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The Surface Dielectric Function and Its Sum Rule for a Semi-Infinite Electron System

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In this paper we define a surface dielectric function for a semi-infinite electron system and a sum rule involving the imaginary part of the inverse of the surface dielectric function is derived. The sum rule has almost exactly the same form as the well-known dielectric function f-sum rule in a bulk system, with the bulk quantities replaced by the corresponding surface quantities. However there is an important difference that the surface sum rule applies to all surfaces only in the $Q \rightarrow 0$ limit, where Q is the two-dimensional wavevector parallel to the surface. For small Q, linear and higher order terms of Q will appear in the sum rule whose coefficients may depend on the surface properties of the system considered. This is due to the fact that for $Q = 0$ both the surface dielectric function and the surface plasma frequency depend on the average electron density only, independent of the surface properties; however for $Q \neq 0$, the Q-dependence of the above two quantities both depend sensitively on the surface properties of the system considered.

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I. INTRODUCTION

There are several well-known dielectric function sum rules for bulk metallic materials [1]. These sum rules relate the dielectric function and the plasma frequency and are useful for checking results obtained from approximations or model calculations. Among these sum rules the most important and fundamental one is, perhaps, the so-call longitudinal f-sum rule. While all sum rules may be derived from the Kramers-Kronig relations and the known bulk dielectric function, the longitudinal f-sum rule can also be derived from microscopic theory without knowing the expression of the bulk dielectric function [1]. The f-sum rule therefore can be considered as a rigorous way to calculate the plasma frequency. The bulk longitudinal f-sum rule has the following form

$$\int_0^\infty d\omega\, \omega\, \mathrm{Im}\left[\frac{1}{\epsilon(q,\omega)}\right] = -\frac{\pi}{2}\,\omega_p^2(0)\,, \tag{1}$$

where $\epsilon(q,\omega)$ is the bulk dielectric function with wavevector q and frequency ω; Im stands for the imaginary part; and $\omega_p(0) = (4\pi ne^2/m)^{1/2}$ is the bulk plasma frequency with electron mass m and density n for the $q = 0$ mode.

It is interesting to ask if the electron system occupies only half space and possesses a planar surface, would the sum rule as in Eq. (1) still hold for the semi-infinite system? If the sum rule does exist, it would relate a quantity called the *surface* dielectric function to the surface plasma frequency. The sum rule would provide a guideline for approximations or models in constructing the surface dielectric function, and it may be important in the studies of the particle-surface interactions, such as the van Der Waals interaction [2]. The purpose of this paper is to search for the existence of such a sum rule and to see what we can learn from the sum rule. Our answer to this question is that a sum rule like Eq. (1) for a semi-infinite system does exist and in general it has the following form (in the samll Q limit),

$$\int_0^\infty d\omega\, \omega\, \mathrm{Im}\left[\frac{1}{\epsilon_s(Q,\omega)}\right] = -\frac{\pi}{2}\,\omega_s^2(0)(1+\alpha Q+\cdots)\,, \tag{2}$$

where $\epsilon_s(Q,\omega)$ may be interpreted as the *surface* dielectric function, which depends on the frequency ω and the two-dimensional wavevector $\boldsymbol{Q}$ parallel to the surface; $\omega_s(0)$ is the surface plasma frequency for the $Q = 0$ mode and is known to equal to $\omega_p(0)/\sqrt{2}$; α is a constant (with a dimension of length) and its sign and magnitude may be different for different surface considered. The surface sum rule Eq. (2) is identical to the bulk sum rule Eq. (1) only in the $Q \to 0$ limit. And it is only in this limit that all surfaces obey the same sum rule. For small but finite Q, the right-hand side of Eq. (2) contains a linear (and higher order) term of Q whose coefficient depend sensitively on the surface properties, such as the surface charge density profile. In this paper we will derive the sum rule Eq. (2) and study its physical significances.

We use the infinite potential barrier jellium model (IPBJM) to derive the sum rule Eq. (2) by a microscopic analytical calculation. We follow closely the approach used by Mahan [1] in his derivation of the bulk sum rule Eq. (1). For IPBJM we find that $\alpha = 0$, and all higher order terms of Q are also zero, therefore for this particular model the surface sum rule has exactly the same form as that of the bulk sum rule. However in Sec. III we will use a different approach, other than microscopic calculations, to give evidence that for more realistic surface models the right-hand side of Eq. (2) will, to lowest order, contain a linear term of Q whose coefficient depends on the surface properties of the system considered, in particular the surface charge density profile. The surface dependence of the sum rule is closely related to the local nature of the surface dielectric function $\epsilon_s(Q,\omega)$ appeared in Eq. (2) and the fact that the surface plasmon dispersion relation depends sensitively on the surface charge density profile [3-5].

