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Van Hove correlation functions for identical fermions

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For a quantum system of identical fermions a partition of the density-density correlation function in its "self" and "distinct" part is presented. These quantities show different properties than their classical counterparts, e.g., they violate the "detailed balance" and are not necessarily real. Nevertheless it can be expected that they will provide a good tool for a better description of the self-motion in many-particle systems and are therefore investigated in second-order perturbation theory of the interparticle potential.

I. INTRODUCTION

The main interest in the description of quantum many-particle systems nowadays lies on their dynamic aspects. Probably the most important quantity, as directly measurable through scattering experiments,[1,2] is the *dynamic structure factor* $S(q,\omega)$ originally introduced by van Hove.[1] In classical statistics many successful theories for S have been presented,[2-4] and the dynamics of simple liquids is fairly well understood. The situation for quantum liquids is much worse; for classical theories based on the hierarchical equations of motion for reduced densities, efforts have been made to generalize these approaches to their quantum analog[5,6] (the Wigner functions) and were in general quite satisfactory.[7] One important concept of classical statistics, however, the so-called *self-motion* of a particle,[2-4] has not yet been applied in quantum mechanics. This is due to the fact that there a clear definition of a self and distinct part of $S(q,\omega)$ is a nontrivial problem. This question is our main interest.

After a short description of the classical quantities in Sec. II, we calculate in Sec. III the self and distinct parts of the free-fermion structure factor. It turns out that the fundamental properties known for correlation functions are violated; this problem is examined in Sec. IV. In Sec. V we redefine the van Hove functions in the formalism of second quantization thus providing a physically meaningful description of S^s and S^d. The corresponding susceptibilities finally are discussed in Sec. VI. Throughout the paper we restrict ourselves to the case of fermions (electrons); the spin indices are omitted for brevity.

II. CLASSICAL VAN HOVE CORRELATION FUNCTIONS

The coherent dynamic structure factor S is defined as the density-density correlation function of the system, namely

$$S(q,\omega)=\frac{1}{N}\int dt\, e^{i\omega t}\langle \delta\rho_{\mathbf{q}}(t)\delta\rho_{-\mathbf{q}}\rangle \ , \tag{2.1}$$

where $N \gg 1$ is the number of particles in the system and $\delta\rho$ is the Fourier transform of the particle-density fluctuation $\delta\rho(\mathbf{r})=\rho(\mathbf{r})-n$ ($n=N$ per unit volume)

$$\delta\rho_{\mathbf{q}}(t)=\int d^3\mathbf{r}\, e^{-i\mathbf{q}\cdot\mathbf{r}}\delta\rho(\mathbf{r},t) \ . \tag{2.2}$$

Its time dependence is determined by the Liouville operator $iL \equiv [\ ,H]_{\mathrm{PB}}$ (Poisson bracket)

$$\rho(\mathbf{r},t)=e^{-iLt}\sum_i \delta(\mathbf{r}_i-\mathbf{r})=\sum_i \delta(\mathbf{r}_i(t)-\mathbf{r}) \ . \tag{2.3}$$

This leads immediately to the space-time Fourier transform of $S(\mathbf{q},\omega)$ [in the literature[2-4] often denoted as $G(\mathbf{r},t)$]

$$S(\mathbf{r},t)=\frac{1}{N}\left\langle \sum_{i,j} \delta(\mathbf{r}_i(t)-\mathbf{r}_j-\mathbf{r})\right\rangle -n \ . \tag{2.4}$$

From this, the interpretation is quite clear; S denotes essentially the probability of finding both a particle at time $t=0$ in $\mathbf{r}_i$, and one at time t in $\mathbf{r}_j+\mathbf{r}$. It is convenient to split this quantity in the two parts of finding there the *same* and a *different* particle, S^s and S^d [again equivalent to $G^s(\mathbf{r},t)$ and $G^d(\mathbf{r},t)$ in the literature]

$$S^s(\mathbf{r},t)=\frac{1}{N}\left\langle \sum_{i} \delta(\mathbf{r}_i(t)-\mathbf{r}_i-\mathbf{r})\right\rangle \ , \tag{2.5}$$

$$S^d(\mathbf{r},t)=\frac{1}{N}\left\langle \sum_{i\neq j} \delta(\mathbf{r}_i(t)-\mathbf{r}_j-\mathbf{r})\right\rangle -n \ . \tag{2.6}$$

They have the following initial values:

$$S^s(\mathbf{r},t=0)=\delta(\mathbf{r})$$

and (2.7)

$$S^d(\mathbf{r},t=0)=n[g(r)-1] \ ,$$

where g is the pair distribution function of the system. In the simple case of a perfect gas these quantities are easily evaluated: The pair distribution $g^0(\mathbf{r})$ is simply equal to one and $S^{d0}(\mathbf{r},t=0)$ vanishes. As there are no interactions which could build up correlations, this has to be valid for all t

$$S^{d0}(\mathbf{r},t)=0 \Longrightarrow S^{s0}(\mathbf{r},t)=S^0(\mathbf{r},t) \ . \tag{2.8}$$

The self part is thus equal to the full structure factor ($\beta \equiv 1/k_BT$)

$$S^0(\mathbf{r},t)=\left[\frac{m\beta}{2\pi}\right]^{3/2} e^{-r^2 m\beta/2t^2} \ . \tag{2.9}$$

For later comparison we also report the space Fourier transform [in the literature often $F^s(q,t)$]

$$S^{s0}(\mathbf{q},t)=\int d^3\mathbf{k}\left[\frac{\beta}{2m\pi}\right]^{1/2} e^{-\beta\mathbf{k}^2/2m}e^{-it(\mathbf{kq}/m)} . \tag{2.10}$$

So far all the relations are valid for classical systems, or—as pointed out by van Hove[1]—for *distinguishable* quantum-mechanical particles. However, problems arise, if one tries to describe identical particles; how can a self part of S be meaningful, if exchange effects make it impossible to decide whether after time t a particle is the same, or not. ("You can't paint a quantum particle green.") Certainly a different definition for S^s has to be found. On the other hand, at first sight there is no reason[2] why it should be impossible—if the wave functions are assumed to be known—to calculate S^s and S^d according to Eqs. (2.5) and (2.6). (Of course with the correct quantum-mechanical time dependence in the Heisenberg picture, $\hbar\equiv 1$). For identical fermions without interactions this procedure and its consequences are discussed in the following section.

