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Series Expansion in the Variational Approach to Many-Boson Problems[*]

Deok Kyo Lee[†]
Department of Physics, University of California, Berkeley, California 94720

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The ground state of a many-boson system is studied within the range of the Bijl-Dingle-Jastrow–type description when the radial distribution function $g(r)$ differs little from its asymptotic value. The treatment of the problem is based on the development of power series in $\alpha = 1 - g(0)$ for all physical quantities which depend on the particle density. The n-particle distribution functions $p^{(n)}$ are evaluated to order α^4 as functionals in the $g(r)$ function for $n = 3$ and 4 using the cluster-expansion procedure outlined by Abe. These results are used in connection with the improvement of the ground-state description when the wave function is not the optimum choice. Using $p^{(3)}$ function obtained, the Bogoliubov-Born-Green-Kirkwood-Yvon equation is solved, also to order α^4, for the two-particle correlation function $\mathcal{U}(r)$, and the first two leading corrections to the hypernetted-chain (HNC) approximation are obtained. The variational calculation along with the series expansion for $\mathcal{U}(r)$ yields formulas for the ground-state properties, including some corrections to known results. For a charged boson gas, numerical values of $\mathcal{U}(r)$, $p^{(3)}$, $p^{(4)}$, and the ground-state energy are computed using the Gaussian approximation for $g(r)$, and the results show that the errors associated with the HNC approximation are small. A brief discussion is presented on the method of determining the general expansion coefficients of the correlation functions of $p^{(n)}$ in terms of $g(r)$.

I. INTRODUCTION

In recent years, the theoretical study of a many-particle boson problem has been approached with a great variety of approximation methods. In particular, the variational procedure based on the Bijl-Dingle-Jastrow (BDJ) type of correlated trial wave function of the form

$$\Psi_0=\prod_{i<j}^{N}\exp\tfrac{1}{2}\mathcal{U}(r_{ij})$$

$$\times\Big/\left(\int\prod_{m<n}^{N}\exp\mathcal{U}(r_{mn})d\vec{r}_{12\cdots N}\right)^{1/2}\qquad(1)$$

has been widely used to calculate the ground-state properties of a system of N bosons interacting in pairs through a radial potential.[1] While it is a formidable task to minimize the expectation value of Hamiltonian directly with respect to the variational function $\mathcal{U}(r)$, a slightly different approach in which the radial distribution function $g(r)$ serves as an indirect variational function is particularly useful, since it is convenient to describe the ground-state and low-lying excited states of the system in terms of $g(r)$, which can be determined from experiments. Nevertheless, this indirect variational method suffers from lack of our sufficient understanding about the expression for the correlation function $\mathcal{U}(r)$ as an explicit functional in g.

The problem is, however, amenable to solution if the deviation of $g(r)$ from its asymptotic value unity is small (i.e., in the uniform limit), since the deviation at the origin $\alpha=1-g(0)$ can be used as an expansion parameter for $\mathcal{U}(r)$ and other quantities of interest.[2] In this paper, we present an extensive analysis of the many-boson system using the method of series expansion in powers of α for physical quantities which depend on the particle density, such as the ground-state energy, the mean number of particles in nonzero-momentum states, the correlation function $\mathcal{U}(r)$, and n-particle distribution functions.

II. BASIC RELATIONS

We consider an extended uniform system of N bosons interacting in a cubic box of volume Ω through a two-body potential $v(r)$. Many important properties of the system can be described in terms of n-particle distribution functions[3]

$$p^{(n)}(1,2,\ldots,n)$$

$$=N(N-1)\cdots(N-n+1)\int\Psi_0^{2}d\vec{r}_{n+1,n+2,\ldots,N},\qquad(2)$$

which satisfy the sequential relation

$$p^{(n-1)}(1,2,\ldots,n-1)$$

$$=\frac{1}{N-n+1}\int p^{(n)}(1,2,\ldots,n)d\vec{r}_{n}\;.\qquad(3)$$

For $n=2$, Eq. (3) yields the normalization condition[4]

$$\rho\int[g(r)-1]d\vec{r}=-1\;,\qquad(4)$$

where $\rho=N/\Omega=p^{(1)}(1)$,

and $g(r_{12})=p^{(2)}(1,2)/\rho^{2}$

are the number density and the radial distribution function, respectively. The simple notation $p^{(n)}(1,2,\ldots,n)=p(1,2,\ldots,n)=p^{(n)}$ will be used hereafter.

The expectation values of the kinetic and potential energies per particle are given by

$$\frac{\langle\mathrm{KE}\rangle}{N}=\frac{\hbar^{2}\rho}{8m}\int\vec{\nabla}\mathcal{U}(r)\cdot\vec{\nabla}g(r)d\vec{r}\;,\qquad(5)$$

$$\frac{\langle\mathrm{PE}\rangle}{N}=\tfrac{1}{2}\rho\int g(r)v(r)d\vec{r}\;.\qquad(6)$$

The function $\mathcal{U}(r)$ in Eq. (5) arises from the use of the BDJ-type wave function (1). The best variational ground state is determined by minimizing $E=\langle\mathrm{KE}\rangle+\langle\mathrm{PE}\rangle$ with the aid of a relation connecting $\mathcal{U}(r)$ and $g(r)$. The useful connection is ordinarily given by one of the following three approximate forms:

(i) Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) equation[3]

$$g(r_{12})\vec{\nabla}_{1}\mathcal{U}(r_{12})=\vec{\nabla}_{1}g(r_{12})$$

$$-\frac{1}{\rho^{2}}\int[p(1,2,3)-\rho^{3}g(r_{12})g(r_{13})]\vec{\nabla}_{1}\mathcal{U}(r_{13})d\vec{r}_{3}\qquad(7)$$

in conjunction with the Kirkwood superposition approximation[3]

$$p_{K}(1,2,3)=\rho^{3}g(r_{12})g(r_{23})g(r_{31})\;;\qquad(8)$$

(ii) Hypernetted chain (HNC) equation[5]

$$\mathcal{U}(r)=\ln g(r)-\frac{1}{(2\pi)^{3}\rho}\int e^{i\vec{k}\cdot\vec{r}}$$

$$\times\frac{[1-S(k)]^{2}}{S(k)}d\vec{k}\;,\qquad(9)$$

where $S(k)=1+\rho\int e^{i\vec{k}\cdot\vec{r}}[g(r)-1]d\vec{r}$ (10)

is the liquid-structure function;

(iii) Percus-Yevick (PY) equation[6,7]

$$\mathcal{U}(r)=\ln g(r)-\ln\left(1+\frac{1}{(2\pi)^{3}\rho}\int e^{i\vec{k}\cdot\vec{r}}\right.$$

$$\times \frac{[1-S(k)]^2}{S(k)}\, d\vec{k} \Bigg) . \tag{11}$$

In the uniform limit, defined by the condition $|1-g(r)| \ll 1$, it proves convenient to introduce the dimensionless variable $s=(\alpha\rho)^{1/3}r$ and the dimensionless expansion parameter $\alpha = 1-g(0)$.[2a] The new functions in $\vec{s}$ space are defined by

$$g(r) = 1-\alpha G(s), \qquad G(0)=1 , \tag{12}$$

$$\mathcal{Y}(s) = \mathcal{U}(r) . \tag{13}$$

In terms of Fourier transforms

$$F(q) = \int e^{i\vec{q}\cdot\vec{s}} G(s)\, d\vec{s} = 1-S(k) , \tag{14}$$

$$Z(q) = \int e^{i\vec{q}\cdot\vec{s}}\, \mathcal{Y}(s)\, d\vec{s} \equiv \alpha W(k) , \tag{15}$$

$$\nu(k) = \int e^{i\vec{k}\cdot\vec{r}}\, V(r)\, d\vec{r} , \tag{16}$$

Eqs. (5) and (6) become

$$\frac{\langle \mathrm{KE}\rangle}{N} = -\frac{1}{4(2\pi)^3}\, \frac{\hbar^2(\alpha\rho)^{2/3}}{2m} \times \int q^2 Z(q) F(q)\, d\vec{q} , \tag{17}$$

$$\frac{\langle \mathrm{PE}\rangle}{N} = \tfrac{1}{2}\rho\nu(0) - \frac{\alpha\rho}{2(2\pi)^3} \times \int F(q)\, \nu(\alpha^{1/3}\rho^{1/3} q)\, d\vec{q} . \tag{18}$$

Denoting the mean number of particles in zero-momentum state by N_0, we observe from Eq. (17) that the mean kinetic energy in a moving reference frame (with velocity $-\vec{v}$) is given by

$$\langle \mathrm{KE}\rangle_{\substack{\text{moving}\\ \text{frame}}} = \tfrac{1}{2} N_0 m v^2 - \frac{N}{4(2\pi)^3}\, \frac{\hbar^2(\alpha\rho)^{2/3}}{2m} \times \int \left(\vec{q} + \frac{m}{(\alpha\rho)^{1/3}\hbar}\, \vec{v}\right)^2 Z(q) F(q)\, d\vec{q} ,$$

$$= \tfrac{1}{2} N m v^2 - \frac{N}{4(2\pi)^3}\, \frac{\hbar^2(\alpha\rho)^{2/3}}{2m} \times \int q^2 Z(q) F(q)\, d\vec{q} ;$$

hence the mean number of particles in states of nonzero momentum is immediately found to be[8]

$$N - N_0 = \sum_{\vec{k}\neq 0} n(k) = -\frac{N}{4(2\pi)^3} \int Z(q) F(q)\, d\vec{q} \tag{19a}$$

$$= -\tfrac{1}{4} N\rho \int \mathcal{U}(r)[1-g(r)]\, d\vec{r} .$$

Equations (17) and (19a) imply that the momentum-distribution function is of the form

$$n(k) = -\tfrac{1}{4} N W(k)[1-S(k)] + N\phi(k) , \tag{19b}$$

where $\phi(k)$ is not determined in our present analysis, but we surmise that $\phi(k)=0$ on the ground that it satisfies

$$\int \phi(k)\, d\vec{k} = \int \phi(k) k^2\, d\vec{k} = 0 ,$$

and $\phi(k)=0$ in the Bogoliubov approximation (Sec. V). It is, however, to be noted that Eq. (19) cannot be used in the realistic problem of liquid He^4, in which case $W(k)$ is not believed to exist.

