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Hydrodynamic model of linear response for a jellium surface: Nonretarded limit

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The response of a jellium surface to an external longitudinal perturbation is obtained using a hydrodynamic model to describe the bounded electron gas. The general irreducible response function, which describes the response of the system to the local self-consistent field, is written down. The reducible density-density and density-potential response functions are obtained by solving the response equations for several simple models of the electron density at the surface. The collective modes of the surface are investigated by examining the poles of the response functions. It is shown that the nonlocal effects associated with hydrodynamic dispersion give rise to new structure in the imaginary part of the response functions for the case of nonabrupt surfaces. This structure is then related to the "higher-multipole" modes which may exist in addition to the regular surface plasmon for a sufficiently diffuse surface. The dynamic structure factor is investigated and related to experiments on the energy loss of fast electrons. The effect on these experiments of the existence of "higher-multipole" surface modes is discussed.

I. INTRODUCTION

The response of a metal surface to an external electromagnetic perturbation is of considerable theoretical and experimental interest. In the study of a number phenomena, as for example the Schottky effect,[1] chemisorption,[2] low-energy scattering,[3] field emission,[4] field desorption,[5,6] field evaporation,[7] etc., it is important to understand the surface response to a static external charge. In contrast with these phenomena, the dynamical response is of fundamental importance in the study of surface collective oscillations,[8] fast-electron energy loss,[9] and optical reflectivity and absorption.[10]

The formalism developed by Hohenberg, Kohn, and Sham[11,12] (HKS) for the ground state of an inhomogeneous electron gas has been used successfully in problems involving the response of a metal surface to a static external charge.[13] Qualitative and in some cases even quantitative understanding of experimental results has been obtained. Other calculations[14,15] based on a self-consistent-field approach give qualitative results in the static response case.

Unfortunately, there has not been equal success in dealing with the problem of dynamic response of metal surfaces. Several authors[14,16–18] have applied the random-phase approximation (RPA) to the problem of surface collective oscillations. With the RPA, one usually has to do a high-frequency expansion or to resort to numerical methods very early in the calculation. The problem with high-frequency expansion is that if only the lowest-order terms are retained, all nonlocal effects are lost and the theory essentially becomes a local one. Use of numerical methods right from the beginning of the calculation tends to hide the essential physics of the dynamic problem. In view of the fact that one is forced to use some kind of a simplified model for the metal surface, it would be of considerable value to obtain closed-form expressions for surface response functions which indicate their qualitative nature.

An alternative way of treating the dynamic surface response is to use the hydrodynamic model for an electron gas. Several authors[19–24] have applied the hydrodynamic theory to the surface collective excitation problem. The great advantage of the hydrodynamic theory over RPA is that one can do a reasonable amount of analytical work giving one a qualitative feel about the nature of the calculation. Ying[25] first wrote down a generalization of the HKS theory for the dynamic case which became equivalent to a generalized hydrodynamic theory for inhomogeneous electron gas. This becomes equivalent to conventional hydrodynamics[19–24] when one uses the Thomas-Fermi form[23] for the exchange-correlation functional. Throughout our work we employ this particular hydrodynamic model to obtain the response functions of a metal surface. In this sense our work is a generalization of the work done by Eguiluz *et al.*[23] for the problem of surface collective excitations. Heinrich[21,26] took a different hydrodynamic approach to the problem of surface response. We believe that his use of bulk hydrodynamic dielectric function in dealing with the surface problem is somewhat *ad hoc* and some nonlocal effects may be lost through his constitutive equations.

We shall restrict ourselves to the problem of linear response of the surface to an external dynamic perturbation in the nonretarded ($c \rightarrow \infty$) limit. As such, we shall be dealing primarily with the longitudinal response to a self-consistent field. In the future we shall generalize our work to include the effects of retardation. We believe that even in the nonretarded limit, our work is the first one dealing with the response of a diffuse surface to an external dynamic perturbation which includes the nonlocal hydrodynamic dispersion effects in a comprehensive fashion.

The plan of the paper is the following. In Sec. II, we write down the fundamental hydrodynamic equations governing the response of the system to an external perturbation. We combine the hydrodynamic equations with the nonlocal consitutive equation for the surface response to obtain the general conductivity tensor (for the total self-consistent field) of the system. Taking the nonretarted ($c \to \infty$) limit, we then write down the response equations for density fluctuation in presence of an external longitudinal perturbation.

In Sec. III we explicitly solve for the response functions by invoking the hydrodynamical boundary conditions. We investigate two different simple models for the surface, the single-step and two-step models. In the single-step model the electron density drops abruptly from its bulk value to zero at the surface. In the two-step model the electron density goes to zero in two steps, the distance between the steps being a measure of the diffusivity of the surface. We discuss the pole structure of the response functions and show for the first time that the surface response functions indeed have poles at the "higher-multipole" modes[20,23] in addition to the poles associated with the regular surface plasmon modes. In Sec. IV, we write down the dynamic structure factor of the surface and relate it to fast-electron energy loss experiments. We conclude in Sec. V with a discussion of some problems remaining to be studied. These are inclusion of retardation effects (finite velocity of light) so that a theory of optical properties of metal surface containing nonlocal hydrodynamic dispersion effects can be developed, and extension of the surface density models considered to more realistic smooth electron density profiles.

