PHYSICAL REVIEW B VOLUME 25, NUMBER 12 15 JUNE 1982

Phonons at metal surfaces

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(Received 3 December 1981)

A hydrodynamic model of collective motion at a metal surface is presented which treats ion and electron degrees of freedom on the same basis. In order to examine modes at a surface, the bulk equations of motion must be supplemented by additional boundary conditions. It is argued that at a free surface, continuity of surface traction is more appropriate than continuity of normal current density. The acoustic-phonon modes for several model systems are determined. Both the surface-mode dispersion and the bulk- and surface-mode external coupling to a charged probe show considerable sensitivity to the choice of boundary conditions. The implications of these results for electron-loss spectroscopy are discussed.

I. INTRODUCTION

This paper is concerned with the collective motion of ions and electrons at a metal surface. Our interest in such motions was stimulated by the rapidly growing field of low-energy electron loss spectroscopy.[1,2] In particular we are intrigued by the relative strength of various loss processes. If one allows only a single mechanism—the long-range Coulomb coupling between the external electron and the electric field fluctuations associated with the sample's collective modes—then a unified overview is possible.[3] In an earlier paper Schaich presented a semiclassical, dielectric-function formulation of this overview.[4] Besides treating the well-studied cases of surface plasmons, optical surface phonons on ionic crystals, and adsorbate vibrations, he also discussed within a simple model phonons at metal surfaces. Further work by us on this model indicates that his particular solution, although correct in mathematical detail, is inappropriate in physical content.

The body of this paper presents our arguments in full, but here we wish to make clear what is at issue. In order to determine the strength of coupling to an external charge, one must formulate a description of collective modes which retains the possibility of external electric fields associated with the modes. To satisfy this severe constraint and to still have a tractable model, we consider a hydrodynamic description of electron and ion motion, i.e., we postulate a set of differential equations relating charge and current densities to electric fields and stress gradients. These equations apply in bulk material and have several possible solutions; e.g., plasmons and phonons, with the latter being either longitudinal or transverse. Our method of finding surface collective modes is to form linear combinations of the bulk solutions, fixing coefficients by the imposition of boundary conditions at the surface, where the medium changes abruptly to vacuum. The subtlety of the problem lies in the choice of boundary conditions. It is a disadvantage of our phenomenological model that the appropriate boundary conditions are not obvious. This dilemma is not academic since the physical implications of various choices are widely different, even to the extent of determining whether a mode is or is not possible. In other words, an important part of the physics of the model lies in the choice of the boundary conditions. It is this difficulty that proves to be the major challenge of a quantitative analysis.

In Sec. II we describe our basic model, quoting the bulk equations of motion and listing possible choices of boundary conditions. We also discuss qualitatively the physical justification for some choices. Part of these arguments are relegated to an appendix, where it is shown how they contrast with an earlier discussion by Forstmann.[5] Then in Sec. III we outline our mathematical methods for calculating the collective mode dispersion and external coupling. Two basic techniques are used: One involves the calculation of an effective surface dielectric function and the other requires a second quantization procedure. Finally in Sec. IV we present some numerical results that illustrate possible solutions. We discuss their implications, both in the context of electron loss spectroscopy and more generally.

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II. MODEL

We consider the metal to be a continuum, and treat the electron and ion motion on the same footing. In equilibrium there is a charge density ρ_0 of ions and $-\rho_0$ of electrons. The deviations from equilibrium are described by displacement fields which depend on position and time: $\vec{\xi}_i(\vec{x},t)$ for the ions and $\vec{\xi}_e(\vec{x},t)$ for the electrons. Hence in linear order the current densities for the ions and electrons are $\vec{j}_i=\rho_0(\partial/\partial t)\vec{\xi}_i$ and $\vec{j}_e=-\rho_0(\partial/\partial t)\vec{\xi}_e$, respectively; while the charge-density deviations (derived from the equations of continuity) are $\delta\rho_i=-\rho_0\vec{\nabla}\cdot\vec{\xi}_i$ and $\delta\rho_e=\rho_0\vec{\nabla}\cdot\vec{\xi}_e$, respectively. The displacement of charge induces an electric field $\vec{E}$ where

$$\vec{\nabla}\cdot\vec{E}=4\pi\rho_0\vec{\nabla}\cdot(\vec{\xi}_e-\vec{\xi}_i)\ . \tag{1}$$

If we neglect retardation $\vec{E}$ is longitudinal and completely determined by (1). The ions and electrons are driven not only by the long-range $\vec{E}$ but also by short-range forces. The explicit equations of motion for the displacement fields are in linear order taken to be

$$\frac{\partial\vec{j}_i}{\partial t}=(\Omega_P^2/4\pi)\vec{E}+\rho_0[c_L^2\vec{\nabla}(\vec{\nabla}\cdot\vec{\xi}_i) -c_T^2\vec{\nabla}\times(\vec{\nabla}\times\vec{\xi}_i)]\ , \tag{2}$$

$$\frac{\partial\vec{j}_e}{\partial t}=(\omega_p^2/4\pi)\vec{E}-\rho_0[\beta^2\vec{\nabla}(\vec{\nabla}\cdot\vec{\xi}_e)]\ . \tag{3}$$

Here, $\Omega_p^2/4\pi=\rho_0Q/M$, where Q is the charge and M the mass of an ion and similarly $\omega_p^2/4\pi=-\rho_0e/m$, where $e<0$ is the charge and m the mass of an electron. The short-range forces are parametrized by the c's and β, all of which have the units of velocity.

The physical origin of these parameters in a solid is different for ions and electrons. The c's derive from elastic restoring forces between near neighbors in a lattice, while β is a measure of statistical repulsion among electrons. Note that only the ions experience transverse forces, via c_T.

