$$

$$\theta_i^2 = \zeta_i^{-1} \mathscr{L}_{1/2}'(a_i) = \mathscr{L}_{-1/2}(a_i)/\mathscr{L}_{1/2}(a_i). \tag{18}$$

If (17) is used, the linearized equations obtained from (15) are:

$$A \left\{ \begin{array}{l} \nabla^2 \psi_+ = 4\pi \beta e^2 [z_i^2 \theta_i^2 n_{+o} + \theta_e^2 n_{-o}] \psi_+ \\[2ex] \nabla^2 \psi_- = 4\pi \beta e^2 \theta_e^2 [z_i^2 n_{+o} \psi_+ - n_{-o} \psi_-] , \end{array} \right. \tag{19}$$

and from (16):

$$B \left\{ \begin{array}{l} \nabla^2 \psi_- = 4\pi \beta e^2 [z_i^2 \theta_i^2 n_{+o} + \theta_e^2 n_{-o}] \psi_- \\[2ex] \nabla^2 \psi_+ = 4\pi \beta e^2 \theta_i^2 [z_i^2 n_{+o} \psi_+ - n_{-o} \psi_-] . \end{array} \right. \tag{20}$$

The solutions of the linearized equations are designated with ψ_+ and ψ_-, to distinguish them from Ψ_+ and Ψ_- for the nonlinear equations, where ψ_+ and ψ_- are the asymptotic forms of Ψ_+ and Ψ_- for large r. The δ functions expressing the boundary conditions at $r = 0$ have not been written in the linearized equations, since these boundary conditions are of no help in determining the integration constants in ψ_+ and ψ_-.

The general solutions of the linear equations A, subject only to the requirement that ψ_+ and ψ_- vanish at ∞, are:

$$\psi_+ = \frac{z_i e}{r} C_{A+} e^{-\kappa r}$$

$$\psi_- = -\frac{e}{r}\left[C_{A-} e^{-\kappa_- \theta_e r} + C_{A+}\left(\theta_e^2/\theta_i^2\right) e^{-\kappa r}\right],$$

$$(21)$$

where

$$\kappa = \left(\kappa_-^2 \theta_e^2 + \kappa_+^2 \theta_i^2\right)^{1/2} = 1/\lambda$$

$$\kappa_-^2 = 4\pi e^2 \beta n_{-o} \qquad (22)$$

$$\kappa_+^2 = 4\pi e^2 \beta z_i^2 n_{+o} .$$

Here, C_{A+} and C_{A-} are arbitrary constants, and κ is the reciprocal of the Debye screening length λ, generalized to include the modifications due to quantum statistics. Similarly, the general solutions of equations B are:

$$\psi_- = -\frac{e}{r} C_{B-} e^{-\kappa r}$$

$$\psi_+ = \frac{z_i e}{r}\left[C_{B+} e^{-\kappa_+ \theta_i r} + C_{B-}\left(\theta_i^2/\theta_e^2\right) e^{-\kappa r}\right].$$

$$(23)$$

By numerical integration of the nonlinear equations (15) and comparison of ψ_+ and ψ_- with (21) for large r, we may find numerical values for C_{A+} and C_{A-}. Similarly, numerical values of C_{B+} and C_{B-} could be found by numerical integration of (16). The solutions, (21) and (23), of the alternative sets of linear equations are different from each other, and hence would lead to different answers for the thermodynamic functions of the gas. Furthermore, ψ_+ and ψ_- have the unsatisfactory feature of behaving differently as r approaches ∞. In (21), ψ_+ vanishes as $e^{-\kappa r}$, while ψ_- vanishes as $e^{-\kappa_- \theta_e r}$, since $\kappa_- \theta_e$ is less than κ.

The only way in which the solutions (21) and (23) can be identical is to have the condition: $C_{A-} = C_{B+} = 0$. If this requirement is made, then (20) and (23) have the same form and require only one arbitrary constant:

$$\psi_{+} = \frac{z_i e \theta_i^2}{r} C e^{-\kappa r}$$

$$\psi_{-} = -\frac{e \theta_e^2}{r} C e^{-\kappa r} .$$

(24)

In view of the nonuniqueness of the theory, as illustrated by two apparently equally valid sets of equations A and B, the solutions (24) are to be preferred over (21) or (23). In the classical limit, the degeneracy parameters θ_i^2 and θ_e^2 both reduce to 1. The remaining arbitrary constant C is determined by the fact that the Debye-Hückel theory is rigorously valid at sufficiently high temperature. The asymptotic forms ψ_{+} and ψ_{-} are valid arbitrarily close to the origin, and at the origin we must have $r\Psi_{+}$ equal to $z_i e$ and $r\Psi_{-}$ equal to $- e$; hence, C has the value 1 for a nondegenerate gas. It is clear, however, that for a degenerate gas (i.e., $\theta_e^2 \neq \theta_i^2 \neq 1$) the constant C cannot be chosen so that ψ_{+} and ψ_{-} reduce to $z_i e/r$ and $-e/r$, respectively, as r approaches 0.