II. THEORY

A. Basic equations

The basic hydrodynamic equations are the equation of continuity and Euler equation. The latter can be obtained by a generalization of HKS theory to an inhomogeneous electron gas capable of self-oscillations about a ground state.[23,25] Here we simply write down both equations for linearized quantities using a Thomas-Fermi ansatz for the hydrodynamic pressure term

$$\frac{\partial n}{\partial t}(\vec{r},t) + \vec{\nabla}\cdot\vec{J}(\vec{r},t) = 0 \ , \tag{1}$$

$$\frac{\partial}{\partial t}\vec{J}(\vec{r},t) = -n_0(\vec{r})\vec{E}(\vec{r},t) - \beta^2\vec{\nabla}n(\vec{r},t) - \tau^{-1}\vec{J}(\vec{r},t) \ , \tag{2}$$

where $n(\vec{r},t)$ and $\vec{J}(\vec{r},t)$ are the linearized local electron density (*not* charge density) and particle current density fluctuations, respectively. $n_0(\vec{r})$ is the static electron density contour for the surface, and $\vec{E}(\vec{r},t)$, the linear electric field fluctuation, is the total local, self-consistent field containing both the external field and the internal field due to the induced density fluctuation. The term $(1/\tau)\vec{J}(\vec{r},t)$ is the frictional term with $1/\tau$ a phenomenological damping parameter. Finally β^2 in Eq. (2), the coefficient of the hydrodynamic pressure term, is taken to be $\frac{3}{5}v_F^2$ (where v_F is the Fermi velocity of electrons deep inside the metal) so that the bulk plasma dispersion relation given by RPA agrees with that in hydrodynamics. Note that throughout this paper we use atomic units in which $|e| = \hbar = m_e = 1$. A few points are worth noting here. The electron density contour $n_0(\vec{r})$ is itself determined self-consistently from the equation $\vec{E} - \vec{\nabla}v_{\text{back}} + \vec{\nabla}(\delta G/\delta n_0) = 0$ where the subscript 0 denotes that these are zeroth order or equilibrium values. v_{back} is the background ionic potential and $G \equiv G\{n_o(\vec{r})\}$ is the exchange-correlation functional.[11,12] Lang and Kohn[27] have solved this equation in a different but equivalent version to compute the self-consistent electron density contours in the ground state of the metal-vacuum systems. We should point out that instead of solving self-consistently for $n_0(\vec{r})$ (which would be very difficult in the dynamic response case) we use models for $n_0(\vec{r})$, thus assuming $v_{\text{back}}(z)$ to have the particular form which yields the desired electron density contour $n_0(r)$. Second, the magnetic field does not enter Eq. (2) because of the absence of an external static magnetic field in the problem. The total self-consistent field in Eq. (2) is given by

$$\vec{E}(\vec{r},t) = \vec{E}_{ex}(\vec{r},t) + \vec{E}_{\text{ind}}(\vec{r},t) \ . \tag{3}$$

The applied field $\vec{E}_{ex}(\vec{r},t)$ and the induced field $\vec{E}_{\text{ind}}(\vec{r},t)$ are in turn related to the external charge density $\rho_{ex}(\vec{r},t)$ and the induced charge density fluctuation $-n(\vec{r},t)$ respectively, through Maxwell's equations. For longitudinal response there is just one Maxwell equation (Gauss law) relating them

$$\vec{\nabla}\cdot\vec{E}(\vec{r},t) = 4\pi\rho(\vec{r},t) \ , \tag{4a}$$

$$\vec{\nabla}\cdot\vec{E}_{ex}(\vec{r},t) = 4\pi\rho_{ex}(\vec{r},t) \ , \tag{4b}$$

$$\vec{\nabla}\cdot\vec{E}_{\text{ind}} = -4\pi n(\vec{r},t) \ . \tag{4c}$$

We can also introduce electrostatic potentials defined by

$$\nabla^2\phi(\vec{r},t) = -4\pi\rho(\vec{r},t) \ , \tag{5a}$$

$$\nabla^2\phi_{\text{ind}}(\vec{r},t) = 4\pi n(\vec{r},t) \ , \tag{5b}$$

$$\nabla^2\phi_{ex}(\vec{r},t) = -4\pi\rho_{ex}(\vec{r},t) \ , \tag{5c}$$

$$\phi(\vec{r},t) = \phi_{\text{ind}} + \phi_{ex} \ . \tag{5d}$$

Equations (1)–(5) are the basic equations of our theory. They are combined with various constitutive relations to obtain response functions either to the self-consistent field or to the external field.

In our subsequent discussions, we shall find it convenient to proceed in the Fourier space which is easily done by taking $(\vec{k},\omega)$ Fourier transforms of the equations.

B. Conductivity tensor

The conductivity tensor $\overleftrightarrow{\sigma}$ is defined through the constitutive relation

$$J_i(\vec{r},t)=\int d^3r'\,dt'\,\sigma_{ij}(\vec{r},\vec{r}',t-t')\,E_j(\vec{r}',t') \ , \tag{6}$$

where sum over repeated dummy suffix j is understood. In Fourier space Eq. (6) reads

$$J_i(\vec{k},\omega)=\int\frac{d^3k'}{(2\pi)^3}\sigma_{ij}(\vec{k},-\vec{k}',\omega)E_j(\vec{k}',\omega) \ . \tag{7}$$

Taking Fourier transforms of Eqs. (1) and (2) and combining them with Eq. (7) it is easy to obtain

$$\sigma_{ij}(\vec{k},-\vec{k}',\omega)=\left(-\frac{i}{\tilde{\omega}}\right)n_0(\vec{k}-\vec{k}')+\left(-\frac{i\beta^2}{\tilde{\omega}}\right)\frac{n_0(k-k')k_ik_j}{\tilde{\omega}^2-\beta^2k^2} \ , \tag{8}$$

where

$$\tilde{\omega}^2=\omega^2+\frac{i\omega}{\tau} \ . \tag{9}$$

In general $\omega >> 1/\tau$ and hence the imaginary part in Eq. (9) is very small. We should point out that σ_{ij} as defined by Eq. (7) is an irreducible response function, i.e., the response function to the total, local self-consistent field rather than the external electric field.

To discuss the physical properties of σ_{ij} we go back to real space, by taking the inverse Fourier transform of Eq. (8). In doing that we use the fact that our model for surface electron density profile is such that translational invariance is broken only in the direction normal to the surface. We take that to be z direction. Thus,

$$\begin{aligned} n_0(\vec{k}-\vec{k}') &= \int d^3r\, e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}}n_0(\vec{r}) \\ &= \int d^3r\, e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}}n_0(z) \\ &= (2\pi)^2\delta(\vec{q}-\vec{q}')n_0(k_z-k_z') \ , \end{aligned} \tag{10}$$

where $\vec{k}\equiv(\vec{q},k_z)$ and $\vec{q}$ is the wave vector in the plane of the surface. With Eq. (10) in Eq. (8), we find that in addition to ω, $\vec{q}$ is another conserved quantity.

