High-density expansion of the electron-gas correlation function

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A high-density expansion of the electron-gas correlation function $g(r)$ is carried out in powers of the coupling constant αr_s. It is found that at zero interparticle separation, $g(0) = 1/2 - \alpha r_s(\pi^2 + 6\ln 2 - 3)/5\pi$ $-(3\alpha r_s/2\pi)^2 \ln(r_s)(3 - \pi^2/4) + O(r_s^2)$. For large interelectronic separation, the zero-order correction to $g(r)$ is obtained and the correction linear in r_s is estimated.

I. INTRODUCTION

Many of the electron-electron interaction effects in simple metals may be reasonably investigated using the interacting-electron-gas model. A particularly simple function which reflects the effects of these interactions is the two-particle correlation function $g(r)$. This function, which is normalized to one for large r, is proportional to the probability of finding two electrons separated by a distance r.

Approximate calculations of the electron-gas response function can be used to obtain approximate correlation functions.[1-3] The requirement that the derived correlation function be reasonable has turned out to be a sensitive test of the validity of the response function. There are also a number of direct calculations of $g(r)$.[4,5] Thus, it is important to know as many exact properties of the correlation functions as possible. Some of these exact properties are listed here;

(a) $g(r) \geq 0$;

(b) $\dfrac{N}{\Omega} \displaystyle\int_0^\infty [g(r) - 1]4\pi r^2\, dr = -1$,

where N is the number of electrons and Ω is the volume of the system;

(c) $\dfrac{dg(r)}{dr}\bigg|_{r\to 0} = \dfrac{1}{a_0} g(0)$,

where a_0 is the Bohr radius;

(d) $\dfrac{d}{dr_s} \displaystyle\int_0^\infty [g(x) - 1]x\,dx \leq 0$,

where $x = r/r_s a_0$ and $\frac{4}{3}\pi(r_s a_0)^3 = \Omega/N$.

Result (a) follows, simply because $g(r)$ is a probability, and (b) expresses the fact that a given electron in a N-electron system is surrounded by $N - 1$ other electrons. Result (c) can be obtained by noting that for small interelectronic separations, the many-body problem becomes an effective two-body problem.[6] Result (d) states the electrostatic energy per electron decreases as

the density of the system is decreased. This result can be derived by noting that the electrostatic interaction energy per particle is

$$\frac{\epsilon_{\text{int}}}{N} = \frac{e^2}{r_s a_0} \int \left(\frac{g(x) - 1}{x}\right) d^3x,$$

and ϵ_{int}/N in units of $4\pi e^2/r_s a_0$ gives the left-hand side of (d). If one uses dimensionless units the Hamiltonian for the system can be written

$$H = \frac{1}{r_s^2}\left(-\frac{\hbar^2}{2m}\sum_i \nabla_{x_i}^2 + e^2 r_s \sum_{i<j}(|\vec{x}_i - \vec{x}_j|)^{-1}\right)$$

$$= \frac{1}{r_s^2}(A + B r_s).$$

Because B is a positive perturbation, the expectation value of B must not increase as r_s increases, and $\langle B \rangle = r_s \epsilon_{\text{int}}$.

The main purpose of this paper is to consider properties of the correlation function which can be obtained from a high-density perturbation expansion. These calculations yield results which are exact to the lowest orders in r_s. The results for small r_s are

(i) $g(0) = \frac{1}{2} - (\alpha r_s/5\pi)(\pi^2 + 6\ln 2 - 3)$

$\qquad - (3\alpha r_s/2\pi)^2 \ln(r_s)(3 - \frac{1}{4}\pi^2) + O(r_s^2)$,

where

$$\alpha = (4/9\pi)^{1/3}.$$

(ii) When $q_F r$ (q_F is the Fermi wave vector) is large compared to $1/(r_s)^{1/2}$,

$$g(r) \to 1 + \frac{9\cos(2q_F r)}{4(q_F r)^4} + O(r_s).$$

(iii) When $q_F r$ is large compared to one, the term linear in r_s for $g(r)$ could not be calculated exactly, but it is shown that there is a long-range oscillatory correction to the correlation function proportional to r_s, which does not converge to zero faster than $\ln(r)/r^4$.

