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Method of Correlated Basis Functions for the Ground State of an Electron Gas

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The ground state of an electron gas is studied by means of the method of correlated basis functions developed by Wu and Feenberg. The optimum form of the Bijl-Dingle-Jastrow-type wave function of a charged-boson gas obtained with the application of the paired-phonon analysis is used as the correlation factor in a trial wave function describing the electron gas. Numerical results are given for the correlation energy per particle and the radial distribution function at metallic densities. The high-density limit of the system is briefly discussed.

I. INTRODUCTION

Considerable progress has been made recently in the development of quantum theory of interacting many-particle systems using a wide variety of techniques. In particular, the method of second quantization, quantum field theory, and Green's functions have been used quite extensively. The elegance of this approach lies in the fact that important physical properties can be evaluated without the need for dealing directly with the symmetrical or antisymmetrical wave function, which is rather cumbersome to find from the many-body Schrödinger equation. Yet, in the application of the field-theoretic techniques one is usually confronted with the problem of having to deal with unpleasant divergencies.

The many-body problem has also been approached from a substantially different direction by means of the method of correlated basis functions,[1-10] which does not lead to any divergencies and hence is well adopted to numerical evaluation even if the two-body potential is highly singular so that its Fourier transform does not exist in any form. For a fermion system the starting point of this procedure is the introduction of an antisymmetrical trial wave function[11]

$$\Psi_F = \Psi_B \Phi \ , \tag{1}$$

in which

$$\Phi = \mathrm{Det}[e^{i\vec{k}_i\cdot\vec{r}_j}\chi_i(\sigma_j)] \tag{2}$$

is a Slater determinant constructed from products of plane wave orbitals and spin functions, and the correlation factor Ψ_B is the ground-state boson-type solution of the Schrödinger equation[12]

$$H\Psi_B = E_0^B \Psi_B \ , \tag{3}$$

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i{}^2 + \sum_{i<j}^{N} v(r_{ij}) \ . \tag{4}$$

The description of the ground state of the fermion system in the representation of correlated basis functions is convenient in terms of the boson radial distribution function

$$g_B(r_{12}) = N(N-1)\rho^{-2}\int |\Psi_B|^2 d\vec{r}_{34\cdots N} \ , \tag{5}$$

or, equivalently, the boson liquid structure function

$$S(k) = 1 + \rho \int [g_B(r) - 1]\, e^{i\vec{k}\cdot\vec{r}} d\vec{r} \ , \tag{6}$$

where $\rho = N/\Omega$ is the particle number density. Using a cluster-expansion technique Wu and Feenberg (WF) have evaluated diagonal matrix elements of the identity and the Hamiltonian operator, obtaining the ground-state energy given by

$$E_0^F = E_0^B + E_{01}^F + E_{02}^F + E_{03}^F \ , \tag{7a}$$

$$E_{01}^F = \tfrac{3}{5} N e_F \ , \tag{7b}$$

$$E_{02}^F = -24 N e_F \int_0^1 [1 - S(2k_F x)](1 - \tfrac{3}{2}x + \tfrac{1}{2}x^3)x^4 dx \ , \tag{7c}$$

$$E_{03}^F = -(3/8\pi)^3 N e_F \int_{|x_i|<1} x_{12}^2 S(k_F x_{12}) \times [1 - S(k_F x_{13})][1 - S(k_F x_{23})] d\vec{x}_1 d\vec{x}_2 d\vec{x}_3 \ , \tag{7d}$$

in which E_0^B is the ground-state energy of the boson system and

$$k_F = (3\pi^2\rho)^{1/3}, \quad e_F = \hbar^2 k_F^2/2m \ . \tag{7e}$$

The formula for the fermion radial distribution function based on a similar cluster expansion is

$$\begin{aligned} g_F(r_{12}) = g_B(r_{12})\{1 &- \tfrac{1}{2}h^2(k_F r_{12}) \\ &- \rho\int [g_B(r_{13}) - 1] g_B(r_{23}) h^2(k_F r_{23}) d\vec{r}_3 \\ &+ \tfrac{1}{2}\rho h(k_F r_{12}) \int [g_B(r_{13}) - 1] h(k_F r_{13}) \\ &\times g_B(r_{23}) h(k_F r_{23}) d\vec{r}_3 + \cdots\} \ , \end{aligned} \tag{8}$$

with

$$h(x) = 3(\sin x - x\cos x)/x^3 \ .$$

Corrections to the results of Eqs. (7) and (8) arising from nondiagonal matrix elements are discussed in Refs. 1, 4, and 5.

Applications of the WF formalism to the ground state of liquid ^{3}He have given results in semiquantitative agreement with experimental values.[5,6] However, the method has not yet been tested in the case of the electron gas. The purpose of this paper is to investigate the ground state of the electron gas using the WF theory. The problem of estimating contributions from nondiagonal matrix elements is reserved for a later paper.

