electro-optic absorption using the EMA will appear in a future publication.[15] Some changes from the present results (obtained using the Franz-Keldish theory) have been calculated.[15] It might be possible that one could use a less-strict condition by considering L as the mean free path in a crystal instead of its length. This matter is now under investigation. The second condition (C 2) restricts the range of energy for which the EMA can be applied. It has a simple form and can easily be checked. A similar criterion appears for the impurity problem[3] and for the case of a crystal in a constant magnetic field.[4] In the case of a constant magnetic field, however, this restriction is usually ignored in calculating the optical magnetoabsorption.[16] The condition (C 2) gives also a better qualitative understanding why the EMA cannot be used for the case of an infinite crystal in a constant electric field: It is clear that as the number of nodes of the eigenfunctions increases, the smallest "period" decreases (see the expression for Δx_p above) and the number of Fourier terms needed to represent the function increases. For an infinite crystal, this "period" goes to zero and thus the function cannot be developed in a finite number of terms anymore.

Let us stress again that while for the infinite crystal there is no justification to use the EMA, this approximation was shown to *be* applicable to real (finite) crystals under conditions (C 1) and (C 2).

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Surface-Plasmon Dispersion: A Comparison of Microscopic and Hydrodynamic Theories[*†]

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The hydrodynamic theory of the electron gas, first applied to surface plasmons in metals by Ritchie, is critically examined using the equation of motion for the Wigner distribution function in the random-phase approximation (RPA). It is found that the theory does not agree with the RPA in the case of surface plasmons, though it does for bulk plasmons.

I. INTRODUCTION

In deriving the dispersion relation of surface plasmons in metals, several authors[1-3] have used the hydrodynamical equations for a charged fluid. While one may view with some suspicion the application of these equations to the so-called "collisionless" region, it is nevertheless true that the wave-vector dependence of the bulk-plasmon frequency, calculated by the hydrodynamic theory, is in apparent agreement with the prediction of the random-phase approximation (RPA),[4] to the lowest order in k^2/k_F^2. In addition, the lowest-order correction term in the surface-plasmon dispersion relation is approximately the same as that obtained via an exact solution of the collisionless Boltzmann equation for the case of a sharp metal-vacuum interface.[5]

The present paper constitutes a critical examination of the hydrodynamic theory, taking as a starting point the RPA equation of motion for the Wigner distribution function. It will be shown that an ansatz for the pressure tensor, which is introduced to reduce the hydrodynamic equations to a single equation for the density fluctuation, is valid only when the density fluctuation is spatially slowly varying. This condition is satisfied for long-wavelength bulk plasmons but it is not satisfied for surface plasmons.

Agreement between the hydrodynamical theory and the exact calculation of Wagner[5] is somewhat misleading since it relies on the assumption that a parameter β (which is undetermined by the hydrodynamic theory) is the same for both bulk and surface plasmons. Moreover, the model of the metal surface employed in both calculations is valid only if the detailed behavior of fluctuations in the distribution function is unimportant within a distance $\sim k_F^{-1}$ of the plane surface. For the surface plasmon, this condition is not satisfied and we must conclude that a more careful treatment of the static surface charge density is necessary.

II. HYDRODYNAMIC THEORY

The hydrodynamic equations for a charged fluid are most easily derived from the collisionless Boltzmann equation (or Vlasov equation) for the Wigner distribution function of the system. We have

$$\frac{\partial}{\partial t}+\frac{\vec{p}\cdot\vec{\nabla}_R}{m}\, f(\vec{p},\vec{R},t)=\vec{\nabla}_R U_{\text{eff}}(\vec{R},t)\cdot\vec{\nabla}_p f(\vec{p},\vec{R},t)\ , \tag{2.1}$$

where the Wigner distribution function is given, in terms of the single-particle Green's function, by

$$f(\vec{p},\vec{R},t)\equiv\int d\vec{r}\, e^{-i\vec{p}\cdot\vec{r}}\, G^{<}(\vec{R}+\tfrac{1}{2}\vec{r},t;\vec{R}-\tfrac{1}{2}\vec{r},t)\ , \tag{2.2}$$

and the local effective field is defined by

$$U_{\text{eff}}(\vec{R},t)\equiv U_{\text{ext}}(\vec{R},t)+e^2\int d\vec{R}'\,\frac{n(\vec{R}',t)}{|\vec{R}-\vec{R}'|}\ . \tag{2.3}$$