A good numerical approximation to the linear correction to the zero separation correlation

function in result (i) has been previously obtained by Geldart.[7] The second result is not the standard Hartree-Fock form for $g(r)$, and this result shows that a perturbation expansion can yield zero-order corrections to the correlation function. The third result shows that perturbation corrections to the electron-gas correlation function can be relatively long range.

II. THEORY

The basic result used here is a simple formula [Eq. (6)] relating the structure factor $S(q)$ to the functional dependence of the ground-state energy on the Fourier components of the Coulomb potential. From this result, the direct second-order contribution to the structure factor is obtained explicitly [Eq. (11)]. Using this second-order contribution to $S(q)$, it is possible to obtain the linear dependence of $g(0)$ on r_s [Eq. (12)]. It is also possible to sum an infinite series of ring diagrams for $S(q)$ to obtain the $r_s^2 \ln(r_s)$ contribution to $g(0)$ [Eq. (19)], and the zero-order correction to $g(r)$ for large r [Eq. (18)]. By examining the second-order exchange contribution to the structure factor, it is possible to estimate the lowest-order perturbation correction to the correlation function for large r.

The correlation function $g(r)$ is essentially the Fourier transform of the structure factor,[8] $S(q)$,

$$g(r) - 1 = \frac{1}{N} \sum_q e^{i \vec{q} \cdot \vec{r}} [S(q) - 1]. \tag{1}$$

The structure factor is in turn given by

$$S(q) - 1 = \langle S(q)_{\mathrm{op}} - 1 \rangle, \tag{2}$$

with

$$S(q)_{\mathrm{op}} - 1 = \frac{1}{N} \sum_{K\sigma, K'\sigma'} a_{K,\sigma}^\dagger a_{K',\sigma'}^\dagger a_{K'-q,\sigma'} a_{K+q,\sigma}. \tag{3}$$

The symbols $a_K^\dagger$ and a_K denote the standard creation and annihilation operators, and $\langle \cdots \rangle$ denotes a zero-temperature expectation value.

The Hamiltonian for this system is the sum of kinetic and potential-energy terms. The potential energy or interaction terms can be written in terms of $S(q)_{\mathrm{op}}$, and the total Hamiltonian is

$$H = \sum_{K\sigma} \frac{\hbar^2 K^2}{2m} a_{K\sigma}^\dagger a_{K\sigma} + \frac{N}{2} \sum_q v(q)[S(q)_{\mathrm{op}} - 1], \tag{4}$$

with

$$v(q) = 4\pi e^2 / q^2 \Omega. \tag{5}$$

Because $S(q)_{\mathrm{op}}$ appears in the Hamiltonian, it is possible to obtain the structure factor if one knows how the energy of the system depends on $v(q)$. The structure factor is obtained by using the

"Feynman theorem,"[9] which states that if

$$H\psi = E\psi$$

and

$$H = H_0 + \gamma H_1,$$

then

$$\frac{dE}{d\gamma} = \langle H_1 \rangle.$$

This result can be applied to obtain $S(q)$ by treating one particular term in the sum over q of $v(q)[S(q)_{\mathrm{op}} - 1]$ as H_1, yielding

$$S(q) - 1 = \frac{2}{N} \frac{\partial E}{\partial [v(q)]}. \tag{6}$$

This formula for the structure factor is particularly useful when the energy is calculated as a perturbation series in the interaction terms, because differentiation with respect to $v(q)$ is relatively easy.

The Hartree-Fock approximation to the energy yields the Hartree-Fock approximation for the structure factor

$$[S(q) - 1]_{\mathrm{HF}} = \frac{-1}{N} \sum_{K\sigma} f(K) f(K + q), \tag{7}$$

where $f(K)$ is the Fermi function for the noninteracting system. In terms of the variable $y = q/2q_{\mathrm{F}}$,

$$[S(y) - 1]_{\mathrm{HF}} = \begin{cases} -1 + \frac{3}{2} y - \frac{1}{2} y^3 & \text{for } y < 1, \\ 0 & \text{for } y \geq 1. \end{cases} \tag{7'}$$

The integral form of Eq. (1), written in terms of y, is

$$g(r) - 1 = 12 \int_0^\infty \frac{\sin(2q_{\mathrm{F}} r y)}{2q_{\mathrm{F}} r y} [S(y) - 1] y^2 \, dy. \tag{1'}$$

