PHYSICAL REVIEW B VOLUME 1, NUMBER 3 1 FEBRUARY 1970

Electron Correlations at Metallic Densities. IV*

K. S. Singwi
Northwestern University, Evanston, Illinois and Argonne National Laboratory, Argonne, Illinois 60439

AND

A. Sjölander,† M. P. Tosi,‡ and R. H. Land
Argonne National Laboratory, Argonne, Illinois 60439

(Received 24 September 1969)

This paper presents an extension of an earlier theory of the dielectric function of the electron liquid in the metallic density range, which took into account the short-range correlations arising from both Coulomb and exchange effects through a local-field correction depending on the pair correlation function. The extension consists in allowing for the adjustment of the pair correlation function to the external field and results in a screening of the Coulomb potential entering the local field. Self-consistent numerical calculations have been carried out to evaluate the dielectric function and the density correlation function in the metallic-density range. Results are presented for the static pair correlation function, the correlation energy, the compressibility, the plasmon dispersion, and the screening of a static point charge. In contrast to the earlier theories, the present theory satisfies closely the compressibility sum rule and also gives reasonable values for the pair correlation function. The same approximation has been straightforwardly applied to treat the spin correlations in the paramagnetic state. The calculation yields fair values for the static paramagnetic susceptibility and for the internal field as a function of wave vector. A simple analytic representation is presented for the numerical values of the local-field correction as a function of wave vector over the metallic density range, which should prove useful for applications.

I. INTRODUCTION

THE natural, and a very fruitful, formulation of the theory of screening in the electron liquid is based on the introduction of a wave-vector and frequency-dependent dielectric function.[1] This function enters in a large class of calculations for free-electronlike metals. In an earlier paper,[2] hereafter referred to as I, an improved expression was given for the dielectric function, which includes explicitly the short-range correlations arising from both Coulomb and exchange effects. The theory as outlined in I provided a self-consistent scheme for calculating the dielectric function. The numerical solution of the self-consistent problem, as was shown in I, gave for large wave vectors a marked improvement upon the earlier theories[1,3] of the dielectric function, as evidenced by the behavior of the static pair correlation function at small distances in the metallic density range. However, for small wave vectors the new dielectric function shared with the earlier theories[1,3] the unsatisfactory feature that the compressibility sum rule was strongly violated. This violation would lead to an incorrect value for the velocity of sound in metals. In earlier work,[4] this deficiency in the dielectric function was rectified by introducting in a rather *ad hoc* fashion a parameter in the Hubbard factor, which takes only exchange into account—the value of the parameter could be adjusted so as to give the correct value for the compressibility. However, the introduction of this parameter does not improve the poor behavior of the pair-correlation function at small distances.[5]

In a recent publication[6] the present authors have outlined a refinement of their earlier theory[2] and have shown by a self-consistent numerical calculation that it gives satisfactory values both for the pair correlation function and for the compressibility. This refinement leads to a screening, through the static dielectric function, of the Coulomb interaction entering the local-field term of the effective potential in I. The purpose of this paper is to discuss in detail this modification of our earlier theory and the nature of the approximations involved. We present the results of numerical calculations of the pair correlation function, the screening charge around an impurity, the correlation energy and the compressibility of the electron liquid in the metallic-density range and compare the results with those based on previous theories. We also discuss a similar modification of the expression recently derived[7] for the dynamic paramagnetic susceptibility, and present results for the correlations between different pairs of spins and for the static susceptibility. An interesting

---

* Based on work performed under the auspices of the U. S. Atomic Energy Commission. One of the authors (K. S. S.) was partly supported by the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Center and by the National Science Foundation under Contract No. GP-11054.

† On leave of absence from the Institute of Theoretical Physics, Fack, S-402 20, Göteberg, Sweden.

‡ Present address: Department of Physics, University of Messina, Messina, Italy.

[1] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. **28**, No. 8 (1954); P. Nozières and D. Pines, Nuovo Cimento **9**, 470 (1958).

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

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

[4] L. J. Sham, Proc. Roy. Soc. (London) **A283**, 33 (1965); D. J. W. Geldart and S. H. Vosko, Can. J. Phys. **44**, 2137 (1966).

[5] M. P. Tosi, Nuovo Cimento **1**, 160 (1969).

[6] K. S. Singwi, A. Sjölander, M. P. Tosi, and R. H. Land, Solid State Commun. **7**, 1503 (1969).

[7] R. Lobo, K. S. Singwi, and M. P. Tosi, Phys. Rev. **186**, 470 (1969).

result that emerges from the latter calculation is a very gentle dependence of the molecular field parameter on the wave vector—a result which is in agreement with observations.

II. THEORETICAL FORMULATION

A. Equation of Motion for Density Fluctuations

The equation of motion for the single-particle density matrix $\langle\Psi_\sigma^\dagger(\mathbf{x},t)\Psi_\sigma(\mathbf{x}',t)\rangle$ in the presence of an external potential $V_e(\mathbf{x},t)$ can be written in the following form [see Eq. (A4) of I]:

$$\left\{i\hbar\frac{\partial}{\partial t}-\frac{\hbar^2}{2m}(\Delta_{\mathbf{x}}^2-\Delta_{x'}^2)-V_e(\mathbf{x},t)+V_e(\mathbf{x}',t)\right.$$
$$\left.-\int d\mathbf{x}''[\Phi(\mathbf{x}-\mathbf{x}'')-\Phi(\mathbf{x}'-\mathbf{x}'')]n(\mathbf{x}'',t)\right\}$$
$$\times\langle\Psi_\sigma^\dagger(\mathbf{x},t)\Psi_\sigma(\mathbf{x}',t)\rangle-i\hbar\int d\mathbf{x}''[\Phi(\mathbf{x}-\mathbf{x}'')-\Phi(\mathbf{x}'-\mathbf{x}'')]$$
$$\times\frac{\delta\langle\Psi_\sigma^\dagger(\mathbf{x},t)\Psi_\sigma(\mathbf{x}',t)\rangle}{\delta V_e(\mathbf{x}'',t)}=0. \quad (1)$$

Here, $\Phi(\mathbf{x})$ is the Coulomb potential and $n(\mathbf{x},t)$ is the nonuniform density of electrons. The Wigner phase-space distribution function $f_\sigma(\mathbf{p},\mathbf{R},t)$ is defined by

$$\langle\Psi_\sigma^\dagger(\mathbf{R}+\tfrac{1}{2}\mathbf{r},t)\Psi_\sigma(\mathbf{R}-\tfrac{1}{2}\mathbf{r},t)\rangle$$
$$=\int\frac{d\mathbf{p}}{(2\pi)^3}e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}f_\sigma(\mathbf{p},\mathbf{R},t). \quad (2)$$

In terms of this distribution function, the particle density $n(\mathbf{R},t)$, the particle current $\mathbf{j}(\mathbf{R},t)$, and the momentum current tensor $\pi(\mathbf{R},t)$ are, respectively, given by

$$n(\mathbf{R},t)=\sum_\sigma\int d\mathbf{p}\, f_\sigma(\mathbf{p},\mathbf{R},t), \quad (3a)$$

$$\mathbf{j}(\mathbf{R},t)=\sum_\sigma\int d\mathbf{p}\frac{\mathbf{p}}{m}f_\sigma(\mathbf{p},\mathbf{R},t), \quad (3b)$$

and

$$\pi(\mathbf{R},t)=\sum_\sigma\int d\mathbf{p}\frac{\mathbf{pp}}{m}f_\sigma(\mathbf{p},\mathbf{R},t). \quad (3c)$$

