

Small and large wavelength contributions to the exchange and correlation energy of a nonuniform electron gas

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For the uniform electron gas, the decomposition of the exchange and correlation energy into its individual wave vectors has proved invaluable for both a deeper understanding of its structure as well as its extensions to the metallic range. Similar efforts made in the nonuniform electron gas (and, in particular, surface properties) have also yielded much finer knowledge. However, we show here unequivocally that the particle conservation sum rule does not determine the long-wavelength limit of the structure factor of inhomogeneous many-electron systems in the thermodynamic limit. The short-wavelength region is also examined and shown not to be given rigorously by the local-density approximation.

I. INTRODUCTION

For N electrons in the presence of an external potential $V(\vec{r})$ the exchange and correlation energy can be written in terms of the structure factor $S_\lambda(\vec{r}, \vec{r}')$,¹⁻⁴ i.e.,

$$E_{xc} = \frac{1}{2} \int d^3r \int d^3r' v(\vec{r} - \vec{r}') \int_0^1 d\lambda [NS_\lambda(\vec{r}, \vec{r}') - n_\lambda(\vec{r})\delta(\vec{r} - \vec{r}')], \tag{1}$$

where $\lambda v(\vec{r} - \vec{r}')$ is an arbitrary interparticle interaction of coupling strength λ and $n_\lambda(\vec{r})$ the electron density.

For a uniform system of electrons [$V(\vec{r})=0$] Eq. (1) reduces to⁵

$$E_B^{xc} = -\frac{1}{2} \int \frac{d^3q}{(2\pi)^3} \int_0^1 \frac{d\lambda}{\lambda} \left[\int_C \frac{d\omega}{2\pi i} \frac{1}{\epsilon_\lambda(q, \omega)} + \frac{2\pi N \lambda e^2}{q^2} \right], \tag{2}$$

where C encloses the positive real ω axis in a clockwise direction. In the random-phase approximation (RPA)

$$\epsilon_\lambda(q, \omega) = 1 + \frac{4\pi e^2 \lambda}{q^2} \pi(q, \omega), \tag{3}$$

with

$$\pi(q, \omega) = 2 \int \frac{d^3k}{(2\pi)^3} \frac{[\Theta^<(\epsilon_{\vec{k} + \vec{q}} - \mu) - \Theta^<(\epsilon_{\vec{k}} - \mu)]}{\omega - \epsilon_{\vec{k} + \vec{q}} + \epsilon_{\vec{k}}}, \tag{4}$$

$\epsilon_k = k^2/2m$, $\mu = k_F^2/2m$, $k_F = (3\pi^2 n_0)^{1/3}$, and n_0 the uniform electron density. Also,

$$\Theta^<(x) = \begin{cases} 1 & \text{for } x < 0 \\ 0 & \text{for } x > 0. \end{cases}$$

Sawada *et al.*⁶ was first to recognize that Eqs. (2)–(4) can be written as the difference between

the normal modes $\omega_0(\vec{q}, \vec{k})$ [$\omega_0(\vec{q}, \vec{k}) \equiv \epsilon_{\vec{k} + \vec{q}} - \epsilon_k$] for the noninteracting electron gas and the normal modes $\omega_B(\vec{q}, \vec{k})$ of the interacting electron gas [i.e., the poles of $1/\epsilon_\lambda(q, \omega)$ in Eq. (2)]. In other words,

$$E_B^C = \frac{1}{2} \sum_{\vec{k}, \vec{q}} [\omega_B(\vec{q}, \vec{k}) - \omega_0(\vec{q}, \vec{k})]. \tag{5}$$

The normal modes $\omega_B(\vec{q}, \vec{k})$ can be grouped into two classes. The first contains modes that have a one-to-one correspondence to $\omega_0(\vec{q}, \vec{k})$ and are therefore referred to as the particle-hole continuum (PH). The second are split-off modes or bulk plasmons. The PH continuum exists even at large q while the bulk plasmon poles disappear beyond a cutoff value of q_C .^{5,6}

When $V(\vec{r})$ is not equal to zero the spectrum of excitations $\omega_B(\vec{q}, \vec{k})$ is again going to change; such a potential can again create new split-off modes. The boundary confining an electron gas is one example of such a potential $V(\vec{r})$ which creates new surface-plasmon modes. To see this, consider the case of two infinite barriers separated by a distance $L + \delta$ ($L \rightarrow \infty$),⁷ the infinite barrier model (IBM). If, in addition, we ignore quantum interference effects,⁸⁻¹¹ then one can write the exchange and correlation energy in closed form⁹ as

$$E^C = E_B^C + 2E_S^C, \quad (6)$$

where E_B^C is the bulk correlation energy contribution in Eq. (2) and E_S^C , the surface contribution, is given by

$$2E_S^C = -\frac{1}{2} \sum_{q_{||}} \int_C \frac{d\omega \omega}{2\pi i} \left[\frac{1}{2} \frac{d\epsilon(q_{||}, \omega)/d\omega}{\epsilon(q_{||}, \omega)} + 2 \frac{dD(q_{||}, \omega)/d\omega}{D(q_{||}, \omega)} \right], \quad (7)$$

with

$$D(q_{||}, \omega) = 1 + \frac{1}{L} \sum_{q_z} \frac{2q_{||}}{q_z^2 + q_{||}^2} \frac{1}{\epsilon(q, \omega)}, \quad (8)$$

where $q = (q_{||}^2 + q_z^2)^{1/2}$.

Griffin *et al.*⁹ have made a detailed and lucid study of Eq. (7) by following the treatment of Sawada⁶ for the uniform system. They show that the contribution of the last term in Eq. (7) can again be written as the difference in the normal modes of the interacting uniform electron gas [$\omega_B(\vec{k}, \vec{q})$] and the nonuniform system [$\omega_F(\vec{k}, \vec{q})$],¹² i.e.,

$$2E_S^C = \frac{1}{2} \sum_{q_{||}} \sum_{q_z} \sum_{\vec{k}} [(\omega_F(q_{||}, q_z, \vec{k}) - \omega_B(q_{||}, q_z, \vec{k}))]. \quad (9)$$

Again the normal modes $\omega_F(\vec{q}, \vec{k})$ can be grouped in two categories. The first has a one-to-one correspondence with the PH continuum and the bulk plasmons contributions both in $\omega_B(\vec{q}, \vec{k})$. The

second are split-off modes or a surface plasmon for each wave vector $\vec{q}_{||}$ and these again disappear for $q_{||} > q_c$.

The importance of these surface plasmons¹³⁻¹⁶ and systematic ways for including such contributions in the treatment of *real* metallic surface energies has occupied a considerable amount of surface studies.^{2,3,17-24} In most recent studies the functional density formalism has become a corner stone of such calculations. Since E_{xc} is given uniquely by the electronic density $n(\vec{r})$ (Ref. 25) the first step in such calculations is to use the approximation of Hohenberg and Kohn²⁵ or various derivatives of it,²⁶ i.e.,

$$E_{xc} \approx E_{xc}^{LD} + E_{xc}^{NL}, \quad (10)$$

where E_{xc}^{LD} is the well known local-density approximation (LDA), i.e.,

$$E_{xc}^{LD} = \int d^3r n(\vec{r}) \epsilon_{xc}(n(\vec{r})), \quad (11)$$

and $\epsilon_{xc}(n(\vec{r}))$ is the exchange-correlation energy per electron of a homogeneous electron gas of density $n(\vec{r})$. E_{xc}^{NL} is the nonlocal correction given by

$$E_{xc}^{NL} = -\frac{1}{4} \int d^3r \int d^3r' K_{xc}(\vec{r} - \vec{r}', n(\vec{r}_0)) \times [n(\vec{r}) - n(\vec{r}')]^2, \quad (12)$$