If we set c_T to zero, Eqs. (1)–(3) may be written in terms of $\vec{E}$, $\vec{j}$'s, and $\delta\rho$'s alone and one has an approximate continuum description of a plasma (with no magnetic field) or alternatively of the collective oscillations of two groups of electrons with different effective masses.[6] Thus by suitable parameter choices the model equations have a wide range of qualitative validity. On the other hand, in any particular case, the model is quite crude since it neglects damping (of either Ohmic or Landau type), ignores any background polarization of core electrons, imposes linearization and isotropy, and assumes the validity of a hydrodynamic continuum limit. We shall ignore these defects and focus on how to solve (1)–(3) in bulk and at a surface. For us the overriding advantage of these equations is that they treat ions and electrons as separate degrees of freedom and retain the induced electric field.

Before attacking (1)–(3) at a surface, we first consider their implications in bulk. There one can characterize solutions as either longitudinal or transverse, which amounts to solving separately for $\vec{\nabla}\cdot\vec{\xi}$ or $\vec{\nabla}\times\vec{\xi}$. Assuming all linear deviations from equilibrium are proportional to a plane-wave factor $e^{i(\vec{q}\cdot\vec{x}-\omega t)}$, we find two possible longitudinal modes,

$$(\omega^2-\omega_p^2-\beta^2\vec{q}\cdot\vec{q})(\omega^2-\Omega_p^2-c_L^2\vec{q}\cdot\vec{q})=\omega_p^2\Omega_p^2\ , \tag{4}$$

and two degenerate transverse modes,

$$\omega^2=c_T^2\vec{q}\cdot\vec{q}\ . \tag{5}$$

The latter modes have no induced charge density and, with our neglect of retardation, induce no $\vec{E}$. The former modes correspond to plasmons and phonons and both induce electric fields. From the structure of (4) one sees that these modes arise from the coupling of the electron and ion plasma oscillations. A qualitative picture of the two solutions to (4) is shown in Fig. 1. We have considerably reduced the ion-electron mass ratio from its physical value of 10^4-10^6 in order to show the two branches. Both ω_p^2/Ω_p^2 and β^2/c_L^2 are proportional to this ratio, but in Fig. 1 they have each been set equal to 5. It is interesting that the sound speed of the phonon mode, i.e., $d\omega/d\,|\vec{q}\,|$ on the lower branch, tends as $\omega\to0$ to

$$v_L=(c_L^2+c_s^2)^{1/2} \tag{6}$$

with c_s the Bohm-Staver sound speed[7]

$$c_s=\beta\Omega_p/\omega_p=\Omega_p/k_s\ , \tag{7}$$

where we have introduced the electron-screening wave vector $k_s=\omega_p/\beta$. As $|\vec{q}\,|$ grows through k_s, the electron-screening effect on the ions decreases and the sound speed decreases smoothly from v_L to c_L.

Next consider collective modes near a surface. We use the method of partial waves, writing a general solution as a linear combination of particular solutions consistent with the good quantum numbers and boundary conditions. The good quantum numbers are ω, the mode frequency, and $\vec{Q}$, the two-dimensional mode wave vector parallel to the

surface. Particular solutions adapted to the surface are then obtained by replacing $e^{+i\vec{q}\cdot\vec{x}}$ in the just obtained bulk solutions by, for example, $e^{i\vec{Q}\cdot\vec{X}}e^{Qx}$. Here $\vec{X}$ is the projection of $\vec{x}$ in the plane parallel to the surface and x is the coordinate normal to the surface with the metal in $x<0$. The quantity $\bar{Q}$ follows by replacing $\vec{q}\cdot\vec{q}$ in (4) or (5) by $|\vec{Q}|^2-\bar{Q}^2$. In terms of Fig. 1 one draws a line of constant ω and denotes its intersections with the bulk dispersion curves by $\vec{q}_b\cdot\vec{q}_b$'s. Then the $\bar{Q}^2$ for each partial wave is the algebraic difference between $|\vec{Q}|^2$ and $\vec{q}_b\cdot\vec{q}_b$. For $\bar{Q}^2>0$, $\bar{Q}$ is real and the partial wave may be localized at the surface; while for $\bar{Q}^2<0$, $\bar{Q}$ is pure imaginary and the partial wave propagates into the bulk. Inside the material there is one other partial wave that must be included at a surface: $\vec{\nabla}(e^{i\vec{Q}\cdot\vec{X}}e^{Qx})$. It does not appear via (4) or (5) because it is formally neither longitudinal nor transverse: It has zero divergence and zero curl. Still, substitution in (1)–(3) shows that such a variation of $\vec{E}$ and the $\vec{j}$'s provides a solution for any ω. We call it a Coulomb wave.

The general solution for a surface mode of the ion displacement field is then

$$\vec{\xi}_i(\vec{x},t;\vec{Q},\omega)=-e^{i(\vec{Q}\cdot\vec{X}-\omega t)}\Theta(-x)[\alpha_0(Q,iQ,0)e^{Qx}+\alpha_-(Q_-,iQ,0)e^{Q_-x}+\alpha_+(Q_+,iQ,0)e^{Q_+x}+\alpha_T(Q,iQ_T,0)e^{Q_Tx}], \tag{8}$$

where Θ is the unit step function and the $(\pm)$'s label the two longitudinal waves from (4) and (T) labels the relevant transverse wave from (5). The triplets of numbers give Cartesian components in the coordinate system determined by $\hat{x}$, $\hat{Q}$, and $\hat{t}=\hat{x}\times\hat{Q}$. Thus in (8) we have only retained p waves—those partial waves whose polarization lies in the plane of surface normal $\hat{x}$ and the wave vector $\vec{Q}$. We have found in our model that the s waves, whose polarization is along $\hat{t}$ and which are purely transverse, never couple to p waves or form surface modes or lead to external $\vec{E}$ fields. Hence we will mention them no further.

