

## Electrical resistivity of metallic thin films with rough surfaces

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The electrical resistivity of metallic thin films due to the scattering of conduction electrons with rough surfaces and with a random distribution of static impurities within the film is calculated here quantum mechanically using Mori's formalism. The detailed profiles of the surfaces enter into our theory through the single-particle wave functions and energies, which are calculated with the help of a nonconformal coordinate transformation. A detailed analysis of the roughness contribution to the resistivity is made in the small-roughness regime and with the assumption of a Gaussian form for the surface profile autocorrelation functions. The structures of the Fermi levels are studied, and effects due to the discreteness of the levels are also investigated. Our surface-roughness resistivity does not saturate with decreasing film thickness, in agreement with experimental findings.

### I. INTRODUCTION

It has long been known that the electrical resistivity of metals is higher in thin films and wires than in the bulk. Interpretations of experimental measurements have relied almost exclusively on the size-effect theory (SET) of Fuchs<sup>1</sup> and Sondheimer<sup>2</sup> and many other extensions of it.<sup>3-7</sup> According to Fuchs's theory a fraction  $(1-P_0)$  of the conduction electrons is scattered diffusively at the surfaces of the film and thus gives rise to an extra resistivity. The factor  $P_0$ , which is called the specularity factor, can take on values from zero (for totally diffuse surface scattering) to one (for totally specular scattering).

An incredible amount of experimental data on the electrical resistivity of metal films has been accumulated through the works of different authors on a variety of systems.<sup>4-7</sup> Our concern here is on continuous films of normal metals with clean surfaces. Although certain features of the SET have been verified in certain systems by some experiments, a uniform interpretation of the available results has not been possible, and data obtained even on the same material can show a rather poor consistency. For example, in Au film, the values for  $P_0$  as determined by different authors can vary all the way from zero to one.<sup>7</sup> This is primarily caused by the fact that the films used by different authors often differ in their structural properties as a result of the different conditions under which the samples were prepared. Quantitative analysis of experimental data from better characterized films shows, however, distinct deviations from the available theoretical results.<sup>7</sup>

For example, many theories predict a saturation in the resistivity with decreasing thickness of the film, but this has never been observed experimentally. For almost all cases one finds the data to lie distinctly above the theoretical curves for sufficiently thin samples. For extremely rough films, in order to fit theoretical curves, even negative  $P_0$  values have been deduced from experimental data (see Sec. IV for a possible explanation).

Although these theories offer a simple and physically attractive way of understanding the transport properties

of metal films, they suffer a number of shortcomings from the theoretical viewpoint. (1) All these theories are based on the use of the Boltzmann equation, where the excess resistivity arises solely by imposing a certain boundary condition on the classical distribution function  $f(\vec{r}, \vec{p})$ . The validity of such a method may be questionable since  $\vec{r}$  and  $\vec{p}$  cannot be specified simultaneously for an electron. (2) It is not at all clear that one can characterize the properties of a film by just a single parameter  $P_0$ . Even when it is possible to do so,  $P_0$  should depend on the physical quantities that one measures. For example, the value of  $P_0$  determined from a resistivity measurement is expected to be rather different from that obtained by measuring the optical reflectivity on exactly the same film. The former measurement is sensitive to roughness at the surface down to atomic scales, whereas the latter technique probes only the long-wavelength part of the surface profile. The SET's cannot predict such fine details. (3) Even if we can characterize the surface by a single factor  $P_0$ , the SET's do not provide means for calculating such a quantity.<sup>8</sup> Thus it is not possible to investigate the detailed microscopic mechanisms which give rise to the diffuse scattering of electrons at the surfaces. (4) These theories also assume an effective mean free path which is independent of the thickness of the film, and thus predict no surface contribution to the resistivity if surface scattering is purely specular, i.e.,  $P_0=1$ . There are a few reasons, however, to believe that this is not the case. (a) For an impurity located close to the surface, a conduction electron will scatter off both the impurity and its image. (The presence of a rough surface only makes the image appear more diffuse.) (b) The effects due to electron screening of impurities near the surface should be somewhat different from those in the bulk. The screening electron cloud will not be spherical and screening will be less complete. (c) For very thin films quantization of the electron levels perpendicular to the film become important. As a result the effective Fermi wave vector should become larger (see Appendix C for a more detailed analysis).

