in order to leave the link in a state with a small net phase difference so that the order parameter can have a chance to regrow. A multiple phase slip at a given spot is still highly improbable, however, since $F_{4\pi}$ is much larger than $F_{2\pi}$. Instead, the phase slips by 2π across some small region, and the order parameter in the immediate vicinity of the phase slip begins to grow. If the 2π phase slip were not enough, the phase slips again by 2π at some other spot. The order parameter in the region of the first phase slip begins to grow, so if another 2π phase slip is needed, it cannot happen at the first place since locally the order parameter has grown out of the region in which the thermal fluctuations dominate the behavior. In a long link there can be a fairly large region in which the order parameter is very small. The exact position of the phase slip is determined by the detailed nature of the fluctuations and in this large depressed region is more or less random. All this implies that phase slip is a noisy process in a long weak link.

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Localized Modes of Excitation of an Electron Gas in the Vicinity of an Impurity in Metals

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Modes of vibration of an electron gas in a uniform background of positive charge containing a fixed point charge are investigated. A hydrodynamic model is used in which the electrons are treated as a Fermi fluid. It is found that a localized excitation of electron gas may exist near a positive impurity. Such a local excitation can be detected in characteristic energy losses of fast electrons.

INTRODUCTION

Excitations of a homogeneous electron gas embedded in a uniform background of positive charge have been studied extensively.[1] The excitations of a nonhomogeneous system are not so well understood. We consider the collective oscillations of an electron gas in the presence of a fixed point impurity. Layzer[2] has shown that in the vicinity of a positive impurity localized single-particle excitations may exist. Sziklas[3] and Sham[4] have found that a plasmon-type excitation with frequency $\sim \omega_0/\sqrt{2}$ exists in the vicinity of a negative impurity under appropriate conditions. Here ω_0 is the plasma frequency of the homogeneous medium. The previous authors have used a quantum approach to the problem. However, in using a quantum approach one does not have a physical picture of the processes involved, as one has in the hydrodynamic approach. Hence Sziklas[3] and Sham[4] have also

used crude hydrodynamic models to provide a qualitative check on the results of their microscopic theories. Because of the simplicity and the ease of interpretation of a hydrodynamic model we feel it worthwhile to present a more systematic derivation of the equation for the modes of vibration of an electron gas based on a hydrodynamic model.

We investigate the modes of vibration of small density fluctuations of the nonhomogeneous electron system. We regard the electron system as a charged Fermi fluid, and determine the motion of the fluctuations due to electric and pressure forces through Euler's equation and the equation of continuity. Both the pressure and electrostatic forces are related to the density through Poisson's equation and the equation of state for a Fermi fluid. By assuming a simple periodic time dependence for the density fluctuations and substituting for the forces in terms of the density in the hydrodynamic equations, we are led to an eigenvalue equation for the frequencies of vibration of the electron gas. This equation contains extra terms that do not appear in similar equations obtained by other authors.[3,4] We find that in the presence of a positive impurity, localized modes of excitation of the electron gas exist and that they have frequencies higher than the frequencies of oscillation of the uniform electron gas. The existence of these modes has not been established before.

CALCULATIONS

We present a hydrodynamic treatment of an electron gas interacting with an impurity of charge Ze imbedded in a uniform background of positive charge of density $e\rho_0$. The equilibrium electron number density may be expanded as a Fourier series in a box of volume Ω with periodic boundary conditions as follows:

$$\rho(\vec{r}) = \rho_0 + \sum_{\vec{k}\neq 0} \rho_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}. \tag{1}$$

Associated with the equilibrium charge density is an electric field $\vec{E} = -\vec{\nabla}\Phi$, where Φ is given by Poisson's equation:

$$\nabla^2\Phi = +4\pi e\left(\sum_{\vec{k}\neq 0} \rho_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} - \frac{Z}{\Omega}\sum_{\vec{k}\neq 0} e^{i\vec{k}\cdot\vec{r}}\right). \tag{2}$$

Expanding the potential as

$$\Phi = \sum_{\vec{k}} \phi_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}, \tag{3}$$

we obtain from (2)

$$\phi_{\vec{k}} = (4\pi e/k^2)(Z/\Omega - \rho_{\vec{k}}). \tag{4}$$

If now the electron density is displaced slightly from equilibrium, a small fluctuating density $\delta\rho(\vec{r}, t)$ is induced in the medium. We assume a simple periodic time dependence for $\delta\rho(\vec{r}, t)$, i.e.,

$$\delta\rho(\vec{r}, t) = [\sum_{\vec{k}\neq 0} \sigma_{\vec{k}}(\omega) e^{i\vec{k}\cdot\vec{r}}] e^{i\omega t}. \tag{5}$$

