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Theory of electron correlation in metals*

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A new theory for calculating the effects of electron correlation in metals is described and applied to the electron gas. The method is based upon the derivation of a pseudo-Hamiltonian, which describes the motion of the electrons after long-range collective motions (plasma oscillations) have been accounted for. The partition function is also expressed in terms of this operator. The cohesive energy, the density of states, and the thermodynamic properties are calculated in a self-consistent-field approximation, which takes shifts in the band population at high temperature into account. The calculations are in good agreement with exact high- and low-density expansions.

I. INTRODUCTION

We propose a new approach for calculating the effects of electron correlation on the cohesive energy and thermodynamic properties of metals. Throughout this work, we restrict our attention to the "electron gas," a system of interacting electrons moving about in a uniform background of positive charge. This simple model of a metal has been studied by many theorists, and exact solutions are known in the high- and low-density limits.

The effects of electron correlation in metals were first calculated by Wigner.[1] His work showed that the Hartree-Fock (HF) approximation underestimates the energy of the electron gas by about 35% in the region of maximum binding. Bardeen[2] demonstrated that the HF theory also predicts an unrealistic behavior for the specific heat. Wohlfarth[3] noted that this difficulty with the specific heat arises from the long range of the Coulomb forces, and he suggested that electrons in a metal interact according to a screened Coulomb law.

The explanation for this screening was developed in a series of papers by Bohm and Pines (BP).[4-6] They showed that the electrons in a metal undergo long-range collective motions similar to plasma oscillations. These motions create an oscillating field which cancels the long-wavelength components of the Coulomb interaction. The BP theory eliminated the problems encountered in the HF theory. However, objections to the BP use of an extended variable Hamiltonian[7] and the random-phase approximation have been raised. Coldwell contends that their approach leads to difficulties, particularly at low densities.[8,9]

Since the work of Bohm and Pines, numerous alternative treatments of the electron-correlation problem have been given.[10,11] Of particular interest is the paper by Gell-Mann and Brueckner,[12] who obtained the exact expression for the correlation energy in the high-density limit. Wigner's expression for the low-density limit[1] was improved by the more-accurate calculations of Coldwell-Horsfall and Maradudin.[13]

In our work, we return to the spirit of the BP theory. Our method, like theirs, is based upon separation of the short-range interactions from the long-range interactions which lead to plasma oscillations. However, we do not use either the random-phase approximation or the extended variable Hamiltonian. In Sec. II, we derive a pseudo-Hamiltonian that describes the motion of the electrons after plasma oscillations have been taken into account. The effective electron interaction is related to the ground-state wave function of a charged boson gas, which is derived in Sec. III. In Sec. IV, we propose a method for calculating the partition function, taking into account changes in the band population as the temperature is increased. In Sec. V, we present our results for the energy, the density of states, and the thermodynamic properties. The calculated correlation energy is good at low and intermediate densities. The calculation gives poor results at high densities, but correlation is a very small contribution to the total energy in this region. Moreover, our calculation of the heat capacity is in good agreement with the exact high-density limit.

II. THE PSEUDO-HAMILTONIAN

We consider the Schrödinger equation for N electrons in a box of volume V, with a uniform background of positive charge that makes the system neutral:

$$\mathcal{H}\Psi_n = E_n\Psi_n \,, \tag{1a}$$

$$\mathcal{H} = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + U \,, \tag{1b}$$

$$U = \frac{4\pi e^2}{V}\sum_{i>j}\sum_{\vec{k}}\frac{1}{k^2}e^{i\vec{k}\cdot(\vec{x}_i-\vec{x}_j)} \,. \tag{1c}$$

The indices i and j are summed over the N electrons in the box. Equation (1c) is the Fourier expansion of the potential; the term $\vec{k}=0$ is to be omitted from the sum, since it is cancelled by the positive charges. This restriction will hold for all sums over $\vec{k}$, without being explicitly indicated.

We propose to write correlated wave functions in the form

$$\Psi_n = \chi \Phi_n \;. \tag{2}$$

The function χ, which is the same for all states of the system, is intended to describe the collective features of the electron motion; it is symmetric with respect to exchange of electrons. Φ_n describes the electron motion after the plasma oscillations have been taken into account.

In a variational calculation of the ground-state energy, Φ_0 is approximated by a Slater determinant of plane-wave states.[11,14] This approach requires either the evaluation of many-body integrals or the determination of the two- and three-body distribution functions, so that further approximations must be made. Moreover, this method gives little insight into the band structure and the thermal properties of the electron gas. In our theory, we seek to express the energy and other properties interms of integrals that do not involve the complicated many-body weighting factor.

Substituting Eq. (2) into Eq. (1) and dividing by χ, we obtain an equation for Φ_n:

$$\tilde{\mathcal{H}} \Phi_n = E_n \Phi_n \;, \tag{3a}$$

$$\tilde{\mathcal{H}} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \frac{\hbar^2}{m\chi} \sum_i \vec{\nabla}_i \chi \cdot \vec{\nabla}_i + E_p \;, \tag{3b}$$

$$E_p = U - \frac{\hbar^2}{2m\chi} \sum_i \nabla_i^2 \chi \;. \tag{3c}$$

Provided χ is never zero and is bounded, Eq. (3) is equivalent to Eq. (1), and its solutions completely determine the wave functions and energies of the system. We will regard the operator $\tilde{\mathcal{H}}$ as an effective "Hamiltonian" for the electrons after plasma oscillations have been taken into account. However, $\tilde{\mathcal{H}}$ is not Hermitian and cannot be regarded as a true Hamiltonian. The functions $\{\Phi_n\}$ do not form an orthonormal set. The correct normalization is given by

$$\int \Phi_n^* \Phi_m \chi^2 \, d\tau = \delta_{nm} \;. \tag{4}$$

Next, we propose that χ be the ground-state wave function for the charged boson gas; then E_p is the ground-state energy, a quantity which does not depend upon the electronic coordinates. This prescription may seem arbitrary, but we offer two reasons for our procedure. If E_p is a constant, then the electrons at the bottom of the band will be closely approximated by plane waves, since the operator $\vec{\nabla}_i \chi \cdot \vec{\nabla}_i$ makes no contribution for an electron with zero momentum. Second, this choice for χ insures that our theory will be exact at low densities, where the kinetic energy becomes negligible. Unfortunately, we do not know the exact expression for χ, but in Sec. III we derive a fairly simple approximation that is adequate for our purposes.