Using the Hartree-Fock approximation for $S(q)$ [Eq. (7')] yields

$$[g(r) - 1]_{\mathrm{HF}} = -\frac{9}{2} \left(\frac{\sin(q_{\mathrm{F}} r) - q_{\mathrm{F}} r \cos(q_{\mathrm{F}} r)}{(q_{\mathrm{F}} r)^3} \right)^2. \tag{8}$$

The Hartree-Fock result yields $g(0) = \frac{1}{2}$, and for large r,

$$[g(r) - 1]_{\mathrm{HF}} = -\frac{9}{4} \left(\frac{1}{(q_F r)^4} - \frac{\cos(2q_F r)}{(q_F r)^4} \right). \tag{9}$$

As will be shown later, the lowest-order perturbative correction to $g(r)$ cancels the nonoscillatory term in Eq. (9), when $q_F r$ is much greater than $1/\sqrt{r_s}$ and $r_s \ll 1$.

The second-order perturbative corrections to the the energy yield corresponding corrections to $S(q)$ and $g(r)$. The energy correction consists of both direct and exchange terms which are repre-

sented by the lowest-order "ring diagram," and the corresponding exchange diagram. The resulting direct and exchange corrections to $S(q)$ are denoted as $\Delta S(q)_D$ and $\Delta S(q)_E$. Although the direct

second-order energy is divergent, differentiation with respect to $v(q)$ yields a finite result for $\Delta S(q)_D$, except in the limit when y vanishes. The direct contribution to $S(q)$ is

$$\Delta S(q)_D = \frac{2}{N} \sum_{K\sigma, K'\sigma'} v(q)\ \frac{f(K)f(K')[1-f(K+q)][1-f(K'-q)]}{\hbar^2[K^2+K'^2-(K+q)^2-(K'-q)^2]/2m}\ . \tag{10}$$

The sum can be evaluated, and

$$\Delta S(y)_D = \begin{cases} -\dfrac{\alpha r_s}{40\pi y^2}\left(58y - 6y^3 - 80y\ln2 + \dfrac{\ln(1-y)}{y}(1-y)^3(8+9y+3y^2)\right. \\[4mm] \qquad\qquad \left. + \dfrac{\ln(1+y)}{y}(1+y)^3(8-9y+3y^2)\right)\ \text{for}\ y<1, \\[6mm] -\dfrac{\alpha r_s}{5\pi y^2}\left(\dfrac{11}{2} +y^2+2\ln(y)y^2(5-y^2)\ +\dfrac{\ln(y-1)}{y}(y-1)^3(1+3y+y^2)\right. \\[4mm] \qquad\qquad \left. + \dfrac{\ln(y+1)}{y}(y+1)^3(1-3y+y^2)\right)\ \text{for}\ y\ge1. \end{cases} \tag{11}$$

The exchange contribution to $S(q)$ can be obtained from Eq. (10) if $v(q)$ is replaced by $-\delta_{\sigma,\sigma'}v(q+K-K')$. Unfortunately, I could not evaluate the resulting sum. However, it is still possible to obtain both the second-order direct and exchange corrections to $g(0)$ because the exchange contribution is minus one half the direct contribution. This can be seen because the summation over q is unchanged if q is replaced by $(K'-K-q)$. The restriction expressed by $\delta_{\sigma,\sigma'}$ introduces the factor of $\frac{1}{2}$. The resulting second-order correction to $g(0)$ is

$$\Delta g(0)_2 = 6\int_0^\infty \Delta S(y)_D y^2\,dy\ = -\frac{\alpha r_s}{5\pi}(\pi^2+6\ln2-3)$$

$$= -\frac{r_s}{2}\left(\frac{1}{1.367}\right). \tag{12}$$

A problem associated with $\Delta S(q)_D$ but not $\Delta S(q)_E$ is that it diverges as $1/q$ for small q. An expansion of Eq. (11) for small y yields

$$\Delta S(y)_D \to -(2\alpha r_s/\pi y)(1-\ln2)+O(1). \tag{13}$$

This result can also be obtained using an alternative method for evaluating ring diagrams which was used by Gell-Mann and Brueckner.[10] The alternative expression for small q is

$$\Delta S(y)_D = -\frac{3(\alpha r_s)}{16\pi^4 y}\int_{-\infty}^\infty Q^2(u)\,du, \tag{14}$$

where

$$Q(u) = 4\pi(1 - u\cot^{-1}u). \tag{15}$$

The integral over u in Eq. (14) yields Eq. (13). The divergence in $\Delta S(q)_D$ for small q is eliminated by summing the infinite set of ring diagrams. The result is

$$\Delta S(y)_R = -\frac{3\alpha r_s}{16\pi^4 y}\int_{-\infty}^\infty \left(\frac{Q^2}{1+Q\alpha r_s/4\pi^2 y^2}\right)du. \tag{16}$$