II. NUMERICAL RESULTS AT INTERMEDIATE DENSITIES

At the present time no exact form is available for the boson radial distribution function $g_B(r)$ or the liquid structure function $S(k)$, which contains almost all of the correlation effects of the system (except, of course, the statistical effects). There are, however, some approximate forms considered in variational studies of the charged boson gas[13–15]; in particular, the trial function introduced in Ref. 14 has the form

$$g_B(r) = 1 - \alpha[1 - \gamma(r/b)^p]e^{-(r/b)^p} , \tag{9}$$

where α, γ, and ρ are variational parameters and b is the scale parameter determined by the normalization condition

$$\rho \int [1 - g_B(r)] d\vec{r} = 1 . \tag{10}$$

Quite recently this form has been improved[16] using the paired-phonon analysis[17,18] for optimization of the approximate variational description in the Bijl-Dingle-Jastrow (BDJ) function space.[19] In the present study of the electron gas, we use these improved (optimum) functions $S(k)$ and $g_B(r)$ to evaluate E_0^F and $g_F(r)$. The calculation in Ref. 16 shows that the leading corrections to the optimum energies, which come from three-phonon components,[20] are very small except at very low densities where charged particles crystalize. Therefore, we believe that the use of the optimum $S(k)$ and $g_B(r)$ in Eqs. (7) and (8) is meaningful. Some plots of the optimum $S(k)$ taken from Ref. 16 are shown in Fig. 1 at $r_s = 1$, 3, and 6; here the mean particle separation $r_s = (3/4\pi\rho)^{1/3}$ is given in units of Bohr radius $a_0 = \hbar^2/me^2$.

The form of the integral for E_{03}^F of Eq. (7d) does not seem to be suitable for numerical integration. A more convenient form can be derived first by expanding the functions of the integrand in terms of Legendre polynomials and then by carrying out the angular integrations using the orthogonality properties of the polynomials. The resulting expression is

$$E_{03}^F = -(\tfrac{3}{4})^3 N e_F \sum_{n=0}^{\infty} (2n+1) \int_0^1 dx_1 \int_0^1 dx_2 \int_0^1 dx_3$$

$$\times\, x_1^2 x_2^2 x_3^2\, a_n(x_1, x_2) b_n(x_1, x_3) b_n(x_2, x_3) , \tag{11a}$$

where

$$a_n(x_i, x_j) = (1/x_i x_j) \int_{|x_i - x_j|}^{x_i + x_j} S(k_F \xi) P_n(\cos\theta_{ij}) \xi^3 d\xi ,$$

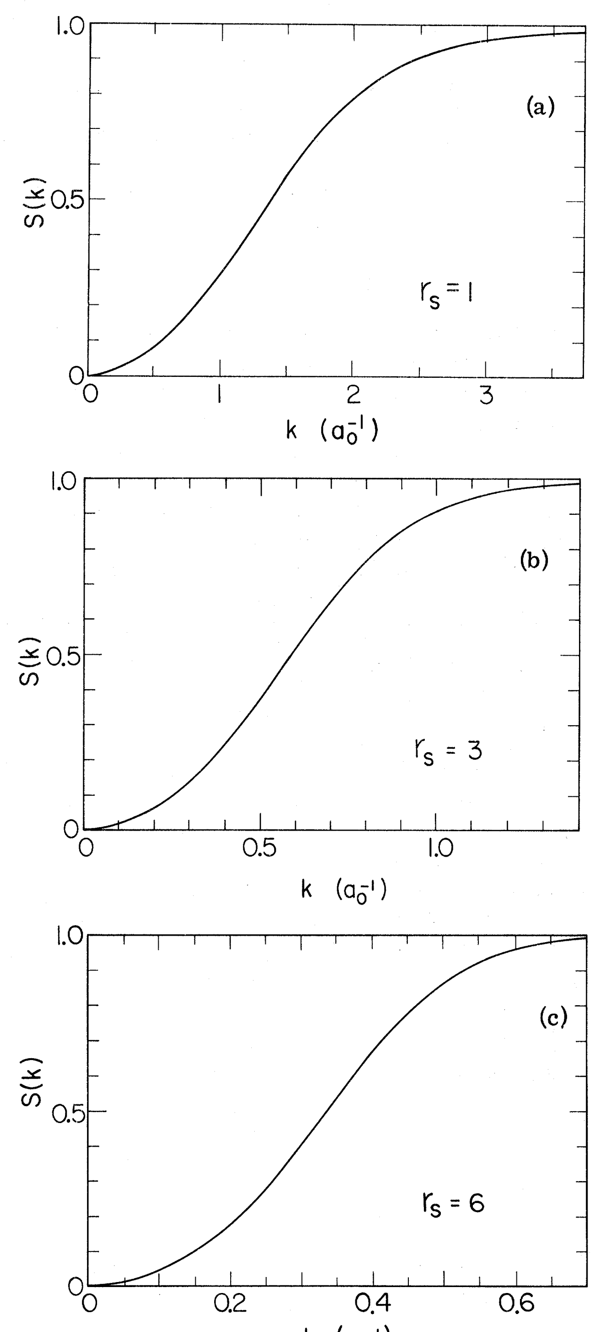

FIG. 1. Liquid structure functions of the charged-boson gas. (a) $r_s = 1$; (b) $r_s = 3$; (c) $r_s = 6$. These results, obtained in Ref. 16, are used in Eqs. (7) and (8) to evaluate the ground-state energies (Table I) and the radial distribution functions (Fig. 2) of the electron gas.