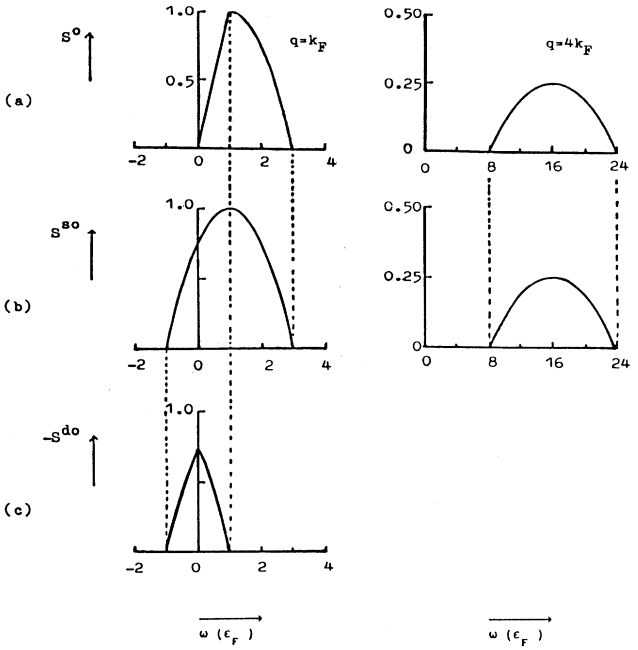

FIG. 1. Van Hove correlation functions for the noninteracting Fermi gas in units of $mk_F/2n\pi$, for $q<2k_F$ (Fermi momentum) and $q>2k_F$. (a) Full structure factor S^0, (b) self part S^{s0}, (c) negative distinct part S^{d0}. For $q>2k_F$, S^{d0} vanishes.

III. S^{s0} AND S^{d0} FOR FERMION SYSTEMS

We start with the calculation of the self part of the density autocorrelation function for identical fermions in $\mathbf{q}$-t space:

$$S^{s0}(\mathbf{q},t)=\frac{1}{N}\sum_i\langle e^{-i\mathbf{q}\cdot\mathbf{r}_i(t)}e^{i\mathbf{q}\cdot\mathbf{r}_i}\rangle^0 . \tag{3.1}$$

With use of the relation

$$e^Ae^B=e^{A+B+([A,B]/2)}\ \text{if } [A,B] \text{ is a } c \text{ number} , \tag{3.2}$$

we get for the expectation value in thermal equilibrium

$$S^{s0}(\mathbf{q},t)=\frac{1}{N}e^{-it(\mathbf{q}^2/2m)} \times\frac{1}{Z}\sum_\nu e^{-\beta E_\nu^0}\left\langle \nu\left|\sum_i e^{-(t\mathbf{q}/m)(\partial/\partial\mathbf{r}_i)}\right|\nu\right\rangle^0 . \tag{3.3}$$

The state $|\nu\rangle^0$ in the ideal system is simply a Slater determinant. Equation (3.3) can, therefore, easily be transformed into a sum over wave vectors with the result

$$S^{s0}(\mathbf{q},t)=\frac{1}{N}\sum_\mathbf{k} n_\mathbf{k}e^{-it[(\mathbf{kq}/m)+(\mathbf{q}^2/2m)]} , \tag{3.4}$$

the quantum analog to Eq. (2.10). The main difference is that the Maxwell distribution is replaced by the Fermi distribution function $n_\mathbf{k}$. Its Fourier transform ($\varepsilon_\mathbf{k}\equiv k^2/2m$)

$$S^{s0}(\mathbf{q},\omega)=\frac{2\pi}{N}\sum_\mathbf{k} n_\mathbf{k}\delta(\omega-(\varepsilon_{\mathbf{k}+\mathbf{q}}-\varepsilon_\mathbf{k})) \tag{3.5}$$

can be integrated explicitly, the result for $T=0$ is shown in Fig. 1(b). The evaluation of the distinct part proceeds exactly the same way, yielding [cf. Fig. 1(c)]

$$S^{d0}(\mathbf{q},\omega)=\frac{2\pi}{N}\sum_\mathbf{k} n_\mathbf{k}n_{\mathbf{k}+\mathbf{q}}\delta(\omega-(\varepsilon_{\mathbf{k}+\mathbf{q}}-\varepsilon_\mathbf{k})) . \tag{3.6}$$

The full coherent structure factor $S^0=S^{s0}+S^{d0}$ then has the well-known behavior of Fig. 1(a).

It should be mentioned that Eq. (3.5) has been derived previously,[2] and it has been argued that Eq. (2.9) should also hold for quantum systems. Consequently, $S^{d0}(\mathbf{q},\omega)$ should vanish for all $\mathbf{q}$ and ω. It can be seen clearly from Fig. 1(c) that this is *not* the case. This is an immediate consequence of the fact that for $t=0$ the probability of finding two particles close together is drastically reduced due to the Pauli exclusion principles as

$$\frac{1}{n}S^{d0}(\mathbf{r},t=0)=[g^0(r)-1]=-\frac{9}{2}\left[\frac{r\cos r-\sin r}{r^3}\right]^2 \tag{3.7}$$

(r is measured in k_F). How these Pauli correlations are reduced with increasing time is then described by $S^{d0}(\mathbf{r},t)$.

Another striking feature of Fig. 1 is that $S^{d0}(\mathbf{q},\omega)$ is an even function of ω and that $S^{s0}(\mathbf{q},\omega)$ is nonzero for negative ω. These two properties are in contradiction with the detailed balance, usually valid for correlation functions. This problem is examined in the following section.

IV. DETAILED BALANCE

This well-known property of correlation functions in thermal equilibrium is given through[2,3]

$$K_{AB}(t) \equiv \langle A_t B \rangle = \frac{1}{Z}\operatorname{Tr} e^{-\beta H} e^{itH} A e^{-itH} B \tag{4.1}$$

$$= \frac{1}{Z}\operatorname{Tr} e^{-\beta H} B e^{itH} e^{-\beta H} A e^{-itH} e^{\beta H}$$

$$= K_{BA}(t+i\beta)\ , \tag{4.2}$$

or, in Fourier space, through

$$K_{AB}(-\omega) = e^{-\beta\omega} K_{AB}(\omega)\ . \tag{4.3}$$

Both the classical and the quantum coherent structure factors obey this relation regulating the ratio of energy absorption and emission in equilibrium, and so do the classical correlation functions S^s and S^d. The reason for its violation in the quantum case is closely related to the symmetry properties of the system; in the *subspace* of identical fermions, the eigenfunctions $|\nu\rangle$ of the Hamiltonian H have to be *antisymmetric* against interchange of particles. The operator

$$\mathbb{1} \equiv \frac{1}{N!}\sum_{\nu} |\nu\rangle\langle\nu| \tag{4.4}$$

then equals unity for any physically meaningful property (i.e., which commutes with the permutation operator P). Application of $\mathbb{1}$ to the individual components of S^s or S^d, however, mixes all the particles, as shown in detail in Appendix A

$$S^s(\mathbf{q},t) = \left\langle \frac{1}{N}\sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i(t)} e^{i\mathbf{q}\cdot\mathbf{r}_i} \right\rangle$$

$$\neq \left\langle \frac{1}{N}\sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i(t)} \mathbb{1} e^{i\mathbf{q}\cdot\mathbf{r}_i} \right\rangle = \frac{1}{N} S(\mathbf{q},t)\ . \tag{4.5}$$