The integrand appears to differ from the standard Gell-Mann-Breuckner logarithm result, because the differentiation with respect to $v(q)$ introduces a factor of n to the nth order diagram. Evaluating Eq. (16) gives

$$\Delta S(y)_R \to -\tfrac{3}{2}y\quad(y\ll\sqrt{r_s}). \tag{17}$$

When this result is added to the Hartree-Fock result [Eq. (7')], the resulting correlation function has only an oscillatory term for large r, i.e.,

$$g(r) - 1 \to -\frac{9}{4}\frac{\cos(2q_F r)}{(q_F r)^4}+O(r_s). \tag{18}$$

This is the second result pointed out in Sec. I.[11] It may at first seem strange that one could obtain a perturbation correction to $g(r)$, which is formally independent of the electron charge. In fact, the charge enters this term because the asymptotic limit is achieved only when $q_F r\gg 1/\sqrt{r_s}$, assuming $r_s\ll1$.

Third- and higher-order perturbation corrections to $g(r)$ are formally divergent, as are the corresponding energies. The divergent terms must be summed to obtain finite results. The correction to $g(0)$ of order $r_s^2\ln(r_s)$ is obtained

as an integral over y of a sum analogous to Eq. (16), except the sum starts at $n=3$, instead of $n=2$. Furthermore, one must also consider diagrams in which the electrons associated with one of the interactions are exchanged. These diagrams do not contribute to the lowest-order Gell-Mann-Brueckner-type divergence, but because of the differentiation with respect to $v(q)$, one of the interaction lines need not contribute to the divergence. The exchange contribution to Δg is $-\frac{1}{2}$ the direct contribution. The total ring diagram correction to $g(r)$ is

$$\Delta g(0)_R = +\frac{9(\alpha r_s)^2}{32\pi^6}\int_0^\infty dy \int_{-\infty}^\infty du \left(\frac{Q^3 y}{y^2 + Q\alpha r_s/4\pi^2}\right)$$

$$= -\left(\frac{3\alpha r_s}{2\pi}\right)^2 (\alpha r_s)^2 \ln(r_s)(3 - \tfrac{1}{4}\pi^2) + O(r_s^2).$$

(19)

When Eqs. (12) and (19) are combined, the first result of Sec. I is obtained.

The final new result mentioned in Sec. I is obtained by returning to the second-order corrections to $S(q)$. The correction, $\Delta S(y)_D$ of Eq. (7') could, in principle, be Fourier transformed to yield a corrections to $g(r)$ for all r, which is proportional to r_s. Such a result would be incomplete because $\Delta S(y)_E$ is unknown. The result would also be incorrect because of the unphysical divergence in $\Delta S(y)_D$ for small y. However, for large r, oscillatory behavior in $g(r)$ is determined by the non-analytic behavior of $S(y)$ at $y=1$. Although $S(y)_D$ and its derivative are continuous at $y=1$, its second derivative is not, and

$$\frac{d^2\Delta S(y)_D}{dy^2}\bigg|_{1+\epsilon} - \frac{d^2\Delta S(y)_D}{dy^2}\bigg|_{1-\epsilon} = -\frac{3\alpha r_s}{\pi}. \qquad (20)$$

This yields a correction to $g(r)$ proportional to $1/r^4$ for large r, but the dominant corrections are obtained from the second-order exchange term.

The function $\Delta S(y)_E$ has not been obtained, but it is possible to qualitatively investigate its analytic structure near $y=1$. Because $v(q+K-K')$ appears in the formula for $\Delta S(y)_E$, which is analogous to Eq. (10), $\Delta S(y)_E$ is more singular than $\Delta S(y)_D$. When y is slightly larger than one, the behavior of $\Delta S(y)_E$ is reflected in the integral

$$I(y) = \int_0^1 dx_1 \int_0^1 dx_2 \frac{1}{x_1 + x_2 + \epsilon}$$

$$\times \int \frac{d^2\rho_1 d^2\rho_2}{(x_1 + x_2 + \epsilon)^2 + (\rho_1 - \rho_2)^2}, \qquad (21)$$

where $\vec{\rho}_1$ and $\vec{\rho}_2$ are two-dimensional vectors which represent the components of $\vec{K}$ and $\vec{K}'$ perpendicular to $\vec{q}$, $\rho_i^2 < x_i$, and $\epsilon = y - 1$. An ap-

proximate solution of this integral yields

$$I(y) \approx (y-1)^2[\ln(y-1)]^2 + \text{(more smoothly}$$

$$\text{varying functions of } y).$$

(22)