The density of particles is

$$n(\vec{R},t)\equiv\int\frac{d\vec{p}}{(2\pi)^3}\, f(\vec{p},\vec{R},t)\ . \tag{2.4}$$

In metallic surface problems, the externally imposed field $U_{\text{ext}}(\vec{R},t)$ can be taken to represent the effect of a static ionic charge background, $-eN_0(\vec{R})$ $(e<0)$, against which the electrons are free to move. It is then often more convenient to write (2.3) in differential form

$$\nabla^2 U_{\text{eff}}(\vec{R},t)=-4\pi e^2[n(\vec{R},t)-N_0(\vec{R})]\ . \tag{2.5}$$

It is not obvious that the collisionless Boltzmann equation is applicable to inhomogeneous systems where the distribution function varies rapidly in space. This question is discussed in Sec. III.

Taking the zero and first moments of (2.1), one easily derives the familiar equations for the so-called local hydrodynamic variables, namely,

$$\frac{\partial}{\partial t}\, n(\vec{R},t)+\vec{\nabla}_R\cdot[n(\vec{R},t)\vec{u}(\vec{R},t)]=0\ , \tag{2.6}$$

$$mn(\vec{R},t)\left(\frac{\partial}{\partial t}+\vec{u}(\vec{R},t)\cdot\vec{\nabla}_R\right)\vec{u}(\vec{R},t)=n(\vec{R},t)\vec{F}(\vec{R},t)-\vec{\nabla}_R\cdot\overleftrightarrow{\Pi}(\vec{R},t)\ , \tag{2.7}$$

where

$$\vec{u}(\vec{R},t)\equiv\int\frac{d\vec{p}}{(2\pi)^3}\,\frac{\vec{p}}{m}\, f(\vec{p},\vec{R},t)\ , \tag{2.8}$$

$$\vec{F}(\vec{R},t)\equiv-\vec{\nabla}_R U_{\text{eff}}(\vec{R},t)\ , \tag{2.9}$$

$$\overleftrightarrow{\Pi}(\vec{R},t)\equiv m\int\frac{d\vec{p}}{(2\pi)^3}\left(\frac{\vec{p}}{m}-\vec{u}\right)\left(\frac{\vec{p}}{m}-\vec{u}\right) f(\vec{p},\vec{R},t). \tag{2.10}$$

We wish to consider small deviations from equilibrium described by the infinitesimal fluctuation in the Wigner distribution function

$$\delta f(\vec{p},\vec{R},t)\equiv f(\vec{p},\vec{R},t)-f_0(\vec{p},\vec{R})\ . \tag{2.11}$$

Linearizing (2.6) and (2.7) in infinitesimals and assuming that $\vec{u}_0(\vec{R})=0$ we have the basic equations of the hydrodynamic theory,

$$\frac{\partial}{\partial t}\delta n(\vec{R},t)+\vec{\nabla}_R\cdot[n_0(\vec{R})\delta\vec{u}(\vec{R},t)]=0\ , \tag{2.12}$$

$$mn_0(\vec{R})\frac{\partial}{\partial t}\,\delta\vec{u}(\vec{R},t)=n_0(\vec{R})\delta\vec{F}(\vec{R},t)+\vec{F}_0(\vec{R})\delta n(\vec{R},t)-\vec{\nabla}_R\cdot\delta\overleftrightarrow{\Pi}(\vec{R},t)\ . \tag{2.13}$$