The corresponding constitutive relation [Eq. (7)] becomes

$$J_i(q,\omega;z)=\int_{-\infty}^{+\infty}dz'\,\sigma_{ij}(q,\omega;z,z')\,E_j(q,\omega;z') \ , \tag{11}$$

where $\vec{E}(q,\omega;z)$ is a Fourier transform in two dimensions (x-y plane) and in time of $\vec{E}(\vec{r},t)$. The components of $\sigma_{ij}(q,\omega;z,z')$ are easily obtained by taking Eq. (8) back to (z,z') space. Without any loss of generality we choose our x,y axes such that q lies entirely along x axis. Then the Fourier transform of Eq. (8) is

$$\sigma_{xx}=-\left(\frac{i}{\omega}\right)n_0(z')\delta(z-z')-\left(\frac{1}{2\omega}\right)\left(\frac{q^2}{\alpha}\right)\times n_0(z')e^{i\alpha|z-z'|}e^{-\xi|z-z'|} \ , \tag{12}$$

$$\sigma_{zz}=-\left(\frac{\alpha}{2\omega}\right)n_0(z')e^{i\alpha|z-z'|}e^{-\xi|z-z'|} \ , \tag{13}$$

$$\sigma_{yy}=-\left(\frac{i}{\omega}\right)n_0(z')\delta(z-z') \ , \tag{14}$$

$$\sigma_{xz}=\sigma_{zx}=-\left(\frac{q}{2\omega}\right)\operatorname{sgn}(z-z')\times n_0(z')e^{i\alpha|z-z'|}e^{-\xi|z-z'|} \ , \tag{15}$$

$$\sigma_{xy}=\sigma_{yx}=\sigma_{yz}=\sigma_{zy}=0 \ , \tag{16}$$

$$\alpha=\frac{1}{\beta}(\omega^2-\beta^2q^2)^{1/2} \ , \tag{17}$$

$$\xi=\frac{\omega}{2\beta\tau(\omega^2-\beta^2q^2)^{1/2}} \ . \tag{18}$$

The exact value of ξ (or τ) is not important for our purpose since we are not interested in the static ($\omega\rightarrow 0$) limit in this work. We may remark that these damping parameters should be small however. With these remarks we shall from now on suppress $e^{-\xi|z-z'|}$ and assume α to contain a small positive imaginary part instead. Equations (12)–(15) are valid for z only within the metal because the hydrodynamic equations themselves are valid only within the metal. The important features of the conductivity tensor are the following:

(i) It leads to the bulk value well inside the solid [deep inside the solid $n_0(z')\rightarrow\bar{n}_0$ where $\bar{n}_0$ is the constant bulk electron density and the conductivity becomes completely translationally invariant].

(ii) It vanishes when it connects points z and z' very far from each other. Typically for $|z-z'| >> 1/\xi$, conductivity is zero. Within our theory this is done by the introduction of a phenomenological hydrodynamic damping term.

(iii) For $q \rightarrow 0$, conductivity tensor becomes diagonal and all components except σ_{zz} take on their local values

$$\sigma_{xx}(q\rightarrow 0)=\sigma_{yy}(q\rightarrow 0)=-\left(\frac{i}{\omega}\right)n_0(z)\delta(z-z') \ .$$

Nonlocal effects are preserved in z direction, a result of hydrodynamic dispersion.

We point out that σ is the response to the self-consistent field and in this sense it is not a true response function as defined in standard texts.[28] The relationship between the corresponding reducible response function (which is the response to the external field) and σ, the irreducible response function can be obtained from Eq. (3) and Maxwell's equation which relates $\vec{J}$ and $\vec{E}_{\text{ind}}$. The relationship is a rather complicated integral equation and since our primary interest in this paper is density response (whereas σ is the current response function), we shall not discuss this point any further.

C. Dielectric response

The dielectric tensor $\overleftrightarrow{\epsilon}$ is defined through the constitutive relation

$$D_i(\vec{r},t)=\int d^3r'\,dt'\,\epsilon_{ij}(\vec{r},\vec{r}';t-t')\,E_j(\vec{r}',t') \ . \tag{19}$$

By taking the Fourier transform of Eq. (19) and using equation of continuity and Maxwell's equations it is easy to show that

$$\epsilon_{ij}(\vec{k},-\vec{k}',\omega)=(2\pi)^3\delta_{ij}\delta(\vec{k}-\vec{k}') + \frac{4\pi}{i\omega}\sigma_{ij}(\vec{k},-\vec{k},\omega) \ . \tag{20}$$

Equation (20) is the generalization of the conventional relationship between the conductivity and dielectric tensors.[28] Following Newns[14] we now define a longitudinal response function χ to the self-consistent or the screened potential by defining the constitutive relation

$$n(q,k_z,\omega)=-\int dk_z'\,\chi(q,k_z,-k_z',\omega)\,\phi(q,k_z',\omega) \ , \tag{21}$$

where the negative sign is to convert n to charge density fluctuation. In Eq. (21), χ is the density response function to the total, self-consistent potential ϕ. Within hydrodynamics, it is possible to get a closed form expression for the screened response function $\chi(q,k_z,-k_z',\omega)$. By taking Fourier transform of Eq. (7), we can obtain

$$\chi(q,k_z,-k_z',\omega)=[q^2(\omega^2-\beta^2k_z^2)+k_zk_z'(\omega^2+\beta^2q^2)] \times\frac{n_0(k_z-k_z')}{2\pi\omega^2(\omega^2-\beta^2q^2-\beta^2k_z^2)} \ . \tag{22}$$

To discuss the screened response function χ, we assume the electron gas to occupy the half space $z<0$ with $\bar{n}_0$ as the uniform bulk electron density for z large and negative. The surface is assumed to be in the vicinity of the plane $z=0$. We can write

$$n_0(z)=\bar{n}_0 f(z)=\bar{n}_0-\bar{n}_0F(z) \ , \tag{23}$$

where $f(z)=1-F(z)\rightarrow 0$ as $z\rightarrow 0$ and $f(z)\rightarrow 1$ as $z\rightarrow -\infty$. Using Eq. (23), we can write Eq. (22)

$$\chi(q,k_z,-k_z',\omega)=\chi_B+\chi_S \ , \tag{24}$$

with

$$\chi_B=\frac{\bar{n}_0(q^2+k_z^2)}{\omega^2-\beta^2q^2-\beta^2k_z^2}\delta(k_z-k_z') \ , \tag{25}$$

and

$$\chi_S=-\frac{\bar{n}_0}{2\pi\omega^2}[q^2(\omega^2-\beta^2k_z^2)+k_zk_z'(\omega^2+\beta^2q^2)] \times\frac{F(k_z-k_z')}{\omega^2-\beta^2q^2-\beta^2k_z^2} \ . \tag{26}$$