In deriving the surface sum rule we find that the dielectric function $\epsilon_s(Q,\omega)$ in Eq. (2) is a position-dependent dielectric function evaluated at the surface, and therefore the nomenclature "surface dielectric function" is an appropriate one to describe it. To understand this more clearly, we recall that the wavevector-dependent dielectric function for a full three-dimensional system is defined as

$$\epsilon(q) = \frac{\phi_{ext}(q)}{\phi_{tot}(q)}\,, \tag{3}$$

where the ω-dependence is omitted for convenience, and for an isotropic system the three-dimensional wavevector $\boldsymbol{q}$ may be replaced by its magnitude q. The functions $\phi_{ext}(q)$ and $\phi_{tot}(q)$ are, respectively, the q-component of the *external* and the *total* potentials, which are expressed in terms of their Fourier components. More explicitly we may say that ϕ_{ext} is the *bare* Coulomb potential and ϕ_{tot} is the *screened* potential due to the presence of the medium. However for a semi-infinite system, the definition of the dielectric function in Eq. (3) has to be modified. This is because now the translational invariance perpendicular to the surface is broken and no Fourier transform for the potentials is taken in that direction. The appropriate expansion of the *bare* Coulomb term for a semi-infinite system with a planar surface is of the form ($\boldsymbol{r}_i = (x_i, y_i, z_i) \equiv (\boldsymbol{R}_i, z_i)$)

$$\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = \int \frac{d^2Q}{(2\pi)^2}\frac{2\pi}{Q}\, e^{i\mathbf{Q}\cdot(\mathbf{R}_1-\mathbf{R}_2)-Q|z_1-z_2|}\,, \tag{4}$$

where the surface is taken to be perpendicular to the z-axis, and $\boldsymbol{Q}$ is the two-dimensional wavevector parallel to the surface. From Eq. (4) $\phi_{ext} = (2\pi/Q)\exp(-Q|z_1 - z_2|)$, and it depends not only on the wavevector Q but also on the coordinates z_1 and z_2. One would expect ϕ_{tot} to depend on Q, z_1 and z_2 in a much more complicated way. By analogy to Eq. (3), the dielectric function for a semi-infinite system will, therefore, depend on Q, z_1 and z_2 and should be expressed as $\epsilon(Q,\omega; z_1, z_2)$ if the frequency dependence is also included. Here we may interpret z_1 as the z-coordinate of the *field* point and z_2 the z-coordinate of the *source* point. An important case, which is relevant to the situation we considered here, is that the source point (the probe) is outside the medium and the field point (the response) is inside the medium. Then we may take $z_1 \leq 0$ and $z_2 > 0$ if $z = 0$ is taken to be the surface and the medium occupies the half-space $z \leq 0$. In this case it is not difficult to see (cf. Sec. II below) that the dielectric function will be independent of z_2, and its expression may be simplified as $\epsilon(Q,\omega;z_1)$ (for $z_1 \leq 0$, $z_2 > 0$). In deriving the surface sum rule we will show that the dielectric function $\epsilon_s(Q,\omega)$ in Eq. (2) should be the position-dependent dielectric function $\epsilon(Q,\omega;z_1)$ evaluated at the surface $z_1 = 0$. The dielectric function evaluated at other locations $\epsilon(Q,\omega;z_1 < 0)$ will not satisfy the sum rule Eq. (2). Therefore the dielectric function $\epsilon_s(Q,\omega)$ in Eq. (2) is really a "surface" dielectric function because it is the dielectric function $\epsilon(Q,\omega;z_1)$ evaluated at the surface $z_1 = 0$.

The local nature of the surface dielectric function $\epsilon_s(Q,\omega)$ implies that the surface plasma excitation is a localized excitation. This can be understood from the relation $\phi_{tot} = \phi_{ext}/\epsilon_s(Q,\omega)$, which is the extension of Eq. (3) to the semi-infinite system. The surface plasma excitation occurs when $\epsilon_s(Q,\omega) = 0$ which is not satisfied by the dielectric function $\epsilon(Q,\omega;z_1)$ evaluated at other locations $z_1 < 0$. However the localization length for the surface plasma excitation is different for different Q modes. This can be seen from the fact (cf. Sec. II) that the difference between $\epsilon(Q,\omega;z_1)$ and $\epsilon_s(Q,\omega)$ may be roughly measured by the factor ($1 - e^{Qz_1}$). For $|z_1| << 1/Q$, we have $\epsilon(Q,\omega;z_1) \approx \epsilon_s(Q,\omega)$. Therefore we may define a *localization length* ξ for mode Q as $\xi_Q \sim 1/Q$. For $Q \rightarrow 0$, ξ_Q becomes very large and the surface plasma excitation extends deep into the interior of the medium. However for small but finite Q, the localization length may become very short. For example, for $Q \sim 0.01\, k_F$ (k_F is the Fermi wavevector) ξ_Q may become only a few lattice constants. For this Q the surface plasma excitation is strongly localized at the surface. From the above analysis of the Q-dependence of the localization length ξ_Q, it is then easy to understand why the surface plasma frequency for the $Q = 0$ mode $\omega_s(0)$ is practically a bulk property and independent of the surface properties, but for the $Q \neq 0$ modes the dispersion relation $\omega_s(Q)$ is strongly dependent on the surface charge density profile [3-5].