We note explicitly the definitions of $\delta\overleftrightarrow{\Pi}(\vec{R},t)$ and $\delta\vec{F}(\vec{R},t)$,

$$\delta\overleftrightarrow{\Pi}(\vec{R},t)\equiv\frac{1}{m}\int\frac{d\vec{p}}{(2\pi)^3}\,\overleftrightarrow{pp}\,\delta f(\vec{p},\vec{R},t)\ , \tag{2.14a}$$

$$\delta\vec{F}(\vec{R},t)\equiv-\vec{\nabla}_R\delta U_{\text{eff}}(\vec{R},t)=-e^2\vec{\nabla}_R\int d\vec{R}'\,\frac{\delta n(\vec{R}',t)}{|\vec{R}-\vec{R}'|}\ . \tag{2.14b}$$

In order to form a closed set of equations it is customary to make an ansatz linking the pressure-tensor fluctuation $\delta\overleftrightarrow{\Pi}$ with the density fluctuation δn, namely,

$$\vec{\nabla}_R\cdot\delta\overleftrightarrow{\Pi}(\vec{R},t)=m\beta^2\vec{\nabla}_R\delta n(\vec{R},t)\ , \tag{2.15}$$

where β is an undetermined constant.

For a truly hydrodynamic mode, where the distribution function is of the local equilibrium form, (2.15) is trivally satisfied since (for zero-temperature fermions)

$$\delta\overleftrightarrow{\Pi}(\vec{R}, t) = \tfrac{1}{3} m v_F^2 \delta n(\vec{R}, t) \overleftrightarrow{I} , \qquad (2.16)$$

where v_F is the Fermi velocity. In such a case the fluctuation in the Wigner function is of the form

$$\delta f(\vec{p}, \vec{R}, t) = [\vec{p} \cdot \vec{u}(\vec{R}, t) - \delta \mu(\vec{R}, t)] \frac{\partial}{\partial \epsilon_p} f(\epsilon_p) , \qquad (2.17)$$

where $f(\epsilon_p)$ is the normalized Fermi function, $\epsilon_p = p^2/2m$, and $\delta \mu(\vec{R}, t)$ is the fluctuation in the local chemical potential. With the aid of the ansatz (2.15), Eqs. (2.12) and (2.13) reduce to a single differential equation for the density fluctuation,

$$m \frac{\partial^2}{\partial t^2} \delta n(\vec{R}, t) = - \vec{\nabla}_R \cdot [n_0(\vec{R}) \delta \vec{F}(\vec{R}, t) + F_0(\vec{R}) \delta n(\vec{R}, t)] + m \beta^2 \nabla_R^2 \delta n(\vec{R}, t) . \qquad (2.18)$$

In a region of constant electron density, (2.18) has the simple solution

$$\delta n(\vec{R}, t) = \delta \bar{n}\, e^{i(\vec{k} \cdot \vec{R} - \omega t)} , \qquad (2.19)$$

provided that

$$\omega^2 = \omega_p^2 + \beta^2 k^2 , \qquad (2.20)$$

where

$$\omega_p^2 \equiv 4\pi \bar{n} e^2 / m .$$

Equation (2.20) is the dispersion relation of bulk plasmons and agrees with that obtained from microscopic theory[4] if one makes the identification

$$\beta^2 = \tfrac{3}{5} v_F^2 . \qquad (2.21)$$

We note that this value of β is not the same as that predicted by (2.16). This is no surprise since the bulk plasmon is not a hydrodynamic mode and is accompanied by a fluctuation in the Wigner distribution function which has a form[6] quite different from that given by (2.17).