III. THREE- AND FOUR-PARTICLE DISTRIBUTION FUNCTIONS

Equations (9) and (11) are simple approximate forms for the correlation function $\mathcal{U}(r)$ as functionals in g; they are widely used in the quantum theory of many-particle systems, and also in the classical theory of imperfect gas or liquid, in which case $\mathcal{U}(r) = -v(r)/k_B T$. A formula for $\mathcal{U}(r)$ with better accuracy may be obtained by solving Eq. (7), which is exact but contains $p(1,2,3)$. The general expression for the $p^{(3)}$ function has the form

$$p(1,2,3) = p_K(1,2,3)\, e^{A(1,2,3)} , \tag{20}$$

and Abe[9] has shown how to exhibit $A(1,2,3)$ as an explicit functional in the hole function

$$h(r) = g(r) - 1 , \tag{21}$$

by deriving the first two leading terms in the formal series expansion in powers of ρ. In terms of $h_{ij} = h(r_{ij})$, Abe's result appears as

$$A(1,2,3) = \rho \int h_{14}h_{24}h_{34}\, d\vec{r}_4 + \rho^2 \iint \Big[h_{24}h_{45}h_{35}(h_{14}h_{15} + h_{14}h_{25} + h_{15}h_{34}) + h_{14}h_{24}h_{34}h_{15}h_{25}h_{35}h_{45} \Big(\sum_{i=1}^{3} \frac{1}{h_{i4}} + \frac{1}{2} \Big) \Big]\, d\vec{r}_{45} + O(\rho^3) . \tag{22}$$

The most serious difficulty in the Abe-type density expansion is the fact that this expansion is not really a true power seris in ρ, since the expansion coefficients are functionals in the hole function which depends, possibly strongly, on density; thus, the condition for the validity of the expansion does not necessarily require low densities. To overcome such a difficulty, we rewrite the ρ expansion with $r = s/(\alpha\rho)^{1/3}$, $h(r) = \alpha G(s)$, and obtain a new series expansion in powers of α. Equation (22) with terms of order ρ and ρ^2 gives the new expansion correct only in the first term which is of order α^2.

In this section, we want to obtain the formula for $A(1, 2, 3)$, correct through order α^4, by including terms through order ρ^5 in the ρ expansion. The derivation is based on the standard cluster-expansion formalism as in the classical statistical mechanics of an imperfect gas. Since the algebra is somewhat lengthy, we give only the result in the form[10]

$$A(1,2,3) = -\alpha^2 A_2(1,2,3) - \alpha^3 A_3(1,2,3) - \alpha^4 A_4(1,2,3) + O(\alpha^5), \tag{23}$$

where the coefficients A_2, A_3, and A_4 are given explicitly by Fig. 1 in a diagrammatic representation. The meaning of the diagrams is the same as in the case of the ordinary cluster integrals. Here, each bond represents a G factor, solid circles represent an operation of integration over the fundamental volume αN of the $\vec{s}$ variable, and open circles represent the particles 1, 2, and 3. Each diagram is in fact a sum over all possible distinct arrangements of the labels 1, 2, and 3 on the open circles.

With the explicit results given by Eq. (23) and Fig. 1, we can show that the $p^{(3)}$ function (20) satisfies the sequential relation (3) for $n = 3$:

$$1 - \alpha G(s_{12}) = \frac{1}{(N-2)\alpha\rho^3} \int p(1,2,3)\, d\vec{s}_3, \tag{24}$$

with an error term of order α^4. The approximation $p_K(1, 2, 3)$ fails in Eq. (24) in the first order in α.

We now turn to the consideration of the four-particle distribution function $p(1, 2, 3, 4)$. This function is as important as $p(1, 2, 3)$ in many instances in the study of many-boson systems. In Sec. VI, we shall see how $p^{(4)}$, in addition to $p^{(3)}$, is used to improve the approximate description of the ground state when the BDJ-type wave function is not the optimum choice. In principle, the procedure of the derivation of $p^{(4)}$ as functional in G is the same as in the case of $p^{(3)}$; to order α^4 the result is

$$\begin{aligned} p(1,2,3,4) &= p_K(1,2,3,4) \times \exp\left(-\sum_{n=2}^{4} \alpha^n B_n(1,2,3,4) + O(\alpha^5)\right) \\ &= \prod_{i<j<k}^{4} p^{(3)}(ijk) \exp\left(-\sum_{n=3}^{4} \alpha^n B_n'(1,2,3,4) + O(\alpha^5)\right) \Big/ \rho^4 p_K(1,2,3,4), \end{aligned} \tag{25}$$

$$p_K(1,2,3,4) = \rho^4 g(r_{12}) g(r_{13}) g(r_{14}) g(r_{23}) g(r_{24}) g(r_{34}),$$

$$B_n(1,2,3,4) = \sum_{i<j<k}^{4} A_n(ijk) + B_n'(1,2,3,4),$$

where $B_2' = 0$ and B_3' and B_4' are given by Fig. 2 in the diagrammatic representation. The meaning of the diagrams is the same as in Fig. 1, with the obvious exception that in each diagram open circles now represent particles 1, 2, 3, and 4.

The two simple approximate forms

$$p(1,2,3,4) = p_K(1,2,3,4), \tag{26a}$$

$$p(1,2,3,4) = \prod_{i<j<k}^{4} p^{(3)}(ijk) \Big/ \rho^4 p_K(1,2,3,4), \tag{26b}$$

correspond to $B_n = 0$ and $B_n' = 0$, respectively. Equation (26b) was first introduced by Fisher and Kopeliovich[11] to improve the Kirkwood superposition approximation (8).

A little algebra shows that Eq. (25) generates $p(1, 2, 3)$ in the sequential relation (3) for $n = 4$:

$$(N-3)^{-1} \int p(1,2,3,4)\, d\vec{r}_4 = p(1,2,3), \tag{27}$$

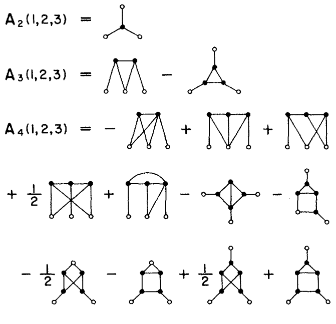

FIG. 1. Diagrammatic representation of $A_n(1,2,3)$ for $n = 2, 3,$ and 4.

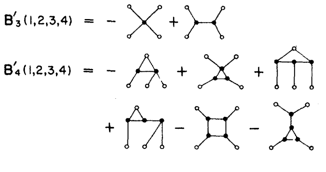

FIG. 2. Diagrammatic representation of $B_n'(1,2,3,4)$ for $n = 3$ and 4.

the error term being of order α^4; Eqs. (26) fail in Eq. (27) by terms of order α and α^2, respectively.

Finally, we remark that the general recipe for determining the coefficient of ρ^n in the expansion of the correlation factor of $p^{(n)}$ [as in Eq. (22)] is given in Appendix A, and thus the general coefficients A_n, B_n', etc., can be obtained through a change of the expansion to the $\vec{s}$ space.

IV. SOLUTION OF BBGKY EQUATION

With $p(1,2,3)$ given by Eqs. (20), (23), and Fig. 1 as an explicit functional in G, we can now proceed to the solution of the BBGKY equation (7), which in $\vec{s}$ space assumes the form

$$\begin{aligned}
&\vec{\nabla}_2\{y(s_{12})-\ln[1-\alpha G(s_{12})]\}=\int[G(s_{23})+\sum_{n=1}^{3}\alpha^n D_n(1,2,3)+O(\alpha^4)]\,\vec{\nabla}_3\, y(s_{13})d\vec{s}_3\ ,\\
&D_1(1,2,3)=A_2(1,2,3)-G(s_{13})G(s_{23})\ ,\\
&D_2(1,2,3)=A_3(1,2,3)-A_2(1,2,3)[G(s_{13})+G(s_{23})]\ ,\\
&D_3(1,2,3)=A_4(1,2,3)-A_3(1,2,3)[G(s_{13})+G(s_{23})]+A_2(1,2,3)[G(s_{13})G(s_{23})-\tfrac{1}{2}A_2(1,2,3)]\ .
\end{aligned}\tag{28}$$

Appendix B discusses the uniqueness of the solution of Eq. (7) with $p(1,2,3)=p_K(1,2,3)$.