with K_{xc} related to the response function of the uniform electron gas.²⁵ While it is likely that such nonlocal corrections (based on properties of the uniform electron gas) can account in a systematic way for the non-split-off modes (see above), they are less likely to give a satisfactory description of the surface plasmons (or any other split-off modes created by an external perturbation). To incorporate such contributions in the framework of the functional density formalism, a new scheme [the wave-vector interpolation (WVI)] was suggested.¹⁷ It relies on the assumption of a universal small- q behavior,¹⁷ dominated by surface plasmons, and an exact large- q behavior given by the LDA,³ and it proposes to interpolate between the two in the intermediate region. This is similar in spirit to the interpolation procedure of Nozières and Pines for $E_{xc}(q)$ in the uniform electron gas.^{27,28} Of course, inhomogeneous systems are more complex and we may expect the determination of the correct small- q and large- q limits of $E_{xc}(q)$ to be much more delicate than for uniform systems, particularly when surface effects or corrections to bulk energies are concerned. The question of the large- q limit and the LDA will be considered later (Sec. IV), and we will focus our present attention on the small- q lim-

it. A major cornerstone of the WVI and its extension is the expectation that for inhomogeneous (bulk or surface) systems, the exchange and correlation hole around an electron will be sufficiently localized so that the limiting value as $q \rightarrow 0$ of the structure factor [directly related to $E_{xc}(q)$] is equal to its value for $q \equiv 0$ which is fixed, by a sum rule, to be zero (see Sec. III). Since a number of serious conclusions follow from this limit behavior, if correct, we have attempted to clarify this crucial point by calculating the q -dependent structure factor for specific well-defined examples to study its explicit form at small q . We show that $\gamma(q)$ [defined in Eqs. (20) and (21)] does *not* vanish in general for $q \rightarrow 0$, even though $\gamma(q \equiv 0) = 0$, and that there is no universal structure for small q . The failure of such expectations is due to subtle differences in pair correlation functions between uniform and inhomogeneous systems. We shall see that these subtle differences are a property of extended

or thermodynamic systems and the systems we examine here are *always* assumed to be of macroscopic size.

In Sec. II, we develop expressions for $E_{xc}(q)$ for both bulk and surface problems. Since one of our objectives is to make as much use as possible of uniform electron-gas results, it is very important to make sure that the q in $E_{xc}(q)$ is the same q entering the corresponding uniform electron-gas result. Therefore we must make a careful connection between Fourier cosine transforms, which are natural in the surface problem, and Fourier exponential transforms, which are natural in bulk problems. This is also done in Sec. II. These results are applied in Sec. III to both surface and bulk density profiles, and it is shown that there exists no universal small- q behavior of $E_{xc}(q)$. In Sec. IV, we show that the LDA is not exact at large q . Section V consists of a summary of results and discussion.

II. q VECTOR DECOMPOSITION OF E_{xc}

Equation (1) can be rewritten in a slightly different form by using the relation

$$NS_{\lambda}(\vec{r}, \vec{r}') = - \int_0^{\infty} \frac{d\omega}{\pi} x_{\lambda}(\vec{r}, \vec{r}', i\omega), \quad (13)$$

then

$$E_{xc} = - \frac{1}{2} \int d^3r \int d^3r' v(\vec{r} - \vec{r}') \int_0^1 d\lambda \left[\int_0^{\infty} \frac{d\omega}{\pi} x_{\lambda}(\vec{r}, \vec{r}', i\omega) + n_{\lambda}(\vec{r}) \delta(\vec{r} - \vec{r}') \right]. \quad (14)$$

We can now write $v(\vec{r} - \vec{r}')$ in terms of any complete basis set $\psi_{\vec{q}}(\vec{r})$, i.e.,

$$v(\vec{r} - \vec{r}') = \sum_{\vec{q}, \vec{q}'} v_{\vec{q}, \vec{q}'} \psi_{\vec{q}}(\vec{r}) \psi_{\vec{q}'}(\vec{r}'). \quad (15)$$

Inserting Eq. (15) in Eq. (14) results in a decomposition of E_{xc} in terms of \vec{q} and \vec{q}' . For a jellium surface, where full translational symmetry exists only in the direction parallel to the surface, a rational choice is

$$\psi_{\vec{q}}(\vec{r}) = \delta(z - z_1) \frac{e^{i\vec{q}_{\parallel} \cdot \vec{x}}}{\sqrt{A}} \quad (16)$$

(with \vec{x} and \vec{q}_{\parallel} two-dimensional vectors parallel to the surface). Then Eq. (14) can be written as

$$E_{xc} = - \frac{1}{2} A \int \frac{d^2q_{\parallel}}{(2\pi)^2} \int dz_1 \int dz_2 v(q_{\parallel}, z_1 - z_2) \times \int_0^1 d\lambda \left[\int_0^{\infty} \frac{d\omega}{\pi} \chi_{\lambda}(q_{\parallel}, z_1, z_2, i\omega) + n_{\lambda}(q_{\parallel} = 0, z_1) \delta(z_1 - z_2) \right], \quad (17)$$

with A the surface area.

Another choice for $\psi_{\vec{q}}(\vec{r})$ is $\psi_{\vec{q}}(\vec{r}) = e^{i\vec{q} \cdot \vec{r}} / \sqrt{V}$; then Eq. (14) becomes

$$E_{xc} = -\frac{1}{2} \int \frac{d^3q}{(2\pi)^3} \int_{\lim\Delta \rightarrow 0} d^3r \int d^3r' v(\vec{q}) e^{i\vec{q} \cdot (\vec{r} - \vec{r}') - \Delta |\vec{r} - \vec{r}'|} \times \int_0^1 d\lambda \left[\int_0^\infty \frac{d\omega}{\pi} \chi_\lambda(\vec{r}, \vec{r}', i\omega) + n_\lambda(\vec{r}) \delta(\vec{r} - \vec{r}') \right]. \quad (18)$$

For a jellium surface this reduces to

$$E_{xc} = -\frac{A}{2} \int \frac{d^3q}{(2\pi)^3} \int_{\lim\Delta \rightarrow 0} dz \int dz' v(\vec{q}) e^{iq_z(z-z') - \Delta |z-z'|} \times \int_0^1 d\lambda \left[\int_0^\infty \frac{d\omega}{\pi} \chi_\lambda(q_{||}, z, z', i\omega) + n_\lambda(q_{||}=0, z) \delta(z-z') \right], \quad (19)$$

with $v(\vec{q}) = 4\pi e^2/q^2$ for a Coulomb interparticle interaction. The appearance of Δ in Eqs. (18) and (19) will be discussed shortly. The choice of this last basis set corresponds to the wave-vector decomposition³ (WVD) and it is this choice we examine almost exclusively in this paper. There is, of course, no *a priori* reason why this should be the best representation for treating either the long- or short-range \vec{q} fluctuations in metallic surface energy calculations. Also, rather than examine the dependence of E_{xc} on each q vector's magnitude and direction we follow the WVI (Ref. 3) and average over angle to define $\gamma_s(q)$ as the spherical decomposition of the surface energy σ_{xc} :

$$\sigma_{xc} \equiv \frac{E_{xc}}{2A} \equiv \int_0^\infty \frac{dq}{k_F} \gamma_S(q). \quad (20)$$

In the case of a bulk system, $\gamma_B(q)$ is defined as the energy per unit volume:

$$\frac{E_{xc}}{V} \equiv \int_0^\infty \frac{dq}{k_F} \gamma_B(q). \quad (21)$$

The quantities $\gamma_S(q)$ and $\gamma_B(q)$ are essentially equivalent to the corresponding averaged structure factors. These results will be used in the following section.