Similarily insertion of $\mathbb{1}$ transforms S^d into $(N-1)S/N$. Any mathematical conversion involving the identity (4.4) [and the equality of Eqs. (4.1) and (4.2) needs exactly this operation] will, therefore, be violated for the self and distinct parts.

At the end of this section we want to stress that S^s, or generally *any* property of the type $A = \sum_i \hat{a}_i$, commutes with P and is therefore an absolutely meaningful quantity. The individual contributions $\hat{a}_i$, of course, are not meaningful quantities and are consequently not considered to be a good description for the quantity of interest, A. How they can be avoided, is demonstrated next.

V. S^s AND S^d IN FIELD QUANTIZATION

An approved description of systems with identical fermions is that of second quantization. Let $\psi_{\mathbf{r}}^\dagger$ and $\psi_{\mathbf{r}}$ be the field operators which create and destroy, respectively, a particle at point $\mathbf{r}$ (with spin s) and $\psi_{\mathbf{r},t}^\dagger$, $\psi_{\mathbf{r},t}$ their Heisenberg representation. The particle-density operator can then be expressed as

$$\rho(\mathbf{r},t) = \psi_{\mathbf{r},t}^\dagger \psi_{\mathbf{r},t}\ , \tag{5.1}$$

and the coherent structure factor for homogeneous systems in thermal equilibrium is

$$nS(\mathbf{r}_{12},t_{12}) = \langle \psi_{\mathbf{r}_1,t_1}^\dagger \psi_{\mathbf{r}_1,t_1} \psi_{\mathbf{r}_2,t_2}^\dagger \psi_{\mathbf{r}_2,t_2} \rangle - n^2$$

$$= nS(-\mathbf{r}_{12},-t_{12})^*\ . \tag{5.2}$$

At $t_1 = t_2$ use of the anticommutation relations of $\psi^\dagger$ and ψ leads to

$$S(\mathbf{r}_{12},0) = \delta(\mathbf{r}_{12}) + n\left[\frac{1}{n^2}\langle \psi_{\mathbf{r}_1}^\dagger \psi_{\mathbf{r}_2}^\dagger \psi_{\mathbf{r}_2} \psi_{\mathbf{r}_1} \rangle - 1\right]\ . \tag{5.3}$$

In the first term of (5.3) we recognize $S^s(\mathbf{r}_{12},0)$ and in the second one the static pair correlations $[g(\mathbf{r}_{12})-1]$. The generalization of this distinct part to arbitrary t is obvious

$$nS^d(\mathbf{r}_{12},t_{12}) = \langle \psi_{\mathbf{r}_1,t_1}^\dagger \psi_{\mathbf{r}_2,t_2}^\dagger \psi_{\mathbf{r}_2,t_2} \psi_{\mathbf{r}_1,t_1} \rangle - n^2$$

$$= nS^d(\mathbf{r}_{12},t_{12})^*\ . \tag{5.4}$$

If we denote for short the state $\psi_{\mathbf{r}_1}|\nu\rangle$ as $|\nu'_{\mathbf{r}_1}\rangle$, nS^d is equal to

$$\langle \nu'_{\mathbf{r}_1}(t_{21}) | \psi_{\mathbf{r}_2}^\dagger \psi_{\mathbf{r}_2} | \nu'_{\mathbf{r}_1}(t_{21}) \rangle\ . \tag{5.5}$$

This quantity has the desired meaning, namely the probability of finding a (necessarily different) particle after a time $t_2 - t_1$ at point $\mathbf{r}_2$, if one has been destroyed at t_1 in $\mathbf{r}_1$. ("Don't paint your particle green—pick it out.") For S^s we were not able to find a closed expression; it is, however, sufficiently defined as the difference of S and S^d, that is

$$nS^s(\mathbf{r}_{12},t_{12}) = \langle \psi_{\mathbf{r}_1,t_1}^\dagger \psi_{\mathbf{r}_1,t_1} \psi_{\mathbf{r}_2,t_2}^\dagger \psi_{\mathbf{r}_2,t_2} \rangle$$

$$- \langle \psi_{\mathbf{r}_1,t_1}^\dagger \psi_{\mathbf{r}_2,t_2}^\dagger \psi_{\mathbf{r}_2,t_2} \psi_{\mathbf{r}_1,t_1} \rangle\ . \tag{5.6}$$

Expressions (5.4) and (5.6) now provide us with an adequate description of Fermi–van Hove correlation functions. Their equivalent formulation in Fourier space and the case of free fermions are listed in Appendix B.

The procedure can easily be extended for arbitrary correlation functions; for single-particle properties A and B (we use for short $\mathbf{1} = \mathbf{r}_1$, etc.)

$$A = \sum_i \hat{a}\left[\mathbf{i}, \frac{\partial}{\partial \mathbf{i}}\right] \triangleq \int d\mathbf{1}\, d\mathbf{1}'\, a_{11'} \psi_1^\dagger \psi_{1'}$$

with (5.7)

$$a_{11'} = \hat{a}\left[\mathbf{1}, \frac{\partial}{\partial \mathbf{1}}\right] \delta(\mathbf{1}-\mathbf{1}')$$

(and analogously for B) the correlation function is given by

$$K_{AB}(t_{12}) = \sum_{ij} \left\langle \hat{a}\left[\mathbf{i}, \frac{\partial}{\partial \mathbf{i}}, t\right] \hat{b}\left[\mathbf{j}, \frac{\partial}{\partial \mathbf{j}}\right] \right\rangle \triangleq \int d\mathbf{1}\, d\mathbf{1}' \int d\mathbf{2}\, d\mathbf{2}'\, a_{11'} b_{22'} \langle \psi_{1,t_1}^\dagger \psi_{1',t_1} \psi_{2,t_2}^\dagger \psi_{2',t_2} \rangle\ . \tag{5.8}$$