It proves convenient to transform Eq. (28) from $\vec{s}$ representation to $\vec{q}$ representation through the repeated application of the Fourier integral theorem. After some algebra, we obtain

$$\begin{aligned}
Z(q)=&\frac{-1}{1-F(q)}\sum_{n=1}^{\infty}\alpha^n F_n(q)-\frac{\alpha}{(2\pi)^3}\frac{F(q)}{1-F(q)}\int\frac{\vec{q}\cdot\vec{q}_1}{q^2}Z(q_1)[1-F(q_1)]F(\vec{q}_1-\vec{q})d\vec{q}_1\\
&-\frac{\alpha^2}{(2\pi)^6}\int\frac{\vec{q}\cdot\vec{q}_1}{q^2}Z(q_1)[1-F(q_1)]F(q_2)F(q_{12})F(\vec{q}_2-\vec{q})\left(\frac{F(q)}{1-F(q)}+F(\vec{q}_1-\vec{q})\right)d\vec{q}_{12}\\
&-\frac{\alpha^3}{(2\pi)^9}\int\frac{\vec{q}\cdot\vec{q}_1}{q^2}Z(q_1)[1-F(q_1)]F(q_{12})F(q_{23})F(\vec{q}_3-\vec{q})\Biggl(\frac{F(q)}{1-F(q)}F(q_2)\\
&\times[F(q_{13})+F(q_3)-F(q_{13})F(q_3)]+F(\vec{q}_2-\vec{q})F(q_3)[-1+F(\vec{q}_1-\vec{q})+F(q_{13})+F(q_2)+\tfrac{1}{2}F(\vec{q}_1-\vec{q}_{23})]+F(\vec{q}_1-\vec{q})\\
&\times F(q_2)F(q_3)[1-F(\vec{q}_2-\vec{q})-F(q_{13})]+F(\vec{q}_1-\vec{q})F(q_2)F(q_{13})[1-F(\vec{q}_2-\vec{q})-\tfrac{1}{2}F(\vec{q}_{32}-\vec{q})]\Biggr)d\vec{q}_{123}\ ,
\end{aligned}\tag{29}$$

with $$F_n(q)=\int e^{i\vec{q}\cdot\vec{s}}G^n(s)d\vec{s}\ ,\qquad F_1(q)=F(q).\tag{30}$$

Introducing the power-series expansion

$$Z(q)=\sum_{n=1}^{\infty}\alpha^n Z_n(q)\ ,\tag{31a}$$

and using identities (C1)–(C6) developed in Appendix C, we find from Eq. (29) the following explicit formulas:

$$Z_1(q)=-F(q)-F^2(q)/[1-F(q)]\ ,\tag{31b}$$

$$Z_2(q)=-\tfrac{1}{2}F_2(q)\ ,\tag{31c}$$

$$Z_3(q)=-\tfrac{1}{3}F_3(q)+\tfrac{1}{2}(2\pi)^{-6}\int F(q_1)F(q_2)F(q_{12})F(\vec{q}_1-\vec{q})F(\vec{q}_2-\vec{q})d\vec{q}_{12}\ ,\tag{31d}$$

$$Z_4(q) = -\tfrac{1}{4}F_4(q) + (2\pi)^{-9}\int F(q_1)F(q_{12})F(q_{23})F(\vec{q}_3-\vec{q})F(\vec{q}_2-\vec{q})\{F(q_{13})F(q_2)[1-F(\vec{q}_1-\vec{q})]$$
$$+F(q_3)F(\vec{q}_1-\vec{q})[1-\tfrac{1}{2}F(q_2)-\tfrac{1}{4}F(\vec{q}_1-\vec{q}_{23})]\}\,d\vec{q}_{123}\ . \tag{31e}$$

The inverse Fourier transformation of Eqs. (31) yields the solution expressed in $\vec{s}$ space, i.e., $\mathcal{Y}(s)$. Thus, writing

$$\mathcal{Y}_n(s) = (2\pi)^{-3}\int e^{-i\vec{q}\cdot\vec{s}}Z_n(q)\,d\vec{q}\ , \tag{32}$$

we obtain $$\mathcal{Y}(s) = \sum_{n=1}^{\infty}\alpha^n\mathcal{Y}_n(s)\ , \tag{33a}$$

$$\mathcal{Y}_1(s) = -G(s) - \frac{1}{(2\pi)^3}\int e^{-i\vec{q}\cdot\vec{s}}\,\frac{F^2(q)}{1-F(q)}\,d\vec{q}\ , \tag{33b}$$

$$\mathcal{Y}_2(s) = -\tfrac{1}{2}G^2(s)\ , \tag{33c}$$

$$\mathcal{Y}_3(s) = -\tfrac{1}{3}G^3(s) + \tfrac{1}{2}\int G(s_1)G(s_2)G(s_{12})G(\vec{s}_1-\vec{s})G(\vec{s}_2-\vec{s})\,d\vec{s}_{12}\ , \tag{33d}$$

$$\mathcal{Y}_4(s) = -\tfrac{1}{4}G^4(s) + \int G(s_1)G(s_{12})G(s_{23})G(\vec{s}_3-\vec{s})G(s_2)G(\vec{s}_1-\vec{s})[G(s_3)+G(s_{13})]\,d\vec{s}_{123}$$
$$-\int G(s_1)G(s_{12})G(s_{23})G(s_{34})G(\vec{s}_4-\vec{s})[G(\vec{s}_1-\vec{s})G(s_{24})G(s_3)+\tfrac{1}{2}G(s_{14})G(s_2)G(\vec{s}_3-\vec{s})$$
$$+\tfrac{1}{4}G(s_{14})G(\vec{s}_2-\vec{s})G(s_3)]\,d\vec{s}_{1234}\ . \tag{33e}$$

The diagrammatic representation of $\mathcal{Y}_n(s)+G^n(s)/n$ for $n=3$ and 4 is given in Fig. 3. A method of determinining diagrams appearing in the general coefficient $\mathcal{Y}_n(s)$ is discussed in Appendix A.

In Eq. (33) the terms $-G^n(s)/n$ of $\mathcal{Y}_n(s)$ simply reproduce the approximate solution

$$\mathcal{U}(r) = \ln g(r)\ , \tag{34}$$

which comes from the crude approximation $p(1,2,3)=\rho^3$ in Eq. (7). The inclusion of the first-order correction from Eq. (33b) yields the HNC approximation (9)

$$\mathcal{U}(r) = \ln g(r) - \frac{1}{(2\pi)^3\rho}\int e^{i\vec{k}\cdot\vec{r}}\,\frac{[1-S(k)]^2}{S(k)}\,d\vec{k}\ , \tag{35}$$

which is in fact correct to order α^2, since there is no second-order correction term as is seen in Eq. (33c). The improved HNC equation with the leading correction is, therefore,

$$\mathcal{U}(r) = \ln g(r) - \frac{1}{(2\pi)^3\rho}\int e^{i\vec{k}\cdot\vec{r}}\frac{[1-S(k)]^2}{S(k)}\,d\vec{k} - \tfrac{1}{2}\rho^2\int h(r_1)h(r_2)h(\vec{r}_1-\vec{r})h(\vec{r}_2-\vec{r})h(r_{12})\,d\vec{r}_{12}\ , \tag{36}$$

and the similar formula with next-higher accuracy is obtained by including two integrals of the right-hand side of Eq. (33e).

Equation (35) was first derived by means of a partial summation in the standard cluster-expansion formalism,[5] and later rederived by Percus[7] using the method of a functional Taylor expansion. A number of encouraging results have been obtained from its application to such systems as classical fluids and liquid He^4, although the radial distribution function $g(r)$ vanishes at the origin, so that the expansion parameter α is not small but $\alpha=1$. Thus, the series expansion in powers of α appears to converge fast even with $\alpha=1$. This is also indicated in Sec. VII by the smallness of the correction terms computed with a Gaussian form for $G(s)$.