We next consider the case of a jellium surface. Now if this potential confines the electron gas between $z=0$ and $z=L+\delta$ then we can write χ in Eq. (13) or (17) in terms of cosine transforms, i.e.,

$$\chi_\lambda(q_{||}, z, z', i\omega) = \left[\frac{2}{L+\delta} \right]^2 \sum_{p_z, p'_z} a_{p_z} a_{p'_z} \cos(p_z z) \cos(p'_z z') \chi_\lambda(q_{||}, p_z, p'_z, i\omega), \quad (22)$$

where p_z and $p'_z = n\pi/(L+\delta)$ with $n=0, 1, 2, \dots$ and $a_{p_z} = 1 - \frac{1}{2}\delta_{p_z, 0}$. We next substitute Eq. (22) in Eq. (19) and ignore the last term of Eq. (19), since it does not participate in the nonuniform contribution to E_{xc} . This yields, after considerable algebra, the following connection between the cosine transform of the susceptibility of a jellium surface and the WVD of E_{xc} ,

$$E_{xc} = -\frac{A}{(L+\delta)^2} \int \frac{d^3q}{(2\pi)^3} \int_{\lim\Delta \rightarrow 0} d\lambda \int_0^\infty \frac{d\omega}{\pi} \sum_{p_z, p'_z} a_{p_z} a_{p'_z} \chi_\lambda(q_{||}, p_z, p'_z, i\omega) \times \left[(L+\delta)2\pi\delta(p'_z - q_z)\delta_{p_z, p'_z} + (L+\delta)2\pi\delta(q_z)\delta_{p_z, 0}\delta_{p_z, p'_z} + \text{Re}' \left\{ \frac{1}{(p'_z + q_z + i\Delta)(p_z + q_z + i\Delta)} - \frac{1}{(p'_z + q_z + i\Delta)(p_z - q_z - i\Delta)} - \frac{1}{(p'_z - q_z - i\Delta)(p_z + q_z + i\Delta)} + \frac{1}{(p'_z - q_z - i\Delta)(p_z - q_z - i\Delta)} \right\} \right], \quad (23)$$

where the prime above the Re restricts the contribution in the following set of parentheses to p_z and p'_z either *both* even or both odd. Two points should be emphasized. Firstly, the variables $\vec{q}_{||}$ and q_z in Eq. (23) correspond precisely to the natural variables for the uniform electron system. Secondly, the connection between these variables and $\vec{q}_{||}, p_z, p'_z$, which are the natural variables for the surface problem, is rather complicated, and the discrete nature of these variables cannot be ignored when extracting surface energies.

Before turning to specific examples, consider a nonuniform electron gas in the presence of a weak external potential $V(\vec{r})$. We demonstrate how the expansion of E_{xc} in Eq. (14) [to second order in $V(\vec{r})$] is related to the usual Feynman graphs and response functions, with the explicit \vec{q} of the structure factor again being that of the uniform electron gas. For simplicity of this discussion, attention is restricted to the self-consistent RPA, and then E_{xc} is approximated by the graphs of Fig. 1. If we expand all the electron propagators to second order in $V(\vec{r})$ then E_{xc} [Eq. (14) or Fig. 1, see also Appendix A] reduces to

$$E_{xc} = -\frac{1}{4} \int K_{xc}(\vec{r} - \vec{r}', n_0) [n(\vec{r}) - n(\vec{r}')]^2, \quad (24)$$

which is the form of Eq. (12) strictly to second order in $V(\vec{r})$. The momentum space representation of Eq. (24) is simply

$$E_{xc} = - \int \frac{d^3h}{(2\pi)^3} K_{xc}(\vec{h}) [n(\vec{h})]^2, \quad (25)$$

with

$$K_{xc}(\vec{h}) = \frac{1}{2} \left[\frac{1}{\pi(\vec{h})} - \frac{1}{\pi_0(\vec{h})} \right]. \quad (26)$$

Here $\pi_0(\vec{h})$ is the Lindhard and $\pi(\vec{h})$ the fully correlated screening functions.

The non-self-consistent (i.e., lowest order RPA) graphs for K_{xc} are shown in Fig. 2(a) and examples of higher order, self-consistent, RPA contributions to K_{xc} are illustrated in Fig. 2(b). The graphs are evaluated in coordinate space by integrating over $\vec{r}_1 \cdots \vec{r}_n$ following the usual Feynman rules.²⁹ To get the WVD of Fig. 1 [or Eqs. (18) and (19)] we replace $v(\vec{r} - \vec{r}')$ by $v(\vec{q})e^{i\vec{q} \cdot (\vec{r} - \vec{r}')}e^{-\Delta|\vec{r} - \vec{r}'|}$

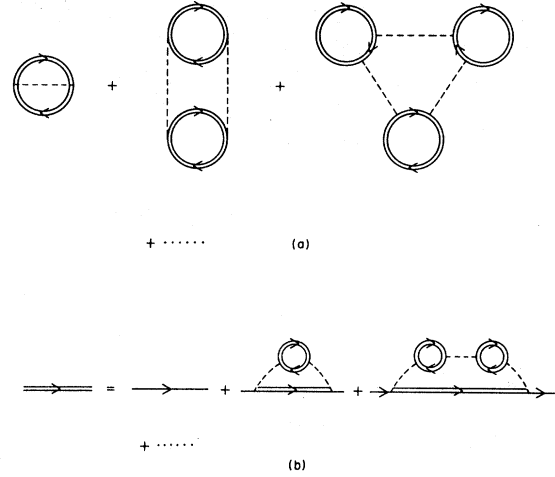


FIG. 1. Set of graphs for the exchange and correlation RPA. The single solid line is the electron propagator in the presence of the electrostatically screened external potential $V(\vec{r})$ [or $V_H(\vec{r})$]. The double solid lines are the self-consistent electron propagators within the RPA as described in (b). The dashed lines are the bare Coulomb potentials.

in Fig. 2 and integrate over all the internal coordinates [including \vec{r} and \vec{r}' ; note that here the \vec{r} and \vec{r}' are not the same as in Eq. (24)]. This then yields the usual momentum space representation of Fig. 3 with the wave vector q labeled explicitly; all other momentum transfers are integrated over. Keeping Δ small and then taking its zero limit gives, of course, the correct momentum conservation at the interaction vertex. In short, the form of Eqs. (18) or (19) in the presence of a weak external potential yields the usual response function³⁰⁻³² with one of the interaction lines carrying the momentum transfer corresponding to the desired wave vector q . For the lowest order RPA terms, only the terms in Fig. 3(b) need be considered.

This completes the formal WVD for a jellium surface [Eq. (23)] or for an electron gas in the presence of a weak external potential [Eq. (25)]. Using these results in the following sections, we proceed to examine the structure of the WVD for both small and large q for several inhomogeneous electron systems.

III. THE SMALL- q LIMIT

A. Surface behavior

To examine the general small- q behavior of $\gamma_s(q)$ for an arbitrary jellium profile is at present an unattainable task. For present purposes, it is sufficient to study $\gamma_s(q)$ within the IBM. We conclude the following:

(i) The $\gamma_s(q)$ for exchange only goes to a finite value as $q \rightarrow 0$.

(ii) The proof of Ref. 3 for the small- q limit of the fully correlated $\gamma_s(q), \gamma_s(q) \rightarrow (k_F/8\pi)q(\omega_s - \omega_B/2)$ for an arbitrary surface profile is incomplete.

To evaluate $\gamma_s(q)$ for exchange only we return to Eq. (23). In the Hartree-Fock (HF) approximation it is not difficult to show that

$$\chi^0(q_{||}, z, z', i\omega) = \frac{2}{(2\pi)^2} \sum_{k_z, k'_z} \left[\int d^2k'_{||} \int d^2k_{||} \delta(\vec{q}_{||} + \vec{k}'_{||} - \vec{k}_{||}) \frac{1}{i\omega + \epsilon_{\vec{k}} - \epsilon_{\vec{k}'}} [\Theta^<(\epsilon_{\vec{k}'}, -\mu) - \Theta^<(\epsilon_{\vec{k}} - \mu)] \right. \\ \left. \times \phi_{k_z}(z) \phi_{k'_z}(z) \phi_{k_z}(z') \phi_{k'_z}(z') \right]. \quad (27)$$

For the IBM

$$\phi_{k_z}(z) = [2/(L + \delta)]^{1/2} \sin k_z z, \quad (28)$$

and $\epsilon_{\vec{k}} = (k_{||}^2 + k_z^2)/2m$ with $k_z = n\pi/(L + \delta)$ ($n = 1, 2, \dots$). If we now perform the integral over frequency and take the cosine transform over z and z' , we get

$$\int_0^\infty \frac{d\omega}{\pi} \chi^0(q_{||}, p_z, p'_z, i\omega) + n(q_{||}, p_z) \delta_{p_z, p'_z} \\ = \frac{1}{8\pi^2} \sum_{k_z, k'_z} H(\vec{q}_{||}, k_z, k'_z) (-\delta_{p_z, -k_z - k'_z} - \delta_{p_z, k_z + k'_z} + \delta_{p_z, k_z - k'_z} + \delta_{p_z, -k_z + k'_z}) \\ \times (-\delta_{p'_z, -k_z - k'_z} - \delta_{p'_z, k_z + k'_z} + \delta_{p'_z, k_z - k'_z} + \delta_{p'_z, -k_z + k'_z}), \quad (29)$$

with

$$H(q_{||}, k_z, k'_z) = \int d^2k'_{||} \int d^2k_{||} \delta(\vec{q}_{||} + \vec{k}'_{||} - \vec{k}_{||}) \Theta^>(k_F^2 - k_z^2 - k_{||}^2) \Theta^>(k_F^2 - k_z'^2 - k_{||}^2), \quad (30)$$

which is given in Ref. 4 (to be referred to as I). Note that although we have included $n(q_{||}, p_z)$ in Eq. (29), this term makes no contribution to the surface energy. If we now introduce Eq. (29) in Eq. (23) and analyze the sum over p_z and p'_z we retrieve the form for the HF contribution to the surface energy of the IBM as given by Eqs. (28)–(32) of I.