In Sec. II we derive the surface dielectric function sum rule by using the IPBJM model. We follow closely the approach used by Mahan[1] to calculate the inverse of the dielectric function for a semi-infinite system and the surface sum rule is then derived. For this particular model we find that the right-hand side of the sum rule Eq. (2) is independent of Q to all orders. In Sec. III we discuss properties of the dielectric function f-sum rule by using a different approach which does not involve any microscopic calculations. We will argue that in general the linear coefficient α in Eq. (2) need not bc zero and it is a surface dependent quantity.

II. INFINITE POTENTIAL BARRIER MODEL

In this Section we use the infinite potential barrier jellium model (IPBJM) to derive the sum rule Eq. (2). For this particular model we find that the right-hand side of Eq. (2) is independent of Q to all orders. We follow closely the method used by Mahan [I] in his derivation of the bulk sum rule Eq. (1). We consider an electron gas in the space

-L $\leq x, y \leq$ L, $-\ell \leq z \leq$ 0, with an infinite potential barrier at both $z = 0$ and $z = -\ell$ surfaces. We assume the positive background is uniformly distributed in the volume to keep the system electrically neutral, and thus we are considering the jellium model. We use periodic boundary conditions in the x- and y-directions to simulate the infinite extended nature in these two directions, and let $\ell \rightarrow \infty$ at the end of the calculations. To shorten our notations we adopt the convention that $\boldsymbol{r} = (x, y, z) \equiv (\boldsymbol{R}, z)$ and $k = (k_x, k_y, k_z) \equiv (\boldsymbol{K}, k)$. The normalized single electron wave function can be written as

$$\psi_{\mathbf{K},k}(\boldsymbol{r}) = \sqrt{\frac{2}{\nu}}\, e^{i\mathbf{K}\cdot\mathbf{R}} \sin kz \,, \qquad -\ell \leq z \leq 0 \,, \tag{5}$$

where $\nu = 4L^2\ell$ is the volume of the system. Periodic boundary conditions in the x- and y-directions and the condition that $\psi_{\mathbf{k}}(\boldsymbol{r}) = 0$ at $z = -\ell$ and $z = 0$ require $k_x, k_y = p\pi/L$, $(p = 0, \pm 1, \pm 2, \cdots)$ and $k = k_z = p\pi/\ell$ $(p = 1, 2, 3, \cdots$, thus $k > 0)$. We follow Newns [6] using $\cos qz$ $(q = p\pi/\ell, p = 0, 1, 2, \cdots$, thus $q \geq 0)$ to be the basis functions for the Fourier transform of functions of z. The electron density operator $\rho(\boldsymbol{r})$ can then be written in terms of the creation (annihilation) operator $C^\dagger_{\mathbf{k}} (C_{\mathbf{k}})$, which creates (annihilates) an electron with wave function $\psi_{\mathbf{k}}(\boldsymbol{r})$,

$$\rho(\boldsymbol{r}) = \frac{2}{\nu} \sum_{\mathbf{Q}, q \geq 0} e^{i\mathbf{Q}\cdot\mathbf{R}} \cos qz \, \rho(\boldsymbol{Q}, q) \,, \qquad -\ell \leq z \leq 0 \,, \tag{6}$$

$$\rho(\boldsymbol{Q}, q) = \frac{1}{2} \sum_{\mathbf{K}, k > 0} [C^\dagger_{\mathbf{K},k} C_{\mathbf{K+Q},k+q} + C^\dagger_{\mathbf{K},k} C_{\mathbf{K+Q},k-q}], \qquad q \geq 0 \,, \tag{7}$$

where we have defined the creation and annihilation operators, $C_{\mathbf{K},k}$ and $C^\dagger_{\mathbf{K},k}$, with negative or zero k by $C_{\mathbf{K},-q} \equiv -C_{\mathbf{K},q}$, and $C^\dagger_{\mathbf{K},-q} \equiv -C^\dagger_{\mathbf{K},q}$, if $q \geq 0$. This is because in the original definition of the electronic state (K, k), that the state with $k \leq 0$ is not defined. Note that the density operator $\rho(\boldsymbol{Q} = 0, q = 0)$ is the state with uniform density (in $-\ell \leq z \leq 0$), which coincides with the positive background density for the jellium model.