χ can be written in the form[15]

$$\chi = c e^{-S} \;, \tag{5}$$

where c is a constant, and S is a function of the electronic coordinates. Using this expression, it is instructive to write $\tilde{\mathcal{H}}$ in the form

$$\tilde{\mathcal{H}} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + E_p + \tilde{U} + \mathfrak{F} \;, \tag{6a}$$

$$\tilde{U} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 S \;, \tag{6b}$$

$$\mathfrak{F} = \frac{\hbar^2}{2m} \sum_i (2\vec{\nabla}_i S \cdot \vec{\nabla}_i + \nabla_i^2 S) \;. \tag{6c}$$

The quantity $\tilde{U}$ can be regarded as the effective potential function after long-range correlations have been taken into account. In Sec. III, we show that $\tilde{U}$ is a sum of screened Coulomb interactions between electron pairs. The operator $\mathfrak{F}$ can be written

$$\mathfrak{F} = -\,[\mathcal{K} S - S \mathcal{K}] \;, \tag{6d}$$

where $\mathcal{K} = -(\hbar^2/2m)\sum_i \nabla_i^2$. From Eq. (6d), we observe that $\mathfrak{F}$ is anti-Hermitian. It is this term which frustrates our efforts to obtain a rigorous solution to Eq. (3). However, we will show that, for many properties of the electron gas, satisfactory results are obtained by neglecting this operator altogether.

III. CHARGED BOSON GAS

Next we derive approximate expressions for the wave function and energy of the charged boson gas. The method used is essentially that proposed by Gross.[15] However, we will adopt a slightly different point of view, in order to bring out the similarity of our approach to the plasma-oscillation theory of Bohm and Pines.

We define the quantities

$$\omega_p^2 = 4\pi e^2 N / mV \;, \tag{7a}$$

$$\rho_{\vec{k}} = (Nk^2)^{-1/2} \sum_i e^{i \vec{k} \cdot \vec{x}_i} \;, \tag{7b}$$

where ω_p is the plasma frequency, and the $\rho_{\vec{k}}$ are Fourier components of the electron density. In terms of these quantities, Eq. (1c) becomes

$$U = (\tfrac{1}{2} m \omega_p^2) \sum_{\vec{k}} (|\rho_{\vec{k}}|^2 - k^{-2}) \;. \tag{8}$$

Equation (8) resembles the potential for an infinite set of harmonic oscillators of frequency ω_p and

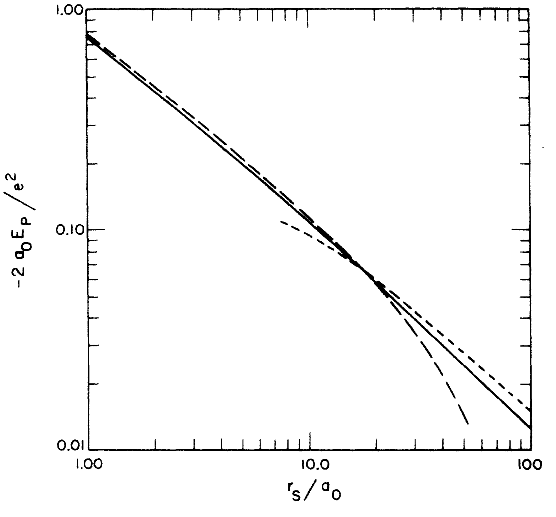

FIG. 1. Ground-state energy of the charged boson gas, according to Brueckner (dashed curve), Coldwell-Horsfall and Maradudin (dotted curve), and Eq. (11) (solid curve).

amplitudes $|\rho_{\vec{k}}|$. This fact suggests that we take χ to be a product of harmonic oscillator functions:

$$\chi = ce^{-S} ,$$

$$S \approx \frac{m\omega_p}{2\hbar} \sum_{\vec{k}} |\rho_{\vec{k}}|^2 .$$

It turns out that the above expression leads to divergence in some of the terms which appear in the theory. Following BP, we could eliminate this divergence by introducing a cutoff in the sum,[6] but we will adopt a procedure similar to that of Gaskell.[16] Let us assume that each Fourier component $\rho_{\vec{k}}$ oscillates with an effective frequency $\omega_k = f_k\omega_p$. Then

$$S \approx \frac{m\omega_p}{2\hbar} \sum_{\vec{k}} f_k |\rho_{\vec{k}}|^2 .$$

Now substituting for $\rho_{\vec{k}}$ from Eq. (7b), and eliminating constant terms from S, we obtain

$$S = \frac{m\omega_p}{\hbar N} \sum_{i>j} \sum_{\vec{k}} \left(\frac{f_k}{k^2}\right) e^{i\vec{k}\cdot(\vec{x}_i - \vec{x}_j)} . \tag{9}$$

Equation (9) agrees with the expression proposed by Gross. We further remark that our method does not allow for the excitation of "plasmons." It may be that we could improve upon the theory by including contributions from "excited" plasma states, but we will not explore that possibility here.

The ground-state energy E_p is found to be

$$E_p = E_{p0} + E_{p3} , \tag{10}$$

where

$$E_{p0} = -\frac{m\omega_p^2}{2} \sum_{\vec{k}} \left(\frac{f_k}{k}\right)^2 , \tag{11}$$

$$E_{p3} = \frac{m\omega_p^2}{2N^2} \sum_{\substack{ijl \\ i\neq j\neq l\neq i,}} \sum_{\vec{k}} \sum_{\substack{\vec{k}' \\ \vec{k}'\neq -\vec{k}}} \frac{f_k}{k^2}\frac{f_{k'}}{k'^2} (\vec{k}\cdot\vec{k}') e^{i\vec{k}\cdot(\vec{x}_i - \vec{x}_j)} e^{i\vec{k}'\cdot(\vec{x}_i - \vec{x}_l)} , \tag{12}$$

and

$$f_k^2 + \frac{\hbar k^2}{m\omega_p} f_k - 1 - \frac{k^2}{N} \sum_{\vec{k}'\neq\vec{k}} \frac{f_{k'}}{k'^2} \times \frac{f_{|\vec{k}-\vec{k}'|}}{|\vec{k}-\vec{k}'|^2} \vec{k}' \cdot (\vec{k}-\vec{k}') = 0 . \tag{13}$$

We see that E_{p0} depends only on the electron density, and that E_{p3} is a sum of three-electron interactions. Following Gross, Eq. (13) is the condition obtained by requiring that all two-electron contributions to E_p vanish.