The $\gamma_s(q)$ corresponding to Eqs. (28)–(32) of I has been calculated numerically and shown to go to a finite value for $q \rightarrow 0$. In other words, the HF structure factor or pair distribution function, in the presence of a surface, shows subtle long-range behavior which renders invalid the intuitive notions concerning small- q limits described in the Introduction. More specifically, define

$$S(\vec{q}, \vec{q}) \equiv \int d^3r \int d^3r' e^{i\vec{q} \cdot (\vec{r} - \vec{r}')} S(\vec{r}, \vec{r}'), \quad (31)$$

which, from Eq. (1), has the same q dependence as $\gamma(q)$ and differs only by a constant factor. Simple conservation of particles yields the sum rule

$$\int d^3r \int d^3r' S(\vec{r}, \vec{r}') = 0. \quad (32)$$

The above Hartree-Fock results, in which particle conservation was carefully maintained (see below), imply that

$$\lim_{q \rightarrow 0} S(\vec{q}, \vec{q}) \neq S(\vec{q} = \vec{0}, \vec{q}' = \vec{0}). \quad (33)$$

Thus, $\gamma(\vec{q})$ exhibits a discontinuity at $\vec{q} = \vec{0}$ in this very explicit example (other examples are discussed in the following). We emphasize that when referring to the $q \rightarrow 0$ limit of the structure factor the thermodynamic limit has been taken as in I.

These results, therefore, do *not* support the general conclusions of Refs. 3 and 24 for the small- q limit of $\gamma(q)$ or $S(q, q)$. For example, the surface contribution of the function $\chi^0(q_{||}, p_z, p'_z, i\omega)$ in Eqs. (27) and (29) is nothing more than the function $\psi_{q, q'}$ of Eq. (3.16) in Ref. 3 (with the notational change $p_z \rightarrow q$, see also Appendix B) within the RPA. But the limiting $q_z \rightarrow 0$ connection between the appropriate WVD and the cosine transform is much more complicated than simply setting $q_z = 0$. To be very explicit, setting $\vec{q}_{||}, p_z, p'_z$ equal to zero in Eq. (29) after summation over k_z and k'_z shows that the sum rule, Eq. (32), is satisfied identically.

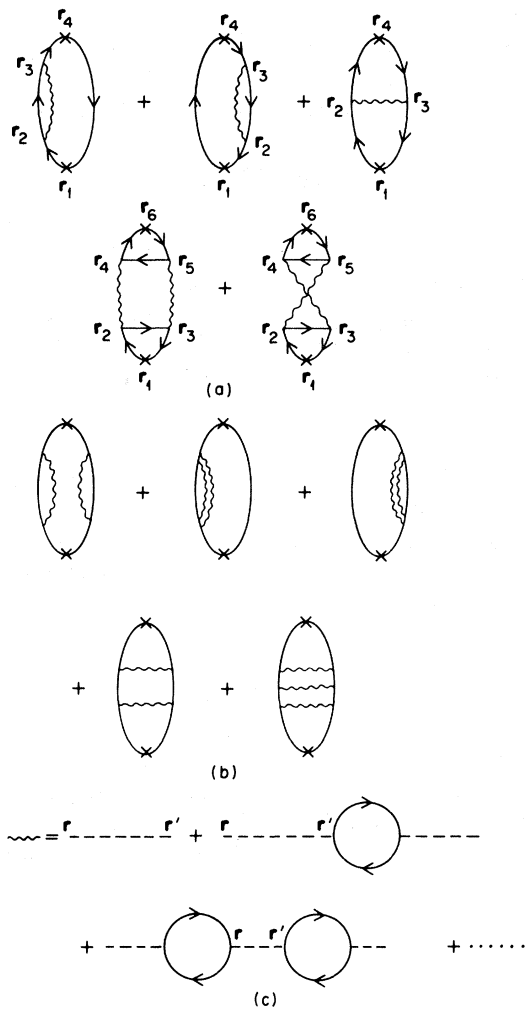


FIG. 2. (a) Contribution of Fig. 1 to *second* order in the screened external potential (represented by the crosses). The solid lines are now the usual uniform noninteracting electron propagators. The graphs are the lowest-order contributions to the irreducible screening function $\pi(\vec{r}, \vec{r}')$ within the RPA before the final integration over \vec{r} and \vec{r}' . (b) Examples of higher-order self-consistent contribution to the RPA irreducible screening function. (c) The dynamically screened interaction within the RPA. The purpose is to show that the structure of $\pi(\vec{r}, \vec{r}')$ involves placing the bare Coulomb line in all possible distinct ways in (a) and (b).

Thus, conservation of particles is strictly maintained but this has no direct bearing at all on the *limiting* value for $q \rightarrow 0$ of $\gamma_S(q)$, which was shown in I to be finite for the IBM. The essential point is that the limiting procedures involved are simply very delicate particularly when account is taken of the discrete nature of certain of the variables involved. A similar problem of different origin (see

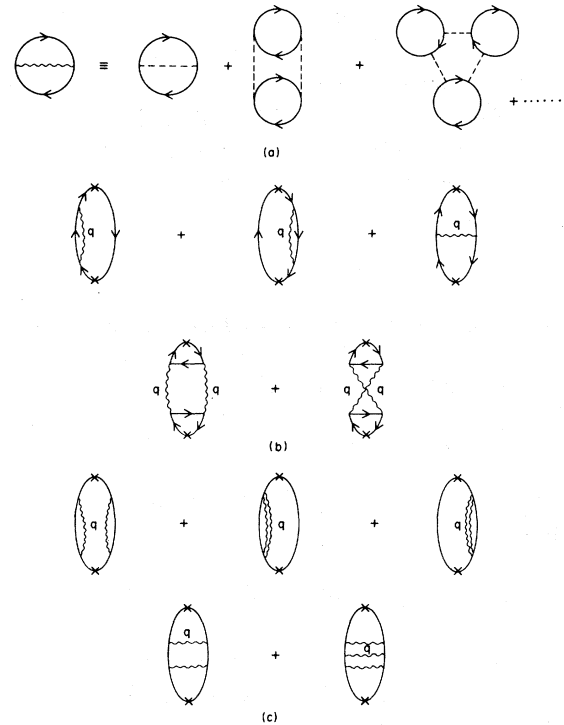


FIG. 3. (a) Contribution to the LDA. (b) All of the contributions from Fig. 2(a) after introduction of $v(\vec{r} - \vec{r}') = v(q)e^{i\vec{q} \cdot (\vec{r} - \vec{r}') - \Delta|\vec{r} - \vec{r}'|}$ and integration over \vec{r} and \vec{r}' . (c) Example of *some* of the contributions from Fig. 2(b). Additional terms will enter by permuting the position of q in the wiggly lines.