TABLE I. Ground-state energies per particle. E_0^B is the ground-state energy of the charged-boson gas. E_{01}^F, E_{02}^F, E_{03}^F, and E_0^F are given by Eqs. (7) and the correlation energy $E_{\rm corr}$ is defined by Eq. (12). Energies and the mean particle distance r_s are given in atomic units.

	Ref. 16	Wu-Feenberg theory					Ref. 22	Hubbard	RPA
r_s	E_0^B/N	E_{01}^F/N	E_{02}^F/N	E_{03}^F/N	E_0^F/N	$E_{\rm corr}/N$	$E_{\rm corr}/N$	$E_{\rm corr}/N$	$E_{\rm corr}/N$
1	−0.7758	2.2099	−0.1749	−0.0309	1.2283	−0.0650	−0.124	−0.131	−0.1578
2	−0.4509	0.5525	−0.0619	−0.0121	0.0278	−0.0667	−0.092	−0.102	−0.1238
3	−0.3264	0.2455	−0.0328	−0.0066	−0.1203	−0.0604	−0.075	−0.086	−0.1058
4	−0.2586	0.1381	−0.0207	−0.0042	−0.1454	−0.0545	−0.064	−0.076	−0.0938
5	−0.2154	0.0884	−0.0144	−0.0029	−0.1443	−0.0494	−0.056	−0.069	−0.0851
6	−0.1853	0.0614	−0.0106	−0.0022	−0.1367	−0.0454	−0.050	−0.064	−0.0784
7	−0.1629	0.0451	−0.0082	−0.0017	−0.1277	−0.0419			−0.0730
8	−0.1456	0.0345	−0.0065	−0.0013	−0.1189	−0.0389			−0.0685
9	−0.1318	0.0273	−0.0054	−0.0011	−0.1109	−0.0364			−0.0647
10	−0.1205	0.0221	−0.0045	−0.0009	−0.1037	−0.0342	−0.036		−0.0615
20	−0.0660	0.0055	−0.0013	−0.0003	−0.0621	−0.0218	−0.022		

$$b_n(x_i, x_j) = (1/x_i x_j)\int_{|x_i-x_j|}^{x_i+x_j}[1-S(k_F\xi)]P_n(\cos\theta_{ij})\,\xi\,d\xi\,, \qquad (11b)$$

$$\cos\theta_{ij} = (x_i^2 + x_j^2 - \xi^2)/2x_i x_j\,.$$

The same type of numerical procedure has been used in the evaluation of virial coefficients in statistical mechanics of classical fluids in equilibrium.[21] Since the method also appears to be useful in various problems of quantum-mechanical many particle systems, we outline the derivation of Eq. (11) in the Appendix.

To examine the convergence of the series of Eq. (11), we write the sum as

$$E_{03}^F = N\sum_{n=0}^{\infty} W_n\,.$$

At the representative density $r_s = 3$ the numerical calculation yields $W_0 = -7.70\times10^{-3}$, $W_1 = 1.08\times10^{-3}$, $W_2 = -6.06\times10^{-6}$, $W_3 = -3.40\times10^{-8}$, and $W_4 = -1.43\times10^{-9}$, in units of Ry $(me^4/2\hbar^2)$. (Henceforth the atomic units a_0 and Ry will be used without further remarks.) The behavior of convergence of the series at other densities in the range $1 \leqslant r_s \leqslant 20$ is very similar to that at $r_s = 3$. Thus, the nearly entire contribution (more than 99%) of E_{03}^F comes from the first two terms W_0 and W_1, indicating that the convergence is quite rapid. Our numerical results for various energy terms evaluated using the WF theory are summarized in Table I and compared with earlier results obtained with different approximation methods based on the dielectric formulations.[22–24] (Here again the mean particle separation r_s and energies are given in atomic units.) In the table E_0^B/N is the boson ground-state energy per particle [Eq. (3)] obtained in Ref. 16 by means of the paired-phonon analysis,[17,18] which optimizes the BDJ-type description of the ground state. The Fermi energy per particle