In this work<sup>9</sup> we shall calculate the resistivity of con-

tinuous metal films due to the scattering of conduction electrons with a random distribution of static impurities within the film and with the rough surfaces. Our results are based on a fully quantum-mechanical calculation of the current-current relaxation function using Mori's projection-operator method.<sup>10</sup> The detailed profiles of the surfaces enter into our theory through the single-particle wave functions and energies, which are computed with the help of a nonconformal coordinate transformation. We find that the effects due to rough surfaces cannot be mimicked by introducing just an effective single-electron potential. There are interesting electron momentum-dependent effects as well. A detailed analysis of the electrical resistivity due to the rough surfaces is made in the small-roughness regime and with the assumption that a Gaussian form for the surface-profile autocorrelation functions. A quantum treatment for this problem is indispensable here since the wavelength of an electron at the Fermi surface can be comparable to the rms height of the roughness at the surface of the film. In fact, this resistivity is found to be proportional to  $\hbar$ . The possibility of having different profiles on the top and the bottom surfaces is taken into account here. The contribution from the scattering with the roughness should have an important angular dependence, and our formalism handles this feature naturally. For very thin films the structures of the Fermi levels are studied in detail. Effects due to the discreteness of the levels and an enlarged effective Fermi sphere are also investigated. In agreement with experimental findings, our surface resistivity does not saturate with decreasing film thickness.

The outline for the rest of this paper is as follows. In Sec. II a coordinate transformation is used to map the free-electron problem of a film with rough surfaces into one where the electrons are not free but the new surfaces are flat. The equation of motion for an electron in the new coordinate system is derived exactly. Section III deals with the single-particle wave functions and energies in the small-roughness regime. A detailed calculation for the resistivity due to scattering with the rough surfaces and with a random distribution of impurities within the film is described in Sec. IV. Section V is used for discussions. In Appendix A we discuss how to incorporate within our formalism some of the effects due to the screening of the impurities by the electrons. The necessary Fermion relaxation functions are computed in Appendix B. Finally, in Appendix C we analyze in detail the Fermi-level structures of an ideal metal thin film within the electron-gas model.

## II. COORDINATE TRANSFORMATION FOR ROUGH SURFACES

In order to calculate the electric conductivity of a thin metallic film using the second quantization formalism, we need to know the one-particle wave functions  $\psi_n(\vec{r})$  and their corresponding energies  $\epsilon_n$ . These quantities obey the Schrödinger equation

$$\mathcal{H}_0\psi_n = \left[ -\frac{\hbar^2}{2m}\vec{\nabla}^2 + U(\vec{r}) \right] \psi_n(\vec{r}) = \epsilon_n\psi_n(\vec{r}), \quad (2.1a)$$

where  $U(\vec{r})$  is the one-particle potential. The mathematical task of solving this equation becomes quite difficult, even within a jellium model, when the surfaces of the system of interest are irregular. This is a very common situation since all realistic surfaces are rough to a certain extent. Although the treatment in this section can be readily adapted to more general situations, we shall confine ourselves to the case of a jellium model of thin films with rough surfaces where  $U$  is given by

$$U(\vec{r}) = \begin{cases} 0 & \text{for } \xi_1(\vec{X}) < z < \xi_2(\vec{X}), \\ U_0 & \text{otherwise.} \end{cases} \quad (2.1b)$$

Throughout this paper we shall use the notation  $\vec{r} \equiv (\vec{X}, z)$  for vectors, where  $\vec{X}$  denotes a two-dimensional vector in the  $x$ - $y$  plane. The film is assumed to have infinite extensions along the  $x$  and  $y$  directions. The two surfaces of the film lie basically perpendicular to the  $z$  axis and are given by  $z = \xi_1(\vec{X})$  and  $z = \xi_2(\vec{X})$ , respectively.