We finally remark that functional derivatives of $Z_n(q)$ and $\mathcal{Y}_n(s)$ satisfy the symmetry relations[12]

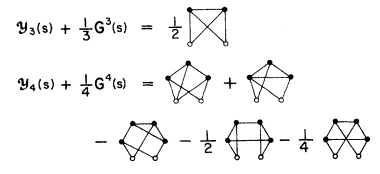

FIG. 3. Diagrammatic representation of $\mathcal{Y}_n(s)+G^n(s)/n$ for $n=3$ and 4.

$$\delta Z_n(q)/\delta F(q') = \delta Z_n(q')/\delta F(q), \qquad \delta \mathcal{Y}_n(s)/\delta G(s') = \delta \mathcal{Y}_n(s')/\delta G(s)\,, \tag{37}$$

for $n \leqslant 4$, which can readily be shown from the explicit formulas given by Eqs. (31) and (33). For an arbitrary n, our analysis merely shows that the dominant terms of $Z_n(q)$ and $\mathcal{Y}_n(s)$ [i.e., $-F_n(q)/n$ and $-G^n(s)/n$, respectively] have the symmetric functional derivatives. It is, however, conjectured, but not proved, that Eq. (37) is correct for all n, or that

$$\delta W(k)/\delta S(k') = \delta W(k')/\delta S(k)\,, \qquad \delta \mathcal{U}(r)/\delta h(r') = \delta \mathcal{U}(r')/\delta h(r)\,, \tag{38}$$

where $W(k)$ is the Fourier transform of $\mathcal{U}(r)$ as defined by Eq. (15). In Sec. VI we show that the symmetry property given by Eq. (38) can be violated only if certain apparently improbable conditions are satisfied. A more intensive analysis of the correlation function $\mathcal{U}(r)$ is necessary to determine if the conjecture (38) is in fact true.

V. VARIATIONAL GROUND STATE

The expectation value of the Hamiltonian as an explicit functional in the liquid-structure function is now readily obtained from Eqs. (17), (18), and (31) with $k = (\alpha\rho)^{1/3}\, q$ and $S(k) = 1 - F(q)$

$$\begin{aligned} E = {} & \tfrac{1}{2} N\rho\nu(0) + \frac{\hbar^2 N}{8(2\pi)^3 m\rho} \int k^2 \left(\frac{[1-S(k)]^2}{S(k)} - \frac{4m\rho}{\hbar^2 k^2} [1-S(k)]\,\nu(k) \right) d\vec{k} \\ & + \frac{\hbar^2 N}{16(2\pi)^6 m\rho^2} \int k_1^2 [1-S(k_1)][1-S(k_2)][1-S(k_{12})]\, d\vec{k}_{12} \\ & + \frac{\hbar^2 N}{8(2\pi)^9 m\rho^3} \int k_1^2 [1-S(k_1)]\,[1-S(k_{12})][1-S(k_{23})][1-S(k_3)] \\ & \times \{ \tfrac{1}{3} - \tfrac{1}{2}[1-S(k_2)][1-S(k_{13})]\}\, d\vec{k}_{123} + \cdots\,, \end{aligned} \tag{39}$$

in which we note that α does not appear explicitly in momentum representation.

By means of the functional series expansion of Eq. (39) we can show that the first-order change in the integral E due to δS – an arbitrary small change of the function S – vanishes if the Fourier transform of the potential is given by

$$\begin{aligned} \nu(k) = {} & \frac{\hbar^2 k^2}{4m\rho} \left(\frac{1}{S^2(k)} - 1 \right) + \frac{\hbar^2}{8(2\pi)^3 m\rho^2} \int (k^2 + 2k_1^2)[1 - S(\vec{k}-\vec{k}_1)][1 - S(k_1)]\, d\vec{k}_1 \\ & + \frac{\hbar^2}{4(2\pi)^6 m\rho^3} \int \{ \tfrac{1}{3} k^2 + k_2^2 - \tfrac{1}{2}(k^2 + 4k_1^2 + k_{12}^2)[1 - S(\vec{k}-\vec{k}_2)][1 - S(k_1)]\} \\ & \times [1 - S(\vec{k}-\vec{k}_1)][1 - S(k_{12})][1 - S(k_2)]\, d\vec{k}_{12} + \cdots = 0\,, \end{aligned} \tag{40}$$

and we can also find that the second-order term in δS is positive.

Thus, Eq. (40) determines the optimum liquid-structure function

$$S(k) = S_0(k) + S_1(k) + S_2(k) + \cdots,$$

$$S_0(k) = [1 + 4m\rho\nu(k)/\hbar^2 k^2]^{-1/2},$$

$$S_1(k) = \frac{S_0^3(k)}{4(2\pi)^3\rho} \int \left(1 + \frac{2k_1^2}{k^2}\right) [1 - S_0(\vec{k}-\vec{k}_1)][1 - S_0(k_1)]\, d\vec{k}_1\,,$$

$$S_2(k) = \frac{3S_1^{\,2}(k)}{2S_0(k)} - \frac{S_0^{\,3}(k)}{2(2\pi)^3\rho}\int\left(1 + \frac{k_1^{\,2}}{k^2} + \frac{(\vec{k}-\vec{k}_1)^2}{k^2}\right)[1-S_0(\vec{k}-\vec{k}_1)]\,S_1(k_1)\,d\vec{k}_1$$
$$+\frac{S_0^{\,3}(k)}{2(2\pi)^6\rho^2}\int\left\{\tfrac{1}{3} + \frac{k_2^{\,2}}{k_2} - \tfrac{1}{2}\left(1+\frac{4k_1^{\,2}}{k^2} + \frac{k_{12}^{\,2}}{k^2}\right)[1-S_0(\vec{k}-\vec{k}_2)]\,[1-S_0(k_1)]\right\}$$
$$\times[1 - S(\vec{k}-\vec{k}_1)]\,[1-S(k_{12})][1-S(k_2)]\,d\vec{k}_{12}\ ; \tag{41}$$

and the minimum energy is found with Eq. (41) to be

$$E = E_0 + E_1 + E_2 + \cdots ,$$

$$E_0 = \tfrac{1}{2}N\rho\nu(0) - \frac{\hbar^2N}{(4\pi)^3m\rho}\int k^2\left(\frac{1-S_0(k)}{S_0(k)}\right)^2 d\vec{k}\ ,$$

$$E_1 = \frac{\hbar^2N}{16(2\pi)^6m\rho^2}\int k_1^{\,2}[1-S_0(k_1)]\,[1-S_0(k_2)]\,[1-S_0(k_{12})]\,d\vec{k}_{12}\ ,$$

$$E_2 = -\frac{\hbar^2N}{(4\pi)^3m\rho}\int\frac{k^2S_1^{\,2}(k)}{S_0^{\,3}(k)}\,d\vec{k} + \frac{\hbar^2N}{8(2\pi)^9m\rho^3}\int k_1^{\,2}\{\tfrac{1}{3} - \tfrac{1}{2}[1-S_0(k_2)]\,[1-S_0(k_{13})]\}$$
$$\times[1-S_0(k_1)]\,[1-S_0(k_{12})]\,[1-S_0(k_{23})]\,[1-S_0(k_3)]\,d\vec{k}_{123}\ . \tag{42}$$

Using the second line of Eq. (41), we may rewrite the leading term of the variational energy as

$$E_0 = \tfrac{1}{2}N\rho\nu(0) - \frac{\Omega}{2(2\pi)^3}\int\left[\frac{\hbar^2k^2}{2m} + \rho\nu(k) - \epsilon(k)\right]d\vec{k}\ , \tag{43}$$

with $h\epsilon(k) = [(\hbar^2k^2/2m)^2 + (\hbar^2k^2/m)\rho\nu(k)]^{1/2}$ (44)

reproducing Bogoliubov's formula for the ground-state energy.[13] Equation (44), which has been shown by Bogoliubov to represent the energy spectrum of elementary excitations, reduces to Feynman's formula[14]

$$\epsilon_0(k) = \hbar^2k^2/2mS(k)\ , \tag{45}$$

if expressed in terms of $S(k) \simeq S_0(k)$, showing the equivalence of the two formulas in the uniform limit. It is to be noted that the relation between Eq. (44) [or (45)] and the excitation spectrum is not made visible by our analysis alone.