$$E_{01}^F/N = \tfrac{3}{5}(\tfrac{9}{4}\pi)^{2/3}(1/r_s^2)$$

is given by Eqs. (7b) and (7e). The quantities E_{02}^F/N and E_{03}^F/N have been evaluated numerically from Eqs. (7c) and (11) with estimated errors less than 0.05% and 0.3%, respectively; for the function $S(k)$ appearing in Eqs. (7c) and (11) we have used the numerical results of the optimum liquid structure function obtained in Ref. 16. E_0^F/N given by Eq. (7a) is the ground-state energy per particle, which does not include contributions from nondiagonal matrix elements. Values of the correlation energy per particle defined by

$$E_{\rm corr}/N = E_0^F/N - E_{\rm HF}/N\,, \qquad (12)$$

with the Hartree-Fock energy per particle

$$\frac{E_{\rm HF}}{N} = \frac{E_{01}^F}{N} - \frac{3}{2\pi}\left(\frac{9\pi}{4}\right)^{1/3}\frac{1}{r_s}\,, \qquad (13)$$

are listed in Table I for comparison with the corresponding values obtained by Singwi *et al.*[22] and also with those resulting from the random phase approximation (RPA)[23] and from the Hubbard approximation.[24,25] From Table I, we find that the WF formalism gives energies higher than those obtained using different techniques. Here we may point out that the actual differences in total energy E_0^F/N are rather small although the corresponding correlation energies differ considerably. At $r_s = 1$, for example, the Hubbard correlation energy is about twice that evaluated with the WF theory, while the difference in total energy is less than 6%. Also we observe that the numerical results for E_{01}^F, E_{02}^F, and E_{03}^F do not show any indication that the WF expansion (7) will not converge. It is interesting to note that the relation

$$E_{03}^F = \tfrac{1}{5}E_{02}^F \qquad (14)$$

is nearly satisfied at all densities in the range $2 \leq r_s \leq 20$.

Using the boson radial distribution function $g_B(r)$ obtained from the optimum boson $S(k)$ through the inverse Fourier transform of Eq. (16), we have also evaluated the fermion radial distribution function $g_F(r)$ numerically from Eq. (8); our results for $r_s = 1$, 3, and 6 are plotted in Fig. 2 against $k_F r$, where the Fermi momentum k_F is given by Eq. (7e). In the figure curve A represents $g_F(r)$ found in the present calculation [Eq. (8)] based on the WF theory, and curve B is the result obtained by Singwi *et al.* using an improved dielectric-function formalism. Curves C and D are those resulting from RPA and the Hubbard approximation, respectively. We may remark here that an important feature of the WF theory is the fact that it never yields negative values of $g_F(r)$ at any distance r and at any density ρ, while other theories previously studied (including those of Refs. 22–24) lead to negative values of $g_F(r)$ for small values of r at all or some values of r_s in the range of metallic densities.

It must be mentioned that examination of Table I and Fig. 2 reveals an interesting fact that of the three calculations[22–24] with which our results are compared for E_{corr}/N and $g_F(r)$, that of Singwi *et al.*[22] disagrees least. It is surely significant in the sense that the calculation of Ref. 22 is apparently most accurate of the three since it attempts to remedy some of the deficiencies (in particular, overestimation of the short-range correlation) of the two earlier treatments.[23,24] Another point calling for explicit notice is that the leading correction to E_0^F/N due to contribution from nondiagonal matrix elements is a negative quantity and hence (if not too large) it will reduce the discrepancy between the correlation energy of the present calculation and that of Singwi *et al.*

We conclude this section with a brief discussion of earlier variational treatments of the electron-gas problem which are, one way or another, related to the WF method used in the present study. It may be pointed out here that if the boson-type solution Ψ_B is approximated by the BDJ-type wave function

$$\Psi_B = \exp\left(\frac{1}{2} \sum_{i<j}^{N} u(r_{ij})\right), \tag{15}$$

the trial wave function (1) becomes in the collective coordinate representation

$$\Psi_F = \Phi \exp\left[\tfrac{1}{4} N^{-1} \textstyle\sum_{\vec{k}} C(k)\left(\rho_{\vec{k}}\rho_{-\vec{k}} - N\right)\right], \tag{16}$$