In order to calculate the dielectric function we put two *external* charges $Z_1 e$ and $Z_2 e$ at $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, respectively. By considering the interactions between the external charges and the charges in the system, the Hamiltonian of the total system is

$$\begin{aligned} H &= H_0 + \frac{Z_1 Z_2 e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} - \sum_{j=1}^{2} Z_j e^2 \int d^3 r \, \frac{\rho(\boldsymbol{r}) - \rho}{|\boldsymbol{r} - \boldsymbol{r}_j|} \\ &= H_0 + Z_1 Z_2 \int \frac{d^2 Q}{(2\pi)^2} \, v(Q) \, e^{i\mathbf{Q}\cdot(\mathbf{R}_1 - \mathbf{R}_2) - Q|z_1 - z_2|} \\ &\quad - \sum_{j=1}^{2} \frac{2Z_j}{\nu} \sideset{}{'}\sum_{\mathbf{Q}, q} v(Q) \rho(\boldsymbol{Q}, q) e^{i\mathbf{Q}\cdot\mathbf{R}_j} \int_{-\ell}^{0} dz \, e^{-Q|z_j - z|} \cos qz \,, \end{aligned} \tag{8}$$

where He is the Hamiltonian for the unperturbed IPBJM system; $v(Q) = 2\pi e^2/Q; \rho_0$ is the positive background density operator and $\sum'$ means that the term $\boldsymbol{Q} = q = 0$ is not included in the sum to account for the uniform positive background density. The second equality is obtained by expanding the factors $1/|\boldsymbol{r}-\boldsymbol{r}'|$ as in Eq. (4).

Now we consider $H -$ He = V *as* the perturbation potential, then the total energy of H can be calculated from the linked cluster theorems [1] as

$$U_{tot} = U_0 - \frac{1}{\beta}\sum_{\ell=1}^{\infty} U_\ell, \tag{9}$$

$$U_\ell = \frac{(-1)^\ell}{\ell}\int_0^\beta d\tau_1 \cdots \int_0^\beta d\tau_\ell \langle T_\tau V(\tau_1)\cdots V(\tau_\ell)\rangle_{d.c.d.}, \tag{10}$$

where *d.c.d.* stands for different connected diagrams. In Eqs. (9) and (10), U_0 is the energy of H when $V = 0$; $\beta = 1/k_B T$ (k_B is the Boltzmann constant and T the absolute temperature); $V(T) \equiv e^{H_0\tau} V e^{-H_0\tau}$ is the perturbation potential V in the interaction picture with imaginary time $t = \tau/i$ ($\hbar = 1$); T_τ denotes r-ordering operator; and *(A)* is the thermal average of A with respect to the unperturbed system. For our purpose it is sufficient to calculate the expansion terms in U_ℓ which are proportional to $Z_1 Z_2$. From the definition of the dielectric function $\epsilon(Q; z_1, z_2)$, *we* have

$$\Delta U = Z_1 Z_2 \int \frac{d^2Q}{(2\pi)^2}\frac{v(Q)}{\epsilon(Q;\, z_1,\, z_2)} e^{i\mathbf{Q}\cdot(\mathbf{R}_1-\mathbf{R}_2)-Q|z_1-z_2|}, \tag{11}$$

where AU is the sum of all terms in (10) which are proportional to $Z_1 Z_2$. Eq. (11) can be easily understood by comparing it with the second term of the right-hand side of Eq. (8) which is the bare interaction energy between $Z_1 e$ and $Z_2 e$; while Eq. (11) is the *screened* interaction energy which involves both of the second and the third terms in Eq. (8).

It is important to note that in calculating the dielectric function $\epsilon(Q; z_1, z_2)$ defined in Eq. (11), we have to express AU to be a double integral over $\boldsymbol{Q}$ whose integrand is proportional to exp(-Q $|z_1 - z_2|$). In evaluating AU from Eq. (10), we find that in general the coefficient of $\exp(-Q|z_1 - z_2|)$ in the integrand will depend on both z_1 and z_2, and therefore the dielectric function will depend on both z_1 and z_2 by Eq. (11). However, it is not difficult to see that if we choose $z_1 \leq 0$ and $z_2 > 0$, then the z_2-dependence disappears. This is because then the absolute signs have no effect on the functions $|z_2 - z_1|$ and $|z_2 - z|$ which appear in Eq. (8). Then both the bare potential and the screened potential will be proportional to e^{-Qz_2} and which is the only z_2-dependence for both potentials. The ratio ϕ_{ext}/ϕ_{tot} then eliminates the z_2-dependence completely. The dielectric function therefore depends on z_1 only (for $z_1 \leq 0$, $z_2 > 0$), and can be written as $\epsilon(Q; z_1)$. The choice of $z_1 \leq 0$ and $z_2 > 0$ not only simplifies the expression of the dielectric function, but also has its physical importance. This choice means that we have a probe outside the medium

