irrelevant that these oscillations are very large. As long as each atom possesses a thermal-equilibrium position and does not wander away never to return, the system is clearly behaving in accordance with our intuitive notion of a solid. According to this criterion, the harmonic one- and two-dimensional systems, the chain and net, are examples of solids.

IV. SUMMARY

In the present work we have shown that to assure consistent statistical-mechanical calculations for a solid, one must include in the Hamiltonian terms explicitly describing the action of the external forces, compression or tension, upon the surface atoms. The physical reason for this requirement is the existence of very long-range correlations between atoms in the solid phase. Although for convenience we selected the linear chain as a model for our analysis, it is clear that the same basic considerations will apply to a three-dimensional solid.

For the one- and two-dimensional systems, the harmonic chain and the harmonic net, although $\langle u_n^2 \rangle$ diverges in the thermodynamic limit, we propose that these systems should be classified as solids. Our proposal is based upon a criterion which is in accord with the usual intuitive notion of a solid.

ACKNOWLEDGMENTS

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[1] Throughout, $V''(d)$ must be assumed independent of d, i.e., $V'''(d)=0$, for otherwise it would be inconsistent to drop anharmonic terms when approximating the Hamiltonian of (1) by (2) or (2′).

[2] The lattice spacing of a solid in the harmonic approximation is well known to be independent of temperature, but of course it is pressure dependent. This result is rederived in the following paragraphs. In particular see (12).

[3] The contradiction $\bar{d} \neq d$ is not unique to the canonical ensemble; it occurs for any ensemble unless the Hamiltonian (1) and (2) is amended as described below.

[4] The constant $F(N-1)d$ is added to ensure that, if $\bar{d}$ indeed equals d, the term $F[x_N - x_1 - (N-1)d]$ added to the Hamiltonian (2) does not alter the energy of the system.

[5] The reason for omitting the $k=0$ term in (15) is that this term corresponds to motion of the center of mass of the chain which is irrelevant to our analysis.

[6] The popular American children's toy "Slinky" displays precisely this behavior when the two ends are held stationary after an internal vibration is excited.

[7] B. Jancovici, Phys. Rev. Letters 19, 20 (1967); N. D. Mermin, Phys. Rev. 176, 250 (1968); Y. Imry and L. Gunther, Phys. Rev. B 3, 3939 (1971).

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Dynamic Contributions to the Surface Energy of Simple Metals

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The contributions of the collective modes to the surface energy of simple metals are calculated. This energy is found to give a relatively good fit to the experimental data indicating that collective contributions must be included in any first-principles calculation.

I. INTRODUCTION

The surface energy is that part of the total energy of condensed matter which is proportional to the surface area of the material in question. Were we to cut a (macroscopic) solid into two (macroscopic) pieces and separate these two pieces the net change in energy would be

$$\Delta E = 2\gamma A ,$$

where A is the area of the cut (the factor of 2 because we create $2A$ new area). The surface energy per unit area or surface tension γ is for macroscopic bodies independent of the size and shape of the body. This quantity γ is of considerable technological interest as there exists a criterion for brittle fracture which balances the energy of new surface produced to the elastic energy released upon the growth of an intrinsic crack.[1]

Suppose we start with a solid which fills all space and then separate this solid into two pieces, each filling one half-space. In doing so we must do work (as $\gamma > 0$); a direct calculation of γ from the work necessary to separate the two pieces would be extremely difficult as the forces between the faces are not particularly well known, especially at small distances. We then look to see what we have done with the solid which may have changed the total energy. Aside from the static redistribution of charge at the surface, one obvious change is that in creating new surface, we have introduced new modes of excitation of the system—surface modes. We now have surface phonons, plasmons, magnons, etc., associated with each mode of which shall be a zero-point energy proportional to the area of the surface. Of these candidates the surface plasmon, being much the highest energy excitation, is the only mode which need be considered. If we naively calculate the zero-point energy of the surface plasmons we get a result which has approximately the proper functional dependence on electron density, but which is about an order of magnitude too large. Clearly, (a) the surface plasmons must be included in the calculations of the surface energy and (b) a better treatment of the surface mode than this simple-minded one is needed.

The naive treatment above treats the surface-collective excitation as in some way divorced from the internal electronic degrees of freedom which gave rise to these excitations. This is, of course, incorrect. We must treat all these excitations (and the changes in these due to the introduction of the surface) on an equal basis.

In an earlier discussion of the surface energy of simple metals, Lang and Kohn[2] use an exact variational theory, the Kohn-Sham-Hohenberg theory[3,4] of an inhomogeneous electron gas, to calculate the surface energy. This theory requires knowledge of the energy as a functional of the electron density. As this functional is not available for the surface geometry, Lang and Kohn approximate it by the energy function for a homogeneous electron gas. The surface modes which would be included in the exact functional are missing in such a treatment. It is not *a priori* clear to what extent ignoring these modes and the dressing of the bulk excitation by these modes is self-compensatory. This approach (with the approximations necessary to do real calculations) does, however, suffer from the same criticism as the naive theory above; it does not treat all the excitations on the same level.

In this work we develop a formalism for obtaining the total energy of a finite system and identify that contribution due to the surface. With this approach, dynamic contributions turn out to be easily identified and isolated. In Sec. II we develop the mathematical background necessary to express the total energy of a finite system in terms of the bulk properties. In Sec. III this calculation is done and the dynamic contribution to the surface energy is computed and compared with the experimental values. These results are discussed in Sec. IV.