The chief criticism of the two sets of nonlinear equations, (15) and (16), for the calculation of thermodynamic functions of a dense gas is that they are unsymmetrical in the way Ψ_{+} and Ψ_{-} are treated. With the set of equations (14) used by Kirkwood and Cowan, Ψ_{+} may be calculated independently of Ψ_{-}, but the calculation of Ψ_{-} requires a knowledge of Ψ_{+}. The same statement applies to the equations (16), but in reverse order. The two ways of doing the calculation, in general, will give different results. Thus, it would seem more reasonable to begin with a symmetrical set of equations in which Ψ_{+} and Ψ_{-} are treated on an equal basis. The first equation of (15) and the first of (16) are symmetrical in this sense. An objection against this symmetrical set of equations for numerical calculations of the type done by Kirkwood and Cowan is that the symmetry requirement, $n_{-+}(r) = z_i n_{+-}(r)$, is violated for r small enough to cause nonlinear effects to be important. We will show, however,

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III. CALCULATION OF THE THERMODYNAMIC FUNCTIONS

The average potential energy of the gas is given by:

$$\bar{U} = \frac{1}{2} N_i \int d\underset{\sim}{r}\, \rho_+(z_i e/r) + \frac{1}{2} N_e \int d\vec{r}\, \rho_-(- e/r)$$

$$= \bar{U}_i + \bar{U}_e \,. \tag{27}$$

The solutions of the linearized equations (24) are valid for sufficiently large r, and with Poisson's equations, they give the asymptotic forms of the charge densities as:

$$\rho_{+\,asy} = -\frac{1}{4\pi} \nabla^2 \psi_+ = -\frac{z_i e\, \theta_i^2}{r} C\, e^{-\kappa r}$$

$$\rho_{-\,asy} = -\frac{1}{4\pi} \nabla^2 \psi_- = \frac{e\, \theta_e^2}{r} C\, e^{-\kappa r} \,. \tag{28}$$

The asymptotic forms (28) are accurate for distances from the central point charges greater than some limit to be denoted as r_c. Inside the sphere of radius r_c, the average potential and charge density are not known, though presumably they may be calculated approximately from the nonlinear equations, either (15) or (16). The average energy integral is thus a sum of two parts:

$$\bar{U}_i = \frac{1}{2} N_i 4\pi \int_0^{r_c} dr\, r^2 \rho_{+\,exact}(z_i e/r) + \frac{1}{2} N_i 4\pi \int_{r_c}^\infty dr\, r^2 \rho_{+\,asy}(z_i e/r) \,. \tag{29}$$

The quantity $\bar{U}_i$ may be estimated by using $\rho_{+\,asy}$ for the entire volume, even for r less than r_c where it is not accurate, since the main contribution comes from r greater than r_c. With this approximation and using (28), we find:

$$\bar{U}_i \cong \frac{1}{2} N_i 4\pi \int_0^\infty dr\, r^2 \rho_{+\,asy}(z_i e/r) = -\frac{1}{2} C N_i z_i^2 e^2 \theta_i^2 \kappa \,. \tag{30}$$

Adding a similar result for $\bar{U}_e$, we have, for the potential energy of the gas due to the particle correlation,

$$\overline{U}/V = - \frac{1}{2} C e^2 (z_i^2 \theta_i^2 n_{+o} + \theta_e^2 n_{-o}) \kappa$$

$$= - \frac{C k T \kappa^3}{8\pi} .$$

(31)

We have seen that the remaining arbitrary constant C must be 1 in the classical limit, but for a degenerate gas, we cannot rule out the possibility that C is a function of temperature in such a way that $\lim C(T)$ is equal to 1 as T approaches ∞. Equation (31), however, agrees with the exact near-classical-limit result for $\overline{U}$ as derived from the grand partition function (Eq. 122 of the previous paper) when C is equal to 1.

The Helmholtz free energy may be obtained from $\overline{U}$ by an integration with respect to the coupling constant from 0 to e^2; this calculation is equivalent to the Debye charging process. Noting that $\overline{U}$ is $0(e^3)$, we easily find the contribution to the Helmholtz free energy to be:

$$F_e = \int_o^{e^2} \frac{d(e'^2)}{(e'^2)} \overline{U}_{e'} = - \frac{V k T \kappa^3}{12\pi} ,$$

(32)

or, in the notation of the previous paper,

$$\frac{F_e}{kT} = - \frac{2}{3} N \Lambda \phi^{3/2} ,$$

(33)

where

$$N = N_e + N_i , \qquad n = n_{+o} + n_{-o} , \qquad f_e = N_e/N$$

$$\Lambda = \sqrt{\pi} \, e^3 \beta^{3/2} n^{1/2} , \qquad \phi = z_i^2 \theta_i^2 f_i + \theta_e^2 f_e .$$