Introducing in Eq. (1) the variables $(\mathbf{R},\mathbf{r},t)$ instead of $(\mathbf{x},\mathbf{x}',t)$ and using Eq. (2), we obtain the equation of motion for $f_\sigma(\mathbf{p},\mathbf{R},t)$. The equation of continuity

$$(\partial/\partial t)n(\mathbf{R},t)+\nabla\cdot\mathbf{j}(\mathbf{R},t)=0 \quad (4)$$

and the equation for the momentum density

$$\mathbf{P}(\mathbf{R},t)=m\mathbf{j}(\mathbf{R},t),$$

$$\frac{\partial}{\partial t}\mathbf{P}(\mathbf{R},t)+\nabla\cdot\pi(\mathbf{R},t)+\int d\mathbf{x}\ \nabla\Phi(\mathbf{R}-\mathbf{x})\langle\rho(\mathbf{x},t)\rho(\mathbf{R},t)\rangle_c$$
$$=-n(\mathbf{R},t)\nabla V_H(\mathbf{R},t), \quad (5)$$

follow immediately. Here, $\langle\rho(\mathbf{x},t)\rho(\mathbf{R},t)\rangle_c=\langle\rho(\mathbf{x},t)\rho(\mathbf{R},t)\rangle-\langle\rho(\mathbf{x},t)\rangle\langle\rho(\mathbf{R},t)\rangle$ is the equal-time density-correlation function, and

$$V_H(\mathbf{R},t)=V_e(\mathbf{R},t)+\int d\mathbf{x}\Phi(\mathbf{R}-\mathbf{x})n(\mathbf{x},t) \quad (6)$$

is the Hartree potential. Combining Eqs. (4) and (5) we have

$$\frac{\partial^2}{\partial t^2}n(\mathbf{R},t)-\frac{1}{m}\nabla_\alpha\nabla_\beta\pi_{\alpha\beta}(\mathbf{R},t)$$
$$-\frac{1}{m}\int d\mathbf{x}\nabla_\alpha\{\nabla_\alpha\Phi(\mathbf{R}-\mathbf{x})\langle\rho(\mathbf{x},t)\rho(\mathbf{R},t)\rangle_c\}$$
$$=\frac{1}{m}\nabla_\alpha\{n(\mathbf{R},t)\nabla_\alpha V_H(\mathbf{R},t)\}, \quad (7)$$

where ∇_α denotes differentiation with respect to the αth Cartesian component of $\mathbf{R}$ and the usual convention of summation over repeated indices is used. We consider the deviation of the density from its uniform equilibrium value n to be caused by an infinitesimal external potential. We can then replace $n(\mathbf{R},t)$ on the right-hand side of Eq. (7) by n.

If one knew the functional dependence of $\pi(\mathbf{R},t)$ and $\langle\rho(\mathbf{x},t)\rho(\mathbf{R},t)\rangle_c$ on the density $n(\mathbf{R},t)$, Eq. (7) would give the relationship between $n(\mathbf{R},t)$ and the Hartree potential $V_H(\mathbf{R},t)$. The dielectric response function $\epsilon(\mathbf{q},\omega)$ is then given by

$$\epsilon(\mathbf{q},\omega)=1-\Phi(q)\alpha(\mathbf{q},\omega), \quad (8)$$

where $\alpha(\mathbf{q},\omega)$ is the Fourier transform of the equilibrium value of $\delta n(\mathbf{R},t)/\delta V_H(\mathbf{R}',t')$ and $\Phi(q)=4\pi e^2/q^2$.

We may introduce an effective potential $V_{\text{eff}}(\mathbf{R},t)$, defined by

$$\nabla V_{\text{eff}}(\mathbf{R},t)=\nabla V_H(\mathbf{R},t)$$
$$+\frac{1}{n}\int d\mathbf{x}\nabla\Phi(\mathbf{R}-\mathbf{x})\langle\rho(\mathbf{x},t)\rho(\mathbf{R},t)\rangle_c. \quad (9)$$

Then Eq. (7) takes the form

$$(\partial^2/\partial t^2)n(\mathbf{R},t)-(1/m)\nabla_\alpha\nabla_\beta\pi_{\alpha\beta}(\mathbf{R},t)$$
$$=(n/m)\nabla_\alpha\nabla_\alpha V_{\text{eff}}(\mathbf{R},t). \quad (10)$$

It should be emphasized that this is the equation of motion for the electron density, which is an average over the momentum distribution of the electrons. $V_{\text{eff}}(\mathbf{R},t)$ is the potential in which the charge density moves, and should not be considered as the potential acting on a particular electron. The second term on the right-hand side of Eq. (9) represents the local-field effects which are neglected in the RPA. Equation (10) is the starting point of our further discussion. We are here not particularly concerned about the momentum-dependent self-energy of an electron, or the momentum-dependent vertex correction entering the expression for the effective interaction between two electrons. In our procedure, we avoid making explicit approximations on these quantities, which are unnecessary for calculating the dielectric response function.

B. Density-Correlation Function

In I, the nonequilibrium density-correlation function $\langle\rho(\mathbf{x},t)\rho(\mathbf{R},t)\rangle_c$ was approximated by

$$\langle\rho(\mathbf{x},t)\rho(\mathbf{R},t)\rangle_c=[g(\mathbf{R}-\mathbf{x})-1]n(\mathbf{x},t)n(\mathbf{R},t)\,, \tag{11}$$

where $g(\mathbf{x})$ is the static pair correlation function in the absence of the external field. This approximation was found to be reasonable at large wave vectors, as one may expect the pair correlation function will be essentially unaffected by a rapidly varying external field. Here we attempt to improve upon the earlier treatment for small wave vectors by taking into account the adjustment of the pair correlation function to the external disturbance. We do this under the assumption that the irreducible part of the density-correlation function is short ranged in space and time, and, therefore, we assume that in the presence of the external field it depends only on the local density.[8] We pursue the formal development and introduce the above assumption at a later stage, in the hope of clarifying its connection with the formal many-body theory.

We express the time-ordered density correlation function $\langle T\rho(\mathbf{R},t)\rho(\mathbf{R}',t')\rangle_c$ in terms of its irreducible part $\alpha(Rt,R't')$ as follows:

$$\langle T\rho(1)\rho(1')\rangle_c=\alpha(1,1')+\int\alpha(1,2)\Phi(2,3)\alpha(3,1')d(2)d(3)+\cdots. \tag{12}$$

Here 1, 2, etc., stand for $(\mathbf{R}_1t_1)$, $(\mathbf{R}_2t_2)$ and so on, and $\Phi(1,2)$ stands for $\Phi(\mathbf{R}_1-\mathbf{R}_2)\delta(t_1-t_2)$. For $t=t'$ we have on the left-hand side of Eq. (12), the equal-time correlation function appearing in Eq. (9). Notice that $\alpha(1,1')$ occurring in Eq. (12) is time-ordered, and so are all the response functions in the rest of this section.