II. MATHEMATICAL BACKGROUND

We want to calculate an expression for the expectation value of the Hamiltonian[5]

$$H=\int \Psi^{\dagger}\,(p^2/2m)\,\Psi+\tfrac{1}{2}\int V(1,2)\,\Psi^{\dagger}(1)\Psi^{\dagger}(2)\Psi(2)\Psi(1) \tag{2.1}$$

for inhomogeneous situations as those where a boundary may be present. As numerous authors have shown,[6]

$$\langle H\rangle=E_0+\int_0^{g_{\text{true}}}\frac{dg'}{g'}\,E_{\text{int}}(g'), \tag{2.2}$$

where

$$\begin{aligned}E_{\text{int}}(g)&=\tfrac{1}{2}\Big\langle\int V(\vec{r}_1-\vec{r}_2)\,\Psi^{\dagger}(1)\Psi^{\dagger}(2)\Psi(2)\Psi(1)\,d^3\vec{r}_1 d^3\vec{r}_2\Big\rangle_g\\&=\tfrac{1}{2}\int d^3\vec{r}_1\,d^3\vec{r}_2\,V_g(\vec{r}_1-\vec{r}_2)\,\big[\langle\Psi^{\dagger}(1)\Psi(1)\Psi^{\dagger}(2)\Psi(2)\rangle-\delta(1,2)\langle\Psi^{\dagger}(1)\Psi(1)\rangle\big]_{t_2=t_1},\end{aligned} \tag{2.3}$$

in which g is the coupling constant and E_0 is the energy of the system in the absence of interactions, i.e., for $g=0$. In the case of the Coulomb interaction between two electrons,

$$V(\vec{r}_1,\vec{r}_2,g)=g/|\vec{r}_1-\vec{r}_2|=g\,v(\vec{r}_1-\vec{r}_2). \tag{2.4}$$

The problem, therefore, reduces to one of determining $E_{\text{int}}(g)$.

To find $E_{\text{int}}(g)$, we use an approach patterned after that of Kadanoff and Baym.[7] To the equilibrium Hamiltonian (2.1) we add a term corresponding to the addition of an external test charge, $\rho(\vec{r},t)_{\text{ext}}$ (assumed positive); that is, one whose position and amplitude we can control explicitly. This adds to the Hamiltonian the term

$$H_{\text{ext}}(t_1)=-\int v(\vec{r}_1-\vec{r}_2)\,\rho_{\text{op}}(1)\rho_{\text{ext}}(\vec{r}_2,t_1)\,d^3\vec{r}_1\,d^3\vec{r}_2, \tag{2.5a}$$

where we have written

$$\rho_{\text{op}}(1)=-e\,\Psi^{\dagger}(1)\,\Psi(1)\ . \tag{2.5b}$$

In the presence of the external test charge, the single-particle propagator (for times on the imaginary axis) becomes

$$iG(1,1')=\frac{\langle T S\Psi(1)\,\Psi^{\dagger}(1')\rangle}{\langle T S\rangle}, \tag{2.6}$$

where

$$S = T \exp\left(\frac{-i}{\hbar}\int_0^{-i\beta} H_{\text{ext}}(t)\,dt\right). \tag{2.7}$$

In (2.6), the operators Ψ and $\Psi^\dagger$ are to be regarded as developing in the interaction representation relative to H_{ext}. That is, they develop according to the full Hamiltonian as given by Eq. (2.1).

Suppose now that we vary the external test charge. We ask how does $G(1,1')$ change to linear order in $\delta\rho_{\text{ext}}$. This change is given by

$$\begin{aligned} i\delta G(1,1') = (i/\hbar) \int d^3\vec{r}_2\, d^3\vec{r}_3\, v(\vec{r}_2 - \vec{r}_3) \\ \times \int_0^{-i\beta} dt_3 \,[\langle T\rho_{\text{op}}(3)\Psi(1)\Psi^\dagger(1')\rangle \\ - \langle\rho_{\text{op}}(3)\rangle\langle T\Psi(1)\Psi(1')^\dagger\rangle]\,\delta\rho_{\text{ext}}(\vec{r}_2, t_3) \end{aligned} \tag{2.8}$$

so that the change in the charge density

$$\rho(1) = -e\,i\,G(1,1')\big|_{1'=1^+} \tag{2.9}$$

induced by the variation in the test charge $\delta\rho_{\text{ext}}$ is

$$\begin{aligned} \delta\rho_{\text{ind}}(\vec{r}_1, t_1) = (1/i\hbar) \int_0^{-i\beta} dt_3 \int d^3\vec{r}_2\, d^3\vec{r}_3\, v(\vec{r}_2 - \vec{r}_3) \\ \times [\langle T\rho_{\text{op}}(3)\rho_{\text{op}}(1)\rangle - \langle\rho_{\text{op}}(3)\rangle\langle\rho_{\text{op}}(1)\rangle]\,\delta\rho_{\text{ext}}(\vec{r}_2, t_3)\,. \end{aligned} \tag{2.10}$$

If now we Fourier transform with respect to the complex "time" variable

$$\begin{aligned} \delta\rho_{\text{ind}}(\vec{r}_1, \Omega) = \int d^3\vec{r}_2 d^3\vec{r}_3 v(\vec{r}_2 - \vec{r}_3) \\ \times \mathfrak{L}(\vec{r}_1, \vec{r}_3, \Omega)\,\delta\rho_{\text{test}}(\vec{r}_2, \Omega), \end{aligned} \tag{2.11}$$

where

$$\mathfrak{L}(\vec{r}_1, \vec{r}_3; t_1, t_2) = \langle T\rho_{\text{op}}(3)\rho_{\text{op}}(1)\rangle - \langle\rho_{\text{op}}(1)\rangle\langle\rho_{\text{op}}(3)\rangle \tag{2.12}$$

is a function only of the time difference $t_1 - t_2$ (although not only of the space differences $\vec{r}_1 - \vec{r}_2$ in an inhomogeneous system) as the expectation values in Eq. (2.12) are evaluated in equilibrium. We note now that if we vary the test charge,

$$\frac{\delta\rho_{\text{ind}}(\vec{r}_1, \Omega)}{\delta\rho_{\text{test}}(\vec{r}_2, \Omega)} = \frac{1}{i\hbar}\int d^3\vec{r}_3\, v(\vec{r}_2 - \vec{r}_3)\mathfrak{L}(\vec{r}_1, \vec{r}_3; \Omega) \tag{2.13}$$

so that

$$\begin{aligned} \frac{i\hbar}{(-i\beta\hbar)}\sum_\Omega \frac{\delta\rho_{\text{ind}}(\vec{r}_1, \Omega)}{\delta\rho_{\text{test}}(\vec{r}_2, \Omega)} \exp[-i\Omega(t_1 - t_2)] \\ = \int d^3\vec{r}_3 v(\vec{r}_2 - \vec{r}_3)\,[\langle\rho_{\text{op}}(3)\rho_{\text{op}}(1)\rangle - \langle\rho_{\text{op}}(3)\rangle\langle\rho_{\text{op}}(1)\rangle] \end{aligned} \tag{2.14}$$

and

$$\begin{aligned} \langle H_{\text{int}}\rangle_g = \frac{i\hbar/2}{(-i\beta\hbar)}\sum_\Omega \int d^3\vec{r}_1 \left(\frac{\delta\rho_{\text{ind}}(\vec{r}_1, \Omega)}{\delta\rho_{\text{test}}(\vec{r}_1, \Omega)}\right)_g \\ + \frac{1}{2}\int v(\vec{r}_1 - \vec{r}_3)[\langle\rho_{\text{op}}(1)\rangle\langle\rho_{\text{op}}(3)\rangle - \delta(1,3)\langle\rho_{\text{op}}(1)\rangle], \end{aligned} \tag{2.15}$$

the expression for H_{int} in (2.15) can now be used to calculate the ground-state energy by inserting this expression into Eq. (2.2). Equation (2.15) is exact and represents the starting point for the remainder of our calculations.