where

$$\rho_{\vec{k}} = \sum_{j=1}^{N} e^{i\vec{k}\cdot\vec{r}_j}, \tag{17}$$

$$C(k) = \rho \int e^{i\vec{k}\cdot\vec{r}} u(r)\, d\vec{r}\,. \tag{18}$$

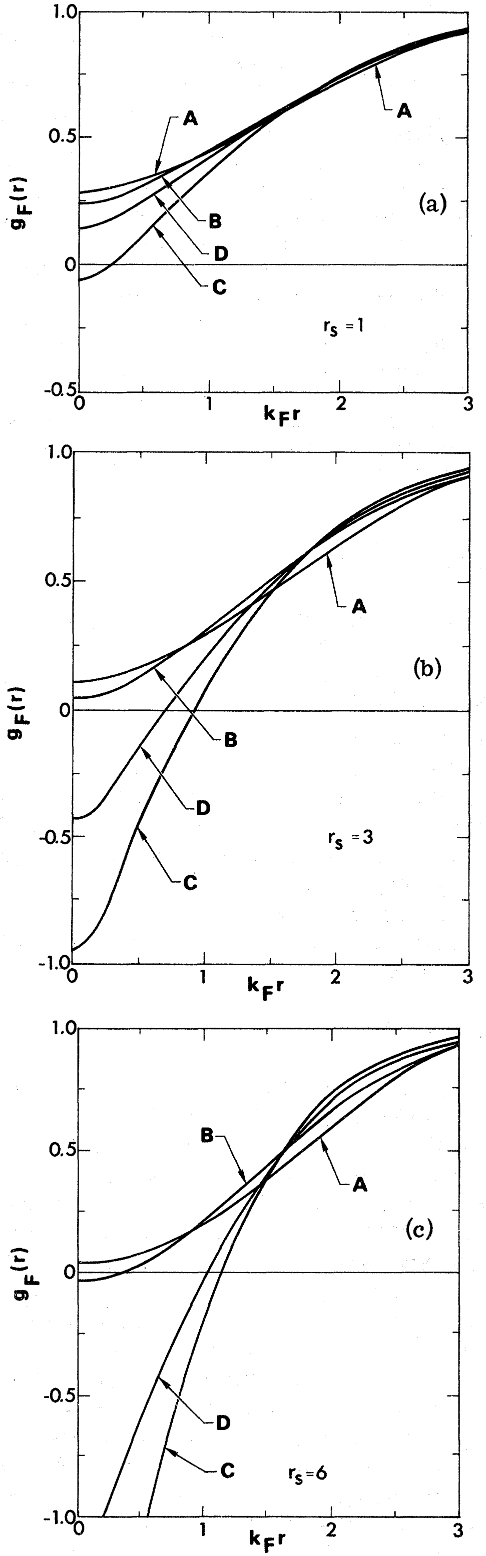

FIG. 2. Radial distribution functions of the electron gas. (a) $r_s = 1$; (b) $r_s = 3$; (c) $r_s = 6$. Lines A are obtained in the present calculation from Eq. (8) and lines B are results of Singwi *et al.* Lines C and D result from RPA and the Hubbard approximation, respectively.

The form of Eq. (16) was used earlier by Edwards,[26] who determined the function $C(k)$ by solving the Schrödinger equation approximately. Later Gaskell[27,28] derived $C(k)$ in a variational calculation which includes effects omitted in the RPA; his results for E_{corr}/N for $2 \leq r_s \leq 5$ agree closely with Hubbard's values listed in Table I, and the corresponding radial distribution function $g(r)$ obtained at $r_s = 2.66$ remains positive definite at all values of r. An interesting variational study was also made by Edwards and Hillel,[29] who, using the determinantal states, examined the possibility of crystalization and magnetic ordering of the electron gas; they introduced the radial distribution function $g(r)$ into the interaction energy between electrons of antiparallel spin, which is neglected in the Hartree-Fock approximation. While the above methods[26-29] make explicit use of the collective variables, Broyles *et al.*[30,31] have developed a useful scheme for approximating the Slater determinant Φ of Eq. (2) by the form of a Boltzmann factor to apply the method of calculating the classical radial distribution function when the ground state is described by the trial wave function of Eq. (1) with Ψ_B given by Eq. (15). Their variational method involves the RPA at high density and the superposition approximation for the three-particle distribution function at metallic densities. We remark finally that our calculation of E_0^F/N and $g(r)$ is an indirect variational treatment in the sense that the unknown function $u(r)$ contained in Ψ_B is determined by minimizing $\langle \Psi_B | H | \Psi_B \rangle$ rather than $\langle \Psi_F | H | \Psi_F \rangle$.

III. HIGH-DENSITY LIMIT

The exact form of the optimum liquid structure function of the charged-boson gas at high density is given by[13,32,33]

$$
\begin{aligned}
S(k) &= \sum_{n=0}^{\infty} S_n(k) , \\
S_0(k) &= (1 + 16\pi e^2 m\rho/\hbar^2 k^2)^{-1/2} , \\
S_1(k) &= \frac{S_0^3(k)}{2(2\pi)^2 \rho} \int \left(\frac{1}{2} + \frac{k'^2}{k^2} \right) [1 - S_0(k')] \\
&\qquad \times [1 - S_0(\vec{k} - \vec{k}')] d\vec{k}' ,
\end{aligned}
\tag{19}
$$

and the exact ground-state energy per particle is[13,34]

$$E_0^B/N = -0.8031/r_s^{3/4} + 0.02749 + O(r_s^{3/4}). \tag{20}$$

Here the leading term of E_0^B/N is obtained from $S(k)$ of Eq. (19), but only a part of the second constant term arises from the variational calculation in the BDJ function space, the remainder being accounted for by the second-order perturbation correction generated by the three-phonon components.[20]