In order to describe surface modes it is necessary to construct a model of the metal surface. A simple and extensively exploited model amounts to representing the equilibrium electronic and ionic densities by step functions,

$$n_0(\vec{R}) = N_0(\vec{R}) \equiv \bar{n} \Theta(Z) . \qquad (2.22)$$

According to (2.3) this assumption implies that $\vec{F}_0(\vec{R}) = 0$, so there is no surface charge dipole, and the metal is bound only by exchange and correlation potentials. This is possible[7] only for $r_s \gtrsim 3$ (r_s = Wigner-Seitz radius). Within the model implied by (2.22), Eq. (2.18) becomes, for $Z > 0$,

$$\frac{\partial^2}{\partial t^2} \delta n(\vec{R}, t) = - \frac{\bar{n}}{m} \vec{\nabla}_R \cdot \delta \vec{F}(\vec{R}, t) + \beta^2 \nabla^2 \delta n(\vec{R}, t) . \qquad (2.23)$$

With the aid of (2.5) it is easy to see that the solution of this equation which oscillates in the (X, Y) direction and vanishes at $Z = +\infty$ is

$$\delta n(\vec{R}, t) = \delta \bar{n} e^{-\gamma Z} e^{i(\vec{k}_{\parallel} \cdot \vec{R}_{\parallel} - \omega t)} , \qquad (2.24)$$

where

$$\gamma^2 \equiv (\omega_p^2 - \omega^2 + \beta^2 k_{\parallel}^2) / \beta^2$$

and $k_{\parallel}$ is the wave vector parallel to the surface. To ensure that electrons do not escape from the half-plane one must impose the boundary condition that the fluid velocity in the Z direction vanishes as $Z \rightarrow 0^+$, that is,

$$u_z(\vec{R}, t) \big|_{Z = 0^+} = 0 . \qquad (2.25)$$

Using (2.25) in the local velocity equation (2.13), it is easy to obtain the dispersion relation of surface plasmons,

$$\omega^2 = \omega_{SP}^2 [1 + (\beta k_{\parallel} / \omega_{SP}) + O(k_{\parallel}^2 / \omega_{SP}^2)] , \qquad (2.26)$$

where $\omega_{SP} = \omega_p / \sqrt{2}$ is the zero-wave-vector surface-plasmon frequency.

It is customary to use the value of β given by (2.21) in order to estimate the contribution of the linear correction term, although there is no *a priori* reason for so doing. The magnitude of the constant multiplying $k_{\parallel}$ then agrees with the value obtained by Wagner,[5] who solved Eq. (1) exactly using the same model and employing the boundary condition of specular reflection at the surface.

Having outlined the hydrodynamical theory, we now turn to the RPA equations and examine the circumstances under which they support the crucial assumption (2.15).

III. RPA EQUATION OF MOTION

The basic equation we will use is derived in Ref. 6, Chap. 7 [Eq. (7.6)] and may be written

$$\left(\frac{\partial}{\partial t} + \frac{\vec{p} \cdot \vec{\nabla}_R}{m}\right) f(\vec{p}, \vec{R}, t) = 2 \int d\vec{R}' \int \frac{d\vec{p}'}{(2\pi)^3} \sin[(\vec{p}' - \vec{p}) \cdot \vec{R}'] \times f(\vec{p}', \vec{R}, t) U_{\text{eff}}\left(\vec{R} + \frac{\vec{R}'}{2}, t\right) , \qquad (3.1)$$

where $U_{\text{eff}}(\vec{R}, t)$ is given by (2.3). The application of this equation to the problem of surface collective modes has been described in detail by Griffin and the author.[8,9] With the assumption that the equilibrium system is spatially inhomogeneous only in the Z direction and that propagating surface modes are described by the distribution function

$$f(\vec{p}, \vec{R}, t) = f_0(\vec{p}, Z) + \delta f(\vec{p}, Z) e^{i(\vec{k}_{\parallel} \cdot \vec{R}_{\parallel} - \omega t)} , \qquad (3.2)$$