χ_B is translationally invariant and can be unambiguously indentified as the hydrodynamic screened density-response function for the bulk metal.[28] For $F\equiv 0$, $\chi=\chi_B$. All the surface effects are in χ_S. Going over to z space, one can easily show that deep inside the metal χ_S vanishes. We note that it is a consequence only of the hydrodynamic approximation employed here that the surface effects enter into the response function in a sufficiently simple fashion as given by Eq. (26). With a more complicated expression for the hydrodynamic pressure term in Euler equation [Eq. (2)], it will not be possible to obtain a simple form like Eq. (26) for the screened response function.

Using $\phi=\phi_{\text{ind}}+\phi_{ex}$ in Eq. (21) along with Poisson's equation, it is easy to demonstrate the self-consistency of the screened response equation and we get

$$\int dk_z'\,\bar{\chi}(q,k_{z},-k_z',\omega)\,\phi_{\text{ind}}(k_z') =\frac{1}{4\pi}\int dk_z'\,\chi(q,k_z,-k_z',\omega)\,\phi_{ex}(k_z') \ , \tag{27}$$

where

$$\bar{\chi}(q,k_{z},-k_z',\omega)=(q^2+k_z'^2)\delta(k_z-k_z') -4\pi\chi(q,k_{z},-k_z',\omega) \ . \tag{28}$$

To find the true response function (response to an external field, rather than the self-consistent field), one has to invert Eq. (27).

We find that the inversion of Eq. (27) is more easily done in the coordinate space. This is because one has to use hydrodynamic boundary conditions in inverting Eq. (21) which are formulated in the z space.

D. Response to external longitudinal field

We begin by defining the density-density response function $R(z,z')$ in the coordinate space by introducing the constitutive relation

$$n(z)=\int_{-\infty}^{+\infty}dz'\,R(z,z')\phi_{ex}(z')\ , \tag{29}$$

where $n(z)$ is the induced electron density due to an external charge-density perturbation $\rho_{ex}(z')$. All quantities in Eq. (29) are Fourier transforms in q-ω space, i.e., we have used the translational invariance parallel to the surface and the homogeneity in time to go over to the corresponding Fourier space. From now on for the sake of brevity, the explicit (q,ω) dependence of our functions will be omitted.

Taking Fourier transforms parallel to the surface and in time of Eqs. (1) and (2) and using Eqs. (3)–(5), one can show that

$$\beta^2\frac{\partial^2}{\partial z^2}n(z)+[\omega^2-\beta^2q^2-\omega_p^2(z)]n(z)+E_z(z)\frac{\partial}{\partial z}n_0(z)+\omega_p^2(z)\rho_{ex}(z)=0\ , \tag{30}$$

and

$$i\omega J_z(z)=n_0(z)E_z(z)+\beta^2\frac{\partial}{\partial z}n(z)\ , \tag{31}$$

where $\omega_p^2(z)=4\pi n_0(z)$ and $E_z(z)$ is the z component of the total, local self-consistent electric field. It is given by

$$E_z(z)=(-2\pi)\int_{-\infty}^{0}dz'e^{-q|z-z'|}\,\mathrm{sgn}(z-z')n(z')+2\pi\int_{-\infty}^{+\infty}dz'\,e^{-q|z-z'|}\,\mathrm{sgn}(z-z')\rho_{ex}(z')\ , \tag{32}$$

where sgn (a) is the sign function being positive for $a>0$ and negative for $a<0$. Equations (30) and (32) define the set of integro-differential equations that must be solved with a specific model for $n_0(z)$, the equilibrium electron density profile to obtain the response function $R(z,z')$ in Eq. (29). We may note that Eq. (31) provides the boundary conditions needed to solve the differential equation (30). Hydrodynamic boundary condition consists of demanding that the normal component of the current, $J_z(z)$, vanishes at the surface which we always take to be the plane $z=0$ with the metal occupying the half space $z<0$. The other boundary condition is obtained by demanding that $n(z)$ goes to zero deep inside the metal $(z\rightarrow-\infty)$. This restricts us to discussion of surface excitations only. Finally, we remark that Eqs. (30) and (31) are valid only inside the metal, i.e., for $z<0$. For $z>0$, $n(z)=0$ since $n_0(z)=0$ for $z>0$ in our model.

Using Eqs. (29) and (32) in Eq. (30) we can write down an integro-differential equation for the response function $R(z,z')$ which is to be solved in conjunction with the hydrodynamic boundary condition. It is easy to see from Eqs. (30)–(32) that the response equations are model dependent and we need to make some specific choice for $n_0(z)$ in order to solve for $R(z,z')$.

In Sec. III we solve for the response function $R(z,z')$ for two different models of the surface electron density contour $n_0(z)$.