Converting the summation in Eq. (13) to an integral, the following result is obtained:

$$g_\lambda(x)^2 + x^2 g_\lambda(x) - 1 - x^2 P(x)/\pi\lambda = 0 , \tag{14}$$

where

$$P(x) = \frac{1}{2\pi} \iiint \frac{g_\lambda(x')g_\lambda(|\vec{x}-\vec{x}'|)}{|\vec{x}-\vec{x}'|^2} \vec{x}' \cdot (\vec{x}-\vec{x}')\, d^3\vec{x}' . \tag{15}$$

We have introduced the definitions

$$\lambda = (\hbar a_0^2/m\omega_p)^{1/2} , \tag{16a}$$

$$g_\lambda(x) = f(\lambda x/a_0) . \tag{16b}$$

a_0 is the Bohr radius. We have solved Eq. (14) numerically; details of the solution are given in the Appendix. We find that $g_\lambda(x) \to 1$ as $x \to 0$ and $g_\lambda(x) \to 1/x^2$ as $x \to \infty$. Because of this asymptotic behavior, there are no diverging terms in our theory.

In Fig. 1, we compare the quantity E_{p0} with Brueckner's exact high-density expansion[17] and the low-density expansion of Coldwell-Horsfall and Maradudin.[13] Brueckner's expansion is of the form

$$E_p = A/(r_S/a_0)^{3/4} + B \text{ Ry/electron,}$$

where $A = -0.8031$, $B = 0.028$, and $r_S = (3V/4\pi N)^{1/3}$ is the Wigner-Seitz cell radius. Our result for the constant A agrees with that of Brueckner, but we obtain $B \approx 0.058$. If our expression for χ were exact, E_p would be completely independent of the electronic coordinates. However, the good agreement shown in Fig. 1 indicates that the term E_{p3} is fairly small. Therefore, we feel that our approximation for χ is adequate, particularly at high densities.

With these results, we can write the pseudo-Hamiltonian $\tilde{\mathcal{H}}$ in the form

$$\tilde{\mathcal{H}} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + E_{p0} + \sum_{i>j} u(|\vec{x}_i - \vec{x}_j|) + E_{p3} + \mathcal{F} , \tag{17a}$$

where

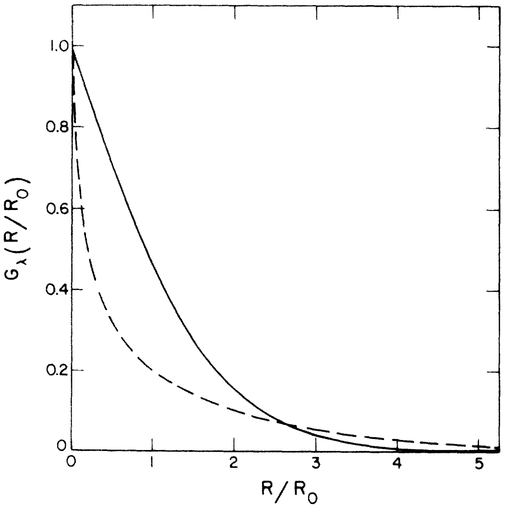

FIG. 2. The function G_λ in the screened Coulomb potential [Eq. (18)] for $r_s = 0.01a_0$ (solid curve) and $r_s = 100a_0$ (dashed curve).

$$u(R) = \frac{\hbar\omega_p}{N} \sum_{\vec{k}} f_k e^{i\vec{k}\cdot\vec{R}} . \tag{17b}$$

$u(R)$ is a screened Coulomb potential. Converting the summation to an integral, Eq. (17b) becomes

$$u(R) = (e^2/R)G_\lambda(R/R_0) , \tag{18a}$$

$$G_\lambda(q) = \frac{2}{\pi}\int_0^\infty g_\lambda(x)x \sin(qx)\, dx , \tag{18b}$$

and $R_0 = a_0\lambda^{-1}$. The screening function G_λ is shown for two densities in Fig. 2.

Before leaving this section, we will make a few more observations about the boson wave function. From Eq. (9), we can write

$$\chi = C \exp\left(-\sum_{i>j} s(|\vec{x}_i - \vec{x}_j|)\right) , \tag{19a}$$

$$s(R) = \frac{m\omega_p}{\hbar N} \sum_{\vec{k}} \left(\frac{f_k}{k^2}\right) e^{i\vec{k}\cdot\vec{R}} . \tag{19b}$$

Converting the summation to an integral, we find

$$s(R) = (A/R)[1 - F_\lambda(R/R_0)] , \tag{20a}$$

$$F_\lambda(q) = \frac{2}{\pi}\int_0^\infty [1 - g_\lambda(x)]x^{-1} \sin(qx)\, dx , \tag{20b}$$

where $R_0 = a_0\lambda^{-1}$ and $A = e^2/\hbar\omega_p$. As $R \to 0$, $s(R)$ approaches a finite value.

$$s(R) \to \frac{2}{\pi\lambda}\int_0^\infty g_\lambda(x)\, dx, \quad R \to 0 . \tag{20c}$$

Hence χ is never zero and is bounded, as is required by our theory. In their variational calculations, Stevens and Pokrant[11] used the expression

$$s(R) = (A/R)(1 - e^{-BR}) .$$

Our value for the constant A agrees with theirs. In Fig. 3, we show the function F_λ for two densities. The exponential formula, while not exact, is a fair approximation to our function F_λ.

IV. CALCULATION OF THE PARTITION FUNCTION

A. No correlation

Although greatest interest in the electronic properties of metals usually centers upon the groundstate, a complete calculation of the thermodynamic properties requires evaluation of the partition function. Our method is a generalization of the Hartree-Fock theory to finite temperatures, and it reduces to the usual HF result at zero temperature. In Sec. IV B we show how the formalism can be modified to include correlation effects.

The partition function is given by

$$Q = \sum_n \int \psi_n^* e^{-\beta\mathcal{H}} \psi_n \, d\tau , \tag{21}$$

where $\beta = 1/kT$ and $\{\psi_n\}$ are any complete set of orthonormal functions. The Hamiltonian is of the form

$$\mathcal{H} = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + \sum_i v(i) + \sum_{i>j} w(ij) . \tag{22}$$

