Self-charging of the surface of a finite-size conductor

V. I. Gorchakov and É. L. Nagaev

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The electrostatic correction to the electron Fermi energy in a conducting thin film is found as a function of the film thickness L for an arbitrary relation between L and r_{sc}. The corresponding behavior of the electrostatic part of the surface energy is also found. Under the condition $L \gg r_{sc}$ the size corrections to the Fermi energy associated with the kinetic energy and with the electrostatic energy may be comparable. For heavily doped semiconductors the electrostatic correction to the Fermi energy is opposite in sign to the surface correction to the kinetic part of the chemical potential and has half the magnitude of the kinetic part. The amplitude of Friedel oscillations of the electron density at the film surface is found; screening is taken into account. As a result, a term with a coordinate dependence different from that in the case of free electrons appears in the asymptotic expression for the amplitude. A mathematical by-product of this study is a generalization of the Euler-Maclaurin summation formula to the case of functions which have a pole near the real axis.

1. INTRODUCTION

The density of conduction electrons near the surface of a sample is known to differ from the bulk density, so the surface of a conductor is charged with respect to the interior. The surface charge results from a difference between the surface potential and the interior potential. This charge is screened by the conduction electrons themselves. As a result, a double layer arises at the surface and has a strong effect on the surface energy of the sample and on its work function.

The size dependence of these properties for conductors of finite dimensions has recently attracted much interest. A size dependence of the work function was first observed experimentally for small particles in Ref. 1. This dependence is usually attributed to the electrostatic energy which the particle acquires after an electron escapes from it.[2] It was stated in Ref. 3 that an even greater contribution to this dependence comes from a spatial quantization of the orbits of the conduction electrons. The second of these mechanisms differs from the first in that it operates also in thin films. In the present paper we propose for a size dependence of the electron chemical potential a new mechanism involving a size dependence of the surface double layer. We will show that this mechanism is fully as significant as the mechanism proposed in Refs. 2 and 3 and that it, too, operates in thin films as well as in small particles.

As we just mentioned, the double layer also has a strong effect on such an important characteristic of a conductor as its surface energy. The calculations below reveal not only this energy but also its size dependence, i.e., the terms of higher order in the reciprocal size of the sample. Finally, a study of the structure of double layers is important in connection with the problem of oscillations in the surface relaxation. If screening is ignored, the electron density near a surface takes the form of Friedel oscillations with an amplitude which falls off by a power law with distance into the sample. Because of the electron-phonon coupling, oscillations of this sort should also be exhibited by the displacements of the atomic layers of the crystal.[4,5] This result applies to samples with a thickness smaller than the screening radius. There is of course the question of whether these oscillations are also found in thicker samples. We show below that the answer to this question is affirmative: The surface-charge density found with allowance for screening also undergoes Friedel oscillations.

2. MODEL AND CALCULATION METHOD

As in Refs. 4 and 5, we consider a plane-parallel sample with a plane face of area S and with a thickness $L \ll S^{1/2}$. In the self-consistent-field approximation, and in the jellium model, the problem reduces to one of solving the one-particle Schrödinger equation and the Poisson equation for the potential φ of the self-consistent electrostatic field:

$$(-\hbar^2\Delta/2m+e\varphi)\hat{\psi}=E\hat{\psi}, \tag{1}$$

$$-\Delta\varphi=(4\pi/\varepsilon_0)\rho,\quad \rho=e(\langle\hat{\psi}^+\hat{\psi}\rangle-n_0), \tag{2}$$

for $0<z<L$. Here $\hat{\psi}$ and $\hat{\psi}^+$ are electron operators in the coordinate representation, n_0 is the density of the "ion background" in the jellium model, and ε_0 is the dielectric constant of this background. If the sample is electrically neutral, a nonvanishing charge density ρ and the electric field φ which it creates arise because of a perturbation of the electron subsystem by the surface of the sample. As a boundary condition on the function φ it is sufficient to require that the potential be symmetric with respect to the middle of the sample and that the average potential over the thickness of the sample vanish. As in Ref. 4, we will be restricting the discussion to the simplest boundary condition on the wave functions:

$$\psi(0)=\psi(L)=0. \tag{3}$$

To put the problem in a form which we can solve analytically, we adopt the condition that the Coulomb interaction is weak. It holds, in particular, for heavily doped semiconductors:

$$\eta\equiv\varkappa/2k_F\ll 1, \tag{4}$$

where $\varkappa\equiv(4e^2mk_F/\varepsilon_0\hbar^2\pi)^{1/2}$ is the Thomas-Fermi parameter, and $\hbar k_F$ is the Fermi momentum. Constructing the electron wave function in (1) in first order in the screened Coulomb field φ, we find the following expression for the charge density:

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$$\rho(r)=\rho_0(z)+\int_0^L dz'K(z,z')\varphi(z')\equiv\rho(z),$$

$$\rho_0(z)\equiv e(\langle\hat{\psi}^+\hat{\psi}\rangle_0-n_0)\equiv\rho_S(z)+\rho_V(z),$$

$$\rho_V(z)=\frac{e}{2\pi L}\sum_{n=1}^{\infty}\theta(k_F-k_n)(k_F{}^2-k_n{}^2)-en_0=e(N/SL-n_0),$$

$$\rho_S(z)=-\frac{e}{2\pi L}\sum_{n=1}^{\infty}\theta(k_F-k_n)(k_F{}^2-k_n{}^2)\cos 2k_Fz, \qquad (5)$$

where

$$K(z,z')=\frac{8e^2m}{\pi\hbar^2L^2}\sum_{n,n'=1;n\neq n'}^{\infty}\theta(k_F-k_n)\frac{k_F{}^2-k_n{}^2}{k_n{}^2-k_{n'}{}^2}$$

$$\times\sin k_nz\cdot\sin k_{n'}z\cdot\sin k_nz'\cdot\sin k_{n'}z'. \qquad (6)$$

Here ρ_0 is a "seed" charge density obtained when the Coulomb interaction is ignored, N is the total number of electrons, which is generally not equal to the number of ions, and $k_n=\pi n/L$ are the quantum-size values of the component of the wave vector normal to the surface ($n=1,2,...$). As a result we find the following expression for the total energy of the conduction electrons:

$$\mathscr{E}=\mathscr{E}_K+\mathscr{E}_Q, \quad \mathscr{E}_Q=\frac{S}{2}\int_0^L dz\,\rho_0(z)\varphi(z), \qquad (7)$$

where $\mathscr{E}_K$ is the energy of the conduction electrons when the electrostatic interaction is ignored. Correspondingly, the electron chemical potential can be written

$$\mu=\mu_K+\Delta\mu_Q, \quad \Delta\mu_Q\equiv\partial\mathscr{E}_Q/\partial N, \qquad (8)$$

where the term $\Delta\mu_Q$ stems from the Coulomb interaction, and μ_K is the kinetic part of the chemical potential. Its size dependence is given by, according to Ref. 3,

$$\mu_K=\mu_0(1+\lambda). \qquad (9)$$

Here $\mu_0=\hbar^2k_0^2/2m$ is the chemical potential of the bulk sample, $k_0=(3\pi^2n_0)^{2/3}$, and the parameter

$$\lambda\equiv\pi/2k_FL\ll1 \qquad (10)$$

is a measure of the extent to which the situation is semiclassical.

The approximation used above leads to reasonable estimates not only under condition (4) but even in the case $\eta\sim1$. One cannot, of course, expect quantitatively correct results in the calculations of the electron energy, but quantitative results are not the goal of this study. The goal is simply to determine how the electrostatic corrections depend on the dimensions of the sample.

To estimate the sums over the discrete variable k_n which arise by virtue of condition (10), we use formulas of the Euler-Maclaurin type. In our notation, the standard form of these formulas[6] would be

$$\sum_{n=1}^{n_F}f(k_n)=\sum_{n=0}^{n_F}f(k_n)-f(k_0)$$

$$=\frac{L}{\pi}\int_0^{k_F}dk\,f(k)+\frac{1}{2}[f(k_F)-f(0)]+O(\lambda), \qquad (11)$$

where $n_F\equiv Lk_F/\pi$ and $f(...)$ is a sufficiently smooth function. As we will see below, this formula is valid only under the condition