III. DENSITY-DENSITY RESPONSE FUNCTION FOR MODEL SURFACES

A. Single-step density model

This is the most widely used model in the study of surface response. The static electron density contour is assumed to have the form

$$n_0(z)=\bar{n}_0\Theta(-z)\ , \tag{33}$$

where $\Theta(z)$ is the unit step function. With this model, Eq. (30) becomes

$$\beta^2\frac{\partial^2}{\partial z^2}n(z)+(\omega^2-\beta^2q^2-\omega_p^2)n(z)=-\omega_p^2\rho_{ex}(z),\ \ z<0\ , \tag{34}$$

where $\omega_p^2=(4\pi\bar{n}_0)^{1/2}$ is the bulk plasma frequency of the metal. It should be noted that the integro-differential response equation [Eq. (30)] becomes a pure differential equation for the step-density model since the term with $E_z(z)$ in Eq. (30) drops out by virtue of the fact that $n_0(z)$ is constant right up to the surface of the metal $z=0$ where it abruptly falls to zero in a single step. The general solution to the inhomogeneous differential equation (34) can be written

$$n(z)=\begin{cases}Ae^{\gamma z}+Be^{-\gamma z}+Ce^{-\gamma z}\int_{-\infty}^{z}dz'f_+(z')+Ce^{\gamma z}\int_{z}^{0}dz'f_-(z'), & z<0\ ,\\ 0,\ \ z>0\ , & \end{cases} \tag{35}$$

where

$$C=\frac{\omega_p^2}{2\gamma\beta^2};\quad \gamma=\frac{1}{\beta}(\omega_p^2+\beta^2q^2-\omega^2)^{1/2}\ , \tag{36}$$

$$f_{\pm}(z')=e^{\pm\gamma z'}\rho_{ex}(z')\ . \tag{37}$$

The unknown constants A and B are independent of z and are determined by the application of boundary conditions.

From the condition that $n(z)$ be bounded as $z\rightarrow-\infty$ we get, $B=0$ in Eq. (35). The other unknown constant A is obtained by applying the hydrodynamic boundary condition that $J_z(z=0^-)=0$. It is straightforward, but rather tedious to obtain A from this boundary condition in conjunction with Eqs. (35), (32), and (31). We get

$$n(z)=Ae^{\gamma z}+\left[\frac{\omega_p^2}{2\gamma\beta^2}\right]\int_{-\infty}^{0}dz'\,e^{-\gamma|z-z'|}\rho_{ex}(z')\ , \tag{38}$$

where

$$A=\frac{q+\gamma}{\omega_p^2/2+\beta^2q^2+\beta^2q\gamma-\omega^2}\left[-\frac{\omega_p^2}{2}\int_{-\infty}^{+\infty}dz'\,F(z')+\frac{\omega_p^2}{2}\int_{-\infty}^{o}dz'\,e^{\gamma z'}\rho_{ex}(z')\right]\ , \tag{39}$$

with

$$F(z')=\left[-\left[\frac{\omega_p^2}{2\gamma\beta^2}\right]\left[\frac{e^{\gamma z'}-e^{qz'}}{q-\gamma}+\frac{e^{qz'}}{q+\gamma}\right]\Theta(-z')+e^{qz'}\Theta(-z')-e^{-qz'}\Theta(z')\right]\rho_{ex}(z')\ . \tag{40}$$

One can combine Eqs. (38)–(40) with the response equation (29) to obtain the response function as

$$\begin{aligned}R(z,z')=&-\frac{(q+\gamma)\omega_p^2}{\omega_p^2/2+\beta^2q^2+\beta^2q\gamma-\omega^2}\,\frac{e^{\gamma z}}{2}\Theta(-z)\left[e^{-q|z'|}\mathrm{sgn}(-z')-\left[\frac{\omega_p^2}{2\gamma\beta^2}\right]\Theta(-z')\right.\\&\left.\times\left[\frac{e^{\gamma z'}-e^{qz'}}{q-\gamma}+\frac{e^{qz'}}{q+\gamma}\right]+\Theta(-z')e^{\gamma z'}\right]\\&+\left[\frac{\omega_p^2}{2\gamma\beta^2}\right]\Theta(-z)\Theta(-z')e^{-\gamma|z-z'|}\ ,\end{aligned} \tag{41}$$

where we have used the fact that $R(z,z')$ is defined only for $z<0$ (inside the metal) to introduce $\Theta(-z)$ in Eq. (41).

We may note that $R(z,z')$ is a true surface response function going rapidly to zero as either z or z' goes very deep inside the bulk. The response function of a single-step surface has only one pole given by

$$\omega_p^2/2+\beta^2q^2+\beta^2q\gamma-\omega^2=0\ . \tag{42}$$

It is easy to see that this implies the usual surface plasmon dispersion relation,

$$\omega=\frac{\omega_p}{\sqrt{2}}\left[1+\frac{\beta q}{\sqrt{2}\omega_p}+O(q^2)+\cdots\right]\ . \tag{43}$$

At this frequency, the induced density fluctuation in the system could be nonzero even in the absence of any external perturbation since the response function is infinite implying a collective excitation of the surface. The abrupt surface (single-step model) thus can have only one kind of normal mode excitation, that given by Eq. (41) which is referred to as the regular surface plasmon.

B. Two-step density model

In this model the electron density goes to zero from its uniform bulk value in two steps and $n_0(z)$ can be written

$$n_0(z)=\bar{n}_0\Theta(-z-a)+\bar{n}_L\Theta(-z)\Theta(z+a)\ . \tag{44}$$

In Eq. (44), $\bar{n}_0$ is the bulk, uniform electron density deep inside the metal (in this model for $z<-a$) and $\bar{n}_L$ is the electron density in a surface layer of thickness a. The two-step model is more realistic than the single-step abrupt surface since in reality the electron density goes from the bulk value to zero in a smooth fashion over a small region near the surface.

The solution of the basic response equation [Eq. (30)] for this model can be written

$$n(z)=Ae^{\gamma_1 z}+\frac{1}{2\gamma_1\beta^2}\int_{-\infty}^{+\infty}dz'\,e^{-\gamma_1|z-z'|}\times\omega_{p_1}^2(z')\rho_{ex}(z')\ ,\quad\text{for } z<-a\ . \tag{45}$$

We should note that $\omega_{p_1}^2(z')=4\pi\bar{n}_0\Theta(-z'-a)$ in the two-step model. For $-a<z<0$, we can write the density fluctuation as

$$n(z)=Be^{\gamma_2 z}+Ce^{-\gamma_2 z}+\frac{1}{2\gamma_2\beta^2}\times\int_{-\infty}^{+\infty}dz'\,e^{-\gamma_2|z-z'|}\omega_{p_2}^2(z')\times\rho_{ex}(z'),\quad\text{for } -a<z<0\ . \tag{46}$$

Here

$$\omega_{p_2}^2(z')=4\pi\bar{n}_L\Theta(-z')\Theta(z'+a)\ .$$

In Eqs. (45) and (46), γ_1,γ_2 are given by the same equations as in Sec. III A with the electron densities $\bar{n}_0$ and $\bar{n}_L$ respectively.