Now suppose the $\{\psi_n\}$ satisfy eigenvalue equations

$$\mathcal{H}_n^0 \psi_n = E_n^0 \psi_n . \tag{23}$$

Then the Gibbs-Bogoliubov inequality[18] states that

$$Q \geq e^{-\beta W} \sum_n e^{-\beta E_n^0} , \tag{24a}$$

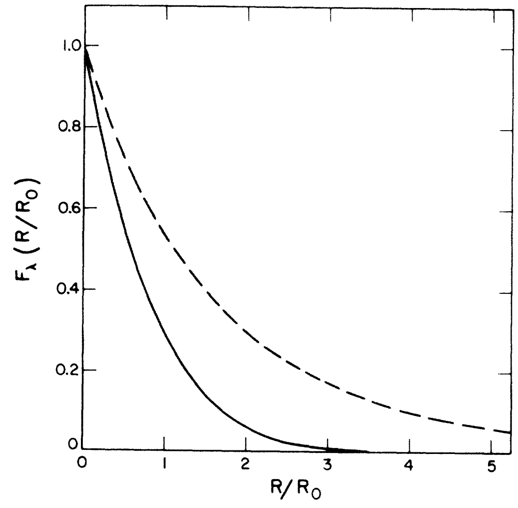

FIG. 3. The function F_λ in the boson wave function [Eq. (20)] for $r_s = 0.01a_0$ (solid curve) and $r_s = 100a_0$ (dashed curve).

$$W = \sum_n e^{-\beta E_n^0} \int \psi_n^* (\mathcal{H} - \mathcal{H}_n^0) \psi_n \, d\tau \Big/ \sum_n e^{-\beta E_n^0} . \tag{24b}$$

We take the $\{\psi_n\}$ to be Slater determinants of one-electron orbitals

$$\psi_n = (N!)^{-1/2} \sum_P (-)^P P[\varphi_{k1}(1)\varphi_{k2}(2) \cdots \varphi_{kN}(N)] , \tag{25}$$

where the sum is taken over all $N!$ permutations P of the electrons. The one-electron orbitals satisfy eigenvalue equations

$$h_{ki}(i)\varphi_{ki}(i) = \epsilon_{ki}(i)\varphi_{ki}(i) , \tag{26a}$$

$$h_{ki}(i) = -(\hbar^2/2m)\nabla_i^2 + v(i) + \omega_{ki}(i) , \tag{26b}$$

and the ω_{ki} are functions to be determined. The operator $\mathcal{H}_n^0$ of Eq. (23) is defined by

$$\mathcal{H}_n^0 \psi_n = (N!)^{-1/2} \sum_P (-)^P P \Big(\sum_i h_{ki}(i) \varphi_{k1}(1) \cdots \varphi_{kN}(N) \Big)$$

$$= \Big(\sum_i \epsilon_{ki} \Big) \psi_n . \tag{27}$$

Now we require that the $\{\psi_n\}$ be an orthonormal set of functions. From Eq. (26), we can show that, if

$$\int \varphi_l^* \omega_k \varphi_k \, d\tau = \int \varphi_k \omega_l^* \varphi_l^* \, d\tau , \tag{28}$$

then the one-electron orbitals $\{\varphi_k\}$ form an orthonormal set, and the $\{\psi_n\}$ are orthonormal. We will see that Eq. (28) is satisfied in our treatment.

Since we are dealing with N electrons, where we are interested in the limit as $N \to \infty$, we can use the formulas of Fermi-Dirac statistics.[19] We define

$$n_k(\beta) = (1 + e^{\alpha + \beta\epsilon_k})^{-1} , \tag{29a}$$

$$N = \sum_k n_k(\beta) . \tag{29b}$$

Then Eq. (24) becomes

$$Q \geq e^{-\beta W} e^{N\alpha} \prod_k (1 + e^{-\alpha - \beta\epsilon_k}) , \tag{30a}$$

$$W = -\sum_k n_k \int \varphi_k^* \omega_k \varphi_k \, d\tau + \frac{1}{2} \sum_k \sum_l n_k n_l \int [\varphi_k^*(1)\varphi_l^*(2) - \varphi_l^*(1)\varphi_k^*(2)] w(12) \varphi_k(1) \varphi_l(2) \, d\tau_1 \, d\tau_2 . \tag{30b}$$

An approximate expression for the Helmholtz free energy A is

$$A = -N\alpha\beta^{-1} + W - \beta^{-1} \sum_k \ln(1 + e^{-\alpha - \beta\epsilon_k}) . \tag{31}$$

We have omitted the inequality sign in Eq. (31), with the understanding that our expression for A is actually an upper limit to the true free energy. Now A is a functional of the quantities $\{\omega_k\}$. Hence our best approximation to the free energy is obtained by minimizing $A\{\omega_k\}$ with respect to all variations in the ω_k:

$$\delta A\{\omega_k\} = 0 . \tag{32}$$

After some manipulation, we find that

$$\omega_k(1) = \sum_l n_l \bigg[\int \varphi_l^*(2) w(12) \varphi_l(2) \, d\tau_2 - \frac{\varphi_l(1)}{\varphi_k(1)} \int \varphi_l^*(2) w(12) \varphi_k(2) \, d\tau_2 \bigg] . \tag{33}$$

Equation (33) is identical to the Coulomb-exchange potential obtained in the usual HF theory,[20] except that the contribution from each electronic state is weighted by its temperature-dependent probability of being occupied. Hence our theory takes into account the dependence of the density of states upon the change in population as the temperature is increased. We also observe that ω_k satisfies the condition imposed by Eq. (28), so that the one-electron orbitals are orthonormal.

As we noted previously, the procedure outlined above is unsatisfactory for the electron gas. In particular, the density of states at the Fermi level vanishes at zero temperature, leading to incorrect behavior for the specific heat.[21] These problems are eliminated when correlation is taken into account.

B. Correlation effects

A generalization of our method to include correlation effects begins with the following theorem:

$$Q = \sum_n \int \psi_n^* e^{-\beta\tilde{\mathcal{H}}} \psi_n \, d\tau . \tag{34}$$

Equation (34) is identical to Eq. (21), except that the true Hamiltonian $\mathcal{H}$ has been replaced by the pseudo-Hamiltonian $\tilde{\mathcal{H}}$, given by Eq. (17). It is interesting to note that Eq. (34) is exact.