$$\varkappa L\gg1, \qquad (12)$$

in which case we have $r_{sc}=\varkappa^{-1}\ll L$. If we do not adopt restriction (12), we find a modification of the standard formula in (11) and of the results found from it, as is shown in the Appendix. In the case in which the function f on the left side of (11) has poles at small values of k, for example, this generalization becomes

$$\sum_{n=1}^{n_F}\frac{Q(2k_n)}{(2k_n)^2+\Delta^2}=\frac{L}{\pi}\int_0^{k_F}dk\frac{Q(2k)}{(2k)^2+\Delta^2}-\frac{Q(0)}{2\Delta^2}$$

$$+\frac{L}{2\Delta}\frac{Q(i\Delta)}{e^{L\Delta}-1}+O(\lambda), \qquad (13)$$

where it is assumed that the function Q satisfies $Q(2k_F)=0$. When condition (12) holds, Eqs. (11) and (13) become the same.

It is sufficient to carry out a transformation of the original equation, (2), with the help of (5), which subsequently leads to an approximate solution of this equation, for the case of an electrically neutral system, in which we have $\rho_V=0$ in (5) and thus $\rho_0\equiv\rho_S$. Since the field vanishes at the boundary and outside the sample in this case, the solution of Eqs. (2) and (5) can be written as the Fourier series

$$\varphi(z)=L^{-1}\sum_{n=-\infty}^{\infty}\varphi_n\cos k_nz, \qquad (14)$$

where $\varphi_{-n}\equiv\varphi_n$ and $k_n=\pi n/L$. From (2), (5), and (14) with $n\neq0$ we find the following equation for the even coefficients φ_{2n}:

$$(2k_n)^2\varphi_{2n}=(4\pi/\varepsilon_0)\rho_{2n}{}^S+(\lambda\varkappa^2/2)\sum_{n'\neq n}\theta(k_F-|k_n-k_{n'}|)$$

$$\times\frac{k_F{}^2-(k_n-k_{n'})^2}{k_nk_{n'}}(-\varphi_{2n}+\varphi_{2n'}). \qquad (15)$$

The odd coefficients are zero. Here ρ_{2n}^S are the Fourier coefficients for the function $\rho_S(z)$, and can be found from (5). The coefficient φ_0 is being set equal to zero (these are boundary conditions on the Poisson equation).

3. CALCULATION OF THE COULOMB SHIFT OF THE FERMI ENERGY

The procedure used for the approximate solution of Eq. (15) is set forth below only for the case in which inequality (12) holds and Eq. (11) can be used. In general, we should use Eq. (13), but since the calculations become laborious we will present only the final results here.

We introduce sufficiently smooth functions $\overline{\varphi}(k)$ and $\overline{\rho}_S(k)$ such that $\overline{\varphi}(k_{2n})=\varphi_{2n}$ and $\overline{\rho}_S(k_{2n})=\rho_{2n}^S$ for $n\neq0$. Applying Eq. (11) to the right side of Eq. (15), and retaining terms of up to first order in the parameter λ in (10), we find the following equation for the function $\overline{\varphi}(k)$:

$$k^2\overline{\varphi}(k)-(4\pi/\varepsilon_0)\overline{\rho}_S(k)=-(\varkappa^2/2k_Fk)\int\limits_{2k_F-k}^{2k_F+k}\frac{d\xi}{\xi}$$
$$\times[\overline{\varphi}(k)-\overline{\varphi}(\xi)](k_F{}^2-k^2/4+k\xi/2-\xi^2/4)$$
$$-(\varkappa^2/2k_F)\int\limits_0^{2k_F-k}d\xi[\overline{\varphi}(k)-\overline{\varphi}(\xi)]+\lambda\varkappa^2[\overline{\varphi}(k)-\overline{\varphi}(0)], \qquad (16)$$

where $\overline{\varphi}(0) = \lim\overline{\varphi}(k)$ as $k\to 0$ but $k\neq 0$.