Given the form of $\vec{\xi}_i$ one can use the equations of motion to determine $\vec{\xi}_e$ and $\vec{E}$. They are

$$\vec{\xi}_e(\vec{x},t;\vec{Q},\omega)=e^{i(\vec{Q}\cdot\vec{X}-\omega t)}\Theta(-x)\left[\frac{\omega_p^2}{\Omega_p^2}\alpha_0(Q,iQ,0)e^{Qx}+\alpha_-\Delta_-(Q_-,iQ,0)e^{Q_-x}+\alpha_+\Delta_+(Q_+,iQ,0)e^{Q_+x}\right] \tag{9}$$

and

$$\vec{E}(\vec{x},t;Q,\omega)=\frac{4\pi\rho_0\omega^2}{\Omega_p^2}e^{i(\vec{Q}\cdot\vec{X}-\omega t)}\{\Theta(-x)[\alpha_0(Q,iQ,0)e^{Qx}+\alpha_-\gamma_-(Q_-,iQ,0)e^{Q_-x}+\alpha_+\gamma_+(Q_+,iQ,0)e^{Q_+x}]+\Theta(x)[\lambda(-Q,iQ,0)e^{-Qx}]\}, \tag{10}$$

where

$$\Delta_\pm=(\omega^2-\Omega_p^2-c_L^2Q^2+c_L^2Q_\pm^2)/\Omega_p^2, \tag{11}$$

$$\gamma_\pm=(1+\Delta_\pm)\Omega_p^2/\omega^2. \tag{12}$$

Note that in (10) we have also allowed for a finite $\vec{E}$ outside the metal, $x>0$. Only a Coulomb wave is possible there. In order that Eqs. (8)–(10) represent a surface collective mode, all the $\bar{Q}$'s, Q, $Q_\pm$, and Q_T, must have positive real parts.

In writing these equations we have introduced five unknowns: α_0, $\alpha_\pm$, α_T, and λ, which must be determined by the boundary conditions. A similar problem arises when one considers the surface part of a bulk mode, or the response of the metal to an external probe. Thus we need to examine what boundary conditions are appropriate. This effort, as discussed in the Introduction, requires a further extension of the model: The boundary conditions are not determined by Eqs. (1)–(3). We feel that the following conditions are appropriate for our model of a free-metal surface: continuity of mechanical traction and parallel electric field plus discontinuity in the normal electric field. Let us define and discuss these in turn.

The main controversial point is the choice of boundary conditions for the displacement fields. They represent the additional boundary conditions (ABC's) made necessary by the inclusion of dispersion (c's and β) in the bulk equations of motion and their general necessity and controversy has been appreciated for some time.[8] Yet for a few physical problems there has developed an apparent consensus as to what is appropriate. For instance to describe the surface response of electrons alone (with the ions held static), the near-universal ABC within a hydrodynamic treatment, such as (3), has been to require continuity of normal current density; i.e., at a free surface $\vec{j}_e\cdot\hat{x}=0$.[9] On the other hand, to describe lattice oscillations at a surface

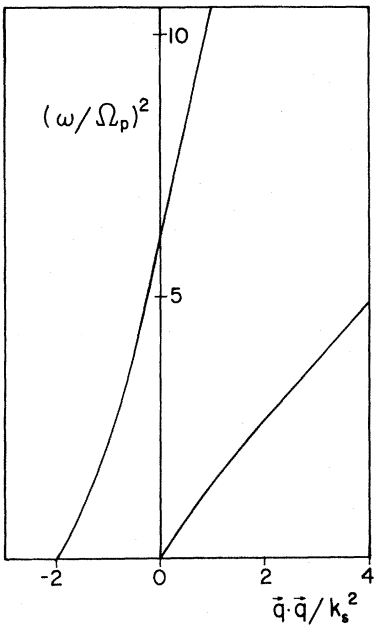

FIG. 1. Bulk dispersion for longitudinal modes. The two solutions of (4) are plotted in reduced units, ω^2/Ω_p^2 and $\vec{q}\cdot\vec{q}/k_s^2$, to suppress some of the arbitrariness of parameter choices. The upper branch is plasmonlike [at $|\vec{q}|=0$, $\omega=(\omega_p^2+\Omega_p^2)^{1/2}$], while the lower branch is phononlike ($\omega\sim v_L|\vec{q}|$ for $|\vec{q}|\sim 0$). We plot both positive and negative values of $\vec{q}\cdot\vec{q}$ to show how to determine surface wave vectors. See text for further discussion.

within the continuum model of elasticity, such as (2) with $\vec{E}=0$, the ABC chosen is continuity of face traction[10]; i.e., $0=\vec{T}_i=\vec{\sigma}_i\cdot\hat{x}$, where $\vec{\sigma}_i$ is the stress tensor whose gradient leads to the short-range forces.

Our dilemma arises from treating the ion and electron motion on an equal basis. We have both $\vec{j}_e,\vec{j}_i$ and $\vec{T}_i,\vec{T}_e$, where

$$\vec{T}_i=\frac{M}{Q}\rho_0\{(c_L^2-2c_T^2)\hat{x}(\vec{\nabla}\cdot\vec{\xi}_i)+c_T^2[(\hat{x}\cdot\vec{\nabla})\vec{\xi}_i+\vec{\nabla}(\vec{\xi}_i\cdot\hat{x})]\}\ , \quad (13)$$

$$\vec{T}_e=-\frac{m\rho_0}{e}[\beta^2\hat{x}(\vec{\nabla}\cdot\vec{\xi}_e)]\ . \quad (14)$$

We believe that at a free surface one should require both $\vec{T}_i$ and $\vec{T}_e$ to vanish, even though this implies that $\vec{j}_i\cdot\hat{x}$ and $\vec{j}_e\cdot\hat{x}$ will be finite there. Only if the medium is clamped by some external means; e.g., capacitor plates confining a plasma, would the condition of zero normal ion and electron current density be appropriate. Our rationale for these choices is not really a proof but rather an assertion that the physical justification given for continuity of surface traction is more compelling than that for any other condition. The basic argument is that one wishes to avoid having a finite force acting on a vanishingly small mass. This argument applies equally well to the ions and to the electrons. They sense different stresses so one obtains potentially four conditions from (13) and (14). On the other hand, when one argues for continuity of normal current density, he is either imagining an infinite barrier that forces specular reflection of all incident particles or attempting to avoid an apparently infinite charge density at the surface. The former picture is invalid in the absence of some external constraint and the latter concern is unnecessary. A finite value of, for example, $\hat{x}\cdot\vec{j}_e$ on the metal side of the surface need not imply a finite amount of charge at $x=0$, but instead only a shift of the true surface location. The physical picture is the same as for water waves: $\hat{x}\cdot\vec{\xi}$ is finite at $x=0$ which means that the surface is undulating.