$(z_2 > 0)$ and measure the response inside the medium $(z_1 \leq 0)$. This represents most of the experimental situations and therefore this is the most important dielectric function we have to consider. The expression of the dielectric function $\epsilon(Q;z_1)$ simplifies further if we choose z_1 to be on the surface ($z_1 = 0$ in our geometry). Other choices of z_1 will make the expression of the dielectric function much more complicated. The main difference between $z_1 < 0$ and $z_1 = 0$ is that the integral over z in the last term of Eq. (8) (with $j = 1$) will result in a term which is proportional to $(1 - e^{Qz_1})$. This term is zero for $z_1 = 0$, but it is a positive and nonzero quantity for $z_1 < 0$.

With the choice of $z_1 = 0$ and $z_2 > 0$, we calculate AU from Eq. (10) by keeping only terms which are proportional to $Z_1 Z_2$, and obtain

$$\Delta U = Z_1 Z_2 \int \frac{d^2Q}{(2\pi)^2} v(Q)\, e^{i\mathbf{Q}\cdot(\mathbf{R}_1-\mathbf{R}_2)-Q|z_1-z_2|} \times \left[1 - \frac{4\,v(Q)}{\nu\ell}\sum_q{}' \int_0^\beta d\tau \frac{Q^2}{(Q^2+q^2)^2}\langle T_\tau \rho(\boldsymbol{Q},q,\tau)\,\rho(-\boldsymbol{Q},q,0)\rangle\right]. \tag{12}$$

By comparing Eqs. (11) and (12) we obtain the inverse of the surface dielectric function $\epsilon_s(Q) \equiv \epsilon(Q;z_1 = 0)$,

$$\frac{1}{\epsilon_s(Q,i\omega)} = 1 - \frac{4\,v(Q)}{\nu\ell}\sum_q{}' \frac{Q^2}{(Q^2+q^2)^2}\int_0^\beta d\tau\, e^{i\omega\tau}\langle T_\tau \rho(\boldsymbol{Q},q,\tau)\,\rho(-\boldsymbol{Q},q,0)\rangle\,, \tag{13}$$

where we have introduced a factor $e^{i\omega\tau}$ in the integrand of Eq. (13) to obtain the frequency dependence of the dielectric function [1]. The integral over τ can easily be carried out by using the definition of the thermal average and the equality $\rho(\tau) = e^{\tau H_0}\rho\, e^{-\tau H_0}$ to obtain (ii = 1)

$$\mathrm{Im}\left[\frac{1}{\epsilon_s(Q,\omega)}\right] = -\pi\,\frac{4\,v(Q)}{\nu\ell}\sum_q{}'\sum_{n,m}\left(e^{-\beta E_n} - e^{-\beta E_m}\right) \times \langle n|\rho(\boldsymbol{Q},q)|m\rangle\langle m|\rho(-\boldsymbol{Q},q)|n\rangle\,\delta(\omega + E_n - E_m)\,. \tag{14}$$

In deriving Eq. *(14) we* have used the following identity

$$\frac{1}{x - x_0 + i\eta} = P\frac{1}{x - x_0} - i\pi\,\delta(x - x_0)\,, \tag{15}$$

where P stands for a Cauchy principal value and η is an infinitesimal positive quantity. In Eq. (14) $|n\rangle$ (or $|m\rangle$) denotes a state of H_0, with total energy E_n (or *E,)*, which is specified by a set of occupation numbers $\{n_{\mathrm{K},k}\}$; and $\langle n|A|m\rangle$ is the matrix element of A between states $|n\rangle$ and $|m\rangle$ (it should not be confused with the thermal average *(A)).* Finally it is easy to obtain

$$\begin{aligned}\int_0^\infty d\omega\,\omega\,\mathrm{Im}\left[\frac{1}{\epsilon_s(Q,\omega)}\right] &= \pi\frac{2v(Q)}{\nu\ell}\sum_{n,m}(e^{-\beta E_n}-e^{-\beta E_m})(E_n-E_m)\\ &\quad\times\sum_q{}'\frac{Q^2}{(Q^2+q^2)^2}\langle n|\rho(\boldsymbol{Q},q)|m\rangle\langle m|\rho(-\boldsymbol{Q},q)|n\rangle \qquad (16)\\ &= \pi\frac{2v(Q)}{\nu\ell}\sum_q{}'\frac{Q^2}{(Q^2+q^2)^2}\langle[[H_0,\rho(\boldsymbol{Q},q)],\rho(-\boldsymbol{Q},q)]\rangle\,.\end{aligned}$$