Because of the presence of the impurity, each Fourier component $\sigma_{\vec{k}}(\omega)$ will not oscillate independently as in the case of a homogeneous medium. In the present case for each frequency ω a set of $\sigma_{\vec{k}}(\omega)$ will contribute to the fluctuating charge density $\delta\rho(\vec{r}, t)$. The time-dependent fluctuation produces a potential

$$\Psi(\vec{r}, t) = (\sum_{\vec{k}\neq 0} \psi_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}) e^{i\omega t}, \tag{6}$$

where from Poisson's equation

$$\psi_{\vec{k}} = -(4\pi e/k^2)\sigma_{\vec{k}}.$$

Φ and Ψ together determine the electric field in the material.

In equilibrium the electric force on a local element of charge density is balanced by a force produced through a pressure gradient. Under nonequilibrium conditions the resultant of these two forces produces local accelerations of the fluid. At high frequencies characteristic of plasma oscillations the expression for pressure as a function of density should be modified from that at equilibrium (see Sham[4] and Jackson[5]). For a noninteracting Fermi gas (assuming an instantaneous local Fermi level) the pressure is

$$\begin{aligned} P_0 &= \tfrac{2}{5}F\rho^{5/3} \quad \text{(equilibrium)}, \\ P(t) &= \tfrac{18}{25}F n^{5/3} \quad \text{(high frequency)}, \end{aligned} \tag{7}$$

where

$$\begin{aligned} F &= (\hbar^2/2m)(3\pi^2)^{2/3}, \\ n(\vec{r}, t) &= \rho(\vec{r}) + \delta\rho(\vec{r}, t). \end{aligned} \tag{8}$$

Use of the high-frequency expression for the pressure leads to a dispersion relation for the plasma oscillations of a uniform system that agrees with the one obtained by a micorscopic treatment.

Euler's equation for the electron fluid is

$$mn\frac{d\vec{v}}{dt} = -\operatorname{grad}P(t) + en\operatorname{grad}(\Phi + \Psi), \tag{9}$$

where $\vec{v}$ is the mean velocity of the fluid at a point $\vec{r}$ and t. We also have the equation of continuity

$$\operatorname{div} n\vec{v} + \dot{n} = 0. \tag{10}$$

Combining Eqs. (9) and (10) and keeping terms linear in $\vec{v}$ and $\dot{n}$, we obtain

$$m\frac{\partial^2 n}{\partial t^2} = \operatorname{div}\{[\operatorname{grad}P(t) - en\operatorname{grad}(\Phi + \Psi)]\}. \tag{11}$$

Substituting for P and n in Eq. (11) from (7) and (8) and keeping terms linear in $\delta\rho(\vec{r}, t)$ and $\Psi(\vec{r}, t)$, we have

$$m\frac{\partial^2}{\partial t^2}\delta\rho(\vec{r},t)=\mathrm{div}\,\mathrm{grad}\left[F[\rho(\vec{r})]^{5/3}\frac{18}{25}\left(1+\frac{5}{3}\frac{\delta\rho(\vec{r},t)}{\rho(\vec{r})}\right)\right]-e\,\mathrm{div}[\rho(\vec{r})\,\mathrm{grad}(\Phi+\Psi)+\delta\rho(\vec{r},t)\,\mathrm{grad}\Phi]\ . \quad (12)$$

The time-independent part of Eq. (12) is not to be considered as the condition for equilibrium in view of the meaning given to $P(t)$.

The equation for the density distribution of the electron gas in equilibrium is

$$0=-\mathrm{grad}P_0+e\rho\,\mathrm{grad}\Phi\ . \quad (13)$$

Equation (13) is the gradient of the Thomas-Fermi condition for equilibrium:

$$F\rho^{2/3}-e\phi=F\rho_0{}^{2/3}\ . \quad (14)$$

The time-dependent part of Eq. (12) gives

$$\frac{\omega^2}{\omega_0^2}\sigma_{\vec{q}}=\frac{9}{5}\frac{q^2}{k_0^2}\sigma_{\vec{q}}+\sigma_{\vec{q}}+\sum_{\vec{k}'\neq\vec{q}}\frac{\vec{q}\cdot\vec{k}'}{k'^2}\frac{\rho_{\vec{q}-\vec{k}'}}{\rho_0}\sigma_{\vec{k}'}+\sum_{\vec{k}'\neq\vec{q}}\frac{\vec{q}\cdot(\vec{q}-\vec{k}')}{|\vec{q}-\vec{k}'|^2}\left(\frac{\rho_{\vec{q}-\vec{k}'}}{\rho_0}-\frac{Z}{\rho_0\Omega}\right)\sigma_{\vec{k}'}$$
$$+\left(\frac{9}{5}\right)\left(\frac{2}{3}\right)\sum_{\vec{k}'\neq\vec{q}}\frac{q^2}{k_0^2}\left(\frac{\rho_{\vec{q}-\vec{k}'}}{\rho_0}\right)\sigma_{\vec{k}'}\ , \quad (15)$$

where

$$\omega_0^2=4\pi\rho_0 e^2/m$$

and

$$k_0^2=4\pi\rho_0 e^2/\tfrac{2}{3}F\rho_0{}^{2/3}\ .$$

In obtaining Eq. (15) we have substituted for $\rho(\vec{r})$, $\Phi(\vec{r})$, $\delta\rho(\vec{r},t)$, and $\Psi(\vec{r},t)$ in (12) from Eqs. (1), (3), (5), and (6), and used Eqs. (4) and (7) to eliminate $\phi_{\vec{k}}$ and $\Psi_{\vec{k}}$.

We note that $\rho_{\vec{q}}(q\neq 0)$ is zero in the absence of an impurity. Hence for a uniform medium the last three terms in Eq. (15) vanish, giving us a dispersion relation $\omega^2=\omega_0^2[1+\frac{9}{5}(q^2/k_0^2)]$.

If we just neglect the last two terms on the right-hand side of Eq. (15) we obtain an equation which would be identical with the equations obtained by Sziklas[3] and Sham,[4] if the term $\frac{9}{5}(q^2/k_0^2)\sigma_{\vec{q}}$ was replaced by $\frac{9}{5}(\omega_0^2/\omega^2)(q^2/k_0^2)\sigma_{\vec{q}}$. The third term in Eq. (15) arises through the Coulomb interaction of the nonuniform (equilibrium) electron charge density with the potential produced by the fluctuations. The origin of the two extra terms is as follows: The first of these arises through the Coulomb interaction of the fluctuation with the potential produced by the nonuniform (equilibrium) electron charge density and by the fixed impurity. The second of these comes from the change in pressure due to fluctuations superimposed on the nonuniform charge density. It will be seen later that these last two terms are comparable with the third term in certain cases.

Equation (15) cannot be solved without the knowledge of $\rho_{\vec{k}}$. In the linearized Thomas-Fermi approximation,

$$\rho_{\vec{k}}=\frac{Z/\Omega}{1+(k^2/k_0^2)}\ . \quad (16)$$

Substituting for $\rho_{\vec{q}-\vec{k}'}$ from (16) we have

$$\left(\frac{\omega^2}{\omega_0^2}-1-\frac{9}{5}\frac{q^2}{k_0^2}\right)\sigma_{\vec{q}}=\frac{Z}{\Omega}\frac{1}{\rho_0}$$
$$\times\sum_{\vec{k}'}\left(\frac{\vec{q}\cdot\vec{k}'[(k_0^2/k'^2)+1]+\frac{1}{5}q^2}{k_0^2+|\vec{q}-\vec{k}'|^2}\right)\sigma_{\vec{k}'}\ . \quad (17)$$

Expanding $\sigma_{\vec{k}}$ in spherical harmonics, we get

$$\sigma_{\vec{q}}=\sum_{lm}=\sigma_q(lm)\,Y_l^m(\theta_{q'},\phi_q)\ , \quad (18)$$

where θ_q and ϕ_q are the polar angles of the vector $\vec{q}$ with respect to some arbitrary axis.