Separating $\alpha(1,2)$ into its equilibrium part, $\alpha_{\text{eq}}(1,2)$, and its deviation from equilibrium, $\bar{\alpha}(1,2)$, and linearizing with respect to $\bar{\alpha}(1,2)$, Eq. (12) can be written in the form

$$\langle T\rho(1)\rho(1')\rangle_c-\langle T\rho(1)\rho(1')\rangle_c^{\text{eq}}=\int\epsilon^{-1}(1,2)\bar{\alpha}(2,3)\alpha_{\text{eq}}^{-1}(3,4)\langle T\rho(4)\rho(1')\rangle_c^{\text{eq}}\times d(2)d(3)d(4)\,, \tag{13}$$

where $\epsilon(1,2)$ is the (time-ordered) equilibrium dielectric function, and the inverse $\epsilon^{-1}(1,2)$ is defined by

$$\int\epsilon(1,3)\epsilon^{-1}(3,2)d(3)=\delta(1,2)\,. \tag{14}$$

Introducing the notation

$$\bar{h}(1,2)=\int\bar{\alpha}(1,3)\alpha_{\text{eq}}^{-1}(3,2)d(3)\,, \tag{15}$$

and expressing this quantity as a functional of the mean density, we can write, in general,

$$\bar{h}(\mathbf{x}_1t_1,\mathbf{x}_2t_2)=\int\Gamma[\mathbf{x}_1-\mathbf{x}_2,\,t_1-t_2|\,\tfrac{1}{2}(\mathbf{x}_1+\mathbf{x}_2)-\mathbf{x}_3,\,\tfrac{1}{2}(t_1+t_2)-t_3]\times n(\mathbf{x}_3,t_3)d\mathbf{x}_3dt_3\,, \tag{16}$$

where $\Gamma(\cdots)$ is the equilibrium value of the functional derivative of $\bar{h}$ with respect to the mean density. Here we have used the fact that the system in equilibrium is homogeneous.

Inserting Eqs. (13) and (16) into Eq. (9), the effective potential in Fourier space becomes

$$V_{\text{eff}}(\mathbf{q},\omega)=V_H(\mathbf{q},\omega)+\Phi(q)\left(\frac{1}{n}\int\frac{d\mathbf{q}'d\omega'}{(2\pi)^4}\frac{\mathbf{q}\cdot\mathbf{q}'}{q'^2\epsilon(\mathbf{q}',\omega')}\times\Gamma(\mathbf{q}'-\tfrac{1}{2}\mathbf{q},\,\omega'-\tfrac{1}{2}\omega|\,\mathbf{q},\,\omega)S(\mathbf{q}'-\mathbf{q},\,\omega'-\omega)\right)n(\mathbf{q},\omega)\,, \tag{17}$$

where $S(\mathbf{q},\omega)$ is the Fourier transform of $\langle T\rho(1)\rho(1')\rangle_c^{\text{eq}}$, and $\Gamma(\mathbf{q}'\omega'|\mathbf{q}\omega)$ is the Fourier transform of $\Gamma(\mathbf{r}t|\mathbf{x}t)$.

The approximation (11) implies that Eq. (12) is approximated as

$$\langle T\rho(1)\rho(1')\rangle_c=\frac{\langle\rho(1)\rangle}{n}\left(\alpha_{\text{eq}}(1,1')+\int\alpha_{\text{eq}}(1,2)\Phi(2,3)\alpha_{\text{eq}}(3,1')d(2)d(3)+\cdots\right)\frac{\langle\rho(1')\rangle}{n} \tag{18}$$

for $t=t'$. This leads to an effective potential of the form

$$V_{\text{eff}}(\mathbf{q},\omega)=V_H(\mathbf{q},\omega)+\Phi(q)\left(\frac{1}{n}\int\frac{d\mathbf{q}'d\omega'}{(2\pi)^4}\frac{\mathbf{q}\cdot\mathbf{q}'}{q'^2}S(\mathbf{q}'-\mathbf{q},\,\omega'-\omega)\right)n(\mathbf{q},\omega)\,, \tag{19}$$

which is to be compared with the exact expression (17).

---

[8] Our approach can be considered to be an extension to the dynamical situation of the treatment given in the static case by P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964). These authors calculate the electron density in the presence of a static, nonuniform potential, including many-body effects, by considering the total energy to be a functional of the density $n(\mathbf{R})$. They derive the equation $\mu(\mathbf{R})+V_H(\mathbf{R})=\text{const}$ for the density distribution, where $\mu(\mathbf{R})=\delta E/\delta n(\mathbf{R})$. This equation follows from Eq. (7) in the static case by considering $\pi(\mathbf{R})$ and $\langle\rho(R)\rho(R')\rangle_c$ to be functionals of the density $n(\mathbf{R})$.

On integrating with respect to ω', we have

$$V_{\mathrm{eff}}(\mathbf{q},\omega)=V_H(\mathbf{q},\omega)+\Phi(q)\left(\frac{1}{n}\int\frac{d\mathbf{q}'}{(2\pi)^3}\frac{\mathbf{q}\cdot\mathbf{q}'}{q'^2}[S(\mathbf{q}'-\mathbf{q})-1]\right)n(\mathbf{q},\omega)\,,\quad(20)$$

where $S(\mathbf{q})$ is the usual static structure factor.

As mentioned earlier, we here assume that $\bar{h}(1,2)$ is short range in both space and time, and depends only on the local density. We assume

$$\bar{h}(1,2)=\mathrm{const}\,\delta(1,2)\bar{n}(1)/n\,.\quad(21)$$

This means that the relative change of $\alpha(1,2)$ is assumed to be proportional to the relative change in the local density. It implies that the function Γ entering Eq. (17) is a constant. We take the constant in Eq. (21) to be unity, so that we recover our previous approximation for the effective potential Eq. (20) in the limit of large wave vectors. This choice has been dictated by the success of our numerical calculations of the pair correlation function as presented in I. Using these assumptions, the effective potential becomes

$$V_{\mathrm{eff}}(\mathbf{q},\omega)=V_H(\mathbf{q},\omega)+\Phi(q)\left(\frac{1}{n}\int\frac{d\mathbf{q}'d\omega'}{(2\pi)^4}\frac{\mathbf{q}\cdot\mathbf{q}'}{q'^2}\frac{1}{\epsilon(\mathbf{q}',\omega')}\times S(\mathbf{q}'-\mathbf{q},\,\omega'-\omega)\right)n(\mathbf{q},\omega)\,.\quad(22)$$

Clearly, the adjustment of the pair correlation function to the external disturbance leads to a dynamical screening of the Coulomb potential in the integrand in Eq. (19).