The expression (19b) for the mean number of particles in state of momentum $\vec{k}\,(\vec{k}\neq 0)$ now becomes, with the assumption $\phi(k) = 0$,

$$\frac{n(k)}{N} = \frac{[1-S_0(k)]^2}{4S_0(k)} + \frac{[1-S_0(k)]}{8(2\pi)^3\rho}\int\left\{1 - \left(\frac{1}{2} + \frac{k_1^{\,2}}{k^2}\right)S_0(k)\,[1+S_0(k)]\right\}$$
$$\times[1-S_0(\vec{k}-\vec{k}_1)]\,[1-S_0(k_1)]\,d\vec{k}_1 + \cdots\ , \tag{46a}$$

and, for small k,

$$\frac{n(k)}{N} \cong \frac{1}{4S_0(k)} - \frac{S_0(k)}{8(2\pi)^3\rho k^2}\int k_1^{\,2}[1-S_0(k_1)]^2\,d\vec{k}_1 + \cdots\ . \tag{46b}$$

Rewriting Eq. (46a) in the zeroth-order approximation, we have

$$n_0(k)/N = [2\epsilon(k)]^{-1}[\hbar^2k^2/2m + \rho\nu(k) - \epsilon(k)], \tag{47}$$

which agrees with Bogoliubov's result.[13] The integral representation of Eq. (12) for $r=0$ in $\vec{k}$ space leads to the formula for α as a function of ρ

$$\alpha = \frac{1}{(2\pi)^3\rho}\int[1 - S_0(k)]d\vec{k} - \frac{1}{(2\pi)^3\rho}\int S_1(k)d\vec{k} + \cdots . \tag{48}$$

We conclude this section with a brief discussion of the variational procedure used in deriving the energy formula (42). In arriving at the optimum relation of $S(k)$ to $\nu(k)$ and ρ [i.e., Eq. (41)], we have included no terms associated with Lagrange multipliers which take into account the restrictions imposed on $S(k)$, or, equivalently, on $g(r)$. It is, therefore, quite possible that the resulting energy value is even lower than the true eigenvalue, and hence there does not necessarily exist a wave function corresponding to the optimum choice of the indirect variational function $S(k)$. It is to be remembered at this point that in general we do not have a one-to-one correspondence between Ψ_0 and $S(k)$. It seems infeasible to incorporate the supplementary conditions on $S(k)$ in the variational treatment, since we know only a few of a (possibly infinite) number of necessary conditions, and a tractable set of sufficient conditions is not known as yet.

We may, however, remark that the known supplementary conditions, such as $S(k)\geqslant 0$, $S(0)=0$, $S(\infty)=1$, and $G(0)=1$, are satisfied without being incorporated explicitly in the derivation of $S(k)$, and more important, our results agree with those obtained by Bogoliubov [Eqs. (43) and (47)] and by Feynman [Eq. (45)], although the methods appear to be substantially different. The interpretation of Eq. (42) as giving an upper bound to the true eigenvalue of the Hamiltonian will be legitimate if Eq. (31) along with Eq. (41) gives a convergent result for $\mathcal{Y}(s) = \mathfrak{u}(r)$, since the BDJ-type trial wave function (1) is generated through the relation (33), and the functional form of the relation is not modified by the choice of the optimum form for $S(k)$. If the present analysis is applied to a charged boson gas at high density, Eq. (42) yields the ground-state energy $E = E_0 + E_1$, which agrees numerically with the exact result evaluated by Brueckner.[15]

VI. FREE-PHONON APPROXIMATION

While the description of a many-boson system in terms of $S(k)$ is convenient, the exact determination of the optimum $S(k)$ is a difficult task in most cases. Thus, one usually works with an approximate $S(k)$ in calculating the ground-state properties, and consequently the problem of estimating the error introduced with this approximation arises. In connection with this problem, Jackson and Feenberg[16–18] developed a formalism, based on the free-phonon analysis, which gives corrections to such quantities as $S(k)$, $W(k)$, $\epsilon(k)$, and E, within the range of the BDJ-type wave function. The analysis starts with the generalization of the radial distribution function

$$g(r_{12};\beta) = \frac{N(N-1)}{\rho^2 I(\beta)}\int \exp\left(\beta\sum_{i<j}^{N} V^*(r_{ij})\right)\Psi_0^{\,2}\, d\vec{r}_{34\cdots N}, \tag{49}$$

where
$$V^*(r) = v(r) - (\hbar^2/4m)\nabla^2\mathfrak{u}(r), \tag{50}$$

and $I(\beta)$ is the normalization constant with the properties $I(0)=1$ and $I'(0)=E$. The corresponding generalized liquid-structure function is

$$S(k;\beta) = 1 + \rho\int e^{i\vec{k}\cdot\vec{r}}[g(r;\beta) - g(\infty;\beta)]\,d\vec{r}, \tag{51}$$

and of special interest here is the quantity

$$S'(k) = [dS(k;\beta)/d\beta]_{\beta=0}\,. \tag{52}$$

Quantities depending on β serve as generating functions and hence the emphasis of β is not on generalization but on generating.

The corrections to $S(k)$, $W(k)$, and E/N are given by[16–18]

$$\Delta S(k) = -2\epsilon_0(k)\omega(k)S(k)/e(k)[e(k)+\epsilon_0(k)], \tag{53}$$

$$\Delta W(k) = -2\omega(k)/S(k)[e(k)+\epsilon_0(k)], \tag{54}$$

$$\Delta E/N = -[(2\pi)^3\rho]^{-1}\int[\epsilon_0(k)+\omega(k)-e(k)]\,d\vec{k}, \tag{55}$$

where
$$\omega(k) = S'(k)/S(k) + (\hbar^2k^2/4m)[S(k)-1]/S(k), \tag{56}$$

$$e(k) = [\epsilon_0{}^2(k) + 2\epsilon_0(k)\omega(k)]^{1/2}, \tag{57}$$

and $\epsilon_0(k)$ is given by Eq. (45). Equation (57) is the improved energy formula for elementary excitations. The best choice of the BDJ-type wave function is characterized by

$$\omega(k) = 0, \tag{58}$$

and all correction terms vanish in this case. The essential part of the problem is to evaluate the function $S'(k)$, which may be expressed in terms of $p^{(3)}$ and $p^{(4)}$, as

$$\begin{aligned} S'(k) &= \frac{\rho}{\Omega}\int e^{i\vec{k}\cdot\vec{r}_{12}}\left(\frac{d}{d\beta}[g(r_{12};\beta)-g(\infty;\beta)]\right)_{\beta=0} d\vec{r}_{12} \\ &= (N-1)\sum_{i<j}^{N}\int e^{i\vec{k}\cdot\vec{r}_{12}}V^*(r_{ij})\Psi_0{}^2 d\vec{r}_{12\cdots N} - I'(0)[S(k)-1] \\ &= -\tfrac{1}{2}N[S(k)-1]\rho\int g(r)V^*(r)d\vec{r} + \rho\int e^{i\vec{k}\cdot\vec{r}}g(r)V^*(r)d\vec{r} \\ &\quad + 2N^{-1}\int e^{i\vec{k}\cdot\vec{r}_{12}}p(1,2,3)V^*(r_{13})d\vec{r}_{123} + (2N)^{-1}\int e^{i\vec{k}\cdot\vec{r}_{12}}p(1,2,3,4)V^*(r_{34})d\vec{r}_{1234}. \end{aligned} \tag{59}$$

It is to be noted that the first term of the right-hand side of Eq. (59) is proportional to N, but it is canceled by the contribution of the last integral arising from $\rho^4[g(r_{12})-1]g(r_{34})$, which is contained in $p(1,2,3,4,)$ [even with the simple approximations (26a) and (26b)].

The practical usefulness of Eq. (59) is limited because the functions $p^{(3)}$ and $p^{(4)}$ are not known exactly, in general, as explicit functionals in g or S. We can, however, evaluate $S'(k)$ in the uniform limit, using the explicit results for $p^{(3)}$ and $p^{(4)}$ obtained in Sec. III. As was done in solving the BBGKY equation in Sec. IV, integrals of Eq. (59) are evaluated with the use of the Fourier integral theorem. After considerable algebraic manipulation, Eq. (59) becomes

$$\begin{aligned} S'(k) = X(k) &- \frac{S^2(k)}{(2\pi)^3\rho}\int X(k_1)[1-S(\vec{k}_1-\vec{k})]d\vec{k}_1 + \frac{S^2(k)}{(2\pi)^6\rho^2}\int\big(X(k_1)[1-S(k_{12})]\{[1-S(k_2)]+2[1-S(\vec{k}_1-\vec{k})]-2\} \\ &+ \tfrac{1}{2}X(k_{12})[1-S(k_1)][1-S(\vec{k}_1-\vec{k})]\big)[1-S(k_2)][1-S(\vec{k}_2-\vec{k})]d\vec{k}_{12} + \cdots, \end{aligned} \tag{60}$$

where
$$X(k) = S^2(k)\rho\int e^{i\vec{k}\cdot\vec{r}}V^*(r)d\vec{r} = S^2(k)[\rho\nu(k) + (\hbar^2k^2/4m)W(k)], \tag{61}$$

and $W(k) = Z(q)/\alpha$ is given by Eq. (31) with the $\vec{k}$, $S(k)$ notation. If $S(k)$ is generated by the best BDJ-type wave function, Eq. (40) may be substituted for $\nu(k)$ in Eq. (61), and Eq. (60) is found to reduce to

$$S'(k) = (\hbar^2k^2/4m)[1-S(k)] \tag{62}$$

in agreement with Eq. (58).