For the distinct part we find again

$$K^d_{AB}(t_{12})=\sum_{i\neq j}\left\langle \hat{a}\left[\mathbf{i},\frac{\partial}{\partial \mathbf{i}},t\right]\hat{b}\left[\mathbf{j},\frac{\partial}{\partial \mathbf{j}}\right]\right\rangle \hat{=}\int d1\,d1'\int d2\,d2'\,a_{11'}b_{22'}\langle \psi^\dagger_{1,t_1}\psi^\dagger_{2,t_2}\psi_{2',t_2}\psi_{1',t_1}\rangle \ . \tag{5.9}$$

As above, the self part $K^s_{AB}(t_{12})$ is determined by the difference of Eqs. (5.8) and (5.9). Finally we want to apply this to the velocity autocorrelation function, which has proved very successful in the description of diffusion processes in molecular liquids. With use of, in this case, more appropriate creation and annihilation operators in momentum space, we have

$$\Phi(t)\equiv\frac{1}{3N}\sum_i\langle \mathbf{v}_i(t)\mathbf{v}_i\rangle \hat{=}\frac{1}{3N}\sum_{k,k'}\frac{\mathbf{k}\mathbf{k}'}{m^2}(\langle c^\dagger_{\mathbf{k},t}c_{\mathbf{k},t}c^\dagger_{\mathbf{k}'}c_{\mathbf{k}'}\rangle-\langle c^\dagger_{\mathbf{k},t}c^\dagger_{\mathbf{k}'}c_{\mathbf{k}'}c_{\mathbf{k},t}\rangle) \ . \tag{5.10}$$

Further investigations of this function, for instance its long time behavior, would be of interest.

VI. DENSITY RESPONSE FUNCTION

A basic quantity in the description of dynamics in many-body systems is the linear response function for the density in an external potential, connected to the structure factor via

$$\frac{i}{n}\chi(\mathbf{q},t)=\theta(t)[S(\mathbf{q},t)-S(-\mathbf{q},-t)] \ . \tag{6.1}$$

In formal analogy we define its self and distinct part as

$$\frac{i}{n}\chi^{s,d}(\mathbf{q},t)=\theta(t)[S^{s,d}(\mathbf{q},t)-S^{s,d}(-\mathbf{q},-t)] \ , \tag{6.2}$$

which reads in Fourier space

$$\frac{1}{n}\chi(\mathbf{q},\omega)=\int d\omega'\frac{1}{2\pi}\frac{S^{(s,d)}(\mathbf{q},\omega')-S^{(s,d)}(-\mathbf{q},-\omega')}{\omega-\omega'+i\alpha} \ . \tag{6.3}$$

For the structure factor according to Eq. (5.2) holds $S(\mathbf{r},t)=S(-\mathbf{r},-t)^*$, consequently (6.3) can be rewritten as

$$-\frac{2}{n}\operatorname{Im}\chi(\mathbf{q},\omega)=(1-e^{-\beta\omega})S(\mathbf{q},\omega) \ . \tag{6.4}$$

S^d, however, is real in $(\mathbf{r},t)$ space [cf. Eq. (5.4)] and therefore real in $(\mathbf{q},\omega)$ space only if it is additionally an even function in ω, immediately leading to a vanishing χ, [which is, e.g., the case for S^{d0}; therefore,

$$\chi^0(\mathbf{q},\omega)=\chi^{s0}(\mathbf{q},\omega) \tag{6.5}$$

holds, in quantum as in classical systems]. This cannot be expected *a priori*, however, so that definition (6.2) remains meaningful [*not*, however, (6.4) for the self- and distinct-parts alone].

Concerning the approximations for χ, among others, generalized mean-field approaches have proved very powerful. The basic theory,[7,8] the random-phase approximation (RPA), is given by

$$\chi(\mathbf{q},\omega)=\frac{\chi^0(\mathbf{q},\omega)}{1-v_\mathbf{q}\chi^0(\mathbf{q},\omega)}=\frac{\chi^{0s}(\mathbf{q},\omega)}{1-v_\mathbf{q}\chi^{0s}(\mathbf{q},\omega)} \ . \tag{6.6}$$

The effect, that a particle drags along an exchange and correlation hole, can be accounted for by introduction of the (exact) local-field correction $G(\mathbf{q},\omega)$:[7,8]

$$\chi(\mathbf{q},\omega)=\frac{\chi^0(\mathbf{q},\omega)}{1-v_\mathbf{q}[1-G(\mathbf{q},\omega)]\chi^0(\mathbf{q},\omega)} \ . \tag{6.7}$$

The most successful theory for determining G (Singwi, Tosi, Land, and Sjölander and related work[9-12]) is based on the ansatz of local equilibrium for $\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2,t)$ in the first hierarchical equation for the reduced density $\rho^{(1)}(\mathbf{r}_1,\mathbf{p}_1,t)$, leading to a static $G(\mathbf{q})$ as a functional of the static $S(\mathbf{q})$.[9] This forms together with (6.7) and (6.4) a closed set of equations, which can be solved self-consistently. The same ansatz for the Wigner function in the quantum case[12] leads to a much more complicated dynamic $G(\mathbf{q},\omega)$ as $\mathbf{r}$ and $\mathbf{p}$ are no longer decoupled quantities. In the homogeneous-electron-gas numerical evaluation, however, has shown that the results, though slightly better, are only insignificantly different from those obtained with the classical G and use of the quantum χ^0 in (6.7).[12]

It should be noted that in classical statistics the connection between the static structure factor and χ is exceptionally simple, namely[3]

$$S(\mathbf{q})=\int d\omega\frac{1}{2\pi}S(\mathbf{q},\omega)=-\frac{1}{n\beta}\chi(\mathbf{q},t=0) \ . \tag{6.8}$$

For static local-field corrections this has the consequence that Eq. (6.7) corresponds to replacing $v_\mathbf{q}$ in (6.6) by $-c(\mathbf{q})/n\beta$, where the direct correlation function $c(\mathbf{q})$ is defined as

$$nc(\mathbf{q})\equiv\left[\frac{1}{S(\mathbf{q})}-1\right]=-\beta v_\mathbf{q}[1-G(\mathbf{q})] \ . \tag{6.9}$$