Appendix B) also occurs when all correlations are included. For correlation, in addition, to determine the contribution to the energy at small q , it is not sufficient to consider only $\omega=0$ or $\omega=\text{fixed}$ constant. Very important contributions come from frequency ranges which *scale* with wave numbers (i.e., $\omega/p_z, \dots$ are relevant) in the usual way. These properties of χ^0 will be reflected in the fully correlated χ as a consequence of the integral equation (3.18) of Ref. 3. As a consequence of these omissions, we conclude that the proof that $\gamma_S(q) \rightarrow (k_F/8\pi) q(\omega_S - \omega_B/2)$ is incomplete (see Appendix B). There is no reason to expect $\gamma_S(q)$ to have this universal small q structure for an arbitrary density profile. It must be again emphasized that to obtain a correct wave-vector decomposition, it is necessary to make use of Eq. (23) to convert the relevant variables.

Finally, it should be noted that these results are fully consistent with corresponding results for fully correlated inhomogeneous bulk systems.

B. Bulk

We shall now evaluate $\gamma_B(q)$ in bulk situations with sufficiently slowly varying density profiles that a gradient expansion following Hohenberg and Kohn gives an accurate representation, that is,²⁵

$$\begin{aligned} |\nabla n|/n &\ll k_F(n), \\ |\nabla_i \nabla_j n|/|\nabla n| &\ll k_F(n). \end{aligned} \quad (34)$$

Then the form for E_{xc} given by Eqs. (11) and (12) is appropriate. As a first approximation to Eq. (12) we evaluate it in terms of

$$E_{xc}^{NL} = \int d^3r B_{xc}(n(\vec{r})) |\nabla n(\vec{r})|^2 + \dots, \quad (35)$$

where B_{xc} is related to the screening function through³⁰⁻³³

$$\frac{1}{\pi_0(\hbar)} - \frac{1}{\pi(\hbar)} = \text{const} + B_{xc} h^2 + \dots \quad (36)$$

To evaluate the WVD of Eq. (35) we follow the discussion of the preceding section (Fig. 3). Figure 3(a) describes the WVD of Eq. (11) within the non-self-consistent RPA, while Fig. 3(b) does the same for Eq. (35). The q behavior of Eq. (11) was first examined (for the uniform system) by Hubbard²¹ and Nozières and Pines.²⁸ The q behavior of Eq. (35) was first presented in Ref. 23 by its Eqs. (22) and (48). We can now derive some rigorous results for a fully correlated nonuniform electron gas at small q . Suppose we take the limit of a *weak* and *slowly* varying external potential $V(\vec{r})$. Equations (11) and (35) then give a rigorous treatment for E_{xc} . We assume these conditions to be satisfied. Then the WVD of E_{xc} , which is uniquely defined (see Sec. II) permits immediate identification of contributions to $\gamma_B(q)$. For example, the WVD of Eq. (11) leads to $\gamma_B(q) \sim q^2$ at small q in the LDA. Similarly, Eqs. (22) and (48) of II give the small q behavior of the WVD of E_{xc}^{NL} . It is not difficult to show [through a study of z_c , z_δ , and y_c of Eq. (48) of II] that $\gamma_B^{NL}(q)$ goes to a constant for $q \rightarrow 0$ (see also Appendix A). Since the sum rule, Eq. (32), is also satisfied in such systems, the above implies that $\gamma_B(q)$ for inhomogeneous bulk systems has a discontinuity as $q \rightarrow 0$. The finite *limit* of $\gamma_B(q)$ as $q \rightarrow 0$ does *not* indicate a failure of the gradient expansion. Note that in the particular case of the high-density limit (see Appendix A), the entire contribution to the gradient corrections comes from small $s \equiv q/2k_F$. Attempts to force $\gamma_B(q)$ to vanish for $0 < s < s_{\min}$ for any finite s_{\min} would be in disagreement with

the results of Ma and Brueckner.³⁰

We conclude the discussion of the small- q behavior of $\gamma_B^{NL}(q)$ by considering a periodic one-dimensional bulklike density profile of the form

$$n(z) = n_0 \left[1 + \beta \cos \frac{2\pi z}{a} \right]. \quad (37)$$

We choose $\beta=0.5$, $r_s=2.07$ and a as the lattice constant of aluminum. Inserting Eq. (37) in Eq. (35) and integrating over the unit-cell volume gives $\gamma_B^{NL}(q)$ of Fig. 4. For comparison we also display $\gamma_S^{NL}(q)$ for a model surface profile

$$n(z) = n_0 / (1 + e^{-\beta z 2k_F}), \quad (38)$$

(first evaluated in II) with $\beta=0.5$ again adjusted to reflect the aluminum surface jellium variation.²³ The similarity of the two γ 's should be noted, in particular the behavior at small q . We return to these results shortly.

IV. THE LARGE- q LIMIT

The WVD not only allows a detailed study of $E_{xc}(q)$ to be made at small q (Sec. III) but also the treatment of the different contributions at large q . In particular, the fundamental question of whether

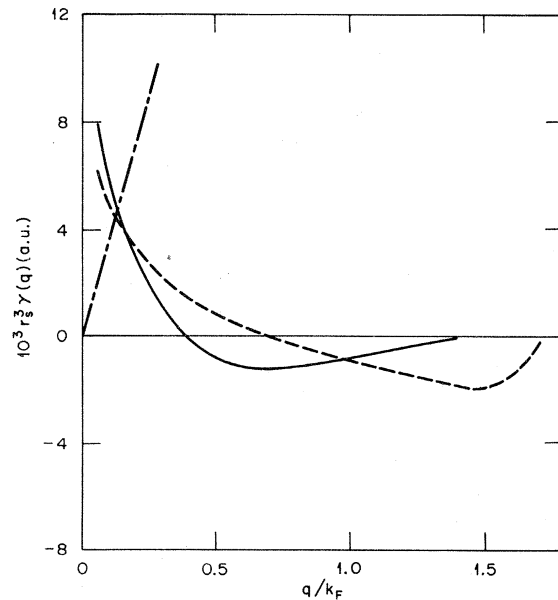


FIG. 4. q vector decomposition of the exchange and correlation contribution from a bulk [$\gamma_B(q)$] and surface density [$\gamma_S(q)$] profiles. The dashed curve is $\gamma_B(q)$ and the solid curve is $\gamma_S(q)$.

the LDA [Eq. (11)] gives a rigorous large- q limit for E_{xc} can be investigated. Again consider the electron gas in the presence of a weak external potential. Focusing on the RPA [Fig. 1(a)], we get for the LDA contribution the results of Fig. 3(a) and for the gradient contribution the results of Fig. 3(b). Now the first term in Fig. 3(a) (the local exchange contribution) is identically zero for $q > 2k_F$ (Ref. 5) and so makes no contribution in the large- q limit. Similarly the exchange contribution in the gradient expression [Eq. (22) of II] does not participate for $q > 2k_F$. In the LDA the leading contribution at large q is well known to give q^{-4} behavior at large q :

$$\gamma(q) \sim \frac{e^4 m k_F}{h^2 q^4} \int d^3 r [n(\vec{r})]^2. \quad (39)$$

Equivalent contributions come from the gradient expansions. It is straightforward [using Eqs. (47) and (48) of II] to show that individual terms in the RPA gradient contributions are also of the order q^{-4} at large q . The contribution to $\gamma(q)$ is

$$\gamma(q) \sim \frac{e^4 m k_F}{h^2 q^4} \int d^3 r \frac{|\nabla n(\vec{r})|^2}{[n(r)]^{2/3}}. \quad (40)$$

Evidently, this result does not support the conclusion that the LDA is exact at large q .³⁴ In fact, it is to be expected, in general, that a given set of graphs in any self-consistent approximation will have gradient corrections to the LDA at large q and that this is not specific to RPA.