Eq. (3.1) leads to the following linearized equation for $\delta f(\vec{p}, Z)$:

$$\left(\omega-\frac{\vec{p}_{\parallel}\cdot\vec{k}_{\parallel}}{m}\right)\delta f(\vec{p},Z)=-i\frac{p_z}{m}\frac{\partial}{\partial Z}\delta f(\vec{p},Z)+2i\int d\vec{R}'\int\frac{d\vec{p}'}{(2\pi)^3}\sin[(\vec{p}'-\vec{p})\cdot\vec{R}']\,e^{ik_{\parallel}\cdot R'_{\parallel}/2}$$
$$\times f_0(\vec{p}',Z)\delta U_{\text{eff}}\left(Z+\frac{Z'}{2}\right)+2i\int dZ'\int\frac{dp'_z}{(2\pi)}\sin[(p'_z-p_z)Z']\,U^0_{\text{eff}}\left(Z+\frac{Z'}{2}\right)\delta f(\vec{p}_{\parallel},p'_z,Z)\;. \qquad (3.3)$$

Equation (3.3) may be used to derive an expression for the surface-plasmon dispersion relation, making no assumption about the static Wigner function and the static self-consistent field $U^0_{\text{eff}}(Z)$ other than that they reach values characteristic of the bulk (vacuum) for $Z>\delta\,(Z<\delta)$, where δ is a "skin-depth" parameter of order k_F^{-1}. One may then show[9] that

$$\omega^2=\omega_{\text{SP}}^2[1+Ak_{\parallel}+O(k_{\parallel}^2/k_F^2)]\;, \qquad (3.4)$$

where

$$A=\lim_{k_{\parallel}\to 0}\left(\int_{-\infty}^{\infty}dZ\,Z\delta n(Z)\Big/\int_{-\infty}^{\infty}dZ\,\delta n(Z)\right)$$
$$+\int_{-\infty}^{\infty}dZ\,[n_0(Z)-\bar{n}\Theta(Z)]\;. \qquad (3.5)$$

Here, $\delta n(Z)\equiv\int[dp/(2\pi)^3]\delta f(\vec{p},Z)$ is the density fluctuation associated with the surface plasmon. It is clear from the form of (3.5) that the value of A may be quite sensitive to the exact form of the density fluctuation, which must be obtained by solving the equation of motion (3.3).

In order to reduce (3.3) to more manageable proportions we note that the fluctuation potential satisfies (2.5), so that

$$\delta U_{\text{eff}}(Z)=(2\pi e^2/k_{\parallel})\int dZ'\,e^{-k_{\parallel}|Z-Z'|}\delta n(Z')\;. \qquad (3.6)$$

The variation of $\delta U_{\text{eff}}(Z)$ in Z is thus governed by $e^{-k_{\parallel}|Z|}$, and a Taylor expansion of the exponential in (3.6) leads to a power series in $k_{\parallel}\delta$, where δ is the skin-depth parameter mentioned earlier. One may retain only the first nonzero term in such an expansion to an accuracy of order $(\delta k_{\parallel})^2$, that is, $k_{\parallel}^2/k_F^2$. If in addition we write

$$f_0(\vec{p}_{\parallel}-\tfrac{1}{2}\vec{k}_{\parallel},p_z,Z)-f_0(\vec{p}_{\parallel}+\tfrac{1}{2}\vec{k}_{\parallel},p_z,Z)$$
$$\simeq-\vec{k}_{\parallel}\cdot\vec{\nabla}_{p_{\parallel}}f_0(\vec{p}_{\parallel},p_z,Z)\;, \qquad (3.7)$$

an approximation correct also to order $k_{\parallel}^2/k_F^2$, the term containing $\delta U_{\text{eff}}(Z)$ on the right-hand side of (3.3) reduces to

$$-\vec{k}_{\parallel}\cdot\vec{\nabla}_{p_{\parallel}}f_0(\vec{p},Z)\delta U_{\text{eff}}(Z)+i\frac{\partial}{\partial p_z}f_0(\vec{p},z)\frac{\partial}{\partial z}\delta U_{\text{eff}}(Z)\;. \qquad (3.8)$$