Based on the physical idea that having taken into account explicitly the *collective* aspects of the motion through the RPA structure of χ, one should also make better allowance for the difference of the *single-particle motion* and its free behavior. Singwi, Tosi, and Sköld[13] suggested the ansatz

$$\chi(\mathbf{q},\omega)=\frac{\chi^s(\mathbf{q},\omega)}{1-v_q[1-G(\mathbf{q})]\chi^s(\mathbf{q},\omega)} \ , \tag{6.10}$$

and were able to obtain better agreement with experiment. It was shown[13] that for $\tilde{S}(\mathbf{q},\omega)$, the Laplace transform of $S(\mathbf{q},t)$, this is equivalent to

$$\tilde{S}(\mathbf{q},\omega)=\frac{S(\mathbf{q})\tilde{S}^s(\mathbf{q},\omega)}{1-nc(\mathbf{q})[i\omega\tilde{S}^s(\mathbf{q},\omega)+1]} \ , \tag{6.11}$$

a result derived earlier by Kerr.[14] More refined theories taking into account both dynamic local-field corrections *and* self-motion corrections through use of χ^s, have proved extremly successful in the description of the classical dynamics in liquids.[15,16] In fermion systems, for instance the electron gas, while many good expressions for static and dynamic local fields have been presented,[7,8] a good theory for the self-motion is missing. Usually it is argued that Eq. (6.7) is exact, used as a definition for G. It has been pointed out by Neilson,[17,18] however, that certain physical effects, e.g., the back flow, should not by force be pressed into the local field, in order to keep their physical meaning as properties of single-particle motion and the one of G as the surrounding correlation hole clear.

From this we expect investigations of S^s and/or χ^s to lead to better descriptions of χ. As a first step we have investigated χ^d in perturbation theory (cf. Appendix C). It turns out that in first order of the interparticle potential $v_{\mathbf{q}}$ still $\chi^s=\chi$ holds, only second-order perturbation theory yields a nonvanishing χ^d. This can be well explained with the help of Feynman diagrams (cf. Fig. 2). First-order polarization diagrams describe intermediate states with only one particle outside the Fermi sphere (and one hole inside). As contributions to χ^d require at least two distinct particles, these graphs are clearly part of χ^s. The same holds for higher-order diagrams obtained from χ^0 but with use of the true single-particle propagator in the place of the free one, as these graphs contain only a better description of the one particle outside the Fermi sphere. From this we can also state that χ^s will certainly contain all the terms of χ^0 with the Fermi function $n_{\mathbf{k}}=n_{\mathbf{k}}^0$ replaced by the true value of the momentum distribution. This form of χ^0 was used previously by Niklasson[19,20] and might be considered as a first application of Eq. (6.10).

In second-order perturbation theory the main contributions to χ^d are of the exchange type of Fig. 2(c). Their detailed derivation and the comparison with the $v_{\mathbf{q}}^2$ contributions[21] to χ is given in Appendix C.

In summary, we have given a precise description of self and distinct van Hove correlation functions for identical fermions in the formalism of second quantization and discussed their main properties. A promising application is their use in generalized mean-field theories to account for a better description of the single-particle motion. First investigations from a perturbation viewpoint have been presented.

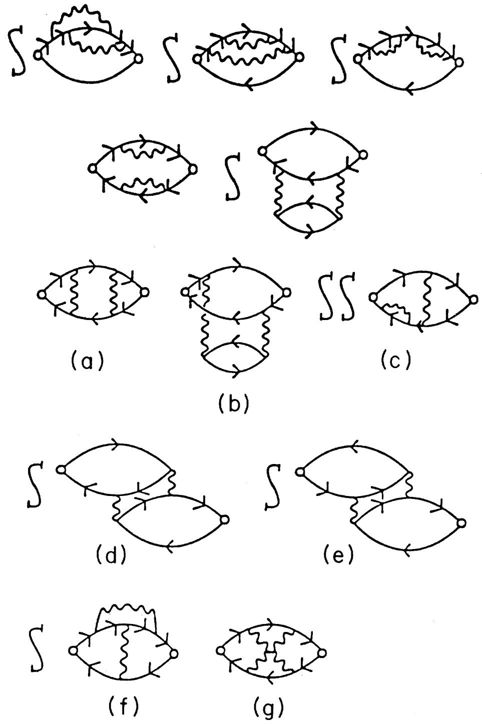

FIG. 2. Proper polarization Feynman diagrams contained in χ. The arrow denotes the free single-particle propagator and the wavy line the bare Coulomb potential. First five graphs: second-order diagrams obtained from χ^0 by use of the true single-particle propagator in place of the free one. (a)–(g) Second-order diagrams which cannot be obtained from χ^0. Diagrams (a)–(g) do not describe real two-particle–two-hole processes and therefore they do not contribute to χ^d. Also the diagrams (d) and (e) give no contributions to χ^d. The main contributions to χ^d come from diagrams (f) and (g) (exchange diagrams).

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APPENDIX A

Our aim is to calculate the expectation value

$$\langle e^{-i\mathbf{q}\cdot\mathbf{r}_i(t)}\mathbb{1}e^{i\mathbf{q}\cdot\mathbf{r}_i}\rangle=\frac{1}{Z}\sum_{\nu'}e^{-\beta E_{\nu'}}\langle\nu'|e^{-i\mathbf{q}\cdot\mathbf{r}_i(t)}\mathbb{1}e^{i\mathbf{q}\cdot\mathbf{r}_i}|\nu'\rangle\ . \tag{A1}$$

In the subspace of identical fermions it can be shown for the operator $\mathbb{1}$ to have the correct antisymmetry against particle interchange

$$\mathbb{1}=\frac{1}{N!}\sum_{\nu}|\nu\rangle\langle\nu|=\frac{1}{N!}\sum_{\nu}f_{\nu}^{*}(1,\ldots,N)f_{\nu}(1',\ldots,N')=\frac{1}{N!}\left\|\begin{bmatrix}\delta_{11'} & \cdots & \delta_{NN'}\\ \vdots & & \vdots\\ \delta_{1N'} & \cdots & \delta_{N1'}\end{bmatrix}\right\|\ . \tag{A2}$$