In our numerical calculations we have made an additional simplifying assumption, in that we have replaced the dynamical screening of the Coulomb potential in Eq. (22) by the static screening. It then follows that

$$V_{\mathrm{eff}}(\mathbf{q},\omega)=V_H(\mathbf{q},\omega)+\Phi(\mathbf{q})\left(\frac{1}{n}\int\frac{d\mathbf{q}'}{(2\pi)^3}\frac{\mathbf{q}\cdot\mathbf{q}'}{q'^2\epsilon(q')}\times[S(\mathbf{q}'-\mathbf{q})-1]\right)n(\mathbf{q},\omega)\,,\quad(23)$$

where $\epsilon(q)$ is the static dielectric function. The static structure factor is related to the retarded dielectric function through the relation

$$S(\mathbf{q})=-\frac{\hbar q^2}{4\pi^2e^2n}\int_0^\infty d\omega\,\mathrm{Im}\left(\frac{1}{\epsilon(\mathbf{q},\omega)}\right).\quad(24)$$

For convenience we introduce the shorter notation

$$G(\mathbf{q})=-\frac{1}{n}\int\frac{d\mathbf{q}'}{(2\pi)^3}\frac{\mathbf{q}\cdot\mathbf{q}'}{q'^2\epsilon(q')}[S(\mathbf{q}'-\mathbf{q})-1].\quad(25)$$

This equation is the same as Eq. (15) of I with the exception of the factor $\epsilon(q')$ in the denominator. We can then write Eq. (23) as[9]

$$V_{\mathrm{eff}}(\mathbf{q},\omega)=V_e(\mathbf{q},\omega)+\Phi(\mathbf{q})[1-G(\mathbf{q})]n(\mathbf{q},\omega)\,.\quad(26)$$

C. Dielectric Response Function

The dielectric response function in the RPA is obtained from Eq. (10) by neglecting the local-field correction, i.e., by putting $G(\mathbf{q})=0$ in Eq. (26) for the effective potential, and by calculating the kinetic part of the pressure tensor $\pi(\mathbf{R},t)$ using the linear-response theory. The electrons are assumed to move as free particles under the influence of the Hartree potential. The Fourier transform of the induced momentum current is then given by

$$\pi_{\alpha\beta}(\mathbf{q},\omega)=\left(\int\frac{p_\alpha p_\beta}{m}\frac{f(\mathbf{p}+\frac{1}{2}\mathbf{q})+f(\mathbf{p}-\frac{1}{2}\mathbf{q})}{\omega-\mathbf{p}\cdot\mathbf{q}/m+i\delta}d\mathbf{p}\right)V_H(\mathbf{q},\omega)\,,\quad(27)$$

where $f(\mathbf{p})$ is the Fermi-Dirac distribution function. Using Eq. (27) and taking the Fourier transform of Eq. (10), we obtain

$$n(\mathbf{q},\omega)=\frac{1}{m\omega^2}\left(nq^2-\int\frac{(\mathbf{p}\cdot\mathbf{q})^2}{m}\times\frac{f(\mathbf{p}+\frac{1}{2}\mathbf{q})-f(\mathbf{p}-\frac{1}{2}\mathbf{q})}{\omega-\mathbf{p}\cdot\mathbf{q}/m+i\delta}d\mathbf{q}\right)V_H(\mathbf{q},\omega)\,.\quad(28)$$

The above expression, after some transformations, can be written in the more familiar form

$$n(\mathbf{q},\omega)=\left(\int\frac{f(\mathbf{p}+\frac{1}{2}\mathbf{q})-f(\mathbf{p}-\frac{1}{2}\mathbf{q})}{\omega-\mathbf{p}\cdot\mathbf{q}/m+i\delta}d\mathbf{p}\right)V_H(\mathbf{q},\omega)=\chi_0(\mathbf{q},\omega)V_H(\mathbf{q},\omega)\,,\quad(29)$$

where $\chi_0(\mathbf{q},\omega)$ is the Lindhard expression for the electron polarizability.

Considering the pressure tensor as a functional of the density, the Fourier transform of its variation in the external field is in general proportional to $V_{\mathrm{eff}}(\mathbf{q},\omega)$, since the latter determines the change in density through Eq. (10). The coefficient of proportionality is assumed to be that for a noninteracting gas, as in Eq. (27). This assumption implies, in particular, that the variation of the equilibrium value of the kinetic

---

[9] Recently, L. Kleinman [Phys. Rev. **160**, 585 (1967)] and D. C. Langreth [Phys. Rev. **181**, 753 (1969)] have discussed the large wave vector behavior of the local-field correction, and they have concluded that $G(\mathbf{q},\omega)$, which in the general case depends on both $\mathbf{q}$ and ω as in Eq. (22), behaves as q^2 for large values of $\mathbf{q}$. We want to point out that, assuming $G(\mathbf{q},\omega)$ to be independent of frequency as in Eq. (25), a q^2 behavior of this function at large wave vector would lead to an unphysical result, in that the static pair correlation function would have a $1/r$ singularity at the origin.

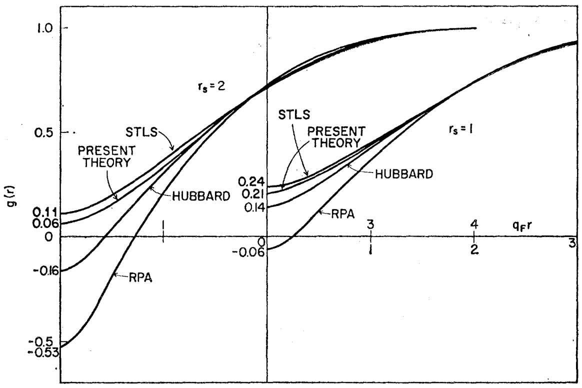

FIG. 1. Pair correlation function $g(r)$ versus $q_F r$ for $r_s=1$ and $r_s=2$.

energy with density is essentially determined by the free-particle kinetic energy—a result which is well confirmed by the calculations. The foregoing assumption implies replacing $V_H(\mathbf{q},\omega)$ by $V_{\mathrm{eff}}(\mathbf{q},\omega)$ in Eq. (27), which leads to

$$n(\mathbf{q},\omega)=\chi_0(\mathbf{q},\omega)V_{\mathrm{eff}}(\mathbf{q},\omega). \qquad (30)$$

The proper response function, which gives the response of the density to the macroscopic Hartree field, is then given by

$$\alpha(\mathbf{q},\omega)=\chi_0(\mathbf{q},\omega)/[1-G(\mathbf{q})Q_0(\mathbf{q},\omega)], \qquad (31)$$

where

$$Q_0(\mathbf{q},\omega)=-\Phi(q)\chi_0(\mathbf{q},\omega). \qquad (32)$$

Hence, using Eq. (8), we have for the dielectric function

$$\epsilon(\mathbf{q},\omega)=1+Q_0(\mathbf{q},\omega)/[1-G(\mathbf{q})Q_0(\mathbf{q},\omega)], \qquad (33)$$

where $G(\mathbf{q})$ is given by Eq. (25) and the structure factor entering in it should be determined self-consistently from Eq. (24).

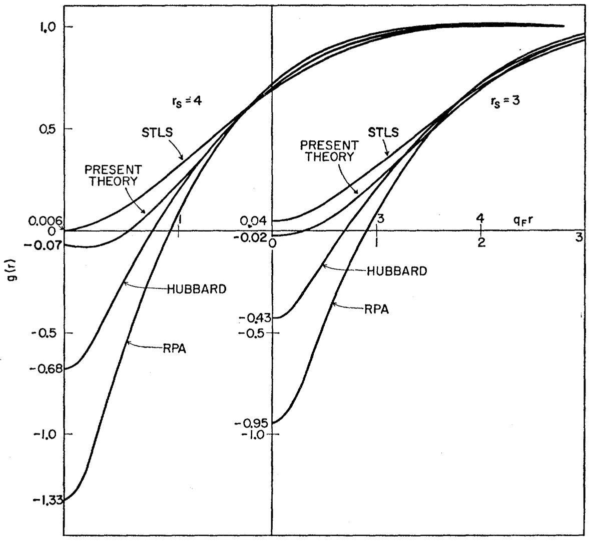

FIG. 2. Pair correlation function $g(r)$ versus $q_F r$ for $r_s=3$ and $r_s=4$.