Once one adopts this viewpoint, then not only the surface traction conditions but also the electric field conditions become easy to understand. The standard pillbox argument for the boundary condition on the normal electric field[11] must take into account the undulating surface. At every $\vec{X}$ and t there are large charge densities, either ρ_0 or $-\rho_0$, extending a small bit, $\hat{x}\cdot\vec{\xi}_i(x=0,\vec{X},t)$ or $\hat{x}\cdot\vec{\xi}_e(x=0,\vec{X},t)$, respectively, beyond $x=0$. We include these extensions inside our pillbox and derive in linear approximation

$$\Delta[\hat{x}\cdot\vec{E}(x=0,\vec{X},t)]=4\pi[\rho_0\hat{x}\cdot\vec{\xi}_i(x=0,\vec{X},t)-\rho_0\hat{x}\cdot\vec{\xi}_e(x=0,\vec{X},t)], \quad (15)$$

where ΔC denotes the jump in C around $x=0$; i.e., from above to below the surface corrugation. The quantity in the square brackets on the right-hand side plays the role of an effective surface charge density, but derives from integrals of bulk charge densities over the amplitudes of surface oscillation. If the same idea is applied to the contour integral argument for the boundary condition on the parallel electric field,[11] one finds in first order

$$\Delta|\hat{Q}\cdot\vec{E}(x=0,\vec{X},t)|=0\ , \quad (16)$$

i.e., no evidence of the surface motion. If we include retardation a similar result is found for the other electromagnetic field components: Only $\hat{x}\cdot\vec{E}$ is discontinuous in a linear theory because only it has inside the pillbox or contour a quantity, $\pm\rho_0$, of zeroth order whose integral is first order.

In the Appendix we discuss the boundary condi-

tions further, showing their generalization to layered media and demonstration their consistency with the conservation of energy.

III. METHODS OF SOLUTION

In this section we outline the methods we have used to solve our model. The partial-wave coefficients are to be determined by applying boundary conditions. We have already listed our preferred choice for these conditions as well as some alternatives. The number of nontrivial equations that need to be simultaneously satisfied for p waves is, in general, five. The electric field conditions (15) and (16) and the surface traction conditions, setting (13) and (14) to zero, give five equations, if we ignore the possibility of s waves. For special cases we will set one or both of the c's to zero, which simultaneously reduces the number of bulk modes (hence partial waves) and the number of boundary conditions. Further, in Sec. IV, we will examine the numerical effect of changing boundary conditions. We describe our solution methods here at a qualitative level which is independent of such particular cases.

We have used two basic methods. The first delivers the external coupling more easily. The idea behind it is to consider not individual collective modes but instead simply the linear response of the metal surface at each $\vec{Q}$ and ω to an external probe. One may use Eqs. (8)–(10) with the single change that the electric field outside the metal is now written as

$$\Theta(x)\vec{E}(\vec{x},t;\vec{Q},\omega) = \frac{4\pi\rho_0\omega^2}{\Omega_p^2} e^{i(\vec{Q}\cdot\vec{X}-\omega t)}[(Q,iQ,0)e^{+Qx} + \lambda(-Q,iQ,0)e^{-Qx}] . \tag{17}$$

The additional partial wave in (17) represents the external perturbation at each $\vec{Q}$ and ω. The relative effect outside the metal of the system's linear response is determined by λ. To make this claim more suggestive we define an effective surface dielectric constant $\bar{\epsilon}(\vec{Q},\omega)$ by

$$\bar{\epsilon}=\frac{1-\lambda}{1+\lambda} . \tag{18}$$

Its definition and symbol are chosen because when the metal response may be described by a local bulk dielectric function $\epsilon(\omega)$, then $\bar{\epsilon}(\vec{Q},\omega)=\epsilon(\omega)$. However, this simple result holds in our model only if both c's and β are zero. It is $\bar{\epsilon}$ that determines a host of physical properties. For example, the differential scattering probability of electron-loss spectroscopy can with the neglect of impact scattering and the use of semiclassical arguments be written as[4]

$$P(\vec{Q},\omega)=\frac{e^2}{\pi^2\hbar Q}\left|\frac{2Qv}{Q^2v^2+(\vec{Q}\cdot\vec{V}-\omega)^2}\right|^2 \times \mathrm{Im}\left[\frac{-1}{1+\bar{\epsilon}(\vec{Q},\omega)}\right] , \tag{19}$$

where the velocity $\vec{v}=(v,\vec{V})$ describes the incoming external electron which will lose energy $\hbar\omega$ and parallel momentum $\hbar\vec{Q}$ in scattering from the surface. One may also express static and dynamic image potentials in terms of $\bar{\epsilon}$ as well as the nonretarded van der Waals interaction between the metal and a neutral molecule.[12] Indeed $\bar{\epsilon}(\vec{Q},\omega)$ is the nonretarded analog of the surface impedance, completely characterizing the external response of the system.