Analogous considerations may not be used to simplify the final term on the right-hand side of (3.3) since the static field is not slowly varying close to the surface. However, if one Taylor expands $U^0_{\text{eff}}(Z+\frac{1}{2}Z')$ about Z, retaining all derivatives, one can reduce this term to

$$i\sum_{n=0}^{\infty}\frac{(-1)^n}{2^{2n}(2n+1)!}\,\frac{\partial^{2n+1}}{\partial Z^{2n+1}}\,U^0_{\text{eff}}(Z)\frac{\partial^{2n+1}}{\partial p_z^{2n+1}}\,\delta f(\vec{p}_{\parallel},p_z,Z)\;. \qquad (3.9)$$

Provided this series converges rapidly, one is justified in replacing the "nonlocal" term on the right-hand side of (3.3) by the "local" term (3.9). Retaining only the first term in (3.9) leads to the result one would obtain starting from the collisionless Boltzmann equation, namely,

$$\left(\omega-\frac{\vec{p}_{\parallel}\cdot\vec{k}_{\parallel}}{m}\right)\delta f(\vec{p},Z)=-\vec{k}_{\parallel}\cdot\vec{\nabla}_{p_{\parallel}}f_0(\vec{p},Z)\delta U_{\text{eff}}(Z)+i\frac{\partial}{\partial p_z}f_0(\vec{p},Z)\frac{\partial}{\partial Z}\delta U_{\text{eff}}(Z)+i\frac{\partial}{\partial Z}\,U^0_{\text{eff}}(Z)\frac{\partial}{\partial p_z}\delta f(\vec{p},z)$$
$$-i\frac{p_z}{m}\frac{\partial}{\partial Z}\delta f(\vec{p},Z)\;. \qquad (3.10)$$

The validity of this approximation is verifiable only by explicit calculation of $\delta f(\vec{p},Z)$ using (3.10), and substitution in (3.9) to check the behavior of higher-order derivatives. Since the coefficients of these derivatives rapidly become very small $(1,\frac{1}{24},\frac{1}{1920}\ldots)$, it is possible that the collisionless Boltzmann equation is a useful approximation even when the effective field is varying quite rapidly in space.

We now return to the step-function density profile model of the metal surface utilized in Sec. II. We recall that the equilibrium distribution function was assumed to be

$$f_0(\vec{p},Z)=\bar{n}f(\epsilon_p)\Theta(Z)\;. \qquad (3.11)$$

From the form of (3.10) it is apparent that an approximation of this kind is only justifiable if the behavior of $\delta f(\vec{p},Z)$ close to the surface is relatively unimportant. In that event, for $Z>0$, we may write (3.10)

$$\delta f(\vec{p},Z)=\left(-\bar{n}\vec{k}_{\parallel}\cdot\vec{\nabla}_{p_{\parallel}}f(\epsilon_p)\delta U_{\text{eff}}(Z)+i\bar{n}\frac{\partial}{\partial p_z}f(\epsilon_p)\frac{\partial}{\partial Z}\delta U_{\text{eff}}(Z)\right)\Big/\left(\omega-\frac{\vec{p}_{\parallel}\cdot\vec{k}_{\parallel}}{m}\right)-i\frac{p_z}{m}\Big/\left(\omega-\frac{\vec{p}_{\parallel}\cdot\vec{k}_{\parallel}}{m}\right)\frac{\partial}{\partial Z}\delta f(\vec{p},Z)\,. \qquad (3.12)$$