The above expression for the dielectric function differs from that in I through the static screening of the Coulomb potential in $G(\mathbf{q})$.

D. Reduction to Modified Hubbard Dielectric Function

In evaluating $G(\mathbf{q})$ in Eq. (25), we use the Thomas-Fermi dielectric function

$$\epsilon_{\mathrm{TF}}(\mathbf{q})=1+q_{\mathrm{TF}}^2/q^2, \qquad (34)$$

where q_{TF} is the Thomas-Fermi screening constant, and further we take the Hartree-Fock value for $S(\mathbf{q})$, i.e.,

$$S(\mathbf{q})=-\frac{2}{(2\pi)^3 n}\int_{|\mathbf{k}|\leq q_F} d\mathbf{k}\int_{|\mathbf{k}'|\leq q_F} d\mathbf{k}' \times\delta(\mathbf{k}-\mathbf{k}'+\mathbf{q}), \qquad (35)$$

where q_F is the Fermi momentum. This leads to

$$G(\mathbf{q})=\frac{2}{(2\pi)^6 n}\int_{|\mathbf{k}|\leq q_F} d\mathbf{k}\int_{|\mathbf{k}'|\leq q_F} d\mathbf{k}' \times\frac{\mathbf{q}\cdot(\mathbf{q}+\mathbf{k}-\mathbf{k}')}{|\mathbf{q}+\mathbf{k}-\mathbf{k}'|^2+q_{\mathrm{TF}}^2}. \qquad (36)$$

If in the above integral we replace $|\mathbf{q}+\mathbf{k}-\mathbf{k}'|^2$ by $(q^2+q_F^2)$, as was also done in the original calculation of Hubbard,[3] we find

$$G(\mathbf{q})=\tfrac{1}{2}q^2/(q^2+q_F^2+q_{\mathrm{TF}}^2). \qquad (37)$$

With this value of $G(\mathbf{q})$, the dielectric function given by Eq. (33) is the same as has been adopted by Sham[4] upon a suggestion by Hubbard. In the context of the present theory, Hubbard's approximation implies that local-field corrections have been included only to the extent that the Pauli exchange hole enters through the free-particle Hartree-Fock pair correlation function, thus neglecting here completely the effect of Coulomb interactions. Also, the screening of the Coulomb potential in $G(\mathbf{q})$ has been taken in the Thomas-Fermi approximation.

III. CALCULATIONS

In this section we present the results of the self-consistent determination of the pair correlation function in the metallic density range, and the pertinent

TABLE I. Correlation energy (Ry/electron).

r_s	1	2	3	4	5	6
Present theory	−0.125	−0.097	−0.080	−0.070	−0.063	−0.057
STLS	−0.124	−0.092	−0.075	−0.064	−0.056	−0.050
Hubbard	−0.131	−0.102	−0.086	−0.076	−0.069	−0.064
Nozières-Pines	−0.115	−0.094	−0.081	−0.072	−0.065	−0.060
RPA	−0.157	−0.124	−0.105	−0.094	−0.085	−0.078

values of the correlation energy. Equations (24), (25), and (33) are solved self-consistently, following the procedure outlined in I. The only comment that we wish to make here is that the numerical work involved in the present calculation is much longer than that in I.

A. Pair Correlation Function

The pair correlation function $g(r)$ is given by

$$g(r)=1+\frac{3}{2r}\int_0^\infty q(\sin qr)[S(q)-1]dq, \tag{38}$$

where q is expressed in units of q_F and r in units of q_F^{-1}. The self-consistent values of $S(q)$ were used in Eq. (38) to calculate $g(r)$. The results are shown graphically in Figs. 1–3 for various values of r_s of interest. For comparison the curves obtained on the basis of our earlier theory,[2] and on the basis of the original Hubbard approximation and of the random-phase approximation (RPA), are also given. It may be mentioned that the inclusion of a screening parameter in the original Hubbard formula for $G(\mathbf{q})$ does actually lead[5] to a worse $g(r)$. It is apparent that, as far as the positiveness of $g(r)$ at small interparticle separation is concerned, there is some deterioration from our earlier results, although there still is a marked improvement over the results based on other approximations. The negative values of $g(r)$ are still small enough that $g(r)$ may be considered to be zero in this region for practical purposes. The price that we have paid here is more than compensated by the marked improvement in the long-wavelength behavior of the dielectric function, as indicated by the excellent values of the compressibility that we have obtained[6] from this limiting behavior. It is this behavior of the dielectric function that plays an important role in many calculations of practical interest.

A numerical interpolation scheme between the present and our earlier values of $G(\mathbf{q})$, that improves the behavior of $g(r)$ at small separations and preserve the compressibility sum rule, has been tried and is discussed in Sec. VII.

B. Correlation Energy

As in I, the correlation energy per particle can be written as

$$E_{\text{corr}}=\frac{1}{r_s^2}\int_0^{r_s}\left[-\frac{4}{\pi}\left(\frac{9}{4}\pi\right)^{1/3}\bar{\gamma}(r_s)+0.9163\right]dr_s\ \text{Ry}, \tag{39}$$

where

$$\bar{\gamma}(r_s)=-\frac{1}{2}\int_0^\infty [S(q)-1]dq. \tag{40}$$

The resulting values of the correlation energy are given in Table I, together with the results of previous approximations. The present values are essentially the same as those given by the interpolation scheme of Nozières and Pines.[10] The present results therefore lead to practically the same values for the cohesive energy of the alkali metals as those obtained by Nozières and Pines. The comparison with the experimental values has already been discussed in I.

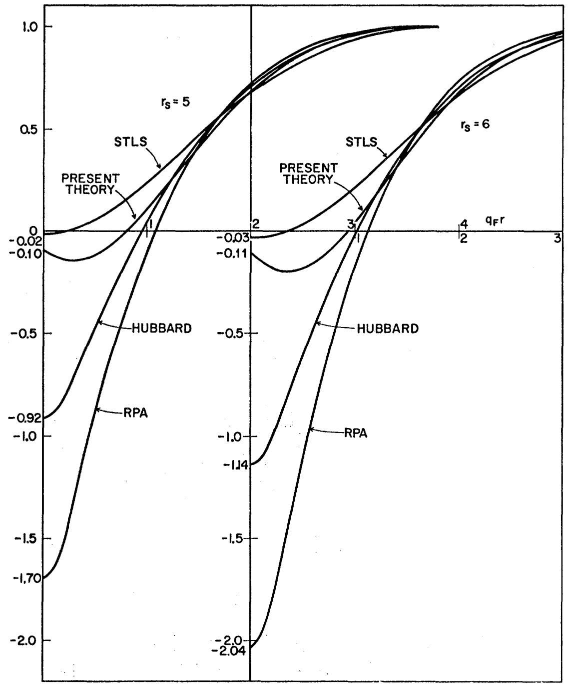

FIG. 3. Pair correlation function $g(r)$ versus $q_F r$ for $r_s=5$ and $r_s=6$.