We end our conclusion of this method by noting two technical points. In solving for λ or $\bar{\epsilon}$, the scheme is not modified when one of the inside $\bar{Q}^2$'s changes sign. The functional form of Eqs. (8)–(10) for $x<0$ is always the same, with the sole constraint that each $\bar{Q}$ as a complex number lies in the fourth quadrant. For our simple model (1)–(3) this means that $\bar{\epsilon}$ is a complex number if one can couple to bulk excitations but a real number otherwise. Surface collective modes are determined by the condition $\lambda\to\infty$, or

$$\bar{\epsilon}(\vec{Q},\omega)=-1 . \tag{20}$$

The other point we mention is that if one has a system where specular reflection is the appropriate ABC, then $\bar{\epsilon}(\vec{Q},\omega)$ can be expressed as an integral of the bulk longitudinal dielectric function $\epsilon(\vec{q},\omega)$[4]:

$$\bar{\epsilon}^{-1}(\vec{Q},\omega)=\frac{2}{\pi}\int_0^\infty dq\,\frac{Q}{Q^2+q^2}\epsilon^{-1}(\vec{q},\omega) , \tag{21}$$

with $\vec{q}=(q,\vec{Q})$. A recent derivation is given by Fuchs and Barrera.[13] The relation holds for any $\epsilon(\vec{q},\omega)$, allowing one the option of considerable generalization beyond our hydrodynamic model, yet it only applies when specular reflection is the ABC. When one requires, as we do here, alternate ABC's, then (21) is irrelevant.

The other basic solution method we have used is to explicitly construct at each $\vec{Q}$ and ω all the possible collective eigenmodes, orthonormalizing them by the technique of second quantization. Thus we

get more information than with the first method, but the scheme is harder to apply and to generalize. If all the $\bar{Q}$'s are real one may use Eqs. (8)–(10) as written to find the surface modes. However, when one chooses $\vec{Q}$ and ω that allow coupling to propagating partial waves, then he must include further partial waves in (8)–(10) that represent incident bulk partial waves. This means physically that a bulk mode contains both incident and reflected partial waves. The subsequent algebra of reduction is not very transparent. Since similar analyses have been published for purely elastic systems[14] (no $\vec{E}$ or $\vec{\xi}_e$), we forego a detailed description. Suffice it to say that the results for the dispersion and external coupling of the totality of the modes is the same as found via $\bar{\epsilon}(\vec{Q},\omega)$, with the additional advantage that one can dissect the coupling into individual-mode contributions.

IV. NUMERICAL RESULTS AND DISCUSSION

Having outlined our solution methods we next present some numerical results. Since our basic equations (1)–(3) are a crude description, we do not attempt to fit parameter values to any material but instead look for qualitative features in the theory. We expect in a metal that all the c's (c_L, c_T, c_S) are roughly comparable, subject to $c_L^2 \geq 2c_T^2$ and that $\omega_p^2 \gg \Omega_p^2$.

In Fig. 2 we plot a sequence of mode dispersions in the phonon regime, showing both bulk- and surface-mode results. The electronic plasmons are off the vertical scale. For the bulk modes we show at each Q just the lower limit of the possible ω values. Only for the panels in the first row is there a natural upper limit Ω_p for the bulk band. For the other cases one would have to impose a Debye cutoff of some sort. The surface modes, if they exist, lie at each Q below all the bulk solutions. This ensures that every $\bar{Q}$ in their partial-wave decomposition is real.

The panels are distinguished by what particles are allowed to move, what forces they are subjected to, and what boundary conditions the solutions must satisfy. The first two aspects are explained in the caption of Fig. 2; we will concentrate on the last one. For all the panels we have required the electric field conditions (15) and (16). The variation comes in whether for the ions or the electrons we can or do require continuity (vanishing) of $\vec{T}_i$, $\vec{T}_e$, $\vec{j}_i \cdot \hat{x}$, or $\vec{j}_e \cdot \hat{x}$ at the surface. When a surface traction condition is imposed we apply the label S (for stress), while a normal current density condition is labeled by C (for current). The first label in a pair refers to the ions, the second to the electrons. The absence of a label means that neither condition can be applied.

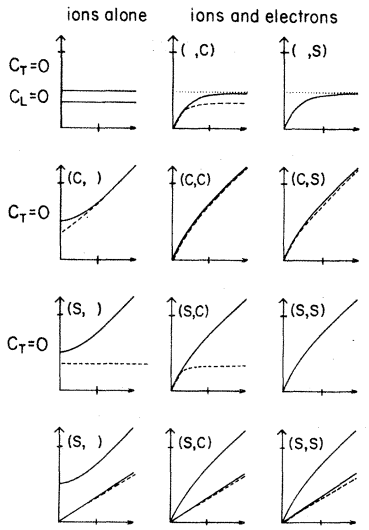

FIG. 2. Mode dispersions for various models. In each case the lower limit of a bulk band is a solid line, the upper limit is a dotted line, and surface modes are dashed lines. All the ordinates are ω/Ω_P, the single tic is at a value of 2. All the abcissae are Q/k_s, the single tic is a value of 2. In the first column of panels the results apply when ions alone are present. The remaining two columns show the effect of adding the electrons under various boundary conditions (see text). In each row of panels the parameter choices are fixed. In the bottom row $c_s^2/c_L^2=3$ and $c_T^2/c_L^2=\frac{1}{3}$. In the middle two rows $c_s^2/c_L^2=3$ and $c_T=0$, while in the first row $c_L=0=c_T$. For all the panels $\omega_P^2/\Omega_P^2=10^4$. Except for the first two panels in the last row, the modes formally exist for all Q or not at all.

The main purpose of Fig. 2 is to show the extreme sensitivity of the surface-mode dispersion to boundary conditions. In contrast the bulk-mode dispersion is independent of boundary conditions. It depends only on what particles are interacting via what forces in the bulk. The primary changes for the bulk modes are that the electrons push the ion plasma oscillations down to phonons as $Q \to 0$ and a transverse mode appears when $c_T \neq 0$.