Therefore we get for the matrix element

$$\frac{1}{N!}\sum_{\nu}\langle\nu'|e^{-i\mathbf{q}\cdot\mathbf{r}_i(t)}|\nu\rangle\langle\nu|e^{i\mathbf{q}\cdot\mathbf{r}_i}|\nu'\rangle=\frac{1}{N!}\int d1\cdots dN\,d1'\cdots dN'\,f^*_{\nu'}(1,\ldots,N)e^{-i\mathbf{q}\cdot\mathbf{r}_i(t)}\|\delta_{j'j}\|e^{i\mathbf{q}\cdot\mathbf{r}_{i'}}f\nu'(1',\ldots,N') \tag{A3}$$

$$=\frac{(N-1)!}{N!}\int d1\cdots dN\,di'\,f^*_{\nu'}(1,\ldots,N)e^{-i\mathbf{q}\cdot\mathbf{r}_i(t)}\sum_j\delta_{i'j}e^{i\mathbf{q}\cdot\mathbf{r}_{i'}}f_{\nu'}(1',\ldots,N') \tag{A4}$$

$$=\frac{1}{N}\left\langle\nu'\left|e^{-i\mathbf{q}\cdot\mathbf{r}_i(t)}\sum_j e^{i\mathbf{q}\cdot\mathbf{r}_j}\right|\nu'\right\rangle . \tag{A5}$$

The sum includes all terms, $i=j$ and $i\neq j$. The insertion of $\mathbb{1}$ has thus caused a "mixing" of the particles in accordance with their indistinguishability.

APPENDIX B

We transform the field operators $\psi^\dagger_{\mathbf{r}},\psi_{\mathbf{r}}$ to $c^\dagger_{\mathbf{k}},c_{\mathbf{k}}$, the creation and annihilation operators of a particle with momentum $\mathbf{k}$

$$\psi_r=\frac{1}{\sqrt{V}}\sum_k e^{i\mathbf{k}\cdot\mathbf{r}}c_{\mathbf{k}} , \tag{B1}$$

immediately leading to

$$S(q,\omega)=\frac{1}{N}\sum_{k,k'}\langle c^\dagger_{\mathbf{k},t}c_{\mathbf{k}+\mathbf{q},t}c^\dagger_{\mathbf{k}'}c_{k'-\mathbf{q}}\rangle-N\delta_{\mathbf{q},0} , \tag{B2}$$

$$S^d(q,\omega)=\frac{1}{N}\sum_{k,k'}\langle c^\dagger_{\mathbf{k},t}c^\dagger_{\mathbf{k}'}c_{\mathbf{k}'-\mathbf{q}}c_{\mathbf{k}+\mathbf{q},t}\rangle . \tag{B3}$$

It will often be convenient to use these expressions instead of (5.2) and (5.3). In the case of free fermions the time dependence of c is simply

$$c_{\mathbf{k}}(t)=e^{i\varepsilon_{\mathbf{k}}t}c_{\mathbf{k}} , \tag{B4}$$

which together with the noninteracting expectation values

$$\langle c^\dagger_{\mathbf{k}}c_{\mathbf{k}+\mathbf{q}}c^\dagger_{\mathbf{k}'}c_{\mathbf{k}'-\mathbf{q}}\rangle=\langle c^\dagger_{\mathbf{k}}c^\dagger_{\mathbf{k}'}c_{\mathbf{k}'-\mathbf{q}}c_{\mathbf{k}+\mathbf{q}}\rangle+\delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}}n_{\mathbf{k}} , \tag{B5}$$

$$\langle c^\dagger_{\mathbf{k}}c^\dagger_{\mathbf{k}'}c_{\mathbf{k}'-\mathbf{q}}c_{\mathbf{k}+\mathbf{q}}\rangle^0=(\delta_{\mathbf{q},0}-\delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}})n_{\mathbf{k}}n_{\mathbf{k}'} \tag{B6}$$

yields straightforwardly Eqs. (3.5) and (3.6). For the perfect Fermi gas we have, therefore, proved rigorously that the description of S^s and S^d in Fock space are correct.

Finally we want to show an interesting feature of the true S^d: Its $t_{12}=t=0$ time derivative is given by

$$-i\frac{\partial}{\partial t_{12}}nS^d(\mathbf{r}_{12},t_{12})=\langle\psi^\dagger_{\mathbf{r}_1}[\rho_{\mathbf{r}_2},H]\psi_{\mathbf{r}_1}\rangle . \tag{B7}$$

The density commutes with the interaction potential, so we can replace H by H^0 and get (using the continuity equation for ρ)

$$i\dot{S}^d(\mathbf{q},t=0)=\frac{1}{N}\sum_{k,k'}\langle c^\dagger_{\mathbf{k}-\mathbf{q}/2}c^\dagger_{\mathbf{k}'+\mathbf{q}/2}c_{\mathbf{k}'-\mathbf{q}/2}c_{\mathbf{k}+\mathbf{q}/2}\rangle\frac{\mathbf{k}'\mathbf{q}}{m} . \tag{B8}$$

In the homogeneous system S^d is a function of the magnitude of $\mathbf{q}$ only and therefore obeys

$$\dot{S}^d(\mathbf{q},t=0)=0=\int d\omega\frac{1}{2\pi}S^d(\mathbf{q},\omega) . \tag{B9}$$

APPENDIX C

The distinct part of the linear response function χ^d is defined as [see Eq. (6.2)]

$$\begin{aligned}i\chi^d&\equiv n\theta(t)[S^d(\mathbf{q},t)-S^d(-q,-t)]\\&=\theta(t)\sum_{\mathbf{k},\mathbf{k}'}\{\langle c^\dagger_{\mathbf{k}-\mathbf{q}/2,t}c^\dagger_{\mathbf{k}'+\mathbf{q}/2}c_{\mathbf{k}'-\mathbf{q}/2}c_{\mathbf{k}+\mathbf{q}/2,t}\rangle\\&\qquad-\langle c^\dagger_{\mathbf{k}'+\mathbf{q}/2}c^\dagger_{\mathbf{k}-\mathbf{q}/2,t}c_{\mathbf{k}+\mathbf{q}/2,t}c_{\mathbf{k}'-\mathbf{q}/2}\rangle\} .\end{aligned} \tag{C1}$$