It is a formidable task to try and solve Eq. (2.1a) directly, with  $U(\vec{r})$  given by Eq. (2.1b), except when  $\xi_1$  and  $\xi_2$  take on extremely simple forms. The idea here is to transform the coordinates in such a way that the film in the new coordinates will have simple flat surfaces. It is obvious that such a transformation has to be nonconformal, since irregularities at the surface must be flattened out by this process. A transformation which will accomplish this is given by<sup>11</sup>

$$\begin{aligned} \vec{X}' &= \vec{X}, \\ z' &= \frac{z - \xi_1(\vec{X})}{\xi_1(\vec{X}) - \xi_2(\vec{X})} l = \frac{z + S_1(\vec{X})}{l + S_1(\vec{X}) + S_2(\vec{X})} l, \end{aligned} \quad (2.2)$$

where the functions  $S_1(\vec{X})$  and  $S_2(\vec{X})$  are defined by

$$\begin{aligned} \xi_1(\vec{X}) &= -S_1(\vec{X}), \\ \xi_2(\vec{X}) &= l + S_2(\vec{X}). \end{aligned} \quad (2.3)$$

Although the value for  $l$ , which gives the new thickness of the film, can be rather arbitrary at this point, there is a natural choice for this value if we want to preserve the electronic and ionic densities. This will be elaborated later in Sec. III [see Eq. (3.10)]. What this transformation does is to stretch and compress the film along the  $z$  direction in such a way that the new surfaces at  $z'=0$  and  $l$  are flat and parallel to each other.

Although the transformed surfaces are now flat, the motion of a single electron within the transformed film is no longer free, which is a direct consequence of the nonconformal nature of our transformation. The departure from a free motion thus represents the scattering of the electron from the rough surfaces of the original film. To describe the motion with the new film we transform Eq. (2.1) into the new coordinate system using Eqs. (2.2) and (2.3). The resulting Schrödinger equation becomes

$$\left[ -\frac{\hbar^2}{2m} \nabla'^2 + A' + U(\vec{r}') \right] \psi_n(\vec{r}') = \epsilon_n \psi_n(\vec{r}'), \quad (2.4)$$

where  $A'$  is an operator given by

$$A' = -\frac{\hbar^2}{2m} \{ [(a')^2 + (b')^2 - c'(2-c')] \partial_z'^2 + 2(a' \partial_{x'z'}^2 + b' \partial_{y'z'}^2) + (\partial_{x'} a' + \partial_{y'} b' + a' \partial_z a' + b' \partial_z b') \partial_z' \} \quad (2.5)$$

and

$$a' = a(\vec{X}', z') = \frac{[(l-z') \partial_{x'} S_1(\vec{X}') - z' \partial_{x'} S_2(\vec{X}')] }{[l + S(\vec{X}')]},$$

$$b' = b(\vec{X}', z') = \frac{[(l-z') \partial_{y'} S_1(\vec{X}') - z' \partial_{y'} S_2(\vec{X}')] }{[l + S(\vec{X}')]}, \quad (2.6)$$

$$c' = c(\vec{X}') = S(\vec{X}') / [l + S(\vec{X}')] = c(\vec{X}),$$

$$S(\vec{X}') = S_1(\vec{X}') + S_2(\vec{X}').$$

The  $U(\vec{r}')$  term now becomes simply

$$U(\vec{r}') = \begin{cases} 0 & \text{for } 0 < z' < l \\ U_0 & \text{otherwise.} \end{cases} \quad (2.7)$$

As a result of the transformation the shape as well as the volume of a differential volume element within the film are changed. The transformation Jacobian is

$$J \equiv \frac{\partial(x', y', z')}{\partial(x, y, z)} = 1 - c(\vec{X}). \quad (2.8)$$

For the case of a semi-infinite slab the above equations simplify to

$$A' = -\frac{\hbar^2}{2m} \{ [(a')^2 + (b')^2] \partial_z'^2 + 2(a' \partial_{x'z'}^2 + b' \partial_{y'z'}^2) \},$$

$$a' = \partial_{x'} S_1(\vec{X}'), \quad b' = \partial_{y'} S_1(\vec{X}'), \quad (2.9)$$

$$U(\vec{r}') = \begin{cases} 0 & \text{for } 0 < z' \\ U_0 & \text{otherwise.} \end{cases}$$

Also, in this case there can be no volume change due to the transformation, and so  $c' = c = 0$  and  $J = 1$ .