A priori this result for E_{int} would appear to have no particular advantage over other more conventional methods of calculating this quantity. As it turns out, in the case of a homogeneous system, (2.15) has no particular advantage or obvious disadvantage, being equivalent to the more conventional expression which expresses the potential energy in terms of the inverse dielectric response of the system, for, in a sense,

$$\delta\rho_{\text{ind}}(\vec{r}, \Omega)/\delta\rho_{\text{test}}(\vec{r}, \Omega)$$

represents the effective inverse dielectric response of the entire inhomogeneous system. That this reduces to the conventional result in the homogeneous limit is shown in the Appendix. For certain inhomogeneous situations, however (namely, those where the physical properties of the dielectric medium change markedly in a relatively short distance), the above formula may be very useful. We shall apply this result to such a situation in a calculation of the surface energy in Sec. III.

III. CALCULATION OF SURFACE ENERGY

In this section we shall calculate the interaction energy in the case where a plane boundary exists. In order to do this we shall need the quantity

$$\delta\rho_{\text{ind}}(\vec{r}, \Omega)/\delta\rho_{\text{test}}(\vec{r}', \Omega)\,.$$

Our approach to calculate this quantity shall be strictly classical and introduces the principal approximations of this work. The approximation involved is that the physical properties of this system change very rapidly in the vicinity of the boundary compared with typical wavelengths and that we may consequently replace the dielectric constants on either side of the boundary by their equilibrium values. This approach is therefore nearly orthogonal to that of Lang and Kohn who used a theory appropriate when the system properties are slowly varying.

Consider the following classical problem [Eq. (3.1)]: A point charge q is located at $\vec{r}_q$ (a distance z_q away from a plane boundary separating dielectrics of dielectric constants $\epsilon^>$ and $\epsilon^<$) and we wish to find the potential $\phi(\vec{r})$ and the induced charge $\rho_{\text{ind}}(\vec{r})$ everywhere. The method for solving this problem is well known[8]: we use an ansatz that the effect of the boundary (for $z>0$) may be replaced by an image charge q' located in the mirror position to the charge in question $\underline{\vec{r}}_q$. For $z>0$ the ansatz claims that the initial charge should be replaced by a charge q'' located at $\vec{r}_q$. When q' and q'' have been chosen to satisfy the appropriate boundary conditions at $z=0$ this leads to a solution

$$\phi(\vec{r}) = \phi^>(\vec{r}) = \frac{q}{\epsilon_>}\left[\frac{1}{|\vec{r} - \vec{r}_q|} + \left(\frac{\epsilon_> - \epsilon_<}{\epsilon_> + \epsilon_<}\right)\frac{1}{|\vec{r} - \underline{\vec{r}}_q|}\right], \quad z>0$$

$$= \phi^{<}(\vec{r}) = \frac{q}{\epsilon_{<}}\left(\frac{2}{\epsilon_{>}+\epsilon_{<}}\right)\frac{1}{|\vec{r}-\vec{r}_q|}, \quad z<0 . \quad (3.1)$$

When we use a dielectric formulism to describe an interacting electron gas we find that ϵ is not local as assumed above, but instead is, in general, a function of frequency and wave vector. It turns out, however, that expressing the right-hand side of (3.1) in its Fourier transformed form and then replacing $\epsilon^{\gtrless}$ by the corresponding wave-vector dependent quantities gives the appropriate solution in this more general case. That is, when a test charge $q(\Omega)$ (oscillating at frequency Ω) is at $\vec{r}_q$ in the right half space, the following occurs:

$$\phi(\vec{r},\Omega) = \phi^{>}(\vec{r},\Omega) = \sum_{\vec{k}} \frac{4\pi q(\Omega)}{k^2\epsilon^{>}(\vec{k},\Omega)}\left[e^{i\vec{k}\cdot(\vec{r}-\vec{r}_q)} + \left(\frac{\epsilon^{>}(\vec{k},\Omega)-\epsilon^{<}(\vec{k},\Omega)}{\epsilon^{>}(\vec{k},\Omega)+\epsilon^{<}(\vec{k},\Omega)}\right)e^{i\vec{k}\cdot(\vec{r}-\underline{\vec{r}}_q)}\right], \quad z>0$$

$$= \phi^{<}(\vec{r},\Omega) = \sum_{\vec{k}} \frac{4\pi q(\Omega)}{k^2\epsilon^{<}(\vec{k},\Omega)}\left(\frac{2}{\epsilon^{>}(\vec{k},\Omega)+\epsilon^{<}(\vec{k},\Omega)}\right)e^{i\vec{k}\cdot(\vec{r}-\vec{r}_q)}, \quad z<0 \quad (3.2)$$

in which we have used the fact that $\epsilon^{\gtrless}(\vec{k},\Omega)$ are even functions of $\vec{k}$. If now we have a distribution of charges

$$\rho_{\text{test}}(\vec{r},\Omega) = \textstyle\sum_i q_i(\Omega)\,\delta(\vec{r}-\vec{r}_i), \quad (3.3a)$$

then we can define

$$\rho^{>}{}_{\text{test}}(\vec{r},\Omega) = \sum_{z_i>0} q_i(\Omega)\,\delta(\vec{r}-\vec{r}_i) \quad (3.3b)$$

as those charges lying to the right of the boundary [and of course

$$\rho^{<}{}_{\text{test}}(\vec{r},\Omega) = \sum_{z_i<0} q_i(\Omega)\,\delta(\vec{r}-\vec{r}_i) \quad (3.3c)$$

as those to the left]. We see that the contribution to $\phi(\vec{r},\Omega)$ from the distribution of charges in the right half space is