To get χ^d exact up to the second order of the interparticle potential v, we use the equation-of-motion method. The second time derivative of Eq. (C1) yields

$$\chi^{d(2)}(\mathbf{q},t)=\chi^{d(2)}_{\mathrm{inh}}(\mathbf{q},t)+\chi^{d(2)}_{\mathrm{hom}}(\mathbf{q},t) , \tag{C2}$$

where

$$\begin{aligned}\chi^{d(2)}_{\mathrm{inh}}(\mathbf{q},t)=\sum_{\mathbf{k},\mathbf{k}',\mathbf{p}}v_{\mathbf{p}}\Bigg[&\left[i\frac{\partial}{\partial t}-\Delta E_{\mathbf{k}+\mathbf{p}/2,\mathbf{q}/2}\right]^{-1}\left[i\frac{\partial}{\partial t}-\Delta E_{\mathbf{k}'-\mathbf{p}'/2,\mathbf{q}/2}\right]^{-1}\\&-\left[i\frac{\partial}{\partial t}-\Delta E_{\mathbf{k}-\mathbf{p}/2,\mathbf{q}/2}\right]^{-1}\left[i\frac{\partial}{\partial t}-\Delta E_{\mathbf{k}'+\mathbf{p}'/2,\mathbf{q}/2}\right]^{-1}\Bigg][-i\theta(t)]\\&\times\langle c^\dagger_{\mathbf{k}-(\mathbf{q}-\mathbf{p})/2}c^\dagger_{\mathbf{k}'+(\mathbf{q}-\mathbf{p})/2}c_{\mathbf{k}'-(\mathbf{q}-\mathbf{p})/2}c_{\mathbf{k}+(\mathbf{q}-\mathbf{p})/2}\rangle^{(1)} .\end{aligned} \tag{C3}$$

As $\chi^{d(2)}_{\mathrm{inh}}\propto v$, the expectation value $\langle c^\dagger c^\dagger cc\rangle$ has to be evaluated in first order of v, whereas $\chi^{d(2)}_{\mathrm{hom}}$ is already proportional to v^2, so that there the expectation values and the time dependence of c, respectively, $c^\dagger$, can be evaluated for free particles:

$$\begin{aligned}\chi_{\text{hom}}^{d(2)}(\mathbf{q},t)=\sum_{\mathbf{k},\mathbf{k}',\mathbf{p},\mathbf{p}'} v_{\mathbf{p}}v_{\mathbf{p}'}&\left[\left[i\frac{\partial}{\partial t}-\Delta E_{\mathbf{k}'-\mathbf{p}'/2,\mathbf{q}/2}\right]^{-1}-\left[i\frac{\partial}{\partial t}-\Delta E_{\mathbf{k}'+\mathbf{p}'/2,\mathbf{q}/2}\right]^{-1}\right]\\
\times\Bigg[\left[i\frac{\partial}{\partial t}-\Delta E_{\mathbf{k}+\mathbf{p}/2,\mathbf{q}/2}\right]^{-1}&\{\langle c^{\dagger}_{\mathbf{k}-(\mathbf{q}-\mathbf{p})/2,t}c^{\dagger}_{\mathbf{k}'+(\mathbf{q}-\mathbf{p}')/2}\rho_{-\mathbf{p}'}c_{\mathbf{k}'-(\mathbf{q}-\mathbf{p}')/2}\rho_{\mathbf{p},t}c_{\mathbf{k}+(\mathbf{q}-\mathbf{p})/2,t}\rangle^{0}\\
&-\langle c^{\dagger}_{\mathbf{k}'+(\mathbf{q}-\mathbf{p}')/2}c^{\dagger}_{\mathbf{k}-(\mathbf{q}-\mathbf{p})/2,t}\rho_{\mathbf{p},t}c_{\mathbf{k}+(\mathbf{q}-\mathbf{p})/2,t}\rho_{-\mathbf{p}'}c_{\mathbf{k}'-(\mathbf{q}-\mathbf{p}')/2}\rangle^{0}\}(-i\theta_t)\\
+\left[i\frac{\partial}{\partial t}-\Delta E_{\mathbf{k}-\mathbf{p}/2,\mathbf{q}/2}\right]^{-1}&\{\langle c^{\dagger}_{\mathbf{k}-(\mathbf{q}-\mathbf{p})/2,t}\rho_{\mathbf{p},t}c^{\dagger}_{\mathbf{k}'+(\mathbf{q}-\mathbf{p}')/2}\rho_{-\mathbf{p}'}c_{\mathbf{k}'-(\mathbf{q}-\mathbf{p}')/2}c_{\mathbf{k}+(\mathbf{q}-\mathbf{p})/2,t}\rangle^{0}\\
&-\langle c^{\dagger}_{\mathbf{k}'+(\mathbf{q}-\mathbf{p}')/2}\rho_{-\mathbf{p}'}c^{\dagger}_{\mathbf{k}-(\mathbf{q}-\mathbf{p})/2,t}\rho_{\mathbf{p},t}\\
&\times c_{\mathbf{k}+(\mathbf{q}-\mathbf{p})/2,t}c_{\mathbf{k}'-(\mathbf{q}-\mathbf{p}')/2}\rangle^{0}\}(-i\theta_t)\Bigg]\,.\end{aligned}\tag{C4}$$

After use of Eq. (B4) and rearranging the factors of the expectation values in such a way that we get terms of the form $\langle c^{\dagger}c^{\dagger}\rho\rho c c\rangle$, which cancel, we transform from time dependence to frequency dependence and have to calculate terms of the form

$$\frac{\langle c^{\dagger}c'^{\dagger}\rho c'c\rangle^{0}}{\omega-\Delta E-\Delta E'}\quad\text{and}\quad\frac{\langle c^{\dagger}c'^{\dagger}c''^{\dagger}c''c'c\rangle^{0}}{\omega-\Delta E-\Delta E''}\,.\tag{C5}$$

The noninteracting expectation values are given by

$$\langle c_1^{\dagger}\cdots c_m^{\dagger}c_{m'}\cdots c_{1'}\rangle^{0}=\|\delta_{ii'}\|n_1\cdots n_m\,.\tag{C6}$$

Some of the δ functions cause a reduction of the long energy denominator, e.g., terms with

$$(\omega-\Delta E_{\ldots,p-q}-\Delta E')\delta_{p,q}=(\omega-\Delta E')\delta_{p,q}\tag{C7}$$

do not describe real two-pair excitations. But an exact evaluation shows that all these contributions cancel. In addition, processes without exchange of the two particles or the two holes involved do not contribute to $\chi^{d(2)}$.