Substitution of Eqs. (19) and (20) into Eq. (7) yields, after some algebra, the ground-state energy per particle in the form

$$E_0^F/N = E_{\text{HF}}/N + A/r_s^{3/4} + B/r_s^{1/2} + \cdots , \tag{21}$$

where A and B are constants. Thus, we find that the Hartree-Fock energy per particle given by Eq. (13) is reproduced exactly by the WF theory, but it fails to give the correct correlation energy since the exact result for the correlation energy[35] does not contain terms of $O(r_s^{-3/4})$ and $O(r_s^{-1/2})$. In a similar way, the value of the radial distribution function at the origin can be determined from Eq. (8) by using Eq. (19). The resulting expression is of the form

$$g_F(0) = \tfrac{1}{2} + C r_s^{3/4} + D r_s \ln r_s + \cdots , \tag{22}$$

C and D being constants. This result agrees only in the lowest order with Wadati and Isihara's formula,[36] which gives a second lowest-order term of $O(r_s)$.

It would be instructive to note that there are at least two approximations involved in obtaining the results for E_0^F/N and $g_F(0)$ given by Eqs. (21) and (22). First, as we have already pointed out, the contribution from nondiagonal matrix elements is not included in the energy formula given by Eq. (7). This contribution accounts for about 24% of the total ground-state energy in the case of liquid ^{4}He at equilibrium density.[5] Thus, it appears that inclusion of the nondiagonal effects can improve the accuracy of the second-order energy term in the problem of the electron gas. The second approximation is related to the fact that $S(k)$ given by Eq. (19) is not exact [except the leading term $S_0(k)$] since it is generated by the BDJ type of variational wave function, which is not general enough to represent the exact solution of the Schrödinger equation (3). Therefore, the failure of the present calculation to yield the correct correlation energy may be partially due to the use of the optimum form in place of the exact form for the boson liquid structure function $S(k)$. No progress has yet been reported to date in the evaluation of the exact correction term to $S(k)$ of Eq. (19) arising from the three-phonon vertex. Further investigation is planned for clarification of the precise source(s) of the discrepancy between our results based on the WF formalism and those obtained previously with different methods[35,36] for E_0^F/N and $g_F(0)$ at high density.

ACKNOWLEDGMENT

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APPENDIX: DERIVATION OF EQS. (11)

The integral for E_{03}^F given by Eq. (7d) is of the form

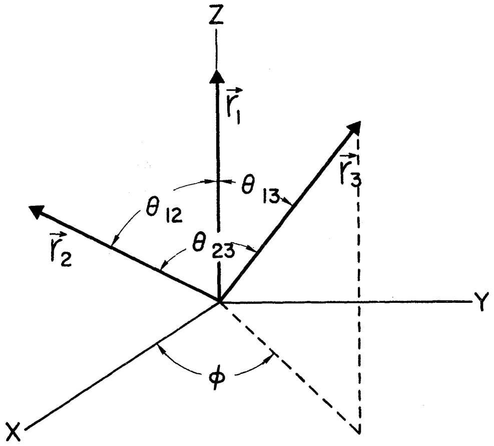

FIG. 3. Vectors $\vec{r}_1$, $\vec{r}_2$, and $\vec{r}_3$.

$$I = \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 f(r_{12}) g(r_{13}) h(r_{23}) \,, \tag{A1}$$

in which the three-dimensional variables of integration $\vec{r}_1$, $\vec{r}_2$, and $\vec{r}_3$ range over a unit sphere. If the integration is performed over variables $\vec{r}_3$, $\vec{r}_2$, and $\vec{r}_1$ in this order, we can, without loss of generality, choose Cartesian coordinates in such a way that $\vec{r}_1$ is along the z axis, $\vec{r}_2$ is on the x-z plane, and $\vec{r}_3$ is in the x-y-z space as shown in Fig. 3, with their volume elements given by

$$\begin{aligned} d\vec{r}_1 &= 4\pi r_1^2 dr_1 \,, \\ d\vec{r}_2 &= 2\pi r_2^2 dr_2 \sin\theta_{12} d\theta_{12} \,, \\ d\vec{r}_3 &= r_3^2 dr_3 \sin\theta_{13} d\theta_{13} d\phi \,. \end{aligned} \tag{A2}$$

Thus Eq. (A1) may be written as

$$\begin{aligned} I = {} & 8\pi^2 \int_0^1 dr_1 r_1^2 \int_0^1 dr_2 r_2^2 \int_0^1 dr_3 r_3^2 \int_0^\pi d\theta_{12} \sin\theta_{12} \\ & \times \int_0^\pi d\theta_{13} \sin\theta_{13} \int_0^{2\pi} d\phi f(r_{12}) g(r_{13}) h(r_{23}) \,. \end{aligned} \tag{A3}$$