Let us now discuss some particular details. Case (,C) in the first row is the one treated earlier by Schaich[4] and others.[15] An initial aim of our work was to generalize this case to finite c_L and c_T. To do so requires a change in the boundary conditions since a (C,C) condition is insufficient to determine collective modes with all c's and β finite. At-

tempting an (S,C) condition is also unsatisfactory since the resulting surface mode only exists above a certain Q. The only satisfactory treatment comes from the (S,S) case in the last row where one finds a surface (Rayleigh) mode for all Q. The propagation speed of this mode in the low-frequency limit is the same as that produced by the theory of elasticity[10] with the use of v_L and c_T. At higher frequencies, as Q becomes greater than k_s, the mode's propagation speed decreases to that appropriate to c_L and c_T.

To make alternate comparisons between the S and C conditions we have considered models with $c_T=0$. Then the S condition reduces to a single equation requiring that the appropriate hydrodynamic pressure vanish at the surface, or equivalently that $\vec{\nabla}\cdot\vec{\xi}_i$ or $\vec{\nabla}\cdot\vec{\xi}_e$ vanish there. These models, which lie in the middle two rows of Fig. 2, correspond to warm plasmas or liquid metals. If one imagines that there is an external constraint forcing all normal current densities to vanish at the surface, then case (C,C) applies and one finds a surface mode extremely close to the bottom of the bulk band. Removing the constraint should switch one to case (S,S) in the third row for which there is no surface mode, certainly a radical change. The same effect occurs when c_L also is zero: first row, $(\ ,C)$ vs $(\ ,S)$. Two hybrid cases, (C,S) and (S,C), are also shown, more as a demonstration of mathematical sensitivity than as a claim of physical relevance.

The external coupling of the collective modes also shows a sensitive dependence on boundary condition. We reported previously the variation of the surface-mode coupling[16]; here we concentrate on the bulk-mode coupling. In Fig. 3 the quantity

$$B(\vec{Q},\omega)=\mathrm{Im}\left[\frac{-1}{1+\bar{\epsilon}(\vec{Q},\omega)}\right] \tag{22}$$

is plotted for several of the cases of Fig. 2. Aside from the wide variety of predictions, one should especially note that B is greatly reduced whenever an S condition is imposed on the electrons. In fact for the (S,S) case with $c_T=0$, B is identically zero. For the (C,S) case with $c_T=0$ and the (S,S) case with $c_T\neq 0$, the size of B is set by $\Omega_p^4/\omega_p^4=10^{-8}$. The same feature is present in the surface-mode coupling.[16] If one includes damping in the model, by adding, for example, $\vec{j}_e/\tau_e$ to the left-hand side of (3), then B acquires a lower limit of roughly $\omega/\omega_p^2\tau_e$, which for the parameters of Fig. 2 and $\omega_p\tau_e=100$ makes $B\gtrsim 10^{-4}$. This bound is certainly much larger than the results shown in Fig. 2

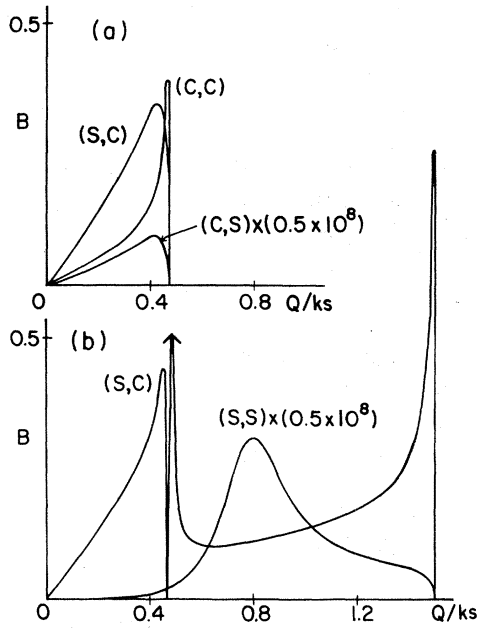

FIG. 3. External Coulomb coupling of bulk modes. In each case $B(\vec{Q},\omega)$ is plotted vs Q/k_s at fixed $\omega/\Omega_P=0.5$. The finite parameter choices and curve labels are as in Fig. 2 and both ions and electrons can respond. In (a) $c_T=0$, while in (b) $c_T\neq 0$. For the (S,C) case in (b), the sharp rise of B to 11.7 has been cut off.

when $\vec{T}_e=0$, but it is still small. Since we earlier argued that the S condition is the appropriate ABC for a free surface, it appears that the Coulomb coupling to the modes at a metal surface is negligible.

There are, however, at least two ways in which experimental consequences of this lack of coupling in our model might be avoided; both involve alternate coupling schemes. The first is to suppose that impact scattering will allow significant coupling. Realistic calculations of the strength of such a scattering mechanism have only recently appeared,[17–19] and have been primarily directed toward adsorbate vibrations rather than towards modes of the clean surface. Although an analytic expression for the scattering strength is not available, it is clear from the calculations and several reported observations with adsorbates[20–24] that impact scattering can be significant.