Finally, we consider the general case when α is not necessarily small. From Eq. (49) one recognizes that $W(k)$ is generalized to a function of β by

$$W(k;\beta) = \rho\int e^{i\vec{k}\cdot\vec{r}}[\mathfrak{u}(r) + \beta V^*(r)]d\vec{r} = W(k) + \beta[\rho\nu(k) + (\hbar^2k^2/4m)W(k)], \tag{63}$$

which, as a functional in S, depends on β only through $S(k;\beta)$. Thus, the first derivative of Eq. (63) with respect to β at $\beta=0$ yields an integral equation of the first kind for $S'(k)$:

$$\rho\nu(k) + (\hbar^2k^2/4m)W(k) = \int K(\vec{k},\vec{k}')S'(k')d\vec{k}', \tag{64}$$

with the kernel given by

$$K(\vec{k},\vec{k}') = \delta W(k)/\delta S(k'). \tag{65}$$

Equation (64) would be difficult to solve unless the kernal K is symmetric, i.e., unless $K(\vec{k},\vec{k}') = K(\vec{k}',\vec{k})$.[19] In the case of liquid He^4, the actual numerical evaluation of $S'(k)$ has been carried out by Campbell[18] using the HNC and the PY approximations. His results show that in both approximations the obtained numerical values of $S'(k)$ differ very little from those given by Eq. (62).

We now rewrite the total energy, from Eqs. (17) and (18), as

$$E/N=\tfrac{1}{2}\rho\nu(0)-[2(2\pi)^3\rho]^{-1}\int[\rho\nu(k)+(\hbar^2k^2/4m)W(k)][1-S(k)]d\vec{k}', \tag{66}$$

and, in the same way as in Sec. V, obtain the necessary condition for the minimum energy

$$\rho\nu(k)+(\hbar^2k^2/4m)W(k)=\int K(\vec{k}',\vec{k})(\hbar^2k'^2/4m)[1-S(k')]d\vec{k}'=\int K(\vec{k}',\vec{k})S'(k')d\vec{k}', \tag{67}$$

where we have used Eq. (62), which holds under this extremum condition. Equations (64) and (67) then combine to yield

$$\int[K(\vec{k},\vec{k}')-K(\vec{k}',\mathrm{k})]S'(\vec{k}')d\vec{k}'=0, \tag{68}$$

from which follows the symmetry of the kernel K as given by Eq. (38), provided that $K(\vec{k},\vec{k}')-K(\vec{k}',\vec{k})$ does not have a zero eigenvalue. Thus, the above analysis supports the conjecture (38) on the symmetry property of $K(\vec{k},\vec{k}')=\delta W(\mathrm{k})/\delta S(k')$, which is an interesting quantity.

VII. GAUSSIAN APPROXIMATION FOR A CHARGED BOSON GAS

In previous sections, we have obtained series expansions in powers of α for various important quantities of a many-boson system. However, the expansion coefficients are of the form of cluster integrals, and the actual evaluation of these integrals for a realistic function $g(r)$, or $S(k)$, is extremely complicated. In this section, we consider the problem of a charged boson gas using the radial distribution function of the form[2a,20]

$$g(r)=1-\alpha e^{-\pi s^2}, \tag{69}$$

and investigate the nature of the α expansion. The evaluation of all the integrals can be carried out in a simple analytic way with $G(s)=e^{-\pi s^2}$, or $F(q)=e^{-q^2/4\pi}$.

In Table I we give numerical values of $\mathcal{Y}(s)$ through the fourth-order approximation for $\alpha=0.5$ and 1.0 using the notations[21]

$$\mathcal{Y}^{(0)}=\ln[1-\alpha G(s)],$$

$$\mathcal{Y}^{(n)}=\mathcal{Y}^{(0)}(s)+\sum_{m=1}^{n}\alpha^m\left[\mathcal{Y}_m(s)+\frac{G^m(s)}{m}\right],\; n=1,2,\cdots.$$

While $\mathcal{Y}^{(0)}$ appears to be a somewhat poor approximation, $\mathcal{Y}^{(1)}=\mathcal{Y}^{(2)}$ differs little from $\mathcal{Y}^{(3)}$, or $\mathcal{Y}^{(4)}$ revealing the accuracy of the HNC equation (35).

TABLE I. Numerical values of $-\mathcal{Y}(s)$.

	$\alpha=0.5$				$\alpha=1.0$			
s	$-\mathcal{Y}^{(0)}$	$-\mathcal{Y}^{(2)}$	$-\mathcal{Y}^{(3)}$	$-\mathcal{Y}^{(4)}$	$-\mathcal{Y}^{(0)}$	$-\mathcal{Y}^{(2)}$	$-\mathcal{Y}^{(3)}$	$-\mathcal{Y}^{(4)}$
0	0.6931	1.499	1.497	1.496	∞	∞	∞	∞
0.1	0.6627	1.464	1.461	1.460	3.476	5.078	5.056	5.044
0.2	0.5815	1.367	1.364	1.364	2.136	3.707	3.687	3.677
0.3	0.4730	1.233	1.231	1.231	1.401	2.922	2.905	2.896
0.4	0.3602	1.088	1.086	1.086	0.9287	2.384	2.371	2.364
0.6	0.1760	0.8238	0.8229	0.8227	0.3897	1.685	1.678	1.675
0.8	0.0693	0.6305	0.6301	0.6300	0.1438	1.266	1.263	1.262
1.0	0.0218	0.5020	0.5019	0.5019	0.0442	1.005	1.004	1.003
1.2	0.0054	0.4169	0.4168	0.4168	0.0109	0.8337	0.8335	0.8335
1.4	0.0011	0.3571	0.3571	0.3571	0.0021	0.7142	0.7142	0.7142

TABLE II. Numerical values of $p(1,2,3)$ for $\alpha=1.0$. The powers of 10 apply to all entries in their rows.

	Straight-line configuration $(s\equiv s_{12}=s_{23}=\frac{1}{2}s_{31})$					Equilateral-triangle configuration $(s\equiv s_{12}=s_{23}=s_{31})$				
s	$p^{(3)}_K$	$p^{(3)}_2$	$p^{(3)}_3$	$p^{(3)}_4$		$p^{(3)}_K$	$p^{(3)}_2$	$p^{(3)}_3$	$p^{(3)}_4$	
0.1	0.2958	0.2455	0.2193	0.2120	$\times 10^{-4}$	1.1295	0.9428	0.8457	0.8184	$\times 10^{-4}$
0.2	0.1647	0.1390	0.1256	0.1218	$\times 10^{-2}$	0.5509	0.4743	0.4347	0.4227	$\times 10^{-2}$
0.3	0.1494	0.1292	0.1188	0.1157	$\times 10^{-1}$	0.4108	0.3683	0.3466	0.3393	$\times 10^{-1}$
0.4	0.6167	0.5489	0.5146	0.5034	$\times 10^{-1}$	0.1352	0.1260	0.1214	0.1197	
0.6	0.3107	0.2920	0.2832	0.2800		0.4537	0.4447	0.4404	0.4385	
0.8	0.6497	0.6331	0.6266	0.6242		0.7499	0.7473	0.7459	0.7453	
1.0	0.8759	0.8686	0.8666	0.8659		0.9154	0.9151	0.9149	0.9147	
1.2	0.4678	0.9658	0.9655	0.9655		0.9784	0.9784	0.9784	0.9784	
1.4	0.9937	0.9933	0.9933	0.9933		0.9958	0.9958	0.9958	0.9958	

TABLE III. Numerical values of $p(1,2,3,4)$ for $\alpha=1.0$. The powers of 10 apply to all entries in their rows.

	Straight-line configuration $(s\equiv s_{12}=s_{23}=s_{34}=\frac{1}{3}s_{41})$					Square configuration $(s\equiv s_{12}=s_{23}=s_{34}=s_{41}=s_{13}/\sqrt{2})$				
s	$p^{(4)}_K$	$p^{(4)}_2$	$p^{(4)}_3$	$p^{(4)}_4$		$p^{(4)}_K$	$p^{(4)}_2$	$p^{(4)}_3$	$p^{(4)}_4$	
0.1	0.3393	0.1622	0.1030	0.1162	$\times 10^{-8}$	1.0160	0.5076	0.3323	0.3654	$\times 10^{-7}$
0.2	0.9604	0.5008	0.3376	0.3633	$\times 10^{-5}$	1.7408	1.0417	0.7676	0.7798	$\times 10^{-4}$
0.3	0.6864	0.4048	0.2962	0.3030	$\times 10^{-3}$	0.6315	0.4578	0.3803	0.3701	$\times 10^{-2}$
0.4	0.9795	0.6606	0.5277	0.5213	$\times 10^{-2}$	0.4576	0.3831	0.3467	0.3365	$\times 10^{-1}$
0.6	0.1689	0.1424	0.1306	0.1275		0.3040	0.2914	0.2851	0.2823	
0.8	0.5427	0.5148	0.5034	0.4992		0.6493	0.6448	0.6423	0.6412	
1.0	0.8349	0.8252	0.8223	0.8212		0.8759	0.8752	0.8748	0.8746	
1.2	0.9571	0.9553	0.9551	0.9551		0.9678	0.9678	0.9677	0.9677	
1.4	0.9915	0.9913	0.9914	0.9914		0.9937	0.9937	0.9937	0.9937	

TABLE IV. Numerical values of $-E/N$ and α for the charged boson system.