An approximate solution of Eq. (16) is found in the leading approximation in the parameter η in (4):

$$\overline{\varphi}(k)\approx\frac{4\pi}{\varepsilon_0}\frac{\overline{\rho}_S(k)-\lambda\overline{\rho}_S(0)}{k^2\varepsilon_\infty(k)-\varkappa^2\lambda}, \qquad (17)$$

where $\varepsilon_\infty(k)$ is the Lindhard dielectric constant.[7] This expression is then used to calculate the correction $\mathscr{E}_Q$ in (7) after the corresponding integral has been converted into a series in Fourier coefficients of the type in (14) for the integrands. The latter is approximated by (11) under conditions (10) and (12). Inequality (4), on the other hand, means that we can restrict the evaluation of the corresponding integrals to the long-wavelength asymptotic expression in (17) for the function $\overline{\varphi}(k)$, in which case we have $|k|\ll\varkappa\ll 2k_F$ [we should actually assume $k^2\varepsilon_\infty(k)\approx k^2+\varkappa^2$ in (17)].

To find the electron chemical potential from (8), we also need an expression for the Coulomb energy in (7) in the case in which the particle is charged. Since the electric field does not vanish at the boundary of the sample in this case [$\varphi'(0) = -\varphi'(L)\neq 0$], Eqs. (14)–(17) cannot be used. However, the approach taken above in the derivation of (17) is still valid, after some modification, in this case.

Since the total seed charge density in (5) is $\rho_0 = \rho_S + \rho_V$, a similar breakup is possible for the total potential $\varphi = \varphi_S + \varphi_V$. Here φ_S is the part of the potential which stems from the density ρ_S, which in turn satisfies the condition of electrical neutrality, as follows from (5). To determine φ_S we can thus use the procedure described above, which leads to an expression of the type in (17) for φ_S. We should then write an expression for the Coulomb energy which follows from (7) and from this breakup of φ:

$$\mathscr{E}_Q=\frac{S}{2}\int\limits_0^L dz\,\rho_S(\varphi_V+\varphi_S)=\frac{S}{2L}\sum_{n\neq 0}\rho_n{}^S(\varphi_n{}^V+\varphi_n{}^S). \qquad (18)$$

For a charged system it is not legitimate to write the potential in Eq. (2) as a Fourier series in (14). The energy $\mathscr{E}_Q$, however, depends on φ_V only through the Fourier coefficients. It turns out that these coefficients can be determined through the use of an expression like (17), in which the only change necessary is to replace $\overline{\rho}_S$ $\overline{\rho}_{\text{eff}}(k) = -\rho_V L$. The sign of $\overline{\rho}_{\text{eff}}$ is opposite that of the net charge of the sample. As a result we find the following expression for the Coulomb energy in (7) and the corresponding correction (8) to the chemical potential:

$$\mathscr{E}_Q/S=\frac{e^2}{16\pi\varepsilon_0}\frac{k_F{}^2}{\Delta}(1-\lambda)\left(k_F{}^2+\frac{4\pi}{e}\rho_VL\right)\left(1-\frac{2}{L\Delta}\right), \qquad (19)$$
$$\Delta^2\equiv\varkappa^2(1-\lambda),$$
$$\Delta\mu_Q=\frac{e^2k_F{}^2}{4\varepsilon_0\varkappa}\left(1-\frac{2}{L\varkappa}\right)\approx\frac{e^2k_F{}^2}{4\varepsilon_0\varkappa}-\frac{1}{2}\lambda\mu_0. \qquad (20)$$

It follows from (19) with $\rho_V = 0$ that the Coulomb energy of the electrically neutral system is proportional to S. As a result, there is a renormalization of the surface energy of the electron gas, which is small to the extent that the parameter in (4) is. Expression (19) also contains a dimensional correction to the surface energy. The leading term in the Coulomb part of the chemical potential, in contrast with that in $\mathscr{E}_Q$, is a bulk term, and the size correction is interpreted as the surface part of the chemical potential.

The physical meaning of expression (20) is as follows. The first term is essentially a well-known result: This term describes the shift of the chemical potential caused by the electrical double layer at the surface of the sample, with a charge density $\propto ek_F^2\propto en^{2/3}$ and a thickness $\varkappa^{-1}$. The double layer arises because under boundary condition (3) the electron density vanishes at the surface, while the neutralizing-charge density does not. The second term in (20) does not depend on the electron charge. This result is a consequence of inequalities (4) and (12), under which this expression was derived (the latter inequality forbids taking the limit $e^2\to 0$). It has the same structure as that of the shift $\lambda\mu_0$ in (9) of the chemical potential, due to the spatial quantization of the electron levels,[3] differing from it only in sign and by a factor of 1/2. The "strength" of the double layer at the surface of the plate thus decreases with decreasing plate thickness. We should stress that both the surface component of the kinetic part of the Fermi energy, $\lambda\mu_0$, and its electrostatic analog, (20), lead to a size dependence of the work function of the films. The same factors should lead to a size dependence of the work function of small particles, but in their case we would also add an electrostatic energy which the particles acquire because of their charging as a result of the escape of electrons from them.