To prove the theorem, we observe that

$$e^{-\beta\tilde{\mathcal{H}}} \Phi_n = e^{-\beta E_n} \Phi_n ,$$

$$\int \Phi_n^* \chi^2 \Phi_n \, d\tau = 1 \ ,$$

where the $\{\Phi_n\}$ are the *exact* eigenfunctions of $\tilde{\mathcal{H}}$, as specified by Eqs. (3) and (4). Hence the partition function is given by

$$Q = \sum_n \int \Phi_n^* \chi^2 e^{-\beta \tilde{\mathcal{H}}} \Phi_n \, d\tau \ . \tag{35}$$

Now expand the $\{\Phi_n\}$ in terms of the orthonormal functions. To simplify the form of the equations, we use Dirac notation $|k\rangle = \psi_k$;

$$\Phi_n = \sum_k |k\rangle A_{kn} \ . \tag{36}$$

From Eq. (4), we have

$$\sum_l \sum_k A_{lm}^* \langle l | \chi^2 | k \rangle A_{kn} = \delta_{mn} \ ,$$

$$\sum_l A_{lm}^* \langle l | \chi^2 | k \rangle = (A^{-1})_{mk} \ .$$

Substituting Eq. (36) into Eq. (35), we find

$$Q = \sum_{lmn} A_{ln}^* \langle l | \chi^2 e^{-\beta \tilde{\mathcal{H}}} | m \rangle A_{mn} \ ,$$

$$= \sum_{klmn} A_{ln}^* \langle l | \chi^2 | k \rangle \langle k | e^{-\beta \tilde{\mathcal{H}}} | m \rangle A_{mn} \ ,$$

$$= \sum_{kmn} (A^{-1})_{nk} \langle k | e^{-\beta \tilde{\mathcal{H}}} | m \rangle A_{mn} \ .$$

Since the trace of a matrix is invariant under a similarity transformation, Eq. (34) is proved.

By analogy to Eq. (24), we make the approximation

$$Q \approx e^{-\beta \tilde{W}} \sum_n e^{-\beta E_n^0} \ , \tag{37a}$$

$$\tilde{W} = \sum_n e^{-\beta E_n^0} \int \psi_n^* (\tilde{\mathcal{H}} - \mathcal{H}_n^0) \psi_n \, d\tau \Big/ \sum_n e^{-\beta E_n^0} \ . \tag{37b}$$

Since $\tilde{\mathcal{H}}$ is not a Hermitian operator, Eq. (37) is not an inequality. However, our approximate expression for Q does not have an upper limit. To see this fact, note that

$$\int \psi_n^* \mathcal{F} \psi_n \, d\tau = 0 \ ,$$

since $\mathcal{F}$ is anti-Hermitian, and all terms which involve $\mathcal{F}$ drop out of Eq. (37). Then Q is a lower bound to the partition function for a system having the Hamiltonian $\tilde{\mathcal{H}} - \mathcal{F}$;

$$\sum_n \int \psi_n^* e^{-\beta(\tilde{\mathcal{H}} - \mathcal{F})} \psi_n \, d\tau \geq e^{-\beta \tilde{W}} \sum_n e^{-\beta E_n^0} \ .$$

Because Q is bounded, we can proceed, as in Sec. IV A, to find an approximate expression for the free energy that is stationary with respect to variations in the one-electron orbitals. Since we do not have a bound to the true free-energy function, however, the validity of our approximation must be judged on pragmatic grounds.

C. The electron gas

In applying our method to the electron gas, we make the additional approximation of neglecting the contribution from the three-electron term E_{p3} in Eq. (17). In Sec. V we will show that this approximation is reasonable. Results for the electron gas are obtained from the equations of Sec. IV A.

From Eq. (33), we find that plane waves, multiplied by appropriate spin functions, are self-consistent solutions for the one-electron orbitals. The dependence of the energy levels on the wave vector $\vec{k}$ is given by

$$\epsilon_k = \hbar^2 k^2 / 2m + \omega_k \ , \tag{38}$$

where

$$\omega_k = -\frac{\hbar \omega_p}{N} \sum_{\vec{q} \neq \vec{k}} f_{|\vec{k} - \vec{q}|} (1 + e^{\alpha + \beta \epsilon_q})^{-1} \ , \tag{39a}$$

$$N = 2 \sum_{\vec{k}} (1 + e^{\alpha + \beta \epsilon_k})^{-1} \ . \tag{39b}$$

The free energy is found to be

$$A = -N\alpha\beta^{-1} + E_{p0} - 2\beta^{-1} \sum_{\vec{k}} \ln(1 + e^{-\alpha - \beta \epsilon_k})$$

$$- \sum_{\vec{k}} \omega_k (1 + e^{\alpha + \beta \epsilon_k})^{-1} \ . \tag{40}$$

The parameter α is related to the Fermi energy μ_F by $\alpha = -\beta\mu_F$. Equations (39) must be solved by iteration, until self-consistent values for α and ω_k are obtained for each temperature.

V. RESULTS

A. Ground state

We define reduced wavevectors $\vec{x} = \vec{k}/k_F$, where $k_F = (3\pi^2 N/V)^{1/3}$ is the wave vector of an electron at the Fermi level. At zero temperature, we obtain the following results. The energy levels (in Ry) are

$$\epsilon(x) = \mu_{F0} x^2 + \omega(x) \ , \tag{41a}$$

$$\omega(x) = -\frac{3\lambda^2}{2x} \int_0^1 y \, dy \int_{|x-y|}^{x+y} g_\lambda(Lz) z \, dz \ , \tag{41b}$$

where $L = a_0 k_F / \lambda$, and $\mu_{F0} = (9\pi/4)^{2/3} / (r_s/a_0)^2$ is the Fermi energy of the noninteracting electron gas. The ground-state energy E_0 is equal to the Helmholtz free energy:

$$E_0 = \tfrac{3}{5} \mu_{F0} + E_{p0} + \frac{3}{2} \int_0^1 \omega(x) x^2 \, dx \ , \tag{42}$$

in Ry/electron. It should be noted that Eq. (42) is the expectation value of the pseudo-Hamiltonian $\tilde{\mathcal{H}}$

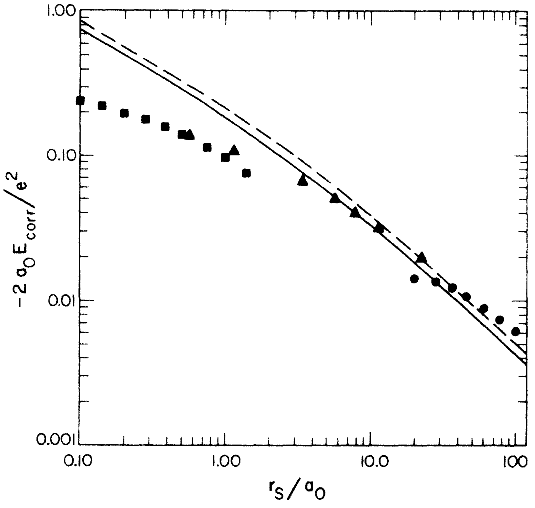

FIG. 4. Correlation energy: squares, Gell-Mann and Brueckner; triangles, Stevens and Pokrant; circles, Coldwell-Horsfall and Maradudin. The solid curve is obtained from Eq. (43). The dashed curve is the correlation energy when the three-body term is included.

(excluding the E_{p3} term) using a Slater determinant of plane-wave states. Hence our approximation to the ground-state energy is just a first-order perturbation approximation to Eq. (3).