To obtain Eq. (45), we have already used the boundary condition that $n(z)\neq\infty$ as $z\rightarrow-\infty$. There are three unknown constants A,B,C in the general solution for the induced density which are to be obtained by using boundary conditions. One of the constants can be elimated by using the hydrodynamic boundary condition $J_z(z=0^-)=0$ whereas the other two are obtained by demanding that the normal component of current density $J_z(z)$ and the density fluctuation $n(z)$ be continuous across the step at $z=-a$. Continuity of $n(z)$ at $z=a$ immediately gives

$$A=Ce^{(\gamma_1-\gamma_2)a}+De^{(\gamma_1+\gamma_2)a}+\frac{e^{\gamma_1 a}}{2\beta^2}\times\int_{-\infty}^{+\infty}dz'\left[\frac{e^{-\gamma_2|z'+a|}}{\gamma_2}\omega_{p_1}^2(z')-\frac{e^{-\gamma_1|z'+a|}}{\gamma_1}\omega_{p_2}^2(z')\right]\rho_{ex}(z')\ . \tag{47}$$

The evaluation of the two constants B and C using the other two boundary conditions viz. $J_z(z=0^-)=0$ and $J_z(z=a^+)=J_z(z=a^-)$, is straightforward but extremely tedious. The final result can be expressed as,

$$B=\frac{C_+D_1-C_-D_2}{\Delta}\ , \tag{48}$$

$$C=\frac{b_-D_2-b_+D_1}{\Delta}\ , \tag{49}$$

where,

$$\Delta=b_-C_+-b_+C_- \tag{50}$$

and b_+,b_-,C_+,C_- are given by

$$b_\pm=\frac{e^{(\pm\gamma_2-q)a}}{q+\gamma_1}+\frac{1-e^{(\pm\gamma_2-q)a}}{q\pm\gamma_2}\pm\frac{2\gamma_2\beta^2}{\omega_{p_2}^2}\ , \tag{51}$$

and

$$C_\pm=\frac{e^{\pm\gamma_2 a}}{q+\gamma_1}+\frac{e^{-qa}-e^{\pm\gamma_2 a}}{q\pm\gamma_2}-\left[\frac{2\beta^2}{\omega_{p_1}^2-\omega_{p_2}^2}\right](\pm\gamma_2+\gamma_1)e^{\pm\gamma_2 a}\ . \tag{52}$$

D_1 and D_2 are rather long and complicated expressions involving integrals over $\rho_{ex}(z)$ and we shall not show them here (Appendix A).

Using Eqs. (47)–(49) in Eqs. (45) and (46), we get $n(z)$ completely in terms of $\rho_{ex}(z)$ and ω_{p_1}, ω_{p_2}, γ_1, γ_2, β, and a. This in turn immediately yields an expression for $R(z,z')$ on comparison with Eq. (29) (Appendix B).

We note that the response function $R(z,z')$ of this system will have poles at frequencies determined by

$$\Delta(q,\omega)=0\ . \tag{53}$$

Since $\Delta(q,\omega)$ is a complicated function of q and ω, we shall investigate the limiting cases $qa\ll 1$ and $qa\gg 1$.

(i) $qa\ll 1$. In this limit, the dispersion relation given by Eq. (53) simplifies to

$$\left[\omega^2-\frac{\omega_{p_1}^2}{2}\right](\gamma_1\sin\tilde{\gamma}_2 a+\tilde{\gamma}_2\cos\tilde{\gamma}_2 a)=0\ , \tag{54}$$

where $\tilde{\gamma}_2=-i\gamma_2$. Thus, in addition to the regular surface plasmon mode (which is given by $\omega=\omega_{p_1}/\sqrt{2}$ in the $q\rightarrow 0$ limit) we may have an additional branch of collective excitation given by,

$$\gamma_1\sin\tilde{\gamma}_2 a+\tilde{\gamma}_2\cos\tilde{\gamma}_2 a=0\ . \tag{55}$$

This is the "higher-multipole" mode of the two-step surface. We may note that the mode vanishes if $a=0$ and thus an abrupt surface cannot support such a mode of collective excitation. We have shown here that the higher multipole mode exists as a genuine pole in the response function of our diffuse surface.

(ii) $qa\gg 1$. This is the limit of a very long step: $a\gg 1/q$. Since we are still interested in the long-wavelength limit we shall first put $qa\rightarrow\infty$ in Eq. (53) and then take $q\rightarrow 0$ limit in the resulting dispersion relation. Doing so gives

$$\left[\frac{1}{q+\gamma_2}-\frac{2\gamma_2\beta^2}{\omega_{p_2}^2}\right]\left[\frac{1}{q+\gamma_1}-\frac{1}{q+\gamma_2}-\frac{2(\gamma_1+\gamma_2)\beta^2}{\omega_{p_1}^2-\omega_{p_2}^2}\right]=0\ . \tag{56}$$

Equation (56) implies two kinds of collective excitations with dispersion relations given by,

$$\frac{1}{q+\gamma_2}-\frac{2\gamma_2\beta^2}{\omega_{p_2}^2}=0 \tag{57}$$

and

$$\frac{1}{q+\gamma_1}-\frac{1}{q+\gamma_2}-\frac{2(\gamma_1+\gamma_2)\beta^2}{\omega_{p_1}^2-\omega_{p_2}^2}=0 \ . \tag{58}$$

Equation (57) can be simplified into

$$\omega_{p_2}^2/2+\beta^2q^2+\beta^2\gamma_2 q-\omega^2=0 \ . \tag{59}$$

This is the dispersion relation of a regular surface plasmon [cf. Eq. (42)] localized at the surface of the metal and with surface plasmon frequency $\omega=\omega_{p_2}/\sqrt{2}+O(q)$ corresponding to the electron density $\bar{n}_L$ in the surface layer of thickness a. Ordinary surface plasmon, however, has a frequency that always corresponds to the density in the bulk metal, independent of surface electron density profile.[18,23] The fact that the surface plasmon in the case of a very long step ($qa \gg 1$) corresponds to the electron density in the surface layer is simply due to the surface at $z=0$ in this case being very far away from the bulk metal essentially has no "memory" of the bulk electron density. The other mode in this case is given by Eq. (58) which can be simpliefied to[29]

$$\omega=\left[\frac{\omega_{p_1}^2+\omega_{p_2}^2}{2}\right]^{1/2}+O(q) \ . \tag{60}$$

This is the well-known interface excitation at a bimetallic junction. Thus, the response function for a two-step model has poles at collective excitations which are a regular surface plasmon and higher multipole modes in the case of $qa \ll 1$ and a regular surface plasmon corresponding to the layer electron density and an interface plasmon in the case of $qa \gg 1$.