If $I(y)$ is continued as smoothly as possible to values of y less than one, and Fourier transformed, the resulting function of $q_F r$ converges as rapidly as possible to zero for large r. For large r, the second-order terms in $S(q)$ yield an oscillatory correction to $g(r)$, given by

$$g(r) - 1 \rightarrow \alpha r_s[f_c(q_F r)\cos(2q_F r) + f_s(q_F r)\sin(2q_F r)].$$

(23)

The approximate knowledge of $\Delta S(y)_E$ implies

$$|f_c(q_F r)| > C\ln(q_F r)/(q_F r)^4, \qquad (24)$$

with the constant C being roughly order of magnitude one.

III. DISCUSSION

A basic problem with the results obtained here is that r_s in real metals is greater than one. The perturbation expansion of $g(r)$ (or the energy) is poorly convergent for metallic electron densities. Thus, the results presented here are useful primarily as checks of other theoretical results in the small r_s range. The r_s^2 correction to $g(0)$ could be calculated only with considerable effort, since several diagrams must be summed.

The correction to $g(r)$ for large r which is proportional to r_s is relatively small, even at metallic electron densities. Nonetheless, this result suggests that higher-order perturbation terms could produce even longer-range corrections to the correlation function. In principle, the perturbation expansion could give a picture of the transition from a gaslike to a liquidlike correlation function.

There has recently been considerable interest in the two-dimensional electron gas. In two dimensions, the same procedure could be followed to obtain an expansion of $g(r)_{2D}$. Although numerical results have not been obtained, we note that

$$g(0)_{2D} = \tfrac{1}{2} - ar_s + br_s^2 + cr_s^3 \ln(r_s) + \cdots.$$

With considerable effort, all the terms up to order $r_s^3 \ln(r_s)$ could be obtained.

It would be desirable to construct a parametrized $g(r)$ which satisfies the rigorous conditions (a)-(d) mentioned in Sec. I, as well as the power series expansion in r_s at low densities. Further conditions on the properties of $g(r)$ could be imposed by the requirement that the ground-state energy derived from $g(r)$ satisfies the exact high-

density expansion. This is a difficult task, since an examination of the power-series expansion of $g(r)$ shows that terms containing $\ln(r_s)$ in the energy expansion are related both to a long-range "tail" in $g(r)$, and a logarithmic dependence of

$g(0)$ on r_s.

[1]K. S. Singwi, M. P. Tosi, R. H. Land, and A. Sjolander, Phys. Rev. 176, 589 (1968); Phys. Rev. B 1, 1044 (1970).

[2]F. Toigo and T. O. Woodruff, Phys. Rev. B 2, 3958 (1970); 4, 371 (1971); 4, 4312 (1971).

[3]D. N. Lowy and G. E. Brown, Phys. Rev. B 12, 2138 (1975).

[4]H. Yasuhura, Solid State Commun. 11, 1481 (1972); J. Phys. Soc. Jpn. 36, 361 (1974).

[5]B. B. J. Hede and J. P. Carbotte, Can. J. Phys. 50, 1756 (1972).

[6]J. C. Kimball, Phys. Rev. A 7, 1648 (1973); J. Phys.

A 8, 1513 (1975).

[7]D. J. W. Geldart, Can. J. Phys. 45, 3139 (1967).

[8]See, for example, D. Pines, Elementary Excitations in Solids (Benjamin, New York, 1962).

[9]C. Kittel, Quantum Theory of Solids (Wiley, New York, 1963), p. 109.

[10]M. Gell-Mann and K. A. Brueckner, Phys. Rev. 106, 364 (1957).

[11]N. H. March, W. H. Young, and S. Sampanthar, The Many-Body Problem in Quantum Mechanics (Cambridge U.P., Cambridge, England, 1967). This result is mentioned but not proven on p. 168.