$$\phi(\vec{r},\Omega) = \phi^{>}(\vec{r},\Omega) = \sum_{\vec{k}} \frac{4\pi e^{i\vec{k}\cdot\vec{r}}}{k^2\epsilon^{>}(\vec{k},\Omega)}\left[\rho^{>}{}_{\text{test}}(\vec{k},\Omega) + \left(\frac{\epsilon^{>}(\vec{k},\Omega)-\epsilon^{<}(\vec{k},\Omega)}{\epsilon^{>}(\vec{k},\Omega)+\epsilon^{<}(\vec{k},\Omega)}\right)\bar{\rho}^{>}{}_{\text{test}}(\vec{k})\right], \quad z>0$$

$$= \phi^{<}(\vec{r},\Omega) = \sum_{\vec{k}} \frac{8\pi e^{i\vec{k}\cdot\vec{r}}}{k^2}\,\frac{\rho^{>}{}_{\text{test}}(\vec{k},\Omega)}{\epsilon^{>}(\vec{k},\Omega)+\epsilon^{<}(\vec{k},\Omega)}, \quad z<0 \quad (3.4)$$

where

$$\bar{\rho}_{\text{test}}(k_x,k_y,k_z) = \rho_{\text{test}}(k_x,k_y,-k_z). \quad (3.5)$$

We can treat a distribution of charges to the left of the boundary in an entirely analogous fashion so that ultimately we get

$$\phi^{>}(\vec{r},\Omega) = \sum_{\vec{k}} \frac{4\pi e^{i\vec{k}\cdot\vec{r}}}{k^2}\left[\frac{\rho^{>}{}_{\text{test}}(\vec{k},\Omega)}{\epsilon^{>}(\vec{k},\Omega)} + \frac{2\rho^{<}{}_{\text{test}}(\vec{k},\Omega)}{\epsilon^{>}(k,\Omega)+\epsilon^{<}(\vec{k},\Omega)} + \bar{\rho}^{>}{}_{\text{test}}(\vec{k},\Omega)\left(\frac{\epsilon^{>}(\vec{k},\Omega)-\epsilon^{<}(\vec{k},\Omega)}{\epsilon^{>}(\vec{k},\Omega)+\epsilon^{<}(\vec{k},\Omega)}\right)\right], \quad z>0 \quad (3.6)$$

with $\phi^{<}(\vec{k},\Omega)$ obtained by interchanging the symbols (>) and (<).

From this expression we can, using Poisson's equation,

$$\Delta^2\phi = -4\pi(\rho_{\text{total}}) = -4\pi(\rho_{\text{test}}+\rho_{\text{ind}}), \quad (3.7)$$

determine the charge density[9]

$$\rho^{\gtrless}_{\text{total}}(\Omega) = \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}\left[\frac{\rho^{\gtrless}_{\text{test}}(\vec{k},\Omega)}{\epsilon^{\gtrless}(\vec{k},\Omega)} + \frac{2\rho^{\lessgtr}_{\text{test}}(\vec{k},\Omega)}{\epsilon^{>}(\vec{k},\Omega)+\epsilon^{<}(\vec{k},\Omega)} + \bar{\rho}^{\gtrless}_{\text{test}}(\vec{k},\Omega)\left(\frac{\epsilon^{\gtrless}(\vec{k},\Omega)-\epsilon^{\lessgtr}(\vec{k},\Omega)}{\epsilon^{>}(\vec{k},\Omega)+\epsilon^{<}(\vec{k},\Omega)}\right)\right], \quad (3.8)$$

so that after some straightforward but tedious algebra,

$$\frac{\delta\rho_{\text{total}}(\vec{r},\Omega)}{\delta\rho_{\text{test}}(\vec{r},\Omega)} = \int\frac{d^3\vec{k}}{(2\pi)^3}\left\{\frac{1}{\epsilon^{\gtrless}(\vec{k},\Omega)}\left[1+e^{2ik_z z}\left(\frac{\epsilon^{\gtrless}(\vec{k},\Omega)-\epsilon^{\lessgtr}(\vec{k},\Omega)}{\epsilon^{>}(\vec{k},\Omega)+\epsilon^{<}(\vec{k},\Omega)}\right)\right]\right\}, \quad z\gtrless 0 . \quad (3.9)$$

When we insert this result into our basic Eq. (2.15), we get

$$E_{\text{int}} = \frac{1}{2}\int v(\vec{r}_1-\vec{r}_2)[\rho(\vec{r}_1)\,\vec{\rho}(r_2) - \delta(1,3)\,\rho(\vec{r}_2)]\,d^3\vec{r}_1\,d^3\vec{r}_2 + \frac{\frac{1}{2}i\hbar}{(-i\beta\hbar)}\sum_{\Omega}\left[V^{>}\int\frac{d^3\vec{k}}{(2\pi)^3}\left(\frac{1}{\epsilon^{>}(\vec{k},\Omega)}-1\right)\right.$$

$$+ V^{<}\int \frac{d^3\vec{k}}{(2\pi)^3}\left(\frac{1}{\epsilon^{<}(\vec{k},\Omega)}-1\right) - \tfrac{1}{4}A\int \frac{d^3\vec{k}}{(2\pi)^3}\left((2\pi)\,\delta(k_z)\frac{[\epsilon^{>}(\vec{k},\Omega)-\epsilon^{<}(\vec{k},\Omega)]^2}{\epsilon^{>}(\vec{k},\Omega)\epsilon^{<}(\vec{k},\Omega)[\epsilon^{>}(\vec{k},\Omega)+\epsilon^{<}(\vec{k},\Omega)]}\right)\Bigg], \tag{3.10}$$

where $V^{\gtrless}$ is the volume of material for $z \gtrless 0$ and A is the area of the boundary.