Now we have to evaluate the right-hand side of Eq. (16) to derive the sum rule. The double commutator in Eq. (16) can be carried out by noting that the density operator commutes with all terms in H_0 except the kinetic energy terms. The result is ($\hbar = 1$)

$$\langle[[H_0,\rho(\boldsymbol{Q},q)],\rho(-\boldsymbol{Q},q)]\rangle = -\frac{1}{2m}\sum_{\mathbf{K},k>0}\langle n_{\mathbf{K},k}\rangle[Q^2\delta_{q,0}+(Q^2+q^2)]\,, \qquad (17)$$

where m is the electron mass, and $n_{\mathbf{K},k}\equiv C^\dagger_{\mathbf{K},k}C_{\mathbf{K},k}$ is the number operator for the State $(\boldsymbol{K},k)$. By substituting Eq. (17) into Eq. (16) and converting the sum over q into an integral, it is then a straightforward matter to derive the sum rule, by letting $\ell\rightarrow\infty$ and noting that Q $\neq$ 0,

$$\int_0^\infty d\omega\,\omega\,\mathrm{Im}\left[\frac{1}{\epsilon_s(Q,\omega)}\right] = -\frac{\pi}{2}\left(\frac{2\pi ne^2}{m}\right) \equiv -\frac{\pi}{2}\omega_s^2(0)\,, \qquad (18)$$

where n is the electron density and the last identity defines the well-known surface plasma frequency w,(O). Therefore we have derived the surface dielectric function sum rule Eq. (18) which is a special form of Eq. (2) with the right-hand side independent of Q to all orders.

The above derivation of the sum rule is based on the simplified IPBJM model, whose surface electron charge density is known not close to that of real metal surfaces. It is known that IPBJM predicts a wrong surface plasmon dispersion relation [3-5], which depends sensitively on the surface charge density profile [3]. Because the surface sum rule involves the surface dielectric function which is a strong localized quantity for Q $\neq$ 0, there are good reasons to ask the question: Will the same sum rule Eq. (18) hold for all surface models even for Q $\neq$ O? This may not be an easy question to answer rigorously, because for other surface models it is not easy to carry out microscopic calculations analytically. However it is not difficult to prove rigorously that in the limit Q $\rightarrow$ 0, the sum rule Eq. (18) will hold for all planar surfaces, regardless of their surface propertities. For small but finite Q, we have no rigorouly answer but there are good reasons to believe that linear and higher order terms of Q will appear in the right-hand side of the sum rule for other surface models, and therefore the general form of the surface sum rule is Eq. (2) rather than Eq. (18). We will use a different approach? other than microscopic calculations, to study this question in the next Section.

III. DISCUSSIONS

In Sec. II we have seen that the dielectric function f-sum rules, Eq. (1) as well as Eq. (18), can be derived by analytic microscopic calculations for some workable models and explicit expressions for the bulk plasma frequency $\omega_p(0)$ and the surface plasma frequency w,(O) can be obtained in terms of the electron mass m and density n. From the sum rule it is readily seen that while the right-hand side of Eq. (1) is independent of q to all orders, but the left-hand side involves the q-dependent bulk dielectric function $\epsilon(q,\omega)$. In other words, the sum rule gives only the plasma frequency $\omega_p(q)$ in the $q \rightarrow 0$ limit, no matter what value of q is given in the dielectric function $\epsilon(q,\omega)$. The q-dependent bulk plasma frequency is known to have the dispersion relation $\omega_p(q) = \omega_p(0)(1+3q^2v_F^2/10\omega_p^2(0)+\ldots)$, which can not be obtained from the sum rule Eq. (1). The above result also occurs for the surface dielectric function sum rule for the IPBJM model. The right-hand side of Eq. (18) is Q-independent while the left-hand side involves the Q-dependent surface dielectric function $\epsilon_s(Q,\omega)$. For the IPBJM model [5], it is known that the Q-dependent surface plasma frequency is $\omega_s(Q) = \omega_s(0)(1 + aQ + \cdots)$, where a is a positive constant. Therefore the the surface sum rule Eq. (18), as in the bulk case, does not give the surface plasmon dispersion relation $\omega_s(Q)$, it gives only the limiting frequency $\omega_s(Q = 0)$. Although microscopic calculations give us the form of the sum rules, it is not easy to see why the above results happen, i.e., why the left-hand side is explictly dependent on q, or Q, but the right-hand side is independent of q, or Q, to all orders. Another related question is: Does the form of the surface sum rule Eq. (18) hold for all surface models? Again it is not easy to answer this question by using analytic microscopic calculations, because for other surface models it is not easy to have analytical expressions for the electron wave functions and therefore no analytic microscopic calculations colud be performed.