Although the formal solution of (3.12) is simple to write down,[5] it is less simple to work with. In order to exhibit the relation between (3.12) and the equations of the hydrodynamic theory, we adopt an iteration procedure to relate $\delta f(\vec{p}, Z)$ to $\delta U_{\text{eff}}(Z)$. That is, writing (3.12) in the symbolic form

$$\delta f(\vec{p}, Z) = \kappa + \hat{\Lambda}\delta f(\vec{p}, Z) , \qquad (3.13)$$

where κ represents the first term on the right-hand side and

$$\hat{\Lambda} \equiv -i\frac{p_z}{m} \bigg/ \left(\omega - \frac{\vec{p}_{\parallel}\cdot\vec{k}_{\parallel}}{m}\right) \frac{\partial}{\partial Z} ,$$

we may generate a series expansion in $(\omega - \vec{p}_{\parallel}\cdot\vec{k}_{\parallel}/m)^{-1}$ by iteration:

$$\delta f = \kappa + \hat{\Lambda}\kappa + \hat{\Lambda}^2\kappa + \cdots . \qquad (3.14)$$

Integrating (3.14) over all momenta and employing (3.6) to link $\delta U_{\text{eff}}(Z)$ to $\delta n(Z)$ we finally arrive at the equation

$$\delta n(Z) = \omega_p^2 \sum_{n=0}^{\infty} (-1)^n (2n+1) \frac{\partial^{2n}}{\partial Z^{2n}} \delta n(Z)$$
$$\times \int \frac{d\vec{p}}{(2\pi)^3} \left(\frac{p_z}{m}\right)^{2n} f(\epsilon_p) \bigg/ \left(\omega - \frac{\vec{p}_{\parallel}\cdot\vec{k}_{\parallel}}{m}\right)^{2n+2} , \qquad (3.15)$$

which the solution of (3.12) must satisfy. For convenience we take the $k_{\parallel} = 0$ limit. This does not affect conclusions and it enables one to simplify (3.15) to

$$\delta n(Z) = \frac{\omega_p^2}{\omega^2} \sum_{n=0}^{\infty} (-1)^n \frac{3}{(2n+3)} \left(\frac{v_F}{\omega}\right)^{2n} \frac{\partial^{2n}}{\partial Z^{2n}} \delta n(Z) . \qquad (3.16)$$

Under the same conditions, the basic equation of the hydrodynamic theory, Eq. (2.18), has the form

$$\delta n(Z) = \frac{\omega_p^2}{\omega^2} \delta n(Z) - \frac{\beta^2}{\omega^2} \frac{\partial^2}{\partial Z^2} \delta n(Z) . \qquad (3.17)$$

Equation (3.17) follows from (3.16) if one neglects all terms on the right-hand side but the first two, and if one makes the identification

$$\beta^2 \equiv \tfrac{3}{5} v_F^2 \, \omega_p^2/\omega^2 . \qquad (3.18)$$

For bulk plasmons (3.18) is the same as (2.21). However, since β is a function of ω, it will be different from (2.21) for surface plasmons [see the comment following (2.26)]. Moreover, the hydrodynamic theory agrees with the RPA only if the expansion on the right-hand side of (3.16) converges rapidly. For bulk plasmons, $\delta n(Z) \sim e^{iZk_z}$ so that for small wave vectors this condition is satisfied, and (3.16) gives the RPA dispersion relation for a bulk-plasmon mode propagating in the Z direction, namely,

$$\omega^2 = \omega_p^2 + \tfrac{3}{5} v_F^2 k_z^2 + O(k_z^4/\omega_p^4) . \qquad (3.19)$$

However, for surface plasmons, the simple exponential decay predicted by the hydrodynamic theory, $\delta n(Z) \sim e^{-\gamma_0 Z}$, where γ_0 is given by (2.24) with $k_{\parallel} = 0$, leads to an expansion parameter $(\gamma_0^2 v_F^2/\omega^2)$ for the right-hand side of (3.16). For $\omega = \omega_{\text{SP}}$, this parameter is of order unity, and the expansion fails. In fact, by rearranging the series into trigonometric form, one can easily show that $e^{-\lambda Z}$ is not a solution of (3.16) whatever the value of λ. The reason for the failure of the hydrodynamic theory is that the ansatz (2.15) for the pressure tensor is not correct for the surface-plasmon mode. One can show this directly by multiplying (3.12) across by p_z^2 and following an equivalent iteration procedure to that outlined above. On differentiating, one obtains an expression for $(\partial/\partial Z)(\delta\Pi_{zz})$ which is in the form of a series expansion in derivatives of $\delta n(Z)$. The first term corresponds to the ansatz (2.15), with β given by (3.18), but the series converges slowly for the surface plasmon.