We see that the exchange and correlation part of $E_{\rm int}$ divides in a rather pleasing manner into two terms dependent upon the properties of the material to the right and left of the boundary, respectively, and which are proportional to the volumes of those pieces, plus a term we can associate with the surface. This latter is proportional to the area of the boundary and will have poles at the surface-plasmon frequency, i.e., those frequencies for which

$$\epsilon^{>}(\vec{k},\Omega)+\epsilon^{>}(\vec{k},\Omega)=0. \tag{3.11}$$

Within our approximation that the material for $z \gtrless 0$ can be described by the bulk properties of the corresponding material, the "Hartree" term

$$\int v(\vec{r}_1-\vec{r}_2)\,\rho(\vec{r}_1)\,\rho(\vec{r}_2)\,d^3\vec{r}_1\,d^3\vec{r}_2$$

cancels against the positive background in the usual way and the singular term

$$\tfrac{1}{2}\int v(\vec{r}_1-\vec{r}_2)\,\delta(\vec{r}_1-\vec{r}_2)\,\rho(\vec{r}_1)\,d^3\vec{r}_1\,d^3\vec{r}_2$$

may also in the usual way be used to cancel the singularities in the corresponding bulk terms. The surface correction to the total energy of the system is then

$$\gamma A=\int_0^{e^2}\frac{dg}{g}\,E_{\rm int}(g)=\frac{-iA(\frac{1}{8})}{(-i\beta)}\sum_{\Omega}\int_0^{e^2}\frac{dg}{g}\int\frac{d^2\vec{k}_{\parallel}}{(2\pi)^2}\,\frac{[\epsilon^{>}(\vec{k},\Omega)-\epsilon^{<}(\vec{k},\Omega)]^2}{\epsilon^{>}(\vec{k},\Omega)\epsilon^{<}(\vec{k},\Omega)[\epsilon^{>}(\vec{k},\Omega)+\epsilon^{<}(\vec{k},\Omega)]}\,. \tag{3.12}$$

Here $\epsilon^{\gtrless}(\vec{k},\Omega)=\epsilon^{\gtrless}(k_x,k_y,0)$ and $\vec{k}_{\parallel}=k_x\hat{\vec{i}}+k_y\hat{\vec{j}}$. (In the remainder of this work we shall take $\hbar=1$.)

At this point we introduce a number of further simplifications. First for convenience and comparison with experiment, we assume that the half space $z>0$ is vacuum so that $\epsilon^{>}=1$. Now we expect that the important contribution to (3.12) will be that due to the high-frequency poles. Accordingly, we shall assume the high-frequency form for $\epsilon^{<}$ is appropriate:

$$\epsilon^{<}=1-\omega p^2/\Omega^2, \tag{3.13}$$

where $\omega_p=\omega_p(g)=(4\pi n g/m)^{1/2}$. We further assume $\epsilon^{<}(k,\Omega)$ to be independent of wave vector up to a cutoff wave vector k_c above which $\epsilon^{<}=1$. This is equivalent to the usual cutoff procedure in the manner of Pines.[10] Finally we assume the system to be at zero temperature. This is always a good approximation for the surface plasmons. When we make the zero-temperature approximation we find that the surface energy becomes

$$\gamma=-i\tfrac{1}{8}\int_0^{e^2}\frac{dg}{g}\int\frac{d^2\vec{k}_{\parallel}}{(2\pi)^2}\int_c\frac{d\omega}{(2\pi)}\,\frac{(1-\epsilon)^2}{\epsilon(1+\epsilon)}\,, \tag{3.14}$$

with a contour c that which goes clockwise about the positive real axis [Fig. 2(a)]. This contour can be deformed into that of Fig. 2(b), thereby isolating the collective poles from those due to individual particle-hole excitations (see the Appendix). The contribution to γ from the high-frequency poles contained within C_2 and C_3, γ_c is seen to be

$$\gamma_c=\int_0^{e^2}\frac{dg}{g}\int_0^{k_c}\frac{d^2k_{\parallel}}{(2\pi)^2}\,\frac{\sqrt{2}-1}{16}\,\omega_p\,. \tag{3.15}$$

The wave-vector and coupling-constant integrals are elementary so this expression is easily evaluated giving

$$\gamma_c=\frac{\omega_p{}^3}{V_F{}^2}\,\frac{\sqrt{2}-1}{96\pi}\,\alpha^2\,, \tag{3.16}$$

where we have set $k_c=\alpha\omega_p/v_F$ in which v_F is the velocity of an electron at the Fermi surface and α is a constant of order unity.[11] Equation (3.16) is an extremely simple result, but one which we would be rather unlikely to guess. There is an additional contribution to γ coming from the particle-hole excitations contained within c_1;

$$\gamma_i=\frac{-i\hbar}{8}\int_0^{e^2}\frac{dg}{g}\int\frac{d^2\vec{k}_{\parallel}}{(2\pi)^2}\int_{c_1}\frac{d\omega}{2\pi}\left(\frac{(1-\epsilon)^2}{\epsilon(1+\epsilon)}\right). \tag{3.17}$$

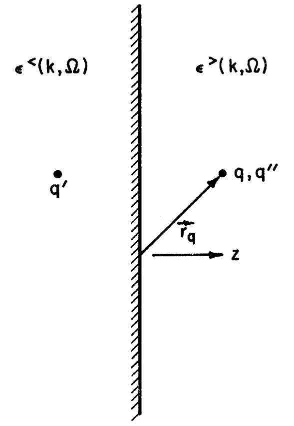

FIG. 1. Image ansatz for solving problem of charge near boundary.

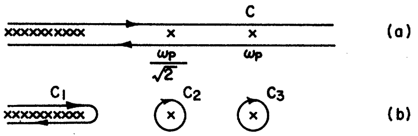

FIG. 2. Contours used with evaluation of γ.

This contribution comes from the low frequency, nearly static region. Consequently, it is this term which will be most sensitive to the "healing" of the surface, i.e., to the fact that the physical surface is not a mathematical surface but instead is spread out over a distance comparable with a Fermi wavelength. This healing will also change the "Hartree" term

$$\int v(\vec{r}_1 - \vec{r}_2)\rho(\vec{r}_1)\rho(\vec{r}_2)\, d^3\vec{r}_1\, d^3\vec{r}_2$$

from zero to some nonzero value and in addition, there will exist contributions to the expression

$$\delta\rho_{\text{ind}}(\vec{r},\Omega)/\delta\rho_{\text{test}}(\vec{r},\Omega)$$

from the surface—induced charge within the boundary layer itself. [Also Bennett[12] has shown that the dispersion of the surface plasma is extremely sensitive to the distribution of charge within the surface layer, although of course it always reduces to the same $k=0$ limit, $\omega_p/\sqrt{2}$. Presumably this should show up as a contribution to (3.14), but we should not see this here as we have taken the high-frequency part of $\epsilon(\vec{k},\Omega)$ to be independent of wave vector.] Now we note that in an expansion in powers of $4\pi\alpha_0(k,\omega)$, the free-electron polarizability, (3.17) is at least of order $(4\pi\alpha_0)^2$, a linear term which appears in the bulk correlation energy being missing. The linear term in $4\pi\alpha_0$ corresponds to the Hartree-Fock approximation for the bulk material in which the electronic density is replaced by its independent particle value. The absence of the linear term indicates that, in a sense, (3.17) is already beyond the lowest-order correction to γ in the static limit.[13]