r_s	$n=2$ (HNC) $-E^{(2)}/N$	α	$n=3$ $-E^{(3)}/N$	α	$n=4$ $-E^{(4)}/N$	α	$p^{(3)}{}_K$ $-E^{(K)}/N$	α
0.01	24.95	0.0159	24.95	0.0159	24.95	0.0159	25.00	0.016
0.03	10.94	0.0360	10.94	0.0360	10.94	0.0360	10.96	0.036
0.1	4.422	0.0877	4.422	0.0877	4.422	0.0877	4.437	0.089
0.3	1.929	0.194	1.929	0.195	1.929	0.195	1.939	0.20
1	0.7692	0.442	0.7696	0.443	0.7697	0.443	0.7764	0.46
3	0.3238	0.807	0.3241	0.811	0.3243	0.813	0.3272	0.83
10	0.1149	1.0	0.1150	1.0	0.1150	1.0	0.1154	1.0
30	0.04034	1.0	0.04034	1.0	0.04035	1.0	0.04039	1.0

Numerical values of $p(1,2,3)$ and $p(1,2,3,4)$ for $\alpha=1.0$ are shown in Tables II and III for two types of configurations of the particles: (1) straight line, and (2) equilateral triangle or square. The notations used in these tables are

$$p_n^{(3)}=p_K(1,2,3)\exp\left[-\sum_{m=2}^{n}\alpha^m A_m(1,2,3)\right],$$

$$p_n^{(4)}=p_K(1,2,3,4)\exp\left[-\sum_{m=2}^{n}\alpha^m B_m(1,2,3,4)\right],$$

where $p_K(1,2,3)$ and $p_K(1,2,3,4)$ are superposition approximations given by Eqs. (8) and (25), respectively. We may observe that the relative corrections in two successive approximations are always larger in the case of straight-line configurations, and hence these approximations should fail less seriously for the equilateral triangle and square configurations.

Finally we list in Table IV the energies of the charged boson system and the optimum values of the variational parameter α. Energies obtained using $\mathcal{Y}^{(n)}$ are denoted by $E^{(n)}$, and $E^{(K)}$ denotes the energy obtained by solving the BBGKY equation (7) using the Kirkwood superposition approximation $p_K(1,2,3)$.[2] The mean-particle separation $r_s=(3/4\pi\rho)^{1/3}$ and the energy are given in a.u. (Bohr radius and rydberg). The inspection of the results reveals that leading corrections to $E^{(2)}$ are negative and small, the largest first and second corrections being -0.1 and -0.05%, respectively, both at $r_s=3.0$. This seems to be an indication that the error introduced through the use of the HNC equation (35) in computing the expectation value of the Hamiltonian does not falsify the interpretation of the computed energy as an *upper bound* on the true eigenvalue.[22] On the other hand, a simple algebra shows that the leading correction to $E^{(K)}$ in the α expansion is positive and not small [$E^{(K)}$ begins to fail at the second term]; note that in Table IV, $E^{(K)}<E^{(n)}$, the difference being 1% at $r_s=3.0$. Consequently, the ground-state energy obtained using $p_K(1,2,3)$ in the BBGKY equation should not be interpreted as an upper bound, unless it can be shown otherwise.

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APPENDIX A: EXPANSION RULES FOR CORRELATION FACTORS

In Secs. III and IV, we considered the problem of expressing functions $p^{(3)}$, $p^{(4)}$, and $\mathcal{U}(r)$ as functionals in the hole function h, and obtained a few leading expansion coefficients for the correlation factors A, B', and $\mathcal{U}$, as given in the diagrammatic representation by Figs. 1, 2, and 3, respectively. To determine the general coefficient of the correlation factor for any n, we introduce the following four rules for diagrams appearing in the expansion: (1) Solid circles are directly connected among themselves; (2) open circles are not directly connected among themselves; (3) each open circle is connected to at least one solid circle; (4) each diagram cannot be obtained from a simpler diagram (having fewer bonds) by replacing a bond with a diagram (having two or more bonds).

Except for the condition (4) being much stronger here, the rules are the same as those in Meeron's expansion,[23] in which case coefficients are given in terms of $f(r)=e^{\mathfrak{u}(r)}-1$. Thus, our new expansion coefficients are obtained from Meeron's expansion by dropping diagrams which do not satisfy the condition (4). As an illustration consider a diagram representing the integral $\int h_{14}h_{24}h_{35}h_{54}d\vec{r}_{45}$. This can be obtained from $\int h_{14}h_{24}h_{34}d\vec{r}_4$ by replacing the bond h_{34} with $\int h_{35}h_{54}d\vec{r}_5$, and hence does not occur in the new series for $A(1,2,3)$. It may readily be seen that diagrams appearing in Figs. 1, 2, and 3 are consistent with the above rules.

When $n=2$, the actual quantity given by these new expansion rules is

$$-\mathfrak{u}(r)+\ln g(r)-\frac{1}{(2\pi)^3\rho}\int e^{i\vec{k}\circ\vec{r}}\frac{[1-S(k)]^2}{S(k)}d\vec{k},$$

and the condition (4) is equivalent to: (4a) Each solid circle is connected to open circles by at least three independent paths, and each open circle is connected to solid circles by at least two independent paths.

Finally, we remark that the expansion rules presented here can be shown to be in agreement with, and equivalent to, the prescriptions given by Stell for classical systems.[24] He gives two different prescriptions, one for $n=2$ and the other for $n\geqq 3$.

APPENDIX B. UNIQUENESS OF SOLUTION OF BBGKY EQUATION

The radial distribution function (69) used in Sec. VII is never greater than its asymptotic value unity, and this condition has the consequence that Eq. (7) [with $p(1,2,3)=p_K(1,2,3)$]

$$g(r_{12})\vec{\nabla}_1\mathfrak{u}(r_{12})=\vec{\nabla}_1 g(r_{12})$$
$$+\rho g(r_{12})\int[1-g(r_{23})]g(r_{13})\vec{\nabla}_1\mathfrak{u}(r_{13})d\vec{r}_3 \qquad \text{(B1)}$$

has a unique solution.[25] In order to prove this we observe from the theory of linear integral equations[19] that either the inhomogeneous equation (B1) has a unique solution [for a given $g(r)$] or its associated homogeneous form has a finite number of linearly independent solutions, in which case Eq. (B1) has no solution or an infinite number of solutions.

Let us consider the homogeneous form

$$g(r_{12})\vec{\nabla}_1\mathfrak{u}(r_{12})$$
$$=\lambda\rho g(r_{12})\int[1-g(r_{23})]g(r_{13})\vec{\nabla}_1\mathfrak{u}(r_{13})d\vec{r}_3, \qquad \text{(B2)}$$

where λ is a fixed dimensionless parameter. Multiplying Eq. (B2) by $\vec{\nabla}_1\mathfrak{u}(r_{12})$, and integrating over $\vec{r}_2$, we find

$$\int g(r_{12})[\vec{\nabla}_1\mathfrak{u}(r_{12})]^2 d\vec{r}_2$$
$$\leqq |\lambda|\rho\int|1-g(r_{23})|\,|[g(r_{12})\vec{\nabla}_1\mathfrak{u}(r_{12})]$$
$$\circ[g(r_{13})\vec{\nabla}_1\mathfrak{u}(r_{13})]|d\vec{r}_2d\vec{r}_3<|\lambda|\rho\int|1-g(r_{23})|d\vec{r}_3$$
$$\times\int[g(r_{12})\vec{\nabla}_1\mathfrak{u}(r_{12})]^2d\vec{r}_2\ . \qquad \text{(B3)}$$

If we now impose the restriction[26]

$$g(r)\leqq 1\ , \qquad \text{(B4)}$$

Eq. (B3) immediately yields, with the aid of the normalization condition (4),

$$|\lambda|>1\ , \qquad \text{(B5)}$$

which shows that Eq. (B2) does not have nontrivial solutions when $\lambda=1$ (i.e., $\lambda=1$ is not an eigenvalue), and hence the solution of Eq. (B1) is unique. The several inequalities employed in deriving (B5) may be strong enough to compensate for the assumption of (B4). We have not, however, been able to prove (B5) without the condition (B4).