There occur only terms which are part of the exchange contributions evaluated by Gasser,[21] namely

$$\begin{aligned}\chi_{\text{hom}}^{d(2)}(q,\omega)=\sum_{\mathbf{p},\mathbf{k},\mathbf{k}'}\delta_{\sigma,\sigma'}v_{\mathbf{p}}&\frac{1}{\omega-\Delta E_{\mathbf{k},(\mathbf{q}-\mathbf{p})/2}-\Delta E_{\mathbf{k}',\mathbf{p}/2}}\\
\times\Bigg[V_{\mathbf{k}-\mathbf{k}'+\mathbf{q}/2}&\Bigg[\frac{n_{\mathbf{k}-(\mathbf{q}-\mathbf{p})/2}n_{\mathbf{k}+(\mathbf{q}-\mathbf{p})/2}\Delta N_{\mathbf{k}',\mathbf{p}/2}}{(\omega-\Delta E_{\mathbf{k}-\mathbf{p}/2,\mathbf{q}/2})(\omega-\Delta E_{\mathbf{k}+\mathbf{p}/2,\mathbf{q}/2})}-\frac{n_{\mathbf{k}-(\mathbf{q}-\mathbf{p})/2}n_{\mathbf{k}'-\mathbf{p}/2}(n_{\mathbf{k}+(\mathbf{q}-\mathbf{p})/2}-n_{\mathbf{k}'+\mathbf{p}/2})}{(\omega-\Delta E_{\mathbf{k}-\mathbf{p}/2,\mathbf{q}/2})(\omega-\Delta E_{\mathbf{k}'-(\mathbf{q}-\mathbf{p})/2,\mathbf{q}/2})}\\
&+\frac{n_{\mathbf{k}-(\mathbf{q}-\mathbf{p})/2}n_{\mathbf{k}'+\mathbf{p}/2}(n_{\mathbf{k}+(\mathbf{q}-\mathbf{p})/2}+n_{\mathbf{k}'-\mathbf{p}/2})}{(\omega-\Delta E_{\mathbf{k}+\mathbf{p}/2,\mathbf{q}/2})(\omega-\Delta E_{\mathbf{k}'-(\mathbf{q}-\mathbf{p})/2,\mathbf{q}/2})}\Bigg]\\
+v_{\mathbf{k}-\mathbf{k}'-\mathbf{q}/2}&\Bigg[-\frac{n_{\mathbf{k}-(\mathbf{q}-\mathbf{p})/2}n_{\mathbf{k}+(\mathbf{q}-\mathbf{p})/2}\Delta N_{\mathbf{k}',\mathbf{p}/2}}{(\omega-\Delta E_{\mathbf{k}-\mathbf{p}/2,\mathbf{q}/2})(\omega-\Delta E_{\mathbf{k}+\mathbf{p}/2,\mathbf{q}/2})}-\frac{n_{\mathbf{k}+(\mathbf{q}-\mathbf{p})/2}n_{\mathbf{k}'+\mathbf{p}/2}(n_{\mathbf{k}-(\mathbf{q}-\mathbf{p})/2}-n_{\mathbf{k}'-\mathbf{p}/2})}{(\omega-\Delta E_{\mathbf{k}+\mathbf{p}/2,\mathbf{q}/2})(\omega-\Delta E_{\mathbf{k}'+(\mathbf{q}-\mathbf{p})/2,\mathbf{q}/2})}\\
&+\frac{n_{\mathbf{k}+(\mathbf{q}-\mathbf{p})/2}n_{\mathbf{k}'-\mathbf{p}/2}(n_{\mathbf{k}-(\mathbf{q}-\mathbf{p})/2}-n_{\mathbf{k}'+\mathbf{p}/2})}{(\omega-\Delta E_{\mathbf{k}-\mathbf{p}/2,\mathbf{q}/2})(\omega-\Delta E_{\mathbf{k}'+(\mathbf{q}-\mathbf{p})/2,\mathbf{q}/2})}\Bigg]\Bigg]\,.\end{aligned}\tag{C8}$$

Equations (C3) and (C8) are our final result for the distinct part of the susceptibility. Its self part is obtained by taking the difference with the full χ in second-order perturbation theory as given in Ref. 21.

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[1] L. Van Hove, Phys. Rev. **95**, 249 (1954).

[2] S. W. Lovesey, *Theory of Neutron Scattering from Condensed Matter* (Clarendon, Oxford, 1984).

[3] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, New York, 1976), and references therein.

[4] J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).

[5] O. T. Valls, G. F. Mazenko, and H. Gould, Phys. Rev. B **18**, 263 (1978).

[6] C. D. Boley and J. B. Smith, Phys. Rev. A **12**, 661 (1975).

[7] K. S. Singwi and M. P. Tosi, Solid State Phys. **36**, 177 (1981).

[8] S. Ichimaru, Rev. Mod. Phys. **54**, 1017 (1982); Phys. Rep. **149**, 93 (1987), and references therein.

[9] K. S. Singwi, M. P. Tosi, R. H. Land, and A. Sjölander, Phys.

Rev. **176**, 589 (1968).

[10] K. F. Berggren, Phys. Rev. A **1**, 1783 (1970).

[11] T. Schneider, Physica **52**, 481 (1971); P. Vashishta and K. S. Singwi, Phys. Rev. B **6**, 857 (1972).

[12] T. Hasegawa and M. Shimizu, J. Phys. Soc. Jpn. **35**, 18 (1973); **38**, 965 (1975); **39**, 569 (1975); **48**, 16 (1980).

[13] K. S. Singwi, K. Sköld, and M. P. Tosi, Phys. Rev. Lett. **21**, 881 (1970); Phys. Rev. A **1**, 454 (1970).

[14] W. C. Kerr, Phys. Rev. **174**, 316 (1968).

[15] A. Sjölander and L. S. Jögren, Ann. Phys. (N.Y.) **110**, 122 (1978); **110**, 173 (1978); **113**, 304 (1978).

[16] A. Sjölander, in *Atomic Motions in Liquids, Proceedings of the NATO Advanced Study Institute, Trentino, Italy, 1985* (Martinus Nijhoff, Dordrecht, 1987).

[17] F. Green, D. Neilson, and J. Szymanski, Phys. Rev. B **35**, 133 (1987); **35**, 142 (1987).

[18] D. Neilson, F. Green, and J. Szymanshi, in *Recent Progress in Many Body Theories* (Plenum, New York, 1988), Vol. 1, p. 235.

[19] G. Niklasson, Phys. Rev. B **10**, 3052 (1974).

[20] A. Holas, Proceedings of the 15th Symposium on Electronic Structures of Metals and Alloys, Johnsbach, 1985 (unpublished).

[21] W. Gasser, Z. Phys. B **57**, 15 (1984).