We are now in a position to evaluate the contribution γ_c as a function of the free electron density. It is conventional to express the electron density in terms of the volume per electron, $\frac{4}{3}\pi r_s^3$ measured in atomic units. In terms of these units,

$$\gamma_c = \frac{\sqrt{2}-1}{12\pi}\left(\frac{3}{16\pi^4}\right)^{1/6} \frac{\alpha^2}{r_s^{5/2}} \frac{\text{Ry}}{(\text{a.u.})^2}. \qquad (3.18)$$

Equation (3.18) is plotted in Fig. 3 as a function of r_s, together with various experimental values of surface energy. The selection of experimental values for γ presents certain difficulties. The most accurate measurements of the surface energy are those done by the sessile drop method in which the profile of a drop of the molten material is examined in detail. This, of course, requires that the material be molten and therefore obviously not at absolute zero (as far as the collective modes are concerned, the temperature is still zero). We could extrapolate the linear part of the surface energy to $T=0$ across the liquid-solid phase transition and call this our surface energy. This, in fact, is what Lang and Kohn have done. There is no particular reason to believe that this extrapolation across the phase transition is correct. If one is to do this extrapolation he should extrapolate

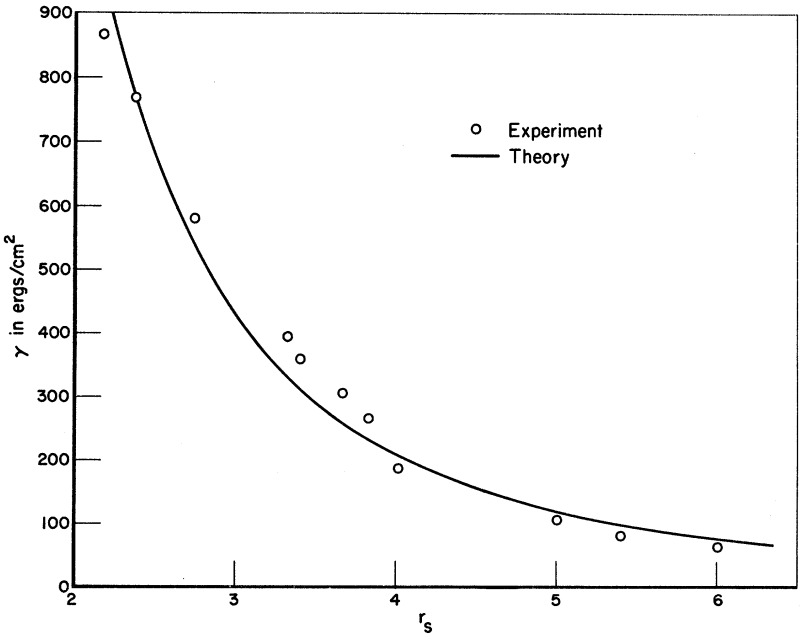

FIG. 3. Experimental and theoretical values of the surface energy. The theoretical value plotted here is that due to dynamic contribution only.

the density as well to $T=0$ to determine the proper value of r_s. The procedure used here was to select that surface energy and density (and therefore r_s) appropriate to the melting temperature. The values used for γ and r_s at the melting temperature are shown in Table I.

IV. CONCLUSION

The collective part of the surface energy is evidently a major contribution to the total surface energy, as consideration of this term alone gives remarkably good agreement with experiment especially when considering the approximations involved. Clearly, therefore, such contribution must be included *a priori* in a better calculation of the surface energy. The Kohn-Sham-Hohenberg theory as used does not include the energy of new normal modes of the system introduced by the variation of the density of electron gas. The reason for this is easy to understand and suggests how the Lang and Kohn procedure might be improved. Hohenberg and Kohn[3] showed that the energy is a unique functional $E(n(\vec{r}))$ of the electronic density $n(\vec{r})$. If we knew what this functional was there would be no difficulty (in principle) in calculating the surface energy. This functional would have contained within it all possible information at all possible electronic density distributions including the one where the electronic system has a surface (as well as more complicated arrangements) and would contain therefore the surface plasmons. Clearly we do not know this $E(n(\vec{r}))$ and must in some way estimate it. If we replace the functional $E(n(\vec{r}))$ by a function of $n(\vec{r})$, $\bar{E}(n(\vec{r}))$ according to the approximation scheme of Hohenberg and Kohn, we introduce certain approximations. If, in addition, we use for $\bar{E}(n(\vec{r}))$ that appropriate to a uniform electron gas (as did Lang and Kohn), we no longer have any information at all about the surface modes.[19]

TABLE I. Experimental data.

	$r_s(T_m)$	$\gamma(T_m)$ (erg/cm^2)
Al [a]	2.17	865
Zn	2.37 [b]	768 [c]
Mg [d]	2.74	583
Li [e]	3.32	397
Ca [d]	3.40	360
Sr [d]	3.67	304
Ba [d]	3.83	267
Na [e]	4.04	186
K [e]	5.02	104
Rb [e]	5.40	79
Cs [e]	5.78	65

[a] Reference 14.
[b] Reference 15.
[c] Reference 16.
[d] Reference 17.
[e] Reference 18.

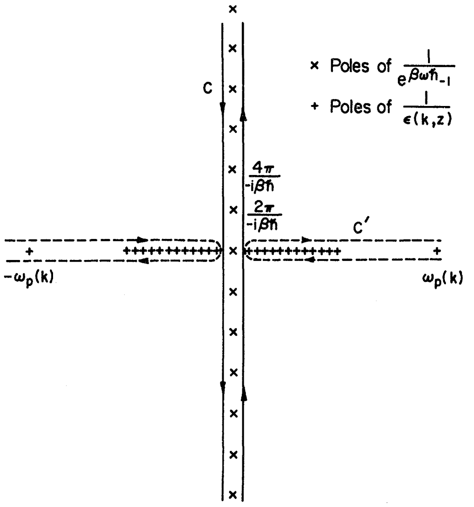

FIG. 4. Integration contours used in conversion of the frequency sum in (A5) to an integral.