The second alternate coupling scheme we consider involves going beyond a linearized treatment. Even within our hydrodynamic model such an extension is a difficult task. However, some estimates have appeared of the coupling due to nonlinear Coulomb interactions,[25,26] calculated within

still simpler models. We focus on the work of Rahman and Mills,[25] who estimate the coupling of an external charge to a Rayleigh mode by calculating the change in the image potential to first order in the surface ripple. The latter amplitude is readily found from elasticity theory, and indeed the theory can be applied not only to surface phonons but also to bulk phonons, which ripple the surface too. To illustrate the essence of this coupling scheme, consider an external charge q fixed at $(R,\vec{X})$ above the (flat) metal surface. The simplest image interaction of this charge is given by $-q^2/4R$. If one allows the surface to be rippled by a phonon of wavelength $2\pi/Q$ much greater than R, but of amplitude $\xi_i(\vec{X})$ much less than R, then the new image potential is well approximated by $-q^2/4(R-\xi_i)$. Hence the change in the image potential is, to first order in ξ_i,

$$V=-(q^2/4R^2)\xi_i(\vec{X})=-(q^2/4R^2)\xi_i^0 e^{i\vec{Q}\cdot\vec{X}} \tag{23}$$

This result is to be contrasted to our prediction which involves the electrostatic potential $\Phi(\vec{E}=-\vec{\nabla}\Phi)$ of the surface phonon:

$$V'=q\Phi(R,\vec{X})=q\Phi^0 e^{i\vec{Q}\cdot\vec{X}}e^{-QR}\ . \tag{24}$$

Note that Φ^0 is linear in ξ_i^0, but independent of q. From our point of view the result (23), which agrees with the more general formula of Rahman and Mills[25] in the limit $QR\ll 1$, follows from a nonlinear interaction between the surface plasmon modes (which are primarily responsible for the image potential), the surface-phonon modes, and the external charge. Its calculation directly from our model would not be easy, and one might imagine the appearance of additional nonlinear terms. Still the formula (23) is not unreasonable for metals, and one should estimate its scattering strength. For electron-loss spectroscopy even this task is quantitatively difficult because of the singularity in (23) at $R\to 0$. We earlier made a rough estimate[16] and in terms of the B used here, we found a scattering strength comparable to the (S,C) case in the lower part of Fig. 3; i.e., this scattering mechanism is much stronger than what we believe is the best estimate, the case (S,S) of the linear coupling. In the absence of further detailed calculations, it is difficult to say whether there are qualitative differences between the linear and nonlinear spectra aside from overall strength that could be probed experimentally.

We can only offer the following qualitative argument to suggest that the linear coupling is negligible. Focus on the suppressed value of B in our model. It derives from the equation of motion for the electrons. From their viewpoint the screening of phonons is nearly an adiabatic process, which means in terms of (3) that one may ignore $\partial\vec{j}_e/\partial t$ when $\omega\lesssim\Omega_p$. In this approximation, (3) reduces to the static Thomas-Fermi equation, which if we use the electrostatic potential Φ instead of $\vec{E}$, may be expressed as

$$\delta\rho_e=-(k_s^2/4\pi)\Phi\ . \tag{25}$$

Now notice [e.g., (14)] that $\delta\rho_e$ also determines the electron stress or pressure. Hence when one requires zero stress for the electrons at the metal surface, (25) implies Φ is zero just inside the metal. Then continuity of Φ—an equivalent statement of (16)—requires Φ to vanish outside the metal. In terms of an $\bar{\epsilon}(\vec{Q},\omega)$ calculation, one deduces that $\lambda=-1$ in (17), or $\bar{\epsilon}=-\infty$ in (18), or finally $B=0$ in (22). By this argument a finite B via linear coupling when $\vec{T}_e=0$ is only a measure of nonadiabatic effects, which diminish when the electron-mass ratio does. Our numerical results are consistent with this conclusion.

Thus the theoretical situation may be summarized as follows. The coupling scheme that we have developed here combined with the favored boundary conditions leads to negligible interaction between surface phonons and external charges. Alternate choices of boundary conditions or alternate coupling schemes can lead to significant interaction but further calculations are necessary to carefully quantify these other schemes. On the experimental side, we know of no reported observations of acoustic-phonon losses at flat, clean metal surfaces via electron-loss spectroscopy. There have been several cases where bulk-phonon losses were observed with the aid of either steps or special adsorbate layers,[27–29] but our model is probably too crude to be applied to these situations. The absence of acoustic-phonon observations on flat, clean metal surfaces would imply no coupling, but such experiments are difficult and too few cases have been examined with sufficient resolution to justify any conclusion yet. Certainly more loss data would be welcome. In the same sense, thermal diffuse scattering spectra at low incident elec-

tron energies would be helpful.[4]

To recapitulate the effort of this paper, we have examined the collective-mode dispersion and external (linear) coupling of a simple hydrodynamic model of a metal surface. The results, as illustrated in Figs. 2 and 3, are remarkably sensitive in the range of phonon frequencies to the choice of ABC. We have given arguments in support of a particular choice of ABC—zero surface traction for both ions and electrons—that has not been used before. This ABC leads to a prediction of negligible long-range Coulomb coupling in linear order to both bulk- and surface-phonon modes. However, it is as yet not clear whether experiment or more sophisticated theory support or contradict this prediction. Alternate coupling mechanisms have been suggested but their detailed quantitative implications remain to be explored. Further work is certainly required, but it should be done with a cautious eye on the sensitivity of results to surface boundary conditions.

ACKNOWLEDGMENTS

This work was supported in part by the NSF under Grant No. DMR 78-10235.

APPENDIX: FURTHER BOUNDARY CONDITION ARGUMENTS

We consider several extensions of our model and their implications for the boundary conditions. First include retardation and allow for several interfaces between uniform layers. Within each layer the bulk equations (1)–(3) still apply, with parameters that are layer but not position dependent.[5,30] The electric field now has transverse components, which must be determined consistently from the full set of Maxwell equations, i.e., (1) must be supplemented with

$$\vec{\nabla}\times(\vec{\nabla}\times\vec{\mathrm{E}})-(\omega^2/c^2)\vec{\mathrm{E}}=\frac{-4\pi i\omega}{c}(\vec{\mathrm{j}}_i+\vec{\mathrm{j}}_e)\,, \tag{A1}$$

where c is the speed of light. In a linear theory the induced magnetic field $\vec{\mathrm{B}}$ does not appear in the equations of motion.