V. CONCLUSIONS

We have studied the fundamental question of the behavior of the structure factor, or equivalently $\gamma(q)$, for inhomogeneous many electron system. We have shown that the usual sum rule $\gamma(q \equiv 0) = 0$, which is a reflection of particle conservation, has no bearing on the *limit* of $\gamma(q)$ as $q \rightarrow 0$ for macroscopic systems in the thermodynamic limit. The structure factor is discontinuous at $q = 0$. This was shown in two examples: (1) the exchange contribution to the surface energy of a metal, and (2) the exchange and correlation energy of a fully correlated weakly inhomogeneous bulk electron gas in the presence of a very slowly varying external potential. Furthermore, small- q structure of $\gamma(q)$ is not universal and the LDA is not exact at large q . The small- q limit reflects an important long-range dependence, in the pair correlation function, which is not only governed by intrinsic length scales (like k_F) but by the length scale of the external pertur-

bation. These are general features of inhomogeneous many electron systems. It follows that although the WVD may be a useful tool for studying the accuracy of various approximation methods in different ranges of q , the WVD method is less powerful than has been suggested, particularly in cases such as surfaces where q is not the natural variable to use to describe split-off modes as described in the Introduction. We conclude with a comment concerning finite systems (e.g., atoms and molecules). Clearly from Eq. (31) and the fact that $S(\vec{r}, \vec{r}')$ must be now localized within a finite size L the $\lim_{q \rightarrow 0} S(q, q) = 0$ and $S(q, q) \approx 0$ for all $q \ll 2\pi/L$. In the thermodynamic limit the entire region $q \ll 2\pi/L$ disappears completely and leads to the type of discontinuity in the structure factor discussed above. This reemphasizes^{32,35} the difficulty of extending forms derived from extended systems (where the spectrum of excitations is continuous) to finite systems with discrete spectrum spaced by $2\pi/L$.

ACKNOWLEDGMENTS

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APPENDIX A

In this appendix, we derive Eqs. (25) and (26) (restricting our discussion for simplicity to the RPA) following the formulation given in Sec. III of Ref. 3. In doing so, the objective is to obtain rigorous results for $\gamma(q)$ for weakly inhomogeneous systems and to study how the presence of inhomogeneity is reflected in the frequency and wave-number-dependent response function.

Consider the electron gas, again in the presence of a *weak* external potential $V(\vec{r})$. The response function $\chi^0(\vec{r}_1, \vec{r}_2, i\omega)$ can be written as

$$\chi^0(\vec{r}_1, \vec{r}_2, i\omega) = \chi^0(\vec{r}_1 - \vec{r}_2, i\omega) + \psi^0(\vec{r}_1, \vec{r}_2, i\omega), \quad (A1)$$

where $\chi^0(\vec{r}_1 - \vec{r}_2, i\omega)$ is the irreducible screening

function for the uniform electron gas and $\psi^0(\vec{r}_1, \vec{r}_2, i\omega)$ the change due to the presence of $V(\vec{r})$. The RPA $\chi^0(\vec{r}_1, \vec{r}_2, i\omega)$ is given by a single bubble in Fig. 1(a), $\chi^0(\vec{r}_1 - \vec{r}_2, i\omega)$ by a single bubble of Fig. 3(a), and $\psi^0(\vec{r}_1, \vec{r}_2, i\omega)$ [to second order in $V(\vec{r})$] by Fig. 5. [Note that the crosses are the screened $V(\vec{r})$, or Hartree potential $V_H(\vec{r})$.] It

should be emphasized that $\psi^0(\vec{r}_1, \vec{r}_2; i\omega)$ is precisely the quantity treated in Ref. 3 (see also Appendix B) where the inhomogeneity is due to the presence of a surface. The properties of ψ^0 are very important.

Now $\chi_\lambda(\vec{r}, \vec{r}', i\omega)$ is given by

$$\chi_\lambda(\vec{r}, \vec{r}', i\omega) = \chi^0(\vec{r}, \vec{r}', i\omega) + \int d^3r_1 \int d^3r_2 \chi^0(\vec{r}, \vec{r}_1, i\omega) \lambda v(\vec{r}_1 - \vec{r}_2) \chi_\lambda(\vec{r}_2, \vec{r}', i\omega). \quad (\text{A2})$$

Unlike Ref. 3 the inhomogeneity from $V(\vec{r})$ extends throughout the bulk rather than being present only in the surface region. We therefore simply Fourier transform (A2) to obtain

$$\chi_\lambda(\vec{q}, \vec{q}', i\omega) = \chi^0(\vec{q}, \vec{q}', i\omega) + \sum_{\vec{q}_1} \chi^0(\vec{q}, \vec{q}_1, i\omega) \lambda v(\vec{q}_1) \chi_\lambda(\vec{q}_1, \vec{q}', i\omega). \quad (\text{A3})$$

Define

$$\chi_\lambda(\vec{q}, \vec{q}', i\omega) = \frac{\chi^0(\vec{q}, i\omega)}{\epsilon_\lambda(\vec{q}, i\omega)} \delta_{\vec{q}, \vec{q}'} + \frac{\psi_\lambda(\vec{q}, \vec{q}', i\omega)}{\epsilon_\lambda(\vec{q}, i\omega) \epsilon_\lambda(\vec{q}', i\omega)}, \quad (\text{A4})$$

then with straightforward manipulation (A3) can be rearranged to an integral equation for ψ_λ in terms of ψ_0 , i.e.,

$$\psi_\lambda(\vec{q}, \vec{q}', i\omega) = \psi^0(\vec{q}, \vec{q}', i\omega) + \sum_{\vec{q}_1} \psi^0(\vec{q}, \vec{q}_1, i\omega) \frac{\lambda v(\vec{q}_1)}{\epsilon_\lambda(\vec{q}_1, i\omega)} \psi_\lambda(\vec{q}_1, \vec{q}', i\omega). \quad (\text{A5})$$

Equation (A5) is identical to Eq. (3.18) of Ref. 3 but now applies to bulklike inhomogeneity. Now consider for the moment only the second-order contribution to $\psi^0(\vec{q}, \vec{q}', i\omega)$ [i.e., $\psi_2^0(\vec{q}, \vec{q}', i\omega)$, in Fig. 5(b)]; then to second order in $V(\vec{r})$ no iteration of Eq. (A5) is necessary and $\psi_\lambda = \psi_2^0$. Using Eq. (A4) in Eq. (18) we get for the nonuniform contribution to E_{xc} [corrections to the kinetic energy are contained in Eqs. (A6)–(A9) and are subtracted later]

$$E_{xc} = -\frac{1}{2} \int \frac{d^3q}{(2\pi)^3} \int_0^\infty \frac{d\omega}{\pi} \int_0^1 \frac{d\lambda v(\vec{q}) \psi_2^0(\vec{q}, \vec{q}, i\omega)}{[\epsilon_\lambda(q, i\omega)]^2}. \quad (\text{A6})$$

Now ϵ_λ in the RPA is given by Fig. 2(c), i.e.,

$$\epsilon_\lambda(q, i\omega) = 1 + \lambda v(q) \pi_0(q, i\omega). \quad (\text{A7})$$

Integration over λ in (A6) gives³⁶

$$E_{xc} = -\frac{1}{2} \int \frac{d^3q}{(2\pi)^3} \int_0^\infty \frac{d\omega}{\pi} \frac{\psi_2^0(\vec{q}, \vec{q}, i\omega) v(q)}{\epsilon(q, i\omega)}. \quad (\text{A8})$$

Now for $\psi_2^0(\vec{q}, \vec{q}, i\omega)$ given in Fig. 5(b), Eq. (A8) reduces to the first three terms of Fig. 3(b), i.e.,

$$E_{xc} = -\frac{1}{2} \int \frac{d^3h}{(2\pi)^3} \pi(\vec{h}) [V_H(\vec{h})]^2. \quad (\text{A9})$$

Following the same analysis for the first-order contribution to ψ^0 [i.e., ψ_1^0 in Fig. 5(a)] and iterating Eq. (A5) once we get

$$E_{xc} = -\frac{1}{2} \int \frac{d^3q}{(2\pi)^3} \int \frac{d^3q'}{(2\pi)^3} \int \frac{d\omega}{\pi} \int_0^1 d\lambda \frac{1}{\epsilon_\lambda^2(\vec{q}, i\omega)} \psi_1^0(\vec{q}, \vec{q}', i\omega) \frac{\lambda v(\vec{q}')}{\epsilon_\lambda(\vec{q}', i\omega)} \psi_1^0(\vec{q}', \vec{q}, i\omega). \quad (\text{A10})$$