Let $\mu=\vec{k}\cdot\vec{q}/kq$ and ω be the azimuthal angle in the plane perpendicular to $\vec{q}$. Then following the usual rules,

$$\sum_{\vec{k}}\rightarrow\tfrac{1}{8}(\Omega/\pi^3)\int k^2\,dk\,(\sin\theta_k)\,d\theta_k\,d\phi_k$$
$$=\tfrac{1}{8}(\Omega/\pi^3)\int k^2\,dk\,d\mu\,d\omega\ .$$

Making use of the relation

$$\int_0^{2\pi}Y_l^m(\theta_{k'},\phi_k)\,d\omega=2\pi\,Y_l^0(\mu)\,Y_l^m(\theta_{q'},\phi_q)\ ,$$

we have

$$\left(\frac{\omega^2}{\omega_0^2}-1-\frac{9}{5}x^2\right)\sigma^l_{(x)}=\frac{k_0^3 Z}{\rho_0 4\pi^2}\int_0^1 dx'\,B^l(x,x')\,\sigma^l_{(x')}\ , \quad (19)$$

where

$$x=q/k_0\ ,\quad x'=k'/k_0\ ,$$

and

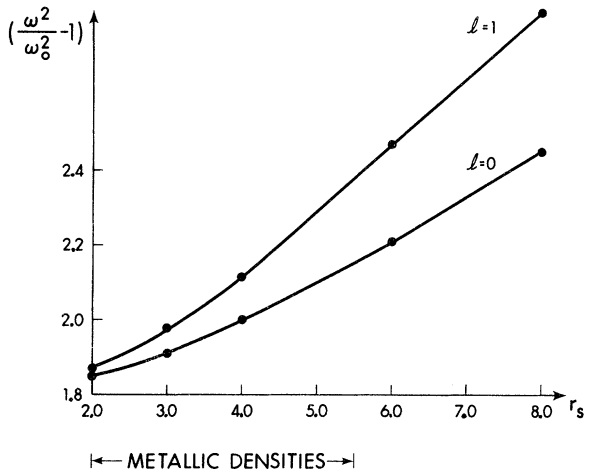

FIG. 1. Plot of ω^2/ω_0^2-1 vs r_s for $Z=+1$ and $l=0$; $+1$ obtained numerically from Eq. (19). Here r_s is defined by $\rho_0=\frac{4}{3}\pi(r_s a_0)^3$, where a_0 is the Bohr radius.

$$B^l(x,x')=xx'\int_{-1}^{+1}\frac{(1+x'^2)\mu P_l(\mu)+\frac{1}{5}xx'P_l(\mu)}{1+x^2+x'^2-2xx'\mu}\,d\mu$$

$$=(1+x'^2)Q_1\left(\frac{1+x^2+x'^2}{2xx'}\right)+\frac{xx'}{5}Q_0\left(\frac{1+x^2+x'^2}{2xx'}\right)\qquad(l=0)$$

$$=\left[(1+x'^2)\left(\frac{x^2+x'^2+1}{2xx'}\right)+\frac{xx'}{5}\right]Q_l\left(\frac{1+x^2+x'^2}{2xx'}\right),\qquad(l\neq 0)\quad.\quad(20)$$

Integral equation (19) can be solved numerically and a frequency spectrum obtained. The range of integration in (19) requires some comment. In the hydrodynamic model the integration should be over values of k from 0 to ∞. However, the collective description of an electron system breaks down for large values of k. We choose a cutoff at $k=k_0$.

DISCUSSION

The classical model used in the present paper is not intended to give better results than those obtained from a microscopic model. However, the microscopic models developed so far do not have all the terms that appear in (15). These extra terms make a significant contribution in the eigenvalue equation for the $l=0$ mode. Their contribution to the $l=1$ mode is comparatively small and therefore the $l=1$ equation is essentially the same as that of Sham[4] or Sziklas.[3]

We have found from Eq. (19) that localized modes of frequency $\sim\sqrt{3}\,\omega_0$ exist in the presence of a positive impurity. Figure 1 displays the frequencies of these modes for $l=0$, $l=1$, as a function of r_s, where r_s is the interparticle spacing measured in units of the Bohr radius. It should be pointed out that the existence of a localized mode in the presence of a positive impurity is not restricted to the hydrodynamic model. The microscopic models mentioned previously will produce such a mode if a cutoff is used in the eigenvalue equation for the mode. Sham[4] has used a cutoff but did not consider the case of a positive impurity. The conclusion by Sziklas[3] that a localized mode does not exist in the presence of a positive impurity is based on the assumption that there is no cutoff in the frequency spectrum.

Characteristic energy losses of fast electrons scattered from thin films have been attributed to plasma excitations. Comparison of results of experiments performed with pure materials and the same materials containing positive impurities should reveal the local frequencies predicted here. Even though the local frequencies may lie close to the continuum they can be detected because they will absorb energy more readily since the impurity can take up momentum.

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