(34)

If the free energy due to the interaction is added to F_o, the free energy of an ideal quantum gas which is given by:

$$\frac{F_o}{kT} = N \{ a - \mathscr{l}_{3/2}(a)/\mathscr{l}_{1/2}(a) \} ,$$

(35)

then the total free energy is given by:

$$F = F_{oi} + F_{oe} + F_e .$$

The pressure and internal energy are obtained from the expressions:

$$\frac{PV}{kT} = - V \frac{\partial}{\partial V} \left(\frac{F}{kT}\right)$$

$$\frac{E}{kT} = \beta \frac{\partial}{\partial \beta} \left(\frac{F}{kT}\right) .$$

(36)

The differentiations of (36) are easily carried out by noting that from the

defining relation for the chemical potential (10) we obtain:

$$V \, \partial a/\partial V = - 1/\theta^2$$

$$\beta \, \partial a/\partial \beta = 3/2\theta^2 .$$

(37)

Also, we need the relation:

$$V \frac{\partial}{\partial V} \left(\frac{\mathscr{l}_{-1/2}(a)}{\mathscr{l}_{1/2}(a)}\right) = \left[\frac{\mathscr{l}_{-3/2}(a)}{\mathscr{l}_{1/2}(a)} - \frac{\mathscr{l}_{-1/2}^2(a)}{\mathscr{l}_{1/2}^2(a)}\right] V \frac{\partial a}{\partial V}$$

$$= - \left(\frac{\mathscr{l}_{-1/2}(a)}{\mathscr{l}_{1/2}(a)} - \frac{\mathscr{l}_{-3/2}(a)}{\mathscr{l}_{-1/2}(a)}\right) \equiv - \eta(a) .$$

(38)

From (36), using (37) and (38), we obtain the following expressions for the

pressure and energy:

$$\frac{PV}{kT} = \Sigma N_i \frac{\mathscr{l}_{3/2}(a_i)}{\mathscr{l}_{1/2}(a_i)} - \frac{1}{3} N \Lambda \phi^{3/2} + N \Lambda \phi^{1/2} \Sigma z_i^2 f_i \eta(a_i)$$

(39)

$$\frac{E}{kT} = \frac{3}{2} \Sigma N_i \frac{\mathscr{l}_{3/2}(a_i)}{\mathscr{l}_{1/2}(a_i)} - N \Lambda \phi^{3/2} + \frac{3}{2} N \Lambda \phi^{1/2} \Sigma z_i^2 f_i \eta(a_i) ,$$

where the sums are over the particle species of a multicomponent gas. Ex-

pressions (39) are identical with (127) and (128) of the previous article, except

for the absence of the exchange interaction term.

IV. CONCLUSION

The pressure and internal energy formulae (39) are exact in the near-classical limit defined by high temperature and low density such that $\Lambda\phi^{3/2} = (8\pi\rho\lambda^3)^{-1} \ll 1$, but $\hbar \neq 0$. In this limit, the ring diagrams of the expansion of the quantum-mechanical grand partition function give the leading contribution to PV/kT after the ideal gas term (namely, $0(\Lambda)$), and the next contribution from non-ring terms is $0(\Lambda^2)$. We have thus shown that the linearized Debye-Hückel-Thomas-Fermi theory is exact in the near-classical limit in the same way in which the Debye-Hückel theory is exact in the classical limit ($\hbar = 0$). To distinguish between the various ways of building up such a theory, we must require that the Poisson equations be symmetrical in the treatment of the average potentials, and preserve the charge-density symmetry, $n_{-+} = z_i n_{+-}$ to $0(\psi)$. The usefulness of the Debye-Hückel method has thus been extended to more dense plasmas, but at the same time the limitations of the method are more apparent. The linearized theory gives the thermodynamic functions of essentially classical particles whose velocity distributions are slightly modified from the Boltzmann form, due to quantum statistics. Exchange interactions and wave-mechanical effects are in no way included in either the linear or the nonlinear equations. Furthermore, it is not clear that the nonlinear equations give any more information than is contained in the linearized forms. The nonlinear effects of the symmetrical nonlinear equations (the final equation of (15) and the first of (16) are not believable, since the charge symmetry, $n_{-+} = z_i n_{+-}$, is violated in $0(\psi^2)$. The set of nonlinear equations (15) used by Cowan and Kirkwood are better in that the charge symmetry is preserved, but the set (16), which gives different answers, would seem to be equally valid. Until more exact results have been obtained from the non-ring terms of the partition function, and can be used for comparison, we conclude that the Debye-Hückel-Thomas-Fermi theory, as applied to plasmas, is useful only in its linearized form.