The correlation energy is found to be

$$E_{\text{corr}} = E_{p0} + \frac{3}{2}\int_0^1 \omega(x)x^2\,dx + \frac{0.91633a_0}{r_s} . \tag{43}$$

The correlation energy is shown in Fig. 4, together with the exact high- and low-density expansions,[12,13] and the variational calculations of Stevens and Pokrant.[11] Upon first examination, the results are somewhat discouraging. Our calculation is good at low and intermediate densities, but the asymptotic behavior at high densities is incorrect. The error at low densities is owing entirely to our use of an approximate boson wave function, for the calculation in this limit would be exact, otherwise. Evidently, the error at high densities is due to our neglect of the anti-Hermitian operator $\mathfrak{F}$.

However, correlation is a very small contribution to the total energy for densities corresponding to $r_s < 1a_0$. Hence the results are more encouraging when we examine the total energy curve shown in Fig. 5. The dotted curve is the HF energy, and the solid curve is our calculation. The dashed curve was obtained by using the interpolation formula of Hedin-Lundqvist[22] for the correlation energy. Their expression, which is fit to the calculations of Singwi *et al.*,[23] gives slightly higher values of the correlation energy than those obtained by Stevens and Pokrant.[11] We estimate the dashed curve of Fig. 5 to have an uncertainty of about 5% in the energy near maximum binding. We observe that our calculation gives a very acceptable result in this region. The error is negligible at higher densities.

The additional contribution of the three-body term E_{p3} to the correlation energy is easy to calculate from first-order perturbation theory. The dashed line in Fig. 4 shows the result when this term is included. Since the correction is fairly small, we feel justified in neglecting it.

It might be thought that the correlation energy could be calculated more accurately by carrying the perturbation-theory solution of Eq. (3) to second order. We will discuss this problem very briefly. The second-order term from the operator $\mathfrak{F}$ is found to cancel the first-order contribution to the correlation energy, and we obtain

$$E_{\text{corr}} = -\sum_{n>0} \frac{|\langle 0|\Omega|n\rangle|^2}{E_n^0 - E_0^0} , \tag{44}$$

where $\Omega = \sum_{i>j} u(|x_i - x_j|) + E_{p3}$, and the sum is taken over all excited states. When this expression is evaluated, it is found that the correlation energy has the correct dependence on the density, but it is too small by roughly a factor of 2. We have not attempted a proof, but we believe that the perturbation solution of Eq. (3) gives the same divergent series as does Eq. (1), although the first diverging term does not appear until fourth order. Hence

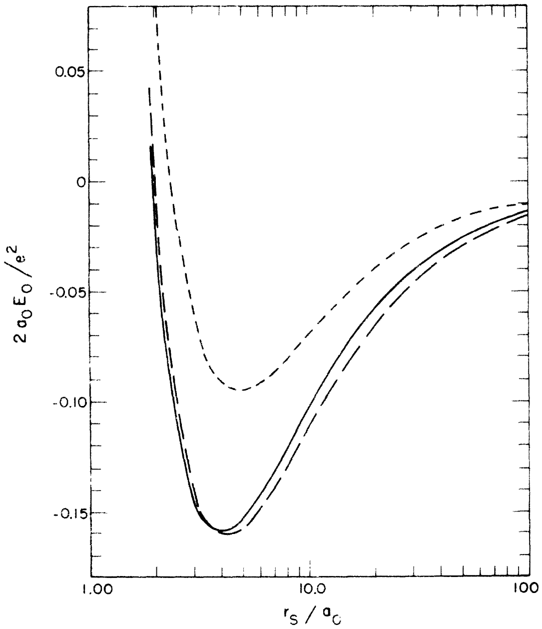

FIG. 5. Cohesive energy of the electron gas: dotted line, HF theory; solid line, Eq. (42); dashed line, Hedin-Lundqvist.

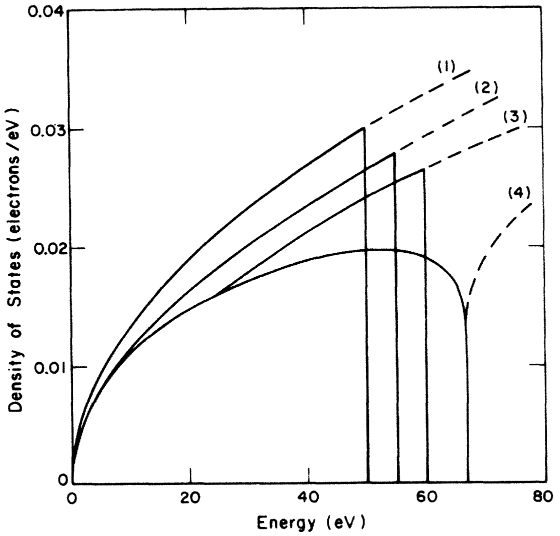

FIG. 6. Density of states for the electron gas at $r_s = 1a_0$: noninteracting gas (1); our calculation (2); BP theory (3); and HF theory (4).

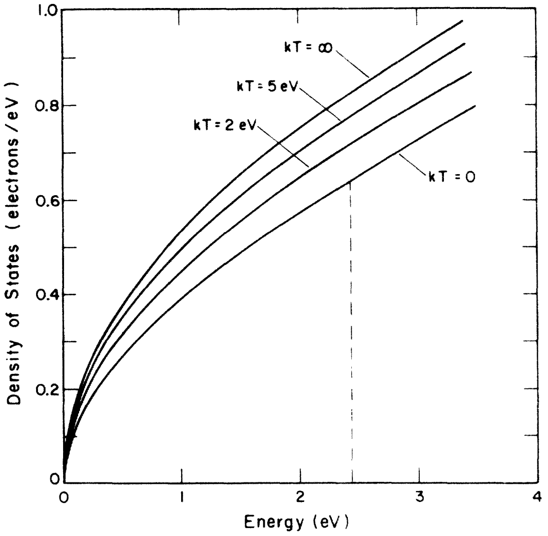

FIG. 8. Density of states as a function of temperature for $r_s = 5a_0$.

the prospects of going beyond our modified HF approach are not encouraging.

The density of states is defined by

$$n(\epsilon_k) = \frac{Vk^2}{N\pi^2}\left(\frac{d\epsilon_k}{dk}\right)^{-1} . \tag{45}$$

Our density-of-states curve for the electron gas at $r_s = 1a_0$ is shown in Fig. 6. Also shown are curves for the noninteracting gas, for the BP theory,[6] and for the HF theory.[21] As in the BP theory, we predict a larger band width and a lower density of states at the Fermi level than for the noninteracting gas. In our case, however, the correlation effects are not as great as those predicted by BP.