Expanding the functions of the integrand in terms of Legendre polynomials, we have

$$\begin{aligned} f(r_{12}) &= \frac{1}{2} \sum_{l=0}^{\infty} (2l+1) a_l(r_1, r_2) P_l(\cos\theta_{12}) \,, \\ g(r_{13}) &= \frac{1}{2} \sum_{m=0}^{\infty} (2m+1) b_m(r_1, r_3) P_m(\cos\theta_{13}), \\ h(r_{23}) &= \frac{1}{2} \sum_{n=0}^{\infty} (2n+1) c_n(r_2, r_3) P_n(\cos\theta_{23}) \,, \end{aligned} \tag{A4}$$

where

$$\begin{aligned} r_{ij}^2 &= r_i^2 + r_j^2 - 2 r_i r_j \cos\theta_{ij} \,, \\ a_l(r_1, r_2) &= \int_0^\pi f(r_{12}) P_l(\cos\theta_{12}) \sin\theta_{12} d\theta_{12} \,, \\ b_m(r_1, r_3) &= \int_0^\pi g(r_{13}) P_m(\cos\theta_{13}) \sin\theta_{13} d\theta_{13} \,, \\ c_n(r_2, r_3) &= \int_0^\pi h(r_{23}) P_n(\cos\theta_{23}) \sin\theta_{23} d\theta_{23} \,, \end{aligned} \tag{A5}$$

and $p_l(\cos\theta)$ is the Legendre polynomial with the well-known property

$$\int_0^\pi P_l(\cos\theta) P_m(\cos\theta) \sin\theta d\theta = [2/(2l+1)] \delta_{lm} \,. \tag{A6}$$

Equation (A3) then becomes

$$\begin{aligned} I = {} & \pi^2 \sum_{l,m,n=0}^{\infty} (2l+1)(2m+1)(2n+1) \int_0^1 dr_1 \int_0^1 dr_2 \\ & \times \int_0^1 dr_3 r_1^2 r_2^2 r_3^2 a_l(r_1, r_2) b_m(r_1, r_3) c_n(r_2, r_3) \\ & \times \int_{-1}^1 d\mu_{12} \int_{-1}^1 d\mu_{13} \int_0^{2\pi} d\phi P_l(\mu_{12}) P_m(\mu_{13}) P_n(\mu_{23}) \,. \end{aligned} \tag{A7}$$

While $P_l(\mu_{12})$ and $P_m(\mu_{13})$ do not depend on ϕ, $P_n(\mu_{23})$ does depend on ϕ through

$$\begin{aligned} P_n(\mu_{23}) = {} & P_n(\mu_{12}) P_n(\mu_{13}) + 2 \sum_{k=1}^{\infty} \frac{(n-k)!}{(n+k)!} \\ & \times P_n^k(\mu_{12}) P_n^k(\mu_{13}) \cos(k\phi). \end{aligned} \tag{A8}$$

But, since

$$\int_0^{2\pi} \cos(k\phi) d\phi = 0, \quad k = 1, 2, \cdots$$

the ϕ integration reduces to

$$\int_0^{2\pi} d\phi P_n(\mu_{23}) = 2\pi P_n(\mu_{12}) P_n(\mu_{13}) \,. \tag{A9}$$

Consequently, we have

$$\begin{aligned} I = {} & 2\pi^3 \sum_{l,m,n=0}^{\infty} (2l+1)(2m+1)(2n+1) \int_0^1 dr_1 \int_0^1 dr_2 \\ & \times \int_0^1 dr_3 r_1^2 r_2^2 r_3^2 a_l(r_1, r_2) b_m(r_1, r_3) c_n(r_2, r_3) \\ & \times \int_{-1}^1 d\mu_{12} P_l(\mu_{12}) P_n(\mu_{12}) \int_{-1}^1 d\mu_{13} P_m(\mu_{13}) P_n(\mu_{13}) \,, \end{aligned}$$

and by Eq. (A6) we obtain finally

$$\begin{aligned} I = {} & (2\pi)^3 \sum_{n=0}^{\infty} (2n+1) \int_0^1 dr_1 \int_0^1 dr_2 \int_0^1 dr_3 r_1^2 r_2^2 r_3^2 \\ & \times a_n(r_1, r_2) b_n(r_1, r_3) c_n(r_2, r_3), \end{aligned} \tag{A10}$$

completing the desired derivation of Eqs. (11).

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[1] E. Feenberg, *Theory of Quantum Fluids* (Academic, New York, 1969).

[2] F. Y. Wu and E. Feenberg, Phys. Rev. 128, 943 (1962).

[3] F. Y. Wu, J. Math. Phys. 4, 1438 (1963).

[4] E. Feenberg and C. W. Woo, Phys. Rev. 137, A391 (1965).

[5] C. W. Woo, Phys. Rev. 151, 138 (1966).

[6] D. Schiff and L. Verlet, Phys. 160, 208 (1967).