IV. LONG-WAVELENGTH LIMIT

A. Compressibility

The dielectric function (33) in the limit $\mathbf{q}\to 0$ at zero ω has the form

$$\lim_{\mathbf{q}\to 0}\epsilon(\mathbf{q},0)=1+\frac{(q_{\text{TF}}/q)^2}{1-\gamma(q_{\text{TF}}/q_F)^2}, \tag{41}$$

where

$$\gamma=-\frac{1}{2}\int_0^\infty dq\frac{S(q)-1}{\epsilon(q)}\left[1-\frac{d\ln\epsilon(q)}{d\ln q}\right]. \tag{42}$$

In our earlier approximation, the expression of γ was the same as the expression of $\bar{\gamma}$ given in Eq. (40). The values of γ for various values of r_s are given in Table

TABLE II. Values of γ.

r_s	1	2	3	4	5	6
γ	0.3341	0.3059	0.2816	0.2601	0.2410	0.2237

---

[10] P. Nozières and D. Pines, Phys. Rev. **111**, 442 (1958).

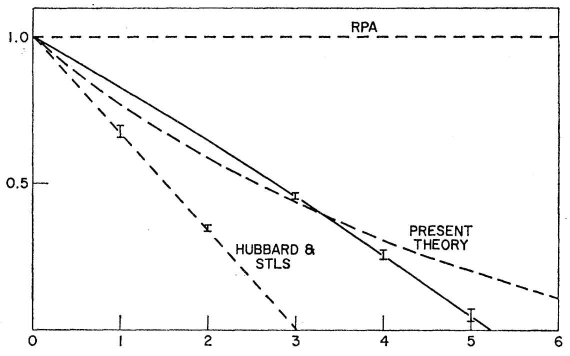

FIG. 4. Ratio between the free-electron compressibility and the compressibility of the electron liquid versus r_s. The full curve is obtained by differentiation of the energy; the bars give the spread of the results obtained from the available approximations to the correlation energy. The broken curves are obtained from Eq. (43).

II. From the compressibility sum rule one finds

$$K_{\rm free}/K=1-\gamma(q_{\rm TF}/q_F)^2, \tag{43}$$

where $K_{\rm free}$ is the compressibility of the noninteracting gas. The values of the compressibility obtained by using Eq. (43) are compared[6] in Fig. 4 with those obtained by differentiating the energy of the system with respect to r_s [see Eq. (43) of I]. As is seen from the figure, the present theory leads to much smaller deviations from the compressibility sum rule than the earlier theories at all values of r_s, and in fact satisfies closely this sum rule up to values of r_s of about 4.

B. Plasmon Dispersion

The dielectric function (33) in the limit $\mathbf{q}\to 0$ and ω finite has the form

$$\lim_{\mathbf{q}\to 0}\epsilon(\mathbf{q},\omega)=1-(\omega_p^2/\omega^2)[1+(9/5)(q/q_{\rm TF})^2-\gamma(q/q_F)^2]+\cdots, \tag{44}$$

where $\omega_p=(4\pi ne^2/m)^{1/2}$. From Eq. (44) follows the plasmon dispersion relation

$$\omega_p(q)=\omega_p+\alpha\hbar q^2/m+\cdots, \tag{45}$$

where

$$\alpha=(\hbar q_F^2/3m\omega_p)[9/10-\tfrac{1}{2}\gamma(q_{\rm TF}/q_F)^2]. \tag{46}$$

In Fig. 5 the quantity $\alpha/\alpha_{\rm RPA}$, where $\alpha_{\rm RPA}=3\hbar q_F^2/(10m\omega_p)$, is plotted as a function of r_s for various theories. The experimental values available[11] for a few metals are also reported in the figure. The comparison between theory and experiment may not have much significance, since the influence of the ion lattice on the measured angular distribution of scattered electrons is not known. If this influence on the scattering were merely a band effect, the discrepancy between theory and experiment would be significant for Al and Na, in which band effects are known to be small.

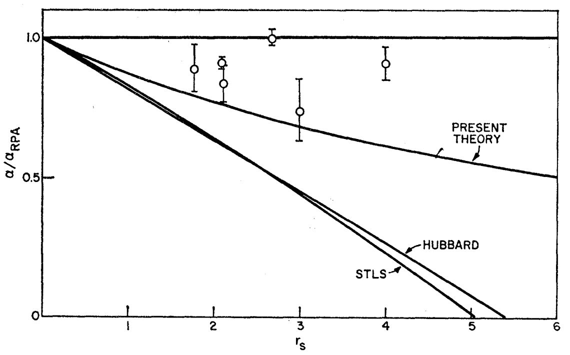

FIG. 5. Coefficient of the leading term in the plasmon dispersion (in units of its RPA value) versus r_s. The experimental values (for Be, Al, Sb, Mg, Li, and Na, in order of increasing r_s) are taken from Ref. 11.

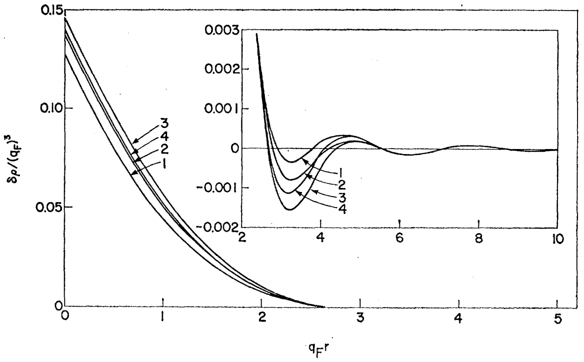

FIG. 6. Screening density $\delta\rho(r)/q_F^3$ versus $q_F r$ for $r_s=3$: curve 1, RPA; curve 2, Hubbard; curve 3, Singwi and Tosi; curve 4, present results.

V. IMPURITY SCREENING

The polarization density at the distance r from a static impurity of unit charge is given by[12,13]

$$\delta\rho(r)=\frac{1}{2\pi^2 r}\int_0^\infty q\sin(qr)\left[1-\frac{1}{\epsilon(q,0)}\right]dq. \tag{47}$$

The results obtained with the present dielectric function at $r_s=3$ and $r_s=6$ are compared in Figs. 6 and 7 with those given by earlier theories. The present results still show a deeper minimum than those based on the Hubbard approximation, although the deviation is smaller than found previously.[13] We expect that the correct polarization density should lie between curves 3 and 4 in this region of intermediate distances.

VI. SPIN CORRELATIONS

Using the formalism of I, the following expression for the dynamic susceptibility of the electron liquid in

---

[11] H. Raether, in *Springer Tracts in Modern Physics* (Springer-Verlag, Berlin, 1965) Vol. 38.

[12] J. S. Langer and S. H. Vosko, J. Phys. Chem. Solids **12**, 196 (1960).