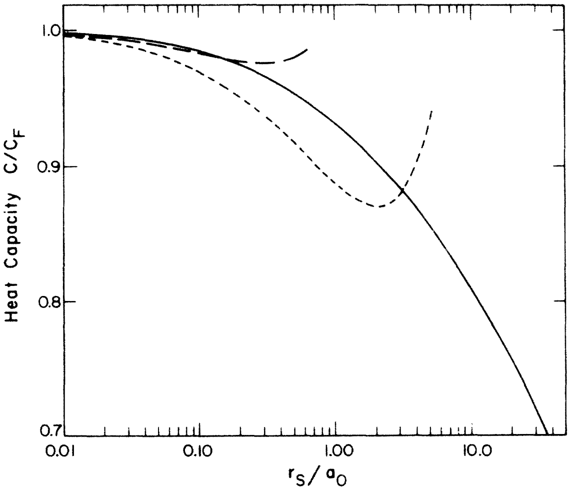

FIG. 7. Heat capacity for the electron gas: dashed line, Brueckner; solid line, our calculation; dotted line, Pines.

At low temperatures, the heat capacity is proportional to the density of states at the Fermi level. Figure 7 depicts the ratio of the heat capacity C to the heat capacity C_F of the noninteracting gas. We also show the exact high-density formula obtained by Gell-Mann,[24] and the result reported by Pines.[6] At high densities our calculation is in fairly good agreement with Gell-Mann's expression. This fact is encouraging, for it is at high densities where our prediction of the correlation energy is poorest. We expect our theory to be even better at low densities. Further discussion of the heat capacity is given in Sec. V B.

Pines[6] has compared the bandwidths predicted by the BP theory with x-ray-emission bands for several metals. His estimates, though much better than those obtained from the HF theory, are still larger than the experimental values. Our bandwidths differ only slightly from those of Pines, being smaller for $r_s < 4a_0$ and larger for $r_s > 4a_0$. In view of the uncertainty caused by the electron-lattice interaction, we have not repeated Pines's analysis.

B. Finite temperatures

We have solved Eqs. (38)–(40) for finite temperatures, using straightforward numerical techniques; only the results are discussed here.

One important feature of our theory is that we take temperature-dependent shifts in the band population into account. In Fig. 8, we show the dependence of the density of states on the temperature for $r_s = 5a_0$. For $kT < 1$ eV, the density of states is essentially unchanged from the zero-temperature result. Then the curve begins to rise with increasing temperature, until it is essentially the same as that of the noninteracting gas, for $kT > 10$ eV. The temperature at which the electrons become "free" decreases with decreasing density.

The dependence of the heat capacity on temperature is shown in Fig. 9, for $r_s = 100a_0$. Also shown are curves for the noninteracting gas and for the Debye law, using the Debye temperature of a Wigner crystal derived by Coldwell-Horsfall and Maradudin.[13] It is interesting to note that the heat capacity reaches a maximum at about 80 K, then decreases to the classical value $C_v = \frac{3}{2}Nk$, at higher temperatures. According to our calculations, the heat capacity at low temperatures does not follow the T^3 law of a crystal. This result may be a failure of our theory. However, the concept of a Wigner crystal implies that the electrons are localized about certain lattice points. Even so, electrons can move about by exchanging positions. It seems likely that there are many delocalized "liquid" states, which are only slightly more energetic than the crystalline ground state. Under these circumstances, the heat capacity should behave as our theory indicates.

To complete our study of the electron gas, we have calculated the Helmholtz free energy, the internal energy, and the pressure at several densities and temperatures. A sample of the results is shown in Fig. 10. Depicted there is the thermal contribution to the free energy (deviation from the ground state) as a function of temperature, for $r_s = 5a_0$. Also shown is the curve for the noninteracting gas. The effect of interaction is seen to be quite small. Similar results are obtained for the energy and the pressure.

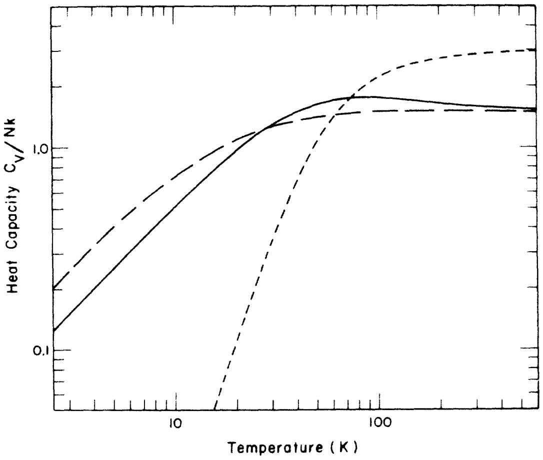

FIG. 9. Heat capacity as a function of temperature for $r_s = 100a_0$: dashed curve, noninteracting gas; solid curve, our calculation; dotted curve, Debye law for the Wigner crystal.

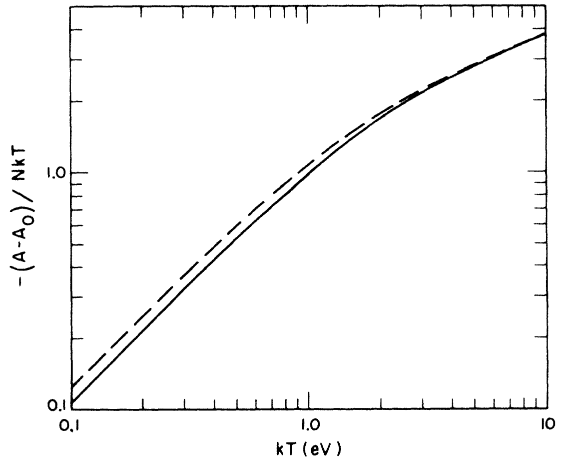

FIG. 10. Thermal contribution to the free energy as a function of temperature at $r_s = 5a_0$: solid curve, interacting electron gas; dashed curve, noninteracting gas.

VI. CONCLUSIONS

We have described a new approach for calculating the effects of electron correlation in metals. The method is based upon the derivation of a pseudo-Hamiltonian $\tilde{\mathcal{H}}$, which describes the motion of the electrons after the plasma oscillations have been taken into account. An exact expression for the partition function can be obtained by substituting this operator for the true Hamiltonian. Approximations to the ground-state energy and wave function of a charged boson gas, which are needed in the expression for $\tilde{\mathcal{H}}$, were also derived.