Integrating Eq. (A10) over the coupling constant³⁶ we retrieve the last two contributions to the RPA in Fig. 3(b). Subtracting the kinetic energy contribution and using the linear screening for $V_H(\vec{h}) = -n(\vec{h})/\pi(\vec{h})$ results in Eqs. (25) and (26). These contributions can be explicitly written down following the usual Feynman rules. The first three graphs in Fig. 5(b) are given by

$$\pi_2(\vec{h}) = \int \frac{d^4q}{(2\pi)^4} \frac{v(\vec{q})}{\epsilon(q)} \int \frac{d^4p}{(2\pi)^4} \{S_0(p)S_0(p+\vec{h})S_0(p+q)[2S_0(p)+S_0(p+q+\vec{h})]\} \quad (\text{A11})$$

and the last two graphs in Fig. 5(b) by

$$\pi_1(\vec{h}) = -2i \int \frac{d^4q}{(2\pi)^4} \frac{v(\vec{q})}{\epsilon(q)} \frac{v(\vec{q}+\vec{h})}{\epsilon(q+\vec{h})} \Lambda_a(q, q+\vec{h}) \Lambda_b(q, q+\vec{h}), \quad (\text{A12})$$

where

$$\Lambda_a(q, q+\vec{h}) = \int \frac{d^4p}{(2\pi)^4} S_0(p)S_0(p-q)S_0(p+\vec{h}), \quad (\text{A13})$$

$$\Lambda_b(q, q+\vec{h}) = \int \frac{d^4p'}{(2\pi)^4} S_0(p')S_0(p'+\vec{h})[S_0(p'-q)+S_0(p'+q+\vec{h})]. \quad (\text{A14})$$

In Eqs. (A11)–(A14), $S_0(p)$ is the noninteracting electron propagator and we make a careful distinction between the three-dimensional \vec{q} and \vec{h} and the four-dimensional vectors $q \equiv (\vec{q}, \omega)$, $p \equiv \vec{p}, p_0$, and $p' \equiv \vec{p}', p'_0$. [Note that the \vec{q} , in Eqs. (A11)–(A14), is of course the same as the one entering Eqs. (A1)–(A10) or equivalently $\gamma(\vec{q})$.]

We can now get a rigorous result for $\gamma(\vec{q})$ in the small- \vec{q} limit for a nonuniform electron gas. Since several different limits will be taken simultaneously

we first define our system with additional care.

(i) Consider a uniform electron gas on which we impose an external potential $V(\vec{r})$ of a single Fourier component \vec{h} , i.e.,

$$V(\vec{r}) = \lambda_{\vec{h}} \cos(\vec{h} \cdot \vec{r}). \quad (\text{A15})$$

(ii) Take the uniform electron gas to the high-density limit (HDL) without changing the value of \vec{h} in the process.

(iii) Restrict $\lambda_{\vec{h}} \ll k_F^2/2m$. From (iii) we can rigorously stop at second-order perturbation in $V(\vec{r})$ so that Eq. (A9) [or Eqs. (25), (26)] gives an exact description for the energy and consequently $\gamma(\vec{q})$.

From (ii) it follows that $|\vec{h}|/k_F$ is small and $\pi(\vec{h})$ can be restricted to small expansions in powers of \vec{h} .³³ In addition, $\pi(\vec{h})$ [$\pi(\vec{h}) = \pi_1(\vec{h}) + \pi_2(\vec{h})$] as given in Eqs. (A11) and (A12) is exact in the HDL. The expansion, to order \vec{h}^2 , of Eqs. (A11) and (A12) have been carefully examined in II. The HDL forms can be extracted from Eq. (47) of Ref. 23 (see Ref. 37) and we list them below.³⁸

We define

$$\pi(\vec{h}) = a^{-1} + b |\vec{h}|^2$$

with

$$b = \frac{e^4 m^3}{(2\pi)^3 k_F^4} Z.$$

Then in the HDL, the contribution of Eq. (A11) to Z_2 is

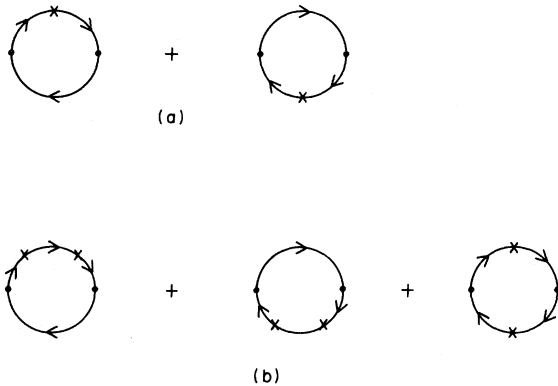


FIG. 5. (a) First-order contributions, in the screened external potential, to the function $\psi^0(\vec{q}, \vec{q}', i\omega)$ (see Appendix A). (b) Second-order contributions, in the screened external potential, to the function $\psi^0(\vec{q}, \vec{q}', i\omega)$.

$$Z_2 = \frac{8k_F^2 a_0}{3\pi} \int_0^\infty \frac{ds}{s} \int_0^\infty dy \left[\frac{-s^2}{\tilde{\epsilon}(s,y)} + 1 \right] \left[\frac{1}{2} \frac{1}{y^2+1} + \frac{\frac{7}{2} - \frac{7}{6}y^2}{(y^2+1)^2} + \frac{4y^2 - 2 + \frac{2}{3}y^4}{(y^2+1)^3} - \frac{2}{3} \frac{17y^2 + 8y^4 + 3}{(y^2+1)^4} \right] \quad (\text{A16})$$

and again from Eqs. (A11) and (A12) the contribution to Z_1 is

$$Z_1 = \frac{8k_F}{3\pi^2} \int_0^\infty ds s \int_0^\infty dy \frac{1}{(y^2+1)^2} \frac{1}{[\tilde{\epsilon}(s,y)]^2} \times \left\{ \left[\frac{\frac{4}{3}y^2 + \frac{1}{2}}{y^2+1} + \frac{2}{3} \frac{y^2(2+y^2)}{(y^2+1)^2} \right] + \frac{1}{k_F a_0 4\pi \tilde{\epsilon}(s,y)} \left[-4 + \frac{7y^2}{y^2+1} - \frac{y^2(3y^2+1)}{(y^2+1)^2} + 6R(y) \right] + \frac{1}{(k_F a_0)^2 4\pi^2} \frac{1}{[\tilde{\epsilon}(s,y)]^2} \left[-1 + \frac{y^2(y^2+2)}{(y^2+1)^2} - 3R(y) \left[\frac{2y^2}{y^2+1} - 2 + 3R(y) \right] \right] \right\}, \quad (\text{A17})$$

where $\tilde{\epsilon}(s,y) = s^2 + (1/k_F a_0 \pi)R(y)$ with $R(y) = 1 - y \tan^{-1}(1/y)$ and $s = q/2k_F$, $y = \omega/(2k_F s)$, $a_0 = \hbar^2/me^2$, and $Z = Z_1 + Z_2$. It is now not difficult to show that the integral over y of Z_1 [Eq. (A17)] is $\lim_{s \rightarrow 0} Z_1 = 2\sqrt{3}\pi(k_F a_0)^{3/2}$ (in agreement with Ref. 24) and that

$$\lim_{s \rightarrow 0} \gamma(q) \approx \lambda_{\vec{h}}^2 |\vec{h}|^2 Z_1 = \text{const.} \quad (\text{A18})$$

Finally we make several comments concerning the validity of the \vec{h} expansion in Eqs. (A11)–(A14). The expansion of the propagator in this order of approximation³³ (lowest-order RPA and to order \vec{h}^2) pose no problem even though at first sight they do seem to produce integrals that seem divergent.³³ One easy way to see this is to observe that the integral over y in the HF contribution [i.e., Z_2 without $s^2/\epsilon(s,y)$] is identically zero as is required to remove the ds/s integral in Z_2 . The second concerns the expansion of $v(\vec{q} + \vec{h})/\epsilon(q + \vec{h})$ in Eq. (A12). From the structure of Z_1 in Eq. (A17) it is apparent that the power expansion in \vec{h} is not valid for $y \rightarrow \infty$ (or equivalently $s \ll |\vec{h}|/k_F$). In keeping \vec{h} fixed, however, this region disappears completely in the HDL. We conclude that the structure factor of a nonuniform electron gas goes to a constant for any finite $s \equiv q/2k_F$ which is the relevant length scale for this problem (see e.g., Fig. 4 or Refs. 23 and 24). For finite densities the above results have the important implication of a strong dependence, in the long-range part of the pair correlation function, on the external environment [i.e., $V(\vec{r})$].