We imagine that the displacement fields in adjoining layers are in perfect contact, which leads to the requirement that components of $\vec{\xi}_i$ and $\vec{\xi}_e$ be continuous. The normal components are always continuous, while the parallel components of a species need by continuous only if there are transverse forces on that species. These conditions imply discontinuities in the normal current densities, that in turn imply an oscillation of the interface location. Retaining only first-order terms, the electromagnetic boundary conditions are that all field components are continuous except the normal component of $\vec{\mathrm{E}}$ for which (13) holds. Finally we require that the surface traction on each species be continuous in order to avoid an imbalance of forces across a boundary.

One might imagine other ways to generalize our model, but the above prescription is at least reasonable and allows us to examine energy conservation. To this end we adapt the analysis of Forstmann.[5] One starts from the Poynting theorem,

$$\int d^{3x}\left[\frac{\partial}{\partial t}\left[\frac{\vec{\mathrm{E}}\cdot\vec{\mathrm{E}}}{8\pi}+\frac{\vec{\mathrm{B}}\cdot\vec{\mathrm{B}}}{8\pi}\right]+\frac{c}{4\pi}\vec{\nabla}\cdot(\vec{\mathrm{E}}\times\vec{\mathrm{B}})\right]=-\int d^3x\,\vec{\mathrm{j}}\cdot\vec{\mathrm{E}}\,, \tag{A2}$$

where $\vec{\mathrm{j}}$ is the total current density, and using equations of motion for $\vec{\mathrm{j}}$ rewrites the right-hand side. To generalize and simplify this analysis we use in the remainder of this paragraph subscripts to denote cartesian components and let $\partial_i a$ mean $\partial a/\partial x_i$ and $\dot{a}$ mean $\partial a/\partial t$. Rather than discussing ions and electrons separately we study the generalized equation of motion for a single species,

$$\frac{\partial}{\partial t}j_i=fE_i+\frac{q}{M}\partial_j c_{ijkl}\partial_k\xi_l\,, \tag{A3}$$

where an Einstein summation convention is presumed, $j_i=\pm\rho_0(\partial/\partial t)\xi_i$ depending on the sign of q, and

$$c_{ijkl}=c_{jikl}=c_{ijlk}=c_{klij}\,. \tag{A4}$$

Equations (2) and (3) are specific examples of (A3). We solve for

$$\begin{aligned}j_iE_i&=\frac{1}{2f}\frac{\partial}{\partial t}(j_ij_i)-\frac{|q\rho_0|}{fM}\left[\frac{\partial}{\partial t}\xi_i\right]\partial_j c_{ijkl}\partial_k\xi_l\\&=\frac{1}{2f}\frac{\partial}{\partial t}(j_ij_i)+\frac{|q\rho_0|}{2fM}\frac{\partial}{\partial t}(\partial_i\xi_j c_{ijkl}\partial_k\xi_l)-\frac{|q\rho_0|}{fM}\partial_i(\dot{\xi}_j c_{ijkl}\partial_k\xi_l)\,.\end{aligned} \tag{A5}$$

Before substituting back into (A2) introduce the stress tensor

$$\sigma_{ij}=c_{ijkl}\partial_k\xi_l \tag{A6}$$

and note that for both ions and electrons $|q\rho_0|/fM=1$.

Now use superscripts to distinguish ions and electrons; e.g., $f^{(i)}=\Omega_P^2/4\pi$ and $f^{(e)}=\omega_P^2/4\pi$. Substitute the appropriate (A5) for each species into (A2) to find

$$\int d^3x\left[\frac{\partial}{\partial t}\left[\frac{\vec{E}\cdot\vec{E}}{8\pi}+\frac{\vec{B}\cdot\vec{B}}{8\pi}+\frac{2\pi}{\Omega_P^2}\vec{j}^{(i)}\cdot\vec{j}^{(i)}+\frac{2\pi}{\omega_P^2}\vec{j}^{(e)}\cdot\vec{j}^{(e)}+\tfrac{1}{2}\partial_i\xi_j^{(i)}c_{ijkl}^{(i)}\partial_k\xi_l^{(i)}+\tfrac{1}{2}\partial_i\xi_j^{(e)}c_{ijkl}^{(e)}\partial_k\xi_l^{(e)}\right]\right.$$
$$\left.+\vec{\nabla}\cdot\left[\frac{c}{4\pi}(\vec{E}\times\vec{B})-\dot{\vec{\xi}}^{(i)}\cdot\overleftrightarrow{\sigma}^{(i)}-\dot{\vec{\xi}}^{(e)}\cdot\overleftrightarrow{\sigma}^{(e)}\right]\right]=0\ . \tag{A7}$$

Compared to (A2) we have acquired new terms in the energy density and energy current density. The latter is defined by

$$\vec{S}=\frac{c}{4\pi}(\vec{E}\times\vec{B})-\dot{\vec{\xi}}^{(i)}\cdot\overleftrightarrow{\sigma}^{(i)}-\dot{\vec{\xi}}^{(e)}\cdot\overleftrightarrow{\sigma}^{(e)} \tag{A8}$$

and contains both electromagnetic and mechanical contributions. From the explicit form of (A8) it is clear, if one imposes the boundary conditions listed above, that the normal component of $\vec{S}$ is continuous through each interface, which has the desired interpretation that the boundaries act as neither a source nor a sink of energy. This criterion has not always been met in previous theories.[30,31]

Although Forstmann also concludes that $\vec{S}\cdot\hat{x}$ should be continuous between layers, he requires in addition that $\vec{j}^{(i)}$ and $\vec{j}^{(e)}$ be continuous. Consequently the surface tractions are discontinuous in his model. We are presently studying the quantitative implications of this difference. Note that it only matters in a layered medium since at the interface between metal and vacuum the mechanical part of $\vec{S}$ is continuous if either one of $\vec{j}$ or $\vec{T}$ vanishes. Finally we remark that a similar discussion of boundary conditions at a free surface or between layers in a hydrodynamic model of electrons alone has recently appeared.[32] The authors, Boardman and Ruppin, also criticize Forstmann and argue for the boundary conditions favored here.

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