How can we improve upon the results of Lang and Kohn? Obviously, we cannot write down the universal functional $E((\vec{r}))$ and must, therefore, settle for an approximation. Equation (3.10) (with the proper added kinetic-energy term) provides a possible starting point, for if we evaluate all the terms of Eq. (3.10) as functions of $n(\vec{r})$, we have an expression for the energy of a system with a surface. In this work we have taken the first step in evaluating (3.10) when the electronic densities are constant on either side of the boundary.

Finally, it should be observed that including core-polarization and effective-mass effects would tend to raise the dynamic contribution to the surface energy, especially to the less ideal metals (lithium and the alkaline earths) as would the inclusion of plasmon dispersion, whereas using the value of the critical wave vector after Sawada *et al.* [20] would tend to lower γ_c. Except possibly for the effective-mass and core-polarization corrections these effects may be neglected for metallic densities. The present theory is a continuum (jellium) model. The inclusion of the ions as discrete (except as already noted above) is unnecessary as, for the wavelengths in question, the collective modes do not see the discrete ions.

APPENDIX

In this Appendix we show how Eq. (2.15) gives the conventional results for homogeneous electron gas. For a translationally invariant system we can Fourier transform in space; then (2.15) becomes

$$E_{\text{int}}(g)=\frac{i\hbar}{2}\,\frac{V}{(-i\beta\hbar)}\sum_{\vec{k},\Omega}\left(\frac{\delta\rho(\vec{k},\Omega)_{\text{ind}}}{\delta\rho_{\text{test}}(\vec{k},\Omega)}\right)_g$$

$$+\tfrac{1}{2}\sum_{\vec{k}} v(\vec{k})\left[\langle\rho(\vec{k})\rangle\langle\rho(\vec{k})\rangle - \langle\rho(0)\rangle\right] . \quad \text{(A1)}$$

Now, defining the frequency and wave-vector-dependent dielectric constant in the conventional manner, that is

$$\epsilon(\vec{k}, \Omega)\, k^2 \varphi(\vec{k}, \Omega) = 4\pi\rho_{\text{test}}(\vec{k}, \Omega) , \quad \text{(A2a)}$$

together with

$$k^2\varphi(\vec{k}, \Omega) = 4\pi[\rho_{\text{test}}(\vec{k}, \Omega) + \rho_{\text{ind}}(\vec{k}, \Omega)] , \quad \text{(A2b)}$$

we have

$$\rho_{\text{ind}}(\vec{k}, \Omega)/\rho_{\text{test}}(\vec{k}, \Omega) = 1/\epsilon(\vec{k}, \Omega) - 1 \quad \text{(A3)}$$

so that

$$\frac{\delta\rho_{\text{ind}}(\vec{k}, \Omega)}{\delta\rho_{\text{test}}(\vec{k}, \Omega)} = 1/\epsilon(\vec{k}, \Omega) - 1 . \quad \text{(A4)}$$

Because of the cancellation against the positive background, the "Hartree" term $\langle\rho\rangle\langle\rho\rangle$ in (A1) vanishes and we find[21]

$$E_{\text{int}} = \frac{i\hbar}{2}\,\frac{V}{(-i\beta\hbar)}\sum_{k,\Omega}\left(\frac{1}{\epsilon} - 1\right) - \sum_{k}\frac{2\pi e^2}{k^2} N . \quad \text{(A5)}$$

When we apply the usual prescription for transforming the sum to an integral,[7] the first term of (A5) becomes

$$\frac{i\hbar}{2} V \int_c \frac{d\omega}{2\pi}\,\frac{1}{(e^{\beta\hbar\omega} - 1)}\left(\frac{1}{\epsilon(\vec{k}, \omega)} - 1\right), \quad \text{(A6)}$$

where the contour c is shown in Fig. 4.

In the simplest approximation in which the electron hole and collective modes of the system are undamped, these excitations appear as poles of $1/\epsilon(\vec{k}, \omega)$ on the real axis. The plasmon pole appears as isolated singularities at $\pm\,\omega_p(\vec{k})$; the particle-hole excitations as a dense set of poles running from $\omega = -\,\omega_{\max}(k)$ to $\omega = \omega_{\max}(k)$. When lifetimes are introduced, we find that these excitations are represented by discontinuities in $1/\epsilon(\vec{k}, \omega)$ across the real axis, i.e., by cuts along the real axis. We can therefore deform the contour in Fig. 4 into C'. When we do this contour deformation, (A6) becomes

$$\frac{i\hbar V}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,\frac{1}{e^{\beta\hbar\omega} - 1}\left(\frac{1}{\epsilon(\vec{k}, \omega + i\epsilon)} - \frac{1}{\epsilon(\vec{k}, \omega - i\epsilon)}\right) , \quad \text{(A7)}$$

but, from the Kramers-Kronig relations

$$\lim_{\epsilon\to 0}\left(\frac{1}{\epsilon(\omega + i\epsilon)} - \frac{1}{\epsilon(\omega - i\epsilon)}\right) = -\,2i\,\text{Im}\,\frac{1}{\epsilon(\vec{k}, \omega)} , \quad \text{(A8)}$$

so that finally (A5) becomes, on using the antisymmetry of $\text{Im}\,1/\epsilon(\vec{k}, \omega)$,

$$E_{\text{int}} = -\frac{\hbar V}{2}\int\frac{d^3\vec{k}}{(2\pi)^2}\int\frac{d\omega}{2\pi}\left(\coth\frac{\hbar\beta\omega}{2}\right)\text{Im}\left(\frac{1}{\epsilon(\vec{k}, \omega)}\right)_g$$

$$-N\int\frac{d^3\vec{k}}{2\pi^3}\,\frac{2\pi g}{k^2} , \quad \text{(A9)}$$

which is the conventional expression for $E_{\text{int}}(g)$.

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[1] J. C. Jaeger, *Elasticity, Fracture and Flow*, 3rd ed. (Methuen, London, 1969).

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[3] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[4] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[5] For simplicity we consider the case of a rigid positive background (jellium). The situation where there may be more than one species of charge (as, for instance, ions) interacting among each other develops in a similar fashion.

[6] Here and in the following, the angular brackets refer to thermal averages: $\langle\cdots\rangle = \text{Tr}(e^{-\beta H}\cdots)\,/\,\text{Tr}(e^{-\beta H})$. For the purpose of this work the zero-temperature limits will ultimately be taken; we shall keep the finite-temperature theory until that time to preserve the generality of the discussion of the mathematical background.