[13] K. S. Singwi and M. P. Tosi, Phys. Rev. **181**, 784 (1969).

the paramagnetic state has been derived[7]

$$\chi(\mathbf{q},\omega)=-g^2\mu_B{}^2\frac{\chi_0(\mathbf{q},\omega)}{1-I(\mathbf{q})\chi_0(\mathbf{q},\omega)},\tag{48}$$

where the internal field correction is given by

$$I(\mathbf{q})=\frac{1}{n}\int\frac{\mathbf{q}\cdot\mathbf{q}'}{q^2}\Phi(q')[\tilde{S}(\mathbf{q}'-\mathbf{q})-1]\frac{d\mathbf{q}'}{(2\pi)^3},\tag{49}$$

with

$$\tilde{S}(\mathbf{q})-1=n\int\tfrac{1}{2}[g_{\uparrow\uparrow}(\mathbf{x})-g_{\uparrow\downarrow}(\mathbf{x})]e^{-i\mathbf{q}\cdot\mathbf{x}}d\mathbf{x}.\tag{50}$$

Here, $g_{\uparrow\uparrow}(\mathbf{x})$ and $g_{\uparrow\downarrow}(\mathbf{x})$ are the correlation functions for a pair of particles with parallel and antiparallel spins, respectively. The structure factor $\tilde{S}(\mathbf{q})$ and the dynamic susceptibility were determined self-consistently using the relation

$$\tilde{S}(\mathbf{q})=\frac{\hbar}{\pi n g^2\mu_B{}^2}\int_0^\infty d\omega\,\mathrm{Im}\chi(\mathbf{q},\omega).\tag{51}$$

It was found that this approximation gives rather good values for the pair correlations, but is inaccurate for small wave vectors. Specifically, it yields values of the static paramagnetic susceptibility for Li and Na which are too large by a factor of 2, and it indicates a rapid decrease of the function $I(\mathbf{q})$ with increasing wave vector.

We have modified Eq. (49) by introducing a screening of the Coulomb potential appearing in the integrand through the static dielectric function, analogously to the screening derived in Sec. II for the dielectric case.

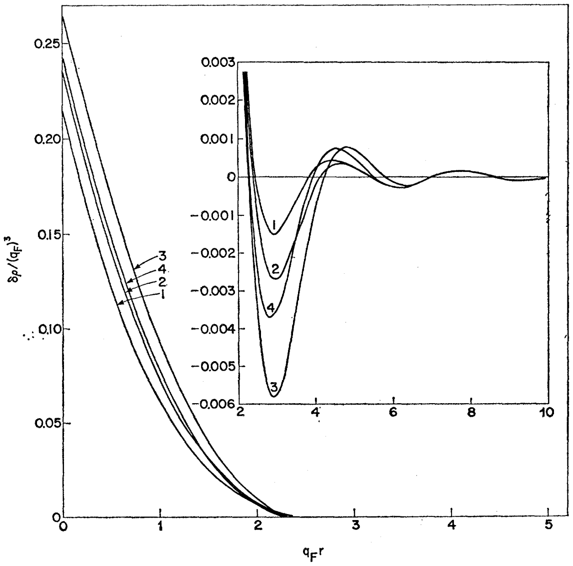

FIG. 7. Screening density $\delta\rho(r)/q_F{}^3$ versus $q_F r$ for $r_s=6$: curve 1, RPA; curve 2, Hubbard; curve 3, Singwi and Tosi; curve 4, present results.

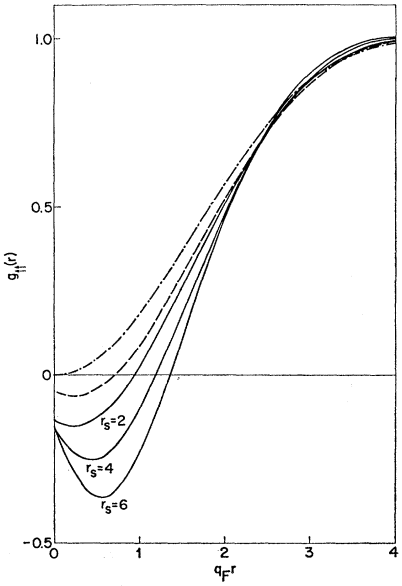

FIG. 8. Pair correlation function $g_{\uparrow\uparrow}(r)$ versus $q_F r$ for various values of r_s. Full curves, present theory; broken curve, Lobo *et al.*; dash-dot curve, Hartree-Fock approximation. The results of Lobo *et al.* are essentially independent of r_s.

The modified expression for $I(\mathbf{q})$ is

$$I(\mathbf{q})=\frac{1}{n}\Phi(q)\int\frac{\mathbf{q}\cdot\mathbf{q}'}{q'^2\epsilon(q')}[\tilde{S}(\mathbf{q}'-\mathbf{q})-1]\frac{d\mathbf{q}'}{(2\pi)^3}.\tag{52}$$

As far as screening is concerned, we have therefore

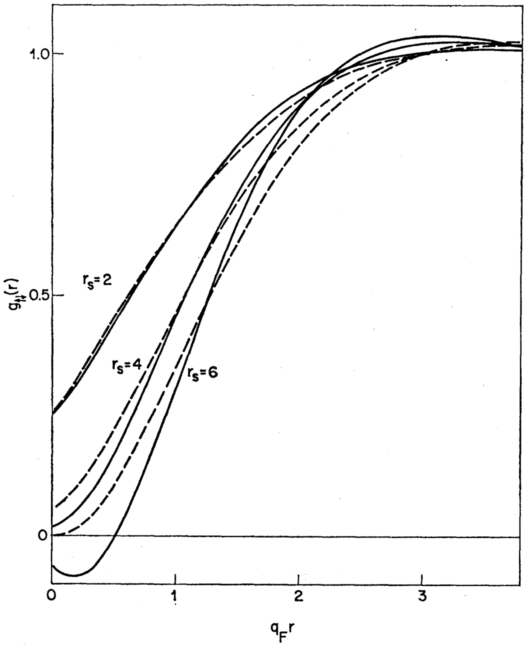

FIG. 9. Pair correlation function $g_{\uparrow\downarrow}(r)$ versus $q_F r$ for various values of r_s. Full curves, present results; broken curves, Lobo *et al.*

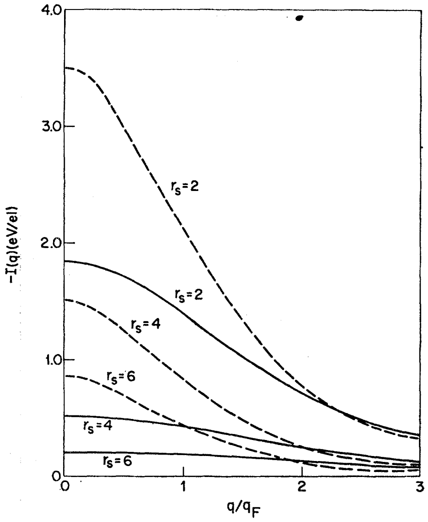

FIG. 10. Function $I(q)$ (in eV/electron) versus q/q_F for various values of r_s. Full curves, present results; broken curves, Lobo *et al.*

treated on the same footing the interactions between pairs of electrons with parallel and with antiparallel spins. Since exchange effects are short range, one might expect that in fact these interactions should be screened in a different manner. Nevertheless, we examine the consequences of our approximate expression (52).