Perhaps the most serious objection to our work is that we have not solved for the eigenvalues and eigenfunctions of $\tilde{\mathcal{H}}$. The difficulty of such a task arises from the nonphysical and anti-Hermitian part of the operator. We have calculated the cohesive energy and thermodynamic properties by a self-consistent-field approximation that has the effect of dropping the anti-Hermitian term.

In spite of its deficiencies, we judge the theory to give satisfactory results for the electron gas. Extension of the technique to include the electron-lattice interaction in real metals is being studied.

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APPENDIX

Rewriting Eqs. (14) and (15), we obtain

$$g_\lambda(x)^2+x^2g_\lambda(x)-1-x^2P(x)/\pi\lambda=0\ , \tag{A1}$$

$$P(x)=\int_0^\infty g_\lambda(y)y\,dy\int_{-1}^1\frac{g_\lambda[(x^2+y^2-2xy\eta)^{1/2}]}{x^2+y^2-2xy\eta}\times(x\eta-y)\,d\eta\ , \tag{A2}$$

where $\lambda=3^{1/4}/(r_s/a_0)^{3/4}$. By a change of integration variables, Eq. (A2) can also be written

$$P(x)=x\int_0^\infty g_\lambda(xy)y^{-1}\,dy\int_{z_0}^{1+y}g_\lambda(xz)\times(1-y^2-z^2)z^{-1}\,dz\ , \tag{A3}$$

where $z_0=\max(y,1-y)$.

First consider the high-density limit of Eq. (A1). Assume that, as $\lambda\rightarrow\infty$, the term involving $P(x)$ can be ignored. Then Eq. (A1) reduces to a quadratic equation for $g_\lambda(x)$. Of the two possible solutions, we take

$$g_\lambda(x)\rightarrow(1+\tfrac{1}{4}x^4)^{1/2}-\tfrac{1}{2}x^2,\quad \lambda\rightarrow\infty\ . \tag{A4}$$

From Eq. (11), E_{p0} becomes

$$E_{p0}=-\frac{2\lambda}{\pi}\int_0^\infty g_\lambda(x)^2\,dx\ , \tag{A5}$$

and

$$E_{p0}\rightarrow-0.8031/(r_s/a_0)^{3/4},\quad r_s\rightarrow0 \tag{A6}$$

which agrees with the exact high-density result for the energy of the charged boson gas.[17] We also find that $P(x)$ is bounded as $\lambda\rightarrow\infty$, so that Eq. (A4) is indeed the correct high-density limit. According to Eq. (A4), we have $g_\lambda(x)\rightarrow1$ as $x\rightarrow0$, $g_\lambda(x)\rightarrow1/x^2$ as $x\rightarrow\infty$.

For finite densities, let us treat the term involving $P(x)$ as a perturbation. The solution of Eq. (A1) can be written

$$g_\lambda(x)=(1+\tfrac{1}{4}x^4+x^2P(x)/\pi\lambda)^{1/2}-\tfrac{1}{2}x^2\ . \tag{A7}$$

To solve for $g_\lambda(x)$, we guess the solution, calculate $P(x)$ from Eq. (A3), then recalculate $g_\lambda(x)$ from Eq. (A7). This procedure is continued until the solution is unchanged by further iteration. Using this method, we have solved Eq. (A1) over the range $0.01\leq r_s/a_0\leq100$.

Next we consider the asymptotic behavior of $g_\lambda(x)$ and $P(x)$. From Eq. (A2) we find that

$$P(x)\rightarrow-2\int_0^\infty g_\lambda(y)^2\,dy,\quad x\rightarrow0\ . \tag{A8}$$

Hence $g_\lambda(x)\rightarrow1$ as $x\rightarrow0$.

It is also possible to show that

$$P(x)\rightarrow C/x^4,\quad x\rightarrow\infty \tag{A9}$$

$$g_\lambda(x)\rightarrow1/x^2+C/\pi\lambda x^4,\quad x\rightarrow\infty\ . \tag{A10}$$

To prove this result, we first note that, if Eq. (A9) holds, then Eq. (A10) follows from Eq. (A7). To prove the converse, we note that, if Eq. (A10) holds, then Eq. (A3) gives

$$P(x)\rightarrow\frac{1}{x}\int_0^\infty g_\lambda(xy)w_2(y)y^{-1}\,dy+\frac{C}{\pi\lambda x^3}\int_0^\infty g_\lambda(xy)w_4(y)y^{-1}\,dy,\quad x\rightarrow\infty \tag{A11}$$

where

$$w_n(y)=\int_{z_0}^{1+y}(1-y^2-z^2)z^{-n-1}\,dz\ . \tag{A12}$$

It can be shown that the second term in Eq. (A11) is of order x^{-5} at most. We also find that

$$\int_0^\infty w_2(y)y^{-3}\,dy=0\ , \tag{A13}$$

$$w_2(y)\rightarrow\tfrac{4}{3}y^3,\quad y\rightarrow0\ . \tag{A14}$$

Hence

$$P(x)\rightarrow-\frac{4}{3x^4}\int_0^\infty[1-y^2g_\lambda(y)]\,dy+\frac{1}{x^3}\int_0^\infty[1-x^2y^2g_\lambda(xy)]\times\left(\frac{4}{3}-\frac{w_2(y)}{y^3}\right)dy,\quad x\rightarrow\infty\ . \tag{A15}$$

It can be shown that the second term in Eq. (A15) is of order x^{-5} at most. Hence Eq. (A9) is proved, and the constant C is given by

$$C=-\frac{4}{3}\int_0^\infty[1-x^2g_\lambda(x)]\,dx\ . \tag{A16}$$

Using Eq. (A1), we also have

$$C=-\frac{4}{3}\int_0^\infty g_\lambda(x)^2\,dx+\frac{4}{3\pi\lambda}\int_0^\infty x^2P(x)\,dx\ . \tag{A17}$$

By a limiting process similar to that used in Eqs. (A11)–(A16), it can be shown that

$$\int_0^\infty x^2P(x)\,dx=-\tfrac{1}{8}\pi^2\ . \tag{A18}$$

Hence we have

$$P(x)\rightarrow x^{-4}[\tfrac{2}{3}P(0)-\pi/6\lambda],\quad x\rightarrow\infty\ . \tag{A19}$$

Finally, we note that solutions to Eq. (A7) will not exist unless

$$P(x)\geq-\pi\lambda x^{-2}(1+\tfrac{1}{4}x^4) \tag{A20}$$

for all x. By explicit calculation, we found this condition to hold over the range of densities considered ($r_s\leq100a_0$). However, we have not been able to demonstrate that Eq. (A20) can be satisfied as $r_s\rightarrow\infty$.

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