We see that the presence of rough surfaces introduces a somewhat complicated momentum- and space-dependent term  $A'$  in the one-particle Hamiltonian. In Eq. (2.5) the first term inside the curly brackets represents an effective-mass term for motions along  $z$  and is dependent on the exact location within the film. The remaining terms describe interferences due to scattering with the top, bottom, or both surfaces. Note that  $A'$  also depends on the thickness of the film,  $l$ . It should be pointed out that the presence of rough surfaces is a purely geometrical effect which, therefore, cannot be represented by any (momentum-independent) effective potentials.

For the special case of a semi-infinite slab, there is only a single surface at  $z = \xi_1(X) = -S_1(x, y)$ . The effects of such a rough surface can be described exactly by a

position-dependent mass tensor [cf. Eq. (2.9)]. This can be understood since the effects due to a surface on the motion of an electron should depend both on how close it is to the surface, as well as on its speed and direction of motion.

All these interesting effects can be computed exactly, at least in principle, once the surface-profile functions  $\xi_1(\vec{X})$  and  $\xi_2(\vec{X})$  are known. These results obviously cannot be characterized by simply introducing a single constant, such as the specularity factor of Fuchs<sup>1</sup> and Sondheimer.<sup>2</sup> (However, see Sec. IV below regarding the surface resistivity.)

### III. ONE-PARTICLE WAVE FUNCTIONS IN THE SMALL-ROUGHNESS REGIME

Although the transformed problem is still rather complicated, it is still comparatively easier to handle than the original problem, since the boundary conditions implicitly given by Eq. (2.7) are now much simpler, and a variety of mathematical techniques for handling the additional term  $A'$  are known. This is especially true, for example, in the so-called small-roughness regime where perturbation theory can be used to obtain approximate but analytic solutions. In order to be in this regime we require that the surfaces be not too jagged so that (i)

$$\max(|\partial_x S_{1,2}|, |\partial_y S_{1,2}|) \ll 1,$$

$$\max(|\partial_x^2 S_{1,2}|, |\partial_y^2 S_{1,2}|) \ll 1.$$

The vertical extension of the irregularities must also be sufficiently small in order that (ii)  $|S_{1,2}|/l \ll 1$ . Condition (ii) is usually met except perhaps for ultrathin films with deep cracks on the surfaces. Hereafter we shall confine ourselves to the small-roughness regime, so we can solve Eq. (2.4) treating  $A'$  perturbatively.

For simplicity, we shall restrict ourselves further to an infinite-hard-wall jellium model by taking  $U_0 \rightarrow \infty$ . In the primed coordinate system the unperturbed wave functions and energies are given by

$$\psi_{\vec{p}}^2(\vec{r}') = \frac{e^{i\vec{p} \cdot \vec{X}}}{(2L^2 l)^{1/2}} \sin(pz'), \quad (3.1)$$

$$\epsilon_{\vec{p}}^0 = \frac{\hbar^2}{2m} (P^2 + p^2), \quad (3.2)$$

where

$$\vec{p} = (\vec{P}, p) = (p_x, p_y, p_z), \quad P \equiv |\vec{P}| \quad (3.3a)$$

$$p_{x,y} = \frac{\pi}{L} m_{x,y}, \quad m_{x,y} = 0, \pm 1, \pm 2, \dots \quad (3.3b)$$

$$p_z = \frac{\pi}{l} m_z, \quad m_z = 1, 2, 3, \dots \quad (3.3c)$$

The wave functions are forced to vanish outside the film, and periodic boundary conditions are imposed along the  $x$  and  $y$  directions with period  $2L$ .