If we lift restriction (12) and replace (11) by (13), we find the following more general expressions in place of (19) and (20):

$$\mathscr{E}_Q/S=\frac{e^2}{16\pi\varepsilon_0}\frac{k_F{}^2}{\Delta}\frac{1-\lambda}{1-\lambda M}\left(k_F{}^2+\frac{4\pi}{e}\rho_VL\right)\left[1-\frac{2}{L\Delta}(1-M)\right], \qquad (21)$$

$$\Delta\mu_Q=\frac{e^2}{4\varepsilon_0}\frac{k_F{}^2}{\Delta}\frac{1-\lambda}{1-\lambda M}\left[1-\frac{2}{L\Delta}(1-M)\right], \qquad (22)$$

where

$$M\equiv L\Delta[\exp(L\Delta)-1]^{-1}.$$

It can be seen from these expressions that if condition (12) does not hold then the expressions for $\mathscr{E}_Q$ and $\Delta\mu_Q$ no longer reduce to a sum of terms having a power-law dependence on the size of the system, L. In the limit $\varkappa L\to 0$, for example, it follows from (21) for an electrically neutral system ($\rho_V = 0$) that

$$\mathscr{E}_Q/S=\frac{e^2k_F{}^4}{16\pi\varepsilon_0}\frac{L}{6}. \qquad (23)$$

In other words, the Coulomb energy converts from a surface energy into a bulk energy. Equation (23) corresponds to a calculation of the Coulomb energy without consideration of screening. This equation can be derived by an alternative rigorous approach. In addition, one can verify that the second term in (22), which competes with the size correction to the kinetic part of the chemical potential under condition (12), actually depends on e^2 and vanishes in the limit $e^2\to 0$.

We have not been able to derive corresponding results for the case of general boundary conditions on the wave functions (as was done in Ref. 5 without consideration of screening). For boundary conditions of a special type, with $\psi'(0) = \psi'(L) = 0$ (these conditions correspond to a surface resonance), however, a solution can be derived without substantial changes in the calculations. It is found as a result that the Coulomb correction to the chemical potential, $\Delta\mu_Q$, simply changes sign, and there is again a partial cancellation of the size dependence of the kinetic part of the chemical potential under condition (12).

4. FRIEDEL OSCILLATIONS OF THE CHARGE DENSITY AT THE SURFACE OF A CONDUCTOR

The charge density of an electrically neutral system can be written as a series like (14):

$$\rho(z)=L^{-1}\sum_n \rho_n \cos k_n z. \qquad (24)$$

An equation for ρ_n can be found from (15) by noting that we have $\varphi_n = (4\pi/\varepsilon_0)\rho_n/k_n^2$:

$$\rho_{2n}=\rho_{2n}{}^0/\varepsilon_L(2k_n)+\frac{\pi}{L}\frac{\varkappa^2}{k_F\varepsilon_L(2k_F)}\sum_{n'\neq n}\theta(k_F-|k_n-k_{n'}|)$$
$$\times\frac{k_F{}^2-(k_n-k_{n'})^2}{2k_n(2k_{n'})^2}\rho_{2n'},\qquad \rho_{2n+1}=0. \qquad (25)$$

Here ε_L is the dielectric constant of a finite-size, plane-parallel plate of thickness L:

$$[\varepsilon_L(2k_n)-1](2k_n)^2=\frac{\varkappa^2}{2k_n}\Big[\frac{k_F{}^2-k_n{}^2}{2k_n}(\psi(n+n_F+1)$$
$$-\psi(n_F-n+1))+(1-\lambda)k_F\Big],$$

where ψ is the digamma function, and $|n|\leqslant n_F = k_F L/\pi$.