[7] L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (Benjamin, New York, 1963).

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[9] This neglects an induced surface charge on the dividing plane $z = 0$. It is possible to show, however, by allowing ϵ to vary linearly over a length a from $\epsilon^<$ to $\epsilon^>$ and taking the limit as $a \to 0$ that this charge makes no contribution to E_{int} and so we ignore it.

[10] D. Pines, *Elementary Excitations in Solids* (Benjamin, New York, 1963).

[11] Here we choose $\alpha = 1.48$ by fitting to the experimental data. The usual practice is to cut off wave-vector integrals of this type at $k = \omega_p/v_f$, i.e., for $\alpha = 1$ as at this value damping of the plasma mode through the creation of particle-hole pairs is first possible. These damped modes do, however, make a contribution to the correlation energy; since detailed investigation of the damped modes is beyond the intended scope of this work, we introduce the parameter α.

[12] A. J. Bennett, Phys. Rev. B 1, 203 (1970).

[13] This does not mean to imply that we are doing (or suggesting) an expansion in powers of $4\pi\alpha_0$; such an expansion is divergent term by term. This argument is only introduced to indicate that it would be inconsistent to keep the static part of γ, (3.17), without healing the "Hartree" term.

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[18] J. Bohdansky and H. E. J. Schins, J. Inorg. Nucl. Chem. 29, 2173 (1967).

[19] It does include, of course, the zero-point energy of the bulk plasmons to the extent that such contributions are included in the bulk correlation energy they use as a starting point.

[20] K. Sawada, K. A. Brueckner, N. Fulcuda, and R. Brout, Phys. Rev. 109, 507 (1957).

[21] A result equivalent to (A5) is derived in a rather different manner by Brout and Carruthers (Ref. 22).

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New Kind of Surface State in Nearly-Free-Electron Metals*

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We show that for a (2, 0, 0) surface of a bcc crystal there exist not only the Goodwin surface states in the (1, 0, 0) energy gap but also a new kind of surface state in the $(\frac{1}{2}, \frac{1}{2}, 0)$ energy gap. Although the Goodwin state exists only when V_{200} is negative, these new surface states exist for either sign of V_{110}.

It has been a third of a century since Goodwin[1] showed the existence of surface states on the (ijk) surface of a nearly-free-electron metal. These states have an energy within the $(\frac{1}{2}i, \frac{1}{2}j, \frac{1}{2}k)$ energy gap and exist only if V_{ijk} [i.e., the (ijk) Fourier transform of the crystal potential] is negative. Goodwin used a model in which the potential was identical to the bulk-crystal potential up to the surface plane and zero beyond the surface plane so that negative V_{ijk} means that the surface plane must be chosen to be at the point where $V(\vec{r})$ is a minimum.[2] In this paper we show, using Goodwin's model, that (2, 0, 0) surface states exist in bcc metals in the $(\frac{1}{2}, \frac{1}{2}, 0)$ energy gap and that their existence is independent of the sign of V_{110} and in all likelihood independent of where in the surface unit cell the surface plane is chosen. Although the discontinuous model potential is not very physical, these facts indicate that they should exist in real metal surfaces. A simple generalization of the following derivation shows that this kind of state exists for an (I, J, K) surface if there exists a set of degenerate energy gaps $(\frac{1}{2}i, \frac{1}{2}j, \frac{1}{2}k)$, $(\frac{1}{2}i', \frac{1}{2}j', \frac{1}{2}k')$, etc. such that $(i+i', j+j', k+k') = (I, J, K)$.

Consider the following wave function inside the crystal (i.e., for $x \leq 0$):

$$\psi = e^{iky}\left(e^{i\pi z/a} + \beta e^{-i\pi z/a}\right)\left(e^{i(\pi x/a+\varphi)} + e^{-i(\pi x/a+\varphi)}\right)e^{qx}. \tag{1}$$

This is a Bloch function in the (k_y, k_z) plane with $k_y = k$, assumed to be small compared to π/a, and $k_z = \pi/a$. Consideration of the continuity of the two-dimensional energy bands, as well as detailed numerical calculations,[3] shows that if Eq. (1) is a surface state at $(k, \pi/a)$ there will also exist surface states at $(k, \pi/a - \delta)$, where $\delta \ll \pi/a$. However if $\delta \neq 0$, the functional form of the surface state becomes much more complicated than Eq. (1) and our simple derivation cannot be made. The Hamiltonian within the crystal is

$$H = -\nabla^2 + V(\vec{r}), \tag{2}$$

where we take the pseudopotential

$$V(\vec{r}) = V_0 + V_{110}\left(e^{i\chi}e^{2\pi i(x+z)/a} + e^{-i\chi}e^{-2\pi i(x+z)/a} + e^{i\chi}e^{2\pi i(x-z)/a} + e^{-i\chi}e^{-2\pi i(x-z)/a}\right). \tag{3}$$

Because the pseudopotential of a nearly-free-electron metal is very weak,[4] we are able to neglect all other Fourier transforms of $V(\vec{r})$ which mix plane waves of much higher kinetic energy into Eq. (1). This is the reason we require $k \ll \pi/a$. The surface plane is taken to be at $x = 0$ but its location with respect to the crystal lattice is determined by χ. Note that in the surface plane, $V(\vec{r}) = V_0 + V_{110} 4\cos\chi\cos 2\pi z/a$. Therefore, we expect our results to be independent of the sign of V_{110} because a change in the sign of V_{110} is equivalent to replacing z by $z + \frac{1}{2}a$ which is of no physical consequence. This differs from the case considered by Goodwin[1] where V_{200} was the important contributor to $V(\vec{r})$; thus $V(\vec{r})$ was a constant in the $x = 0$ plane making the sign of V_{200} of paramount importance.

Inserting (1) into the Schrödinger equation, removing the common factor $e^{iky}e^{qx}$, multiplying through by $e^{\pm i\pi x/a}e^{\pm i\pi z/a}$, and integrating over x and z yield four equations which reduce to the following two if we assume $\beta = \pm 1$:

$$\left[k^2 + (\pi/a)^2 + (\pi/a - iq)^2 + V_0 - E\right]e^{i\varphi} + V_{110}\beta e^{-i(\varphi+\chi)} = 0, \tag{4}$$

$$\left[k^2 + (\pi/a)^2 + (\pi/a + iq)^2 + V_0 - E\right]e^{-i\varphi}$$