IV. DYNAMIC STRUCTURE FACTOR OF SURFACES

The dynamic structure factor[28] contains the maximum information one can deduce from an inelastic scattering experiment. For the surface geometry employed in this paper, we can write down the dynamic structure factor for the surface as[30]

$$S(\vec{k},\omega)=2A\int_{-\infty}^{+\infty}dz\int_{-\infty}^{+\infty}dz'\,e^{-ik_z(z-z')}\,\mathrm{Im}\tilde{R}(z,z') \ , \tag{61}$$

where $\tilde{R}$ is the density-potential response function defined by

$$n(z)=\int_{-\infty}^{+\infty}dz'\tilde{R}(z,z')\phi_{ex}(z') \ . \tag{62}$$

In Eq. (61), A is the total area of the surface and $\vec{k}\equiv(\vec{q},k_z)$ is the three-dimensional wave vector associated with the probe. One has to consider the imaginary part of the retarded response function in Eq. (61).

The response function $\tilde{R}$ can be obtained very simply from R through the following relation:

$$\tilde{R}(z,z')=\frac{1}{4\pi}\left[q^2-\frac{\partial^2}{\partial z'^2}\right]R(z,z') \ . \tag{63}$$

One of the great advantages of the hydrodynamic approximation is that the imaginary part of the response function is known in closed form so that the double integral Eq. (61) can be performed and an analytical expression for the dynamic structure factor can be written down.

We shall illustrate the procedure by an explicit evaluation of the dynamic structure factor of a sharp metal surface. The calculation is straightforward but rather tedious and the result for general (q,ω) is

$$S(\vec{k},\omega)=\frac{A(q+\gamma)\omega_p^2}{4(\omega_p^2-\omega^2+\beta^2k^2)}\times\left[\frac{3\omega_p^2}{\omega^2}-\omega^2+\frac{q\omega_p^2}{2\gamma}\right]\delta(\omega^2-\omega_S^2(q)) \ , \tag{64}$$

where $\omega_S(q)$ is the regular surface plasmon frequency as defined by Eq. (42) and Eq. (43). In the case of a two-step model surface, the dynamic structure factor will have δ-function peaks at the regular surface plasma frequency and at the higher-multipole modes. The peaks in the dynamic structure factor are δ-function-like only because we have neglected any lifetime effects. If we assume ω^2 to contain the damping term so that we replace ω^2 by $\omega^2+i\omega/\tau$, then the δ-function peaks broaden out into Lorentzians.

The dynamic structure factor provides direct information about fast-electron energy loss experiment. Within the Born approximation, the differential cross section for inelastic electron scattering is given by the Van Hove expression,

$$\frac{d^2\sigma}{d\Omega dE}=\frac{m^2}{(2\pi)^3}\frac{k_f}{k_o}V^2(k)S(k,\omega) \ , \tag{65}$$

where ω and $\vec{k}=\vec{k}_f-\vec{k}_o$ are, respectively, the energy and momentum transferred to the solid by the external charge and $V(k)=4\pi/k^2$. Thus in a fast-electron energy loss experiment one expects to see structure around the surface plasma frequency as well as at the higher-multipole frequency.

V. CONCLUSION

In this paper we apply the hydrodynamic model of a bounded electron gas to describe the response of a metal surface to external dynamic perturbation. We write down the general conductivity tensor $\overleftrightarrow{\sigma}(z,z')$ within the hydrodynamic approximation and show that it has the desired physical features of a nonlocal conductivity tensor — it heals to the bulk value deep inside the solid and vanishes when $|z-z'|$ is large. Finally, we obtain explicit expressions for the induced density fluctuation in the system in the presence of an external charge density fluctuation by solving the longitudinal response equations for two different surface models. We show that the nonlocal effects associated with hydrodynamic dispersion may give rise to new structure in response functions of metal surfaces. These structures should show up in the fast-electron energy loss experiments as peaks in scattering cross sections at energies corresponding to higher-multipole modes. We have restricted ourselves only to localized excitations in this paper ignoring the propagating bulk plasma modes completely.

The main advantage of the hydrodynamic theory is that one can write down analytic forms for response functions rather simply. On the other hand, microscopic theories like RPA become very complicated when applied to deal with surface response and even for a sharp surface, it is not possible to write down the response functions explicitly. In the past there has been controversy regarding the validity of hydrodynamic model in surface collective oscillation problem.[31,32] We believe that the simplicity of the approximation makes hydrodynamic theory a particularly appealing alternative to detailed microscopic theories like RPA, the validity of which in the surface region is also questionable. Hydrodynamic theory when applied to a smooth surface electron density profile shows that the slope of the surface plasmon dispersion curve could be negative for sufficiently diffuse profiles, as has been observed experimentally.[33,34] Recently Inglesfield and Wikborg[35] developed an RPA theory to investigate the higher-multipole modes.[20,23] They found that these modes could exist for a two-step model within RPA. This encourages us to believe that the higher-multipole modes are physical features of a diffuse surface and are not peculiar to hydrodynamic model itself. In the final analysis, experiments have to decide whether these modes exist or not. Our work in this paper indicates that inelastic electron scattering experiments on suitable two-step surfaces (like sodium on aluminum) could be one of such experiments looking for these additional poles in the surface response function.

Extension of our theory into the retarded limit remains to be an interesting problem for the future. It is difficult due to the fact that the integrodifferential equations in the presence of a general external electromagnetic field are not explicity soluble even in the hydrodynamic approximation. One can use the general conductivity tensor derived in Sec. II of this paper as a starting point to obtain the surface response to external electromagnetic perturbation. Bagchi[36] has recently given the general RPA theory for the transverse dielectric response function in a bounded electron gas. The hydrodynamic conductivity satisfies the general features outlined in his work.