In this Section we will look at the f-sum rule in a different way which requires no specific models and no microscopic calculations. By using this method we can obtain rigorous results for the sum rules in the limiting cases $q \rightarrow 0$ (for the bulk case) and Q $\rightarrow 0$ (for the surface case). For small values of q or Q there are unknowns in the sum rule by using this approach and these unknowns have to be resolved by microscopic calculations by using specific models. Despite of the shortcoming we think it is worthwhile to introduce the method here as it relates the dielectric function, the plasmon dispersion relation and the j-sum rule, that it may give us more insights about the sum rule. In particular we will use this approach to study how the surface sum rule Eq. (18) may be modified for models other than IPBJRI. To introduce this approach we discuss the bulk case first and it is then a straightforward matter to extend the discussion to the surface case.

It is well known that the q-dependent plasma frequency $\omega_p(q)$ is the frequency for which the dielectric function $\epsilon(q,\omega)$ is zero. Therefore in general we can write the dielectric function, in the frequency regime $qv_F/\omega \ll 1$ (v_F is the Fermi velocity), in the following form

$$\epsilon(q,\omega) = f(q,\omega)\left(1 - \frac{\omega_p^2(q)}{\omega^2}\right), \tag{19}$$

where the function $f(q,\omega)$ is unknown but it maybe written in the form ($qv_F/\omega << 1$)

$$f(q,\omega) = 1 + A\left(\frac{qv_F}{\omega}\right) + B\left(\frac{qv_F}{\omega}\right)^2 + \cdots, \tag{20}$$

where A and B are dimensionless constants. The form of $f(q,\omega)$ satisfies the condition that $\epsilon \rightarrow 1$ as $\omega \rightarrow \infty$. By substituting Eq. (19) into Eq. (15) we easily obtain the sum rule in the following form

$$\int_0^\infty d\omega\,\omega\,\mathrm{Im}\left[\frac{1}{\epsilon(q,\omega)}\right] = -\frac{\pi}{2}\left(\frac{\omega_p^2(q)}{f(q,\omega_p(q))}\right). \tag{21}$$

The applicability of Eq. (15) to the dielectric function is assured by the fact that the dielectric function is a response function and obeys principles of causality. Therefore for a homogeneous electron gas, from Eqs. (1) and (21), we have

$$\frac{\omega_p^2(q)}{f(q,\omega_p(q))} = \omega_p^2(0). \tag{22}$$

The q-dependence of $\omega_p^2(q)$ is exactly cancelled by the factor $f(q,\omega_p(q))$ (it is not easy to understand how or why but it does) and therefore we have a. q-independent right-hand side in the sum rule Eq. (1). By using the relation Eq. (22), one can calculate the coefficients A and B in Eq. (20) from the known bulk plasmon dispersion relation $\omega_p(q)$ to obtain $A = 0$ and $B = 3/5$. The q- and w-dependent dielectric function $\epsilon(q,\omega)$ can then be obtained from Eq. (19) by using the known values of A and B. It is worthwhile noting that with $A = 0$ and $B = 3/5$ the function $f(q,\omega)$ will always be nonzero for all $qv_F/\omega << 1$, and thus the dielectric function $\epsilon(q,\omega)$ has only one root for a given q. Thus for a given q there is only one plasma mode, as predicted by microscopic calculations and experimental observations.

For the surface case, it is still true that $\epsilon_s(Q,\omega) = 0$ when w = w,(Q), and that $\epsilon_s(Q,\omega) \rightarrow 1$ as w $\rightarrow \infty$. Therefore we may write the surface dielectric function ($Qv_F/\omega \ll 1$) as

$$\epsilon_s(Q,\omega) = f_s(Q,\omega)\left(1 - \frac{\omega_s^2(Q)}{\omega^2}\right), \tag{23}$$

where $f_s(Q,\omega)$ is unknown and can be expanded as $f(q,\omega)$ in Eq. (20), if q is replaced by Q. By substituting Eq. (23) into Eq. (15) we easily obtain the surface dielectric function f-sum rule as

$$\int_0^\infty d\omega\,\omega\,\mathrm{Im}\left[\frac{1}{\epsilon_s(Q,\omega)}\right] = -\frac{\pi}{2}\left(\frac{\omega_s^2(Q)}{f_s(Q,\omega_s(Q))}\right) \equiv -\frac{\pi}{2}\omega_s'^2(Q), \tag{24}$$

where $\omega_s'(Q)$ is defined by the last identity. For IPBJM $\omega_s'(Q)=$ w,(O), i.e., the Q-dependence of $\omega_s^2(Q)$ is exactly cancelled by the function $f_s(Q,\omega_s(Q))$ just as the bulk case. From the exact cancellation of the Q-dependence between $\omega_s^2(Q)$ and $f_s(Q,\omega_s(Q))$ and the known surface plasmon dispersion relation $\omega_s(Q)$ for the IPBJM model, one can obtain the surface dielectric function for the IPBJM model as in the bulk case.