The considerations of the preceding paragraph indicate that the hydrodynamical theory does not correctly describe the physics of surface plasmons even for the simplest possible model of the metal surface. That Wagner's calculation[5] of the linear dispersion approximately agrees with (2.26) [with β given by (2.21)] should not be regarded as significant. The reason why one would expect such agreement within the framework of a half-space model will be given in a future paper.[10]

As we observed earlier, the model described by (2.22) or (3.11) is only valid when the detailed spatial variation of $\delta f(\vec{p}, Z)$ or $\delta n(Z)$ close to the surface is unimportant. However, even for the exact calculation of Wagner, the density fluctuation becomes very small at distances greater than v_F/ω_{SP}, which for all metals is $\sim k_F^{-1}$. Thus the fluctuation in density is solely confined to a region of the same spatial extent as the diffuseness in the static electronic density. Insofar as application to a real metal is concerned, the results of these model calculations conflict with the assumption one must make in constructing the model. A more detailed discussion of half-space models and also of infinite-barrier models is given in Ref. 10.

IV. CONCLUDING REMARKS

In this paper, it has been shown that microscopic theory, based on the RPA, does not support the use of Ritchie's hydrodynamic equations[1,3] to calculate dispersion relations for surface plasmons in metals. As shown in Sec. III, it may be possible to approximate the RPA equation of motion (3.1) by the collisionless Boltzmann equation even though the static effective field does not vary slowly in space. The validity of this approximation is only verifiable at the end of a calculation, when the form of $\delta f(\vec{p}, Z)$ has been determined. Although the collisionless Boltzmann equation has been exactly solved for a half-space,[5] one cannot apply the solution to experimental data on metals where the surface diffuseness has the same spatial extent as the calculated density fluctuation.[10]

It is readily apparent that the presence of the term containing $U^0_{\text{eff}}(Z)$ enormously complicates the mathematical problem of solving (3.10). In Wagner's half-space calculation, and in much of the literature on plasma physics, this term is replaced by a boundary condition on $\delta f(\vec{p}, Z)$. As we have argued, this procedure is not self-consistent for the case of surface plasmons in metals. In his hydrodynamical calculation of the surface-plasmon dispersion relation, Bennett[3] includes the effect of the static charge dipole, assuming that the charge density profiles for ions and electrons are linear. However, he uses an ansatz equivalent to (2.15) and determines β for the surface mode by identification with the bulk-mode dispersion relation. Neither assumption appears to be supported by the RPA.

The estimation of correction terms in the surface-plasmon dispersion relation would seem less simple than it may have initially appeared in earlier work. According to the discussion of Sec. III, the very least one has to do is to solve Eq. (3.10) or its equivalent, treating the surface dipole potential $U^0_{\text{eff}}(Z)$ correctly. Since electrons are subject to effects due to changes in exchange and correlation close to the surface, one may also question whether it is sufficient to include only the electrostatic dipole potential $U^0_{\text{eff}}(Z)$. Recent calculations by Lang and Kohn[7] indicate that the contribution of the dipole potential to the work function at "jellium" surfaces is entirely negligible for $r_s \simeq 5$, but becomes comparable with the exchange and correlation contributions for $r_s \lesssim 2.5$. One feels, therefore, that for small r_s, it may be adequate to treat the variation in the exchange and correlation energy close to the surface in a relatively crude fashion. There is no *a priori* reason why this should be true for larger values of r_s.

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