[7] F. Iwamoto and M. Yamada, Progr. Theoret. Phys. (Kyoto) 17, 543 (1957); 18, 345 (1957).

[8] J. B. Aviles, Ann. Phys. (N. Y.) 5, 251 (1958).

[9] C. D. Hartogh and H. A. Tolhock, Physica 24, 721 (1958); 24, 875 (1958); 24, 896 (1958).

[10] J. W. Clark and P. Westhaus, Phys. Rev. 141, 833 (1966).

[11] We present here only a brief outline of the formalism. For further details we refer the reader to Refs. 1 and 2.

[12] In Ref. 6 the correlation factor Ψ_B is taken to be a Bijl-Dingle-Jastrow type of variational function, which is determined by minimizing $\langle H \rangle$ evaluated with Eq. (1).

[13] D. K. Lee and E. Feenberg, Phys. Rev. 137, A731 (1965).

[14] D. K. Lee, Phys. Rev. A 2, 278 (1968).

[15] Reference 1, Appendix 1 B.

[16] D. K. Lee and F. H. Ree, Phys. Rev. A 5, 814 (1972).

[17] H. W. Jackson and E. Feenberg, Ann. Phys. (N. Y.) 15, 266 (1961).

[18] C. E. Campbell and E. Feenberg, Phys. Rev. 188, 396 (1969).

[19] The optimization procedure carried out in Ref. 16 is not exact since the hypernetted chain approximation is used. However, the errors involved are believed to be small in the case of the charged-boson gas (Ref. 14), although the situation appears to be somewhat different in the problem of liquid ^{4}He.

[20] T. B. Davison and E. Feenberg, Ann. Phys. (N. Y.) 53, 559 (1969).

[21] J. A. Barker and J. J. Monaghan, J. Chem. Phys. 36, 2564 (1962); D. Henderson and L. Oden, Mol. Phys. 10, 405 (1966).

[22] K. S. Singwi, M. P. Tosi, R. H. Land, and A. Sjolander, Phys. Rev. 176, 589 (1968).

[23] D. Bohm and D. Pines, Phys. Rev. 92, 609 (1953).

[24] J. Hubbard, Proc. Roy. Soc. (London) A243, 336 (1957).

[25] Numerical values of E_{corr}/N listed in Table I under "Hubbard" and "RPA" are taken, respectively, from Ref. 22 and L. Hedin, Phys. Rev. 139, A796 (1965).

[26] S. F. Edwards, Proc. Phys. Soc. (London) 72, 685 (1958).

[27] T. Gaskell, Proc. Phys. Soc. (London) 77, 1182 (1961).

[28] T. Gaskell, Proc. Phys. Soc. (London) 80, 1091 (1962).

[29] S. F. Edwards and A. J. Hillel, J. Phys. C 1, 61 (1968).

[30] T. Dunn and A. A. Broyles, Phys. Rev. 157, 156 (1967).

[31] M. S. Becker, A. A. Broyles, and T. Dunn, Phys. Rev. 175, 224 (1968).

[32] Reference 1, Chap. 7.

[33] D. K. Lee, Phys. Rev. A 4, 348 (1971).

[34] D. K. Lee, Phys. Rev. A 4, 1670 (1971).

[35] M. Gell-Mann and K. Brueckner, Phys. Rev. 106, 364 (1957); K. Sawada, Phys. Rev. 106, 372 (1957).

[36] M. Wadati and A. Isihara, Phys. Rev. 4, 344 (1971).

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Critical Point in the Percus-Yevick Theory*

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Some consequences of the Percus–Yevick theory are studies in the neighborhood of the critical point for adhesive hard spheres and for the 6 : 12 potential (truncated at 6σ). It is shown that the Percus–Yevick theory gives rise to classical behavior at the critical point. In particular, it is shown that for the compressibility equation of state the critical exponents γ and δ are 1 and 3, respectively, and for the energy equation of state the critical exponents α and β are 0 and $\frac{1}{2}$, respectively. In addition, the behavior of the Percus–Yevick distribution function in the neighborhood of the critical point is examined and it is shown that for the critical isochore the temperature derivative of the distribution function diverges with a critical exponent of $\frac{1}{2}$ which is independent of r and that for the critical isotherm the distribution function is a linear function of the density for all r.

I. INTRODUCTION

The theory of the behavior of a fluid near its critical point is one of the most intensively investigated areas of physics. In this paper we deal with the critical-point behavior of a fluid in the Percus–Yevick (PY) approximation.[1]

Let us consider a fluid of N molecules at a temperature T and occupying a volume V. Thus, the critical point is specified by T_c and ρ_c, where $\rho = N/V$. Experimentally it is found that a number of quantities vanish or diverge at the critical point. Critical exponents can be used to characterize the behavior of these quantities near the critical point. For example, the heat capacity at constant density C is given by

$$C \simeq \text{const} \times |T - T_c|^{-\alpha} \tag{1}$$