The next and more important question is that will the exact cancellation of the Q-dependence between w,“ (Q) and $f_s(Q,\omega_s(Q))$ also happen for all models of surface? It is apparent that in the limit Q → 0 the exact cancellation always happens, and therefore the sum rule Eq. (2) holds for all models of surface in the limit Q → 0. However for Q $\neq$ 0 the situation is quite different. By examining the functional form of the surface dielectric function in Eq. (23), it seems rather unlikely that the exact cancellation will happen for all surfaces, as both the surface dielectric function $\epsilon_s(Q,\omega)$ and the surface plasmon dispersion relation w,(Q) are sensitively dependent on the surface properties for Q $\neq$ 0. We may say that the case of exact cancellation (i.e., the right-hand side of Eq. (2) is independent of Q to all orders) is an exceptional case rather than a general case. Although we cannot prove this statement directly, there is evidence that the general surface dielectric function f-sum rule is of the form of Eq. (2) with the linear coefficient $\alpha \neq 0$. Thus IPBJM is a rather special surface model. We may look at this problem by using a model which has a known surface plasmon dispersion relation. For example we may use a surface model studied by Feibelman [3] which has the surface plasmon dispersion relation $\omega_s(Q)=\omega_s(0)(1-1.5Q+\cdots)$ for a metal with electron density r_s = 4 and Q is in units of Å^{-1}. If a complete cancellation of the Q-dependence occured between $\omega_s^2(Q)$ and $f_s(Q,\omega_s(Q))$ for this surface model, then the function $f_s(Q,\omega)$ appeared in Eq. (23) would be of the following form

$$f_s(Q,\omega) = 1 - 1.3\left(\frac{Qv_F}{}\right) + \cdots . \tag{25}$$

This would imply that $f_s(Q,\omega)$, as well as $\epsilon_s(Q,\omega)$, might become zero with a solution w $\propto$ Q. This is impossible because if this happened, then we would have two surface plasma modes for a given Q, which is certainly not true. Moreover the plasma frequency is known to be a high frequency mode even in the Q → 0 limit. Therefore a solution with w $\propto$ Q for $\epsilon_s(Q,\omega)$ = 0 is not possible, and the complete cancellation of the Q-dependence between $\omega_s^2(Q)$ and $f_s(Q,\omega_s(Q))$ cannot happen for all models of surface. Because the surface plasmon dispersion relation $\omega_s(Q)$ is known to have a linear term in Q whose coefficient depends on the surface properties of the system considered, therefore the general surface dielectric function sum rule Eq. (2) will have a linear term in Q, whose coefficient is a surface dependent quantity. It is worthwhile noting that for IPBJM the surface plasmon dispersion relation w,(Q) has a linear term in Q with a *positive* coefficient. Therefore a complete cancellation between $\omega_s^2(Q)$ and $f_s(Q,\omega_s(Q))$ will not lead to the trouble of $f_s(Q,\omega)=0$ for some ω cx Q.

Finally we remark that theoretical calculations of the surface plasmon dispersion relation [3-5] have shown that w,(Q) may have an imaginary part which, to lowest order, is proportional to Q. It is possible that $f_s(Q,\omega)$ may also have a linear imaginary term. The appearance of the imaginary terms in the surface dielectric function will complicate the application of Eq. (15) to the surface dielectric function. However there is no difficulty in resolving this complication if we keep only first order terms in Q. In the limit Q → 0, both $\omega_s(Q)$ and $f_s(Q,$w) are real and the above derivation of the sum rule holds. Therefore the only effect of the linear imaginary parts is of first order in Q and will only affect the magnitude and/or sign of the linear coefficient α in Eq. (2). This can also be confirmed by explicit application of Eq. (15) if we keep only first order terms in Q.

In conclusion, we have defined a surface dielectric function, for a semi-infinite electron system, which is a function of the frequency ω and the two-dimensional wavevector Q parallel to the surface. A sum rule is derived for the imaginary part of the inverse of the surface dielectric fuction, which involves sum of all frequencies. In the Q → 0 limit, the sum rule has exactly the same form as that of the bulk case, and it is only in this limit that the sum rule applies to all models of surface. For small Q, linear and higher order terms of Q will appear in the sum rule whose coefficients will be sensitive to the surfsce properties of the system considered.

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