Calculation of the reflectivity of a two-step surface for p-polarized light would be of great interest since one can compare it with the results for a one-step model and find out the new features introduced due to the existence of higher-multipole modes. As has been argued by Eguiluz and Quinn,[23] hydrodynamic dispersion remains important in the retarded region. Recent work of Feibelman[37,38] indicates that calculation of surface reflectivity including the nonlocal effects in the theory, is a difficult problem. We hope that the simplicity of the hydrodynamic conductivity tensor will enable us to extend the work into the retarded region in the near future.

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APPENDIX A

Here, we write down the expressions for D_1 and D_2 which enter the response equations [Eqs. (48) and (49)] of the two-step model. They are given by

$$D_1 = \int_{-\infty}^{+\infty} dz' R_1(z') \rho_{ex}(z') \ , \tag{A1}$$

where

$$R_1(z') = \frac{\omega_{p_2}^2(z')}{\omega_{p_2}^2} \operatorname{sgn}(z') e^{-\gamma_2 |z'|} - (I_1 + I_2) + \frac{e^{-qa}}{q+\gamma_1} F - \operatorname{sgn}(z') e^{-q|z'|} \tag{A2}$$

and

$$D_2=\int_{-\infty}^{+\infty} dz'\, R_2(z')\rho_{ex}(z') \quad , \tag{A3}$$

where

$$R_2(z')=\left(\frac{1}{\omega_{p_1}^2-\omega_{p_2}^2}\right)\Bigg[\operatorname{sgn}(z'+a)\,\omega_{p_1}^2(z')e^{-\gamma_1|z'+a|}-\operatorname{sgn}(z'+a)\,\omega_{p_2}^2(z')$$
$$\times e^{-\gamma_2|z'+a|}-2\gamma_1\beta^2F\Bigg]+\left(e^{-qa}I_3-e^{qa}I_1\right)+\frac{F}{q+\gamma_1}-\operatorname{sgn}(z'+a)e^{-q|z'+a|} \tag{A4}$$

I_1, I_2, I_3, and F in Eqs. (A2) and (A4) are given by

$$I_1\equiv I_1(z')=\frac{\omega_{p_1}^2(z')}{2\gamma_1\beta^2}\left(\frac{e^{\gamma_1(z'+a)-qa}-e^{qz'}}{q-\gamma_1}+\frac{e^{qz'}}{q+\gamma_1}\right) \quad , \tag{A5}$$

$$I_2\equiv I_2(z')=\frac{\omega_{p_2}^2(z')}{2\gamma_2\beta^2}\left(\frac{e^{\gamma_2z'}-e^{qz'}}{q-\gamma_2}+\frac{e^{qz'}-e^{-\gamma_2(z'+a)-qa}}{q+\gamma_2}\right) \quad , \tag{A6}$$

$$I_3\equiv I_3(z')=\frac{\omega_{p_2}^2(z')}{2\gamma_2\beta^2}\left(\frac{e^{-qz'}-e^{\gamma_2z'}}{q+\gamma_2}+\frac{e^{-\gamma_2(z'+a)+qa}-e^{-qz'}}{q-\gamma_2}\right) \quad , \tag{A7}$$

$$F\equiv F(z')=\frac{1}{2\beta^2}\left(\frac{e^{-\gamma_1|z'+a|}}{\gamma_1}\omega_{p_1}^2(z')-\frac{e^{-\gamma_2|z'+a|}}{\gamma_2}\omega_{p_2}^2(z')\right) \quad , \tag{A8}$$

where

$$\omega_{p_1}^2(z')=4\pi\bar{n}_0\Theta(z'-a) \quad , \tag{A9}$$

$$\omega_{p_2}^2(z')=4\pi\bar{n}_L\Theta(-z')\Theta(z'+a) \quad . \tag{A10}$$

We point out that I_1, I_2, I_3 defined by Eqs. (A5) – (A7) contain no singularity at $q=\gamma_1$ or γ_2 since in each case the numerator vanishes faster than the denominator at $q=\gamma_{1,2}$.

APPENDIX B

We shall write down the response function for a two-step model in this appendix. We define

$$n(z)=\int_{-\infty}^{\infty} dz'\, R(z,z')\rho_{ex}(z') \quad , \tag{B1}$$

where

$$R(z,z')=\frac{1}{\Delta}\left[\left(C_+R_1-b_+R_2\right)e^{-\gamma_2a}+\left(b_-R_2-c_-R_1\right)e^{\gamma_2a}\right]e^{(\gamma_1+z)a}+\frac{e^{\gamma_1(z+a)}}{2\beta^2}\left(\frac{e^{-\gamma_2|z'+a|}}{\gamma_2}\omega_{p_2}^2(z')-\frac{e^{-\gamma_1|z'+a|}}{\gamma_1}\omega_{p_1}^2(z')\right)$$
$$+\frac{\omega_{p_1}^2(z')}{2\gamma_1\beta^2}e^{-\gamma_1|z-z'|}, \quad \text{for } z<-a \quad , \tag{B2}$$

$$=\frac{e^{\gamma_2z}}{\Delta}(C_+R_1-b_+R_2)+\frac{e^{-\gamma_2z}}{\Delta}(b_-R_2-C_-R_1)+\frac{\omega_{p_2}^2(z')}{2\gamma_2\beta^2}e^{-\gamma_2|z-z'|}, \quad \text{for } -a<z<0 \quad , \tag{B3}$$

$$=0 \text{ for } z>0 \quad . \tag{B4}$$

R_1 and R_2 are defined in Appendix A whereas $\Delta=b_-C_+-C_-b_+$ and $b_\pm$, $C_\pm$ are defined in Eqs. (50) – (52) in the main text of the paper. Equation (B4) follows from the fact that $n(z)=0$ outside the metal, i.e., for $z>0$. One can directly show that in the limit of $a\rightarrow 0$ and/or $\omega_{p_1}\rightarrow\omega_{p_2}$, the response function for the two-step model given by Eqs. (B1)–(B4) reduce to that for the one-step case [Eq. (41)].

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