Equations (48), (51), and (52) have been solved numerically in a self-consistent way. The resulting correlation functions for various values of r_s are compared in Figs. 8 and 9 with the previous results[7] based on Eq. (49). The present approximation leads to a definite deterioration of the pair correlation functions at small separations, although they still compare favorably with the results of other theories,[7] with the exception of $g_{\uparrow\uparrow}(r)$ in the Hubbard approximation. In particular, while the previous values[7] of $g_{\uparrow\uparrow}(r)$ were essentially independent of r_s and quite close to the Hartree-Fock values, this appealing simplicity is now lost, as is apparent from Fig. 8. On the other hand, the long wavelength behavior of the dynamic susceptibility has improved considerably. In Table III we give the values of the static susceptibility.

$$\chi=\lim_{\mathbf{q}\to 0}\chi(\mathbf{q},0) \tag{53}$$

as a function of r_s. The theoretical value at $r_s=4$ is in fair agreement with the average of the experimental values for Na,[14] $\chi=1.04\times10^{-6}$ cgs. A similar comparison can be made for Li if one corrects for the important band effects. The theoretical value, corrected by multiplying the present result by the theoretical cyclotron mass[15] and neglecting the effect of the anisotropy of the Fermi surface, is $\chi=1.76\times10^{-6}$ cgs, to be compared with the experimental value,[16] $\chi=2.08\times10^{-6}$ cgs. Thus, we see that the susceptibility sum rule is approximately satisfied.

TABLE III. Static paramagnetic susceptibility (10^{-6} cgs).

r_s	2	3	4	6
χ	1.65	1.13	0.86	0.55

TABLE IV. Parameters of Eq. (54).

r_s	1	2	3	4	5	6
A	0.7756	0.8994	0.9629	0.9959	1.0138	1.0218
B	0.4307	0.3401	0.2924	0.2612	0.2377	0.2189

In Fig. 10 the present values of $I(\mathbf{q})$ are compared with the previous results.[7] There are two points to notice. First, the greatly improved value of the static susceptibility implies a marked reduction of the value of this function at small wave vectors. Secondly, $I(\mathbf{q})$ has a very gentle dependence on the wave vector. The latter behavior is in general agreement with the experimental observations of Windsor *et al.*[17] on Ni.

VII. INTERPOLATION SCHEME FOR APPLICATIONS

From the foregoing discussion it can be concluded that the present scheme of approximation is quite accurate at small wave vectors, whereas the approximation of I leads to somewhat better results at large

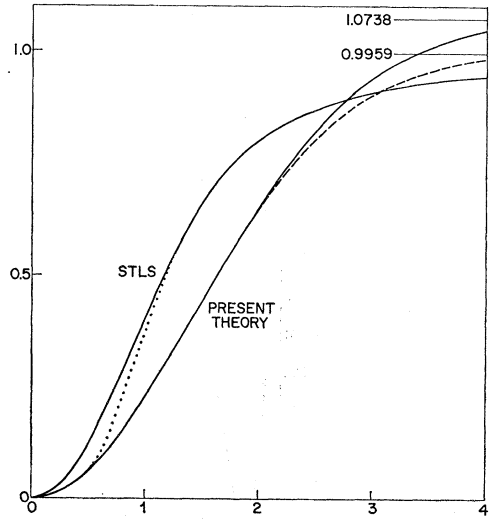

FIG. 11. Function $G(q)$ versus q/q_F for $r_s=4$. The dotted curve indicates the type of interpolation needed to obtain a positive $g(r)$. The broken curve is the fit given by Eq. (54).

---

[14] R. T. Schumacher and C. P. Slichter, Phys. Rev. **101**, 58 (1956); R. T. Schumacher and W. E. Vehse, J. Phys. Chem. Solids 24, 297 (1963).

[15] F. Ham, Phys. Rev. **128**, 2524 (1962).

[16] R. T. Schumacher and C. P. Slichter, Ref. 14.

[17] C. G. Windsor, R. D. Lowde, and G. Allan, Phys. Rev. Letters **22**, 849 (1969).

wave vectors. We have therefore tried a few schemes of interpolation between the present and the previous values of $G(\mathbf{q})$, with the purpose of improving the behavior of the correlation function while at the same time preserving the validity of the compressibility sum rule. It is found that, in order to achieve this end, the interpolation must be started at values of $q\approx\frac{1}{2}q_F$ and must be essentially completed at $q\approx q_F$. This fact is illustrated for $r_s=4$ in Fig. 11, which gives an interpolated curve for $G(\mathbf{q})$ which yields a pair correlation function of quality comparable to our previous results. Analogous results can be achieved at the other values of r_s. It is found,[18] however, that the dielectric function determined by this interpolation scheme does not yield phonon-dispersion curves for sodium as good as those obtained by a direct use of the dielectric function calculated in this paper. It therefore appears that, if one is willing to accept a somewhat poor pair correlation function at small separation, the present dielectric function is adequate for practical applications. We have actually found that the self-consistent values of $G(\mathbf{q})$ can be fitted quite accurately with a simple function of the form

$$G(q)=A[1-e^{-B(q/q_F)^2}], \tag{54}$$

whose parameters are given in Table IV for the values of r_s in the range of metallic densities. As is apparent in Fig. 11, this simple function deviates from the $G(\mathbf{q})$ given in Eq. (25) only at large wave vectors, which do not play any significant role in most practical calculations.

We have also attempted a similar interpolation scheme for the problem of the spin correlations at $r_s=4$. We have found that a considerable improvement in $g_{\uparrow\uparrow}(r)$ can be achieved if we adjust the value of $I(0)$ so that the experimental value of the paramagnetic susceptibility is reproduced and then smoothly go over to the values of $I(q)$ at large q reported previously.[7]

VIII. CONCLUDING REMARKS

The basic result derived in this paper is expression (22) for the effective potential, $V_{\mathrm{eff}}(\mathbf{q},\omega)$, in which the charge density fluctuation induced by an external field moves. This result is obtained by an extension of the treatment given in I, by allowing for the adjustment of the pair correlation function to the external field. The treatment involves the assumption that the irreducible part of the density correlations is so short ranged in space and time that its change in the external field may be taken to depend only on the local density.

This effective potential can be used to derive straightforwardly an expression for the dielectric function of the electron liquid if one makes the additional assumption that the liquid responds to the effective potential via the free-gas response function. The expression (33) for the dielectric function involves the simplifying, but not necessary, approximation of replacing the dynamic screening entering the effective potential by the static screening. The latter approximation has been introduced for the purpose of reducing the numerical work involved in the self-consistent determination of the dielectric function and the pair correlations, with particular emphasis on the low-frequency region. It would, however, be of interest to recalculate the self-consistent dielectric function with the dynamical screening in the local-field correction, especially when one is considering high-frequency phenomena.

We have also considered the spin correlations in the paramagnetic state in the same scheme of approximation as that used for the density correlations, in that we have introduced a static screening in the internal field acting on the spin density. This simple approximation makes no allowance for the fact that the interaction between different pairs of spins should be screened in a different manner. This problem needs further consideration.

Finally, it should be pointed out that there is no unique relation between our $G(\mathbf{q})$ and the momentum-dependent vertex function entering, for instance, the expression of the electron self-energy. This limits the scope of our theory, in that we cannot, within the present treatment, calculate the self-energy correction for arbitrary momentum.

---

[18] D. L. Price, K. S. Singwi, and M. P. Tosi (unpublished).