Under condition (4), an approximate solution can be found iteratively from the right side of Eq. (24):

$$\rho_{2n}=\rho_{2n}{}^{\mathrm{I}}+\rho_{2n}{}^{\mathrm{II}}, \qquad (26)$$
$$\rho_{2n}{}^{\mathrm{I}}=\rho_{2n}{}^0/\varepsilon_L(2k_n),$$
$$\rho_{2n}^{\mathrm{II}}\approx\frac{\pi}{L}\frac{\varkappa^2}{k_F}\sum_{n'\neq n}\theta(k_F-|k_n-k_{n'}|)\frac{k_F{}^2-(k_{n'}-k_n)^2}{2k_n\cdot 2k_{n'}}\frac{\rho_{2n'}{}^0}{(2k_n{}')^2}.$$

Assuming that inequalities (12) and also $k_F L \gg k_F z \gg 1$ hold, and applying Eqs. (11) and (24)–(26), we find, in leading order in the parameter λ in (10),

$$\rho(z)\approx\frac{ek_F}{2\pi^2\varepsilon_\infty(2k_F)}\frac{\cos(2k_F z)}{z^2}$$
$$-\frac{e\varkappa^2}{4\pi^2 k_F\varepsilon_\infty{}^2(2k_F)}\frac{\ln(4k_F z)}{2k_F z^3}\sin(2k_F z), \qquad (27)$$

where ε_∞ is the Lindhard dielectric constant.[7] Essentially the same result would have been derived if we had immediately considered the case of a semi-infinite sample ($L\to\infty$), with a continuous electron spectrum, and if we had stipulated an appropriate procedure for regularizing the singular integrals in the perturbation theory.

With regard to Eq. (27) we note that since the first term appears in the power-law asymptotic behavior it obviously does not stem from a Kohn singularity in the dielectric constant of a degenerate Fermi gas. It arises instead because of the nonanalytic nature of the Fourier transform of the seed density:

$$\bar\rho^0(k)=-(e/2\pi)(k_F{}^2-k^2/4)\theta(2k_F-|k|).$$

A term of the same type arises in the absence of screening.[4,5]

A distinctive feature of the second term in (27) is the appearance of a logarithmic amplitude factor. By way of comparison we note that in the asymptotic expansion for the density of the seed charge, $\rho_0(z)$, the second term is proportional to z^{-3}. The corresponding term in (27) thus falls off more slowly with increasing z, although it does stem from screening effects ($\propto\varkappa^2$). The formal reason for this behavior is that at the point $k = 2k_F$ there are two singularities: the Kohn singularity of $\varepsilon_\infty(k)$ and the singularity of $\bar\rho_0(k)$ which is associated with the nonanalytic behavior at $k=2k_F$. The latter singularity occurs because the seed charge is not a given quantity and instead results from the surface.

We would expect that the lattice surface relaxation due to the electron-photon coupling[4,5] would be determined by expression (27) when screening effects are taken into account.

APPENDIX

Let us explain the derivation of Eqs. (11) and (13) and demonstrate the reason for the difference between them. The sum on the left side of (11) can be written as an integral in the complex k plane:

$$\sum_{n=1}^{n_F} f(k_n)=\frac{1}{2}\sum_{n=-n_F}^{n_F} f(k_n)-\frac{1}{2}f(0)$$
$$=\frac{1}{2}\frac{1}{2\pi i}\oint_C dk\, f(k)\,\omega(k)-\frac{1}{2}f(0),$$

where $f(-k)=f(k)$, and the contour C encircles the values k_n to be summed. The function ω must have simple poles at $k = k_n$, with unit residues. This function can be chosen to be

$$\omega(k)=\frac{d}{dk}\sin(kL).$$

To find an asymptotic estimate of the integral under condition (10), we deform contour C, moving its horizontal part in such a way that we have $\mathrm{Im}k\to\pm\infty$ under the condition $\mathrm{Re}k=\text{const}$. An important point here is whether the contour encounters some singularity of the function $f(k)$. In case (13), these singularities would be poles. Where contour C encounters these poles, we should take account of the contributions from the residues at these points. The technique for deriving asymptotic estimates which was used in Ref. 4 should be used for the integral along deformed contour C.

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