APPENDIX B

In this appendix we examine the small $|\vec{q}|$ limit for a metallic surface inhomogeneity. First we recall two general results for arbitrary nonuniform electron gas.^{39,40}

If we define the function $\Lambda(\vec{r}, \vec{r}', \omega)$ in terms of χ^0 and ψ^0 in Eq. (A1), i.e.,

$$\Lambda(\vec{r}, \vec{r}', \omega) = \int d^3 r'' [\chi^0(\vec{r} - \vec{r}'', \omega) + \psi^0(\vec{r}, \vec{r}'', \omega)] v(\vec{r}'' - \vec{r}'), \quad (\text{B1})$$

then

$$\int d\omega \omega \text{Im} \Lambda(\vec{r}, \vec{r}', \omega) = -2\pi^2 e^2 \delta(\vec{r} - \vec{r}') n(\vec{r}) + \frac{\pi}{2} \frac{\partial v}{\partial \vec{r}}(\vec{r} - \vec{r}') \cdot \frac{\partial n}{\partial \vec{r}}(\vec{r}) \quad (\text{B2})$$

and from the analyticity of Λ

$$\Lambda(\vec{r}, \vec{r}', \omega) = -\frac{2}{\pi \omega^2} \int_0^\infty d\omega' \omega' \text{Im} \Lambda(\vec{r}, \vec{r}', \omega') + O\left[\frac{1}{\omega^4}\right]. \quad (\text{B3})$$

For surface problems where the cosine transform is most natural we can transform Eq. (B1) to get

$$\Lambda(q_{||}, p_z, p'_z, \omega) = \sum_{p_z''} \left[\frac{L 2\pi e^2}{p_z^2 + q_{||}^2} (\delta_{p_z, p_z''} + \delta_{p_z, -p_z''}) - \frac{4\pi e^2 q_{||}}{(p_z^2 + q_{||}^2)(p_z''^2 + q^2)} \right] \times [L\chi^0(q_{||}, p_z'', \omega)\delta_{p_z'', p_z'} + \psi^0(q_{||}, p_z, p'_z, \omega)] . \quad (\text{B4})$$

Inserting Eq. (B4) in Eqs. (B2) and (B3) we can get some rigorous identities for $\Lambda(q_{||}, p_z, p'_z, \omega)$ of a surface nonuniformity. Unfortunately our problem for the exchange-correlation energy (or equivalently for the pair correlation function) requires zeroth moment integrals in the frequency, i.e.,

$$\int d\omega \text{Im} F(q_{||}, p_z, p'_z, \omega) \quad (\text{B5})$$

(where $F = \Lambda + \Delta F$), and exact identities for Eq. (B5) are *not* available.⁴¹ In fact our results for $\gamma(q)$ in the HDL (see Appendix A) show that such identities are not possible. However, in Ref. 3, a universal small- q limit is provided for a metallic surface, i.e.,

$$\lim_{q \rightarrow 0} \gamma_s(q) = \frac{k_F}{8\pi} q (\omega_s - \omega_B / 2) . \quad (\text{B6})$$

We show in this appendix that the derivation suffers from several omissions and thus does not constitute a proof.

The connection between the cosine transforms of the various pieces of the response function and E_{xc} are detailed in Appendix C of Ref. 3 and will not be repeated here. We only wish to examine the contribution to E_{xc} of the last term in Eq. (C4) of Ref. 3; i.e.,

$$E_{xc} = - \int_0^\infty \frac{d\omega}{\pi} \text{Im} \int_0^1 \frac{d\lambda}{\lambda} \sum_{p_z} \frac{4\pi e^2}{p_z^2 + q_{||}^2} \frac{\psi_\lambda(q_{||}, p_z, p_z, \omega)}{\epsilon_\lambda^2(q_{||}, p_z, p_z, \omega)} , \quad (\text{B7})$$

where $\psi_\lambda(q_{||}, p_z, p'_z, \omega)$ satisfies the *same* integral equation in terms of $\psi_\lambda^0(q_{||}, p_z, p'_z, \omega)$ as in the preceding appendix [Eq. (A5)] now for cosine transforms. However, it is *incorrect* to simply replace p_z by q_z , as is clearly shown in Eq. (23) and the discussion following it, unless the functions are properly localized (a contention not supported in the HDL nonuniform electron gas; Appendix A). A second assumption concerns the small p_z, p'_z , and $q_{||}$ structure of ψ^0 , i.e., that

$$\psi^0(q_{||}, p_z, p'_z, \omega) = A(\omega) q_{||}^2 + B(\omega) p_z p'_z . \quad (\text{B8})$$

For the IBM [within the RPA (Ref. 42)] the forms for $\psi^0(q_{||}, p_z, p'_z, \omega)$ have been derived previously⁴³; they are

$$\text{Re}\psi_+^0(q_{||}, p_z, p'_z, \omega) = - \frac{me^2}{\pi q_{||}^2} \Theta^{<}(|p_z''|/2) \{ (pu - p_z p_z'') - \text{sgn}(pu - p_z p_z'') \text{Re}[(p_z'' p - p_z u)^2 + q_{||}^2 (u^2 - 1)]^{1/2} \} \quad (\text{B9})$$

and

$$\text{Im}\psi_+^0(q_{||}, p_z, p'_z, \omega) = \frac{me^2}{\pi q_{||}^2} \Theta^{<}(|p_z''|/2) \text{sgn}\omega \text{Im}[(p_z'' p - p_z u)^2 + q_{||}^2 (u^2 - 1)]^{1/2} \quad (\text{B10})$$

with

$$\psi^0(q_{||}, p_z, p'_z, \omega) = \psi_+^0(q_{||}, p_z, p'_z, +\omega) + \psi_+^0(q_{||}, p_z, p'_z, -\omega)$$

and where $p_z'' = p_z + p'_z$, $p = (q_{||}^2 + p_z^2)^{1/2}$, and $u = p + 2m\omega/p$. At small p_z, p'_z , and $q_{||}$ and finite frequency these forms (of course) reduce to Eq. (B8) but important contributions come as well from intermediate values (i.e., $\omega/p = \text{const}$) in the usual way. In that range these functions [Eqs. (B9)

and (B10)] have no resemblance to Eq. (B8). It is interesting to note that for exchange alone the small- q limit is dominated by χ^0 of Eq. (B4). When correlation is included this contribution will be strongly modified and the small- q limit now dominated by terms like Eq. (B7).

We conclude by making a direct comparison with the discussion in Appendix A. Since both here and in Appendix A the ψ^0 are the response function to an external perturbation we expect the two to reveal similar behaviors. We observed a nonuniversal small- q limit (in Appendix A) considering contributions from second- and higher-order

iterations of Eq. (A5). We, therefore, expect that corrections to Eq. (B6) would appear from such considerations. To demonstrate this, however, must involve a careful treatment of the discrete cosine variable and a transformation like Eq. (23) to the appropriate Fourier components $q_{||}$ and q_{\perp} .

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³⁴As far as we can tell, the numerical corrections from large q in metallic surface profile calculations seem relatively small (see Refs. 20–24). Their numerical importance for more general problems (e.g., adsorbates on metallic surfaces) is unknown.

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³⁶Some care must be exercised in the coupling constant integration when higher-order terms in the screened interaction are considered (Ref. 24). This, however, does not enter in the analysis presented here.

³⁷Equations (25), (34), and (40) of Ref. 23 contain misprints. In Eq. (25) the second term should not have a 2; i.e., it should read $s[g(s,y)/\bar{\epsilon}(s,y)]^2$. In Eq. (34) the last term of the second denominator should read $16y^2s^2(y^2+1-s^2)^2$. In Eq. (40) the last term should read $[s^{-1}Q(s,y)/\bar{\epsilon}(s,y)][\frac{1}{2}H'_1(s,y) - \frac{1}{9}H'_3(s,y)]$.

³⁸Note that these HDL forms are not the same as the ones derived in Ref. 30 although their integrated value (over q) are, of course, the same (see Ref. 23).

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