APPENDIX C: IDENTITIES NEEDED IN DERIVING EQ. (31)

We present here several typical identities employed in reducing the formulas for $Z_n(q)$ to relatively simple expressions (31). The essential part of the derivation of these integral identities is to replace the factor $\vec{q}\cdot\vec{q}_1$ by suitable equivalent ones inside the integral signs, using certain symmetry properties of the integrands. (In this Appendix, equivalence in integrating over variables $\vec{q}_i$ is indicated by an arrow.) Thus, we obtain

from $\vec{q}\cdot\vec{q}_1=\frac{1}{2}q^2+\frac{1}{2}[q_1{}^2-(\vec{q}-\vec{q}_1)^2\rightarrow\frac{1}{2}q^2$,

$$(2\pi)^{-3}\int\frac{\vec{q}\cdot\vec{q}_1}{q^2}F(\vec{q}-\vec{q}_1)F(q_1)d\vec{q}_1=\tfrac{1}{2}F_2(q), \qquad \text{(C1)}$$

and $$\int\frac{\vec{q}\cdot\vec{q}_1}{q^2}F(q_1)F(q_2)F(q_{12})F(\vec{q}-\vec{q}_1)F(\vec{q}-\vec{q}_2)d\vec{q}_{12}$$
$$=\tfrac{1}{2}\int F(q_1)F(q_2)F(q_{12})F(\vec{q}-\vec{q}_1)F(\vec{q}-\vec{q}_2)d\vec{q}_{12}\,; \qquad \text{(C2)}$$

from $\frac{1}{2}\vec{q}\cdot\vec{q}_1=\frac{1}{2}\vec{q}\cdot[\vec{q}_{12}+\vec{q}_2]\rightarrow\vec{q}\cdot\vec{q}_2$,

$$\tfrac{1}{2}\int\vec{q}\cdot\vec{q}_1F(q_1)F(\vec{q}-\vec{q}_1)F(q_{12})F(q_2)d\vec{q}_{12}$$
$$=\int\vec{q}\cdot\vec{q}_2F(q_1)F(\vec{q}-\vec{q}_1)F(q_{12})F(q_2)d\vec{q}_{12}\ ,$$

or

$$\tfrac{1}{2}\int \vec{q}\cdot\vec{q}_1 F(q_1)F(\vec{q}-\vec{q}_1)F_2(\vec{q}_1)d\vec{q}_1$$

$$= (2\pi)^{-3}\int \vec{q}\cdot\vec{q}_1 F(q_1)F(q_2)F(q_{12})F(\vec{q}-\vec{q}_2)d\vec{q}_{12} \quad ; \;|\quad \text{(C3)}$$

from

$$\tfrac{1}{3}\vec{q}\cdot\vec{q}_1 = \tfrac{1}{3}\vec{q}\cdot[\vec{q}_{12}+\vec{q}_{23}+\vec{q}_3] \rightarrow \vec{q}\cdot\vec{q}_3 \rightarrow \tfrac{1}{2}\vec{q}\cdot[\vec{q}_{23}+\vec{q}_3] = \tfrac{1}{2}\vec{q}\cdot\vec{q}_2 \ ,$$

$$\tfrac{1}{3}\int \vec{q}\cdot\vec{q}_1 F(q_1)F(\vec{q}-\vec{q}_1)F(q_{12})F(q_{23})F(q_3)d\vec{q}_{123}$$

$$= \tfrac{1}{2}\int \vec{q}\cdot\vec{q}_2 F(q_1)F(\vec{q}-\vec{q}_1)F(q_{12})F(q_{23})F(q_3)d\vec{q}_{123} \ ,$$

or

$$\tfrac{1}{3}\int \vec{q}\cdot\vec{q}_1 F(q_1)F(\vec{q}-\vec{q}_1)F_3(q_1)d\vec{q}_1$$

$$= \tfrac{1}{2}(2\pi)^{-3}\int \vec{q}\cdot\vec{q}_1 F(q_2)F(\vec{q}-\vec{q}_2)F(q_{12})F_2(q_1)d\vec{q}_{12} \ ; \quad \text{(C4)}$$

from

$$\tfrac{1}{2}\vec{q}\cdot\vec{q}_1 = \tfrac{1}{2}\vec{q}\cdot[\vec{q}_{12}+\vec{q}_2] \rightarrow \vec{q}\cdot\vec{q}_2 \rightarrow \tfrac{1}{3}\vec{q}\cdot[(\vec{q}-\vec{q}_1)+\vec{q}_{12}+\vec{q}_2] = \tfrac{1}{3}q^2,$$

$$\tfrac{1}{2}\int \frac{\vec{q}\cdot\vec{q}_1}{q^2} F(\vec{q}-\vec{q}_1)F(q_{12})F(q_2)d\vec{q}_{12}$$

$$= \tfrac{1}{3}\int F(\vec{q}-\vec{q}_1)F(q_{12})F(q_2)d\vec{q}_{12} \ ,$$

$$\text{or}\quad \tfrac{1}{2}(2\pi)^{-3}\int \frac{\vec{q}\cdot\vec{q}_1}{q^2} F(\vec{q}-\vec{q}_1)F_2(q_1)d\vec{q}_1 = \tfrac{1}{3}F_3(q) \quad ; \quad \text{(C5)}$$

from

$$\tfrac{1}{3}\vec{q}\cdot\vec{q}_1 = \tfrac{1}{3}\vec{q}\cdot[\vec{q}_{12}+\vec{q}_{23}+\vec{q}_3]$$

$$\rightarrow \vec{q}\cdot\vec{q}_3 \rightarrow \tfrac{1}{4}\vec{q}\cdot[(\vec{q}-\vec{q}_1)+\vec{q}_{12}+\vec{q}_{23}+\vec{q}_3] = \tfrac{1}{4}q^2,$$

$$\tfrac{1}{3}\int \frac{\vec{q}\cdot\vec{q}_1}{q^2} F(\vec{q}-\vec{q}_1)F(q_{12})F(q_{23})F(q_3)d\vec{q}_{123}$$

$$= \tfrac{1}{4}\int F(\vec{q}-\vec{q}_1)F(q_{12})F(q_{23})F(q_3)d\vec{q}_{123} \ ,$$

$$\text{or}\quad \tfrac{1}{3}(2\pi)^{-3}\int \frac{\vec{q}\cdot\vec{q}_1}{q^2} F(\vec{q}-\vec{q}_1)F_3(q_1)d\vec{q}_1 = \tfrac{1}{4}F_4(q) \ . \quad \text{(C6)}$$

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[†] Present address: Department of Physics and Astronomy, University of Kansas, Lawrence, Kansas 66044.

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IV and V on convergence of the iteration procedure and uniqueness of the solution for $S'(k)/S^2(k)$.

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Calculated Electrical Resistivity of Liquid Alloys

J. L. Tomlinson*

Naval Weapons Center Corona Laboratories, Corona, California 91720

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The electrical resistivities of several polyvalent alloy liquids were calculated from the pseudopotential form factors and Percus-Yevick hard-sphere structure factors of Ashcroft and Langreth. Good agreement with experiment was obtained by choosing hard-sphere diameter ratios other than one in four of the five systems. It is concluded that the hard-sphere structure factors with the Ashcroft pseudopotential form factors can give better agreement with experiment than have previous calculations.

INTRODUCTION

Tomlinson and Lichter[1] have reported the variation of electrical resistivity with temperature for certain compositions of molten Cd-Bi, Cd-Sn, Cd-Pb, In-Bi, and Sn-Bi. In that paper, the observed electrical resistivity was explained by using a fluctuation scattering model where the electron concentration varied with alloy composition. The deviation in electron-to-atom ratio from the normal valence was then shown to correlate with the excess free energy of mixing. In this paper, the isothermal electrical resistivity of these same alloys is calculated by using the pseudopotential method; in this case, the conduction electrons are considered to be scattered by a weak potential due to the collection of screened ions.

An expression for the electrical resistivity of a liquid binary alloy using pseudopotential form factors and structure factors (or interference functions) was written by Faber and Ziman.[2] Keating[3] had shown that the partial structure factors necessary for writing the electrical resistivity were available from experiment. However, most available structure factors have been calculated from experiments after certain approximations,[4] or are available for a limited number of alloy compositions.[5] Recently, Ashcroft and Langreth[6] and Enderby and North[7] have written partial structure factors for liquid alloys by finding the Fourier transform of the solution of the Percus-Yevick equation for a mixture of hard spheres. These structure factors were then applied to the calculation of the resistivities of several liquid alloys by Ashcroft and Langreth.[8] In this approach, the resistivity depends upon the effective core radius of the constituent potentials, the total packing fraction, the ratio of hard-sphere diameters, and the composition.

Using the notation of Ashcroft and Langreth, we have calculated the electrical resistivities of liquid alloys of the systems Cd-Bi, Cd-Pb, Cd-Sn, Sn-Bi, and In-Bi. The results are compared with the experimental values of Tomlinson and Lichter,[1] Roll and Swamy,[9] Matuyama,[10] Verhoeven and Lieu,[11] and Takeuchi and Endo.[12]

THEORY

The electrical resistivity of a liquid alloy was written by Ashcroft and Langreth[8] as

$$\rho = \frac{4\pi^3\hbar}{e^2 k_F} Z^* \int_0^1 \{X V_2^2(y) S_{22}(y) + 2[X(1-X)]^{1/2} \times V_2(y) V_1(y) S_{12}(y) + (1-X) V_1^2(y) S_{11}(y)\} y^3 dy,$$

where $V_i(y)$ is the electron-ion pseudopotential form factor for component i, Z^* is the effective valence, X is the mole fraction of component 2, $S_{ij}(y)$ is the partial structure factor, and y is the wave number divided by $2k_F$.

In these calculations, the pseudopotential form factor proposed by Ashcroft[13,14] was used. For an alloy, this is written

$$V_i(y) = \{\lambda^2 \cos(s_i y)/[y^2 + \lambda^2 f(y)]\} Z_i/Z ,$$

where $\lambda^2 = 1/\pi a_0 k_F$,