In the small-roughness regime Eq. (2.5) with Eq. (2.6) simplifies to

$$A' = -\frac{\hbar^2}{2m} \left\{ \left[ \partial_x S_1 - \left[ \frac{z'}{l} \right] \partial_x S \right] \partial_{x'z'}^2 + \left[ \partial_y S_1 - \left[ \frac{z'}{l} \right] \partial_y S \right] \partial_{y'z'}^2 \right. \\ \left. + \left[ \partial_x^2 S_1 - \left[ \frac{z'}{l} \right] \partial_x^2 S + \partial_y^2 S_1 - \left[ \frac{z'}{l} \right] \partial_y^2 S \right] \partial_{z'} - 2S \partial_{z'}^2 \right\}. \quad (3.4)$$

To the leading nontrivial order in roughness [cf. conditions (i) and (ii)] the actual wave functions are easily found to be

$$\psi_{\vec{p}}(\vec{r}') = \psi_{\vec{p}}^0(\vec{r}') - \sum_{\vec{k}}' W(\vec{p}, \vec{k}) \psi_{\vec{k}}^0(\vec{r}'), \quad (3.5)$$

where

$$W(\vec{p}, \vec{k}) = \frac{pk}{m_e(\epsilon_{\vec{p}} - \epsilon_{\vec{k}})} \left[ \delta_{m_k m_p} S(\vec{P} - \vec{K}) \left[ 1 + \frac{P^2 - K^2}{4p^2} \right] \right. \\ \left. - \frac{P^2 - K^2}{p^2 - k^2} [S_1(\vec{P} - \vec{K}) + (-1)^{m_p + m_k} S_2(\vec{P} - \vec{K})] \right], \quad (3.6)$$

with  $K \equiv |\vec{K}|$ . The wave functions are clearly normalized to lowest order. The energies are given by the equation

$$\epsilon_{\vec{p}} = \epsilon_{\vec{p}}^0 [1 - 2S(\vec{Q} = \vec{0})/l], \quad (3.7)$$

which has a simple interpretation. Note that the thickness of the film as a function of  $\vec{X}$  is

$$\xi_2(\vec{X}) - \xi_1(\vec{X}) = l + S(\vec{X}),$$

and so the average thickness is

$$l + \frac{1}{4L^2} \int d^2X S(\vec{X}) = l + S(\vec{Q} = \vec{0}),$$

where

$$S(\vec{Q}) = \frac{1}{4L^2} \int d^2X e^{-i\vec{Q} \cdot \vec{X}} S(\vec{X}) \quad (3.8)$$

is the two-dimensional Fourier transform of the sum of the surface-profile functions. In the small-roughness regime we can therefore write

$$\epsilon_{\vec{p}} = \frac{\hbar^2 \pi^2 (m_x^2 + m_y^2 + m_z^2)}{2m [l + S(\vec{0})]^2} \cong \epsilon_{\vec{p}}^0 \left[ 1 - \frac{2S(\vec{0})}{l} \right],$$

which is precisely what we have from perturbation theory in Eq. (3.7). So we see that the first-order energy shift is simply a constant which results from the change in the overall thickness of the film. This constant vanishes, of course, for a semi-infinite slab. For films note that the value for  $l$  has not been specified thus far, but now we see that the most natural choice for it is

$$l = \frac{1}{4L^2} \int d^2X [\xi_2(\vec{X}) - \xi_1(\vec{X})]. \quad (3.9)$$

With this choice of  $l$ ,  $\epsilon_{\vec{p}}$  is then simply equal to  $\epsilon_{\vec{p}}^0$  to first order in the roughness.

Finally we must transform the wave functions back to the original coordinates. The result is

$$\psi_{\vec{p}}(\vec{r}) = \frac{e^{i\vec{p} \cdot \vec{X}}}{(2L^2 l)^{1/2}} \left[ \sin(pz) + p \left[ S_1(\vec{X}) - \frac{z}{l} S(\vec{X}) \right] \cos(pz) \right] \\ - \sum_{\vec{k}}' W(\vec{p}, \vec{k}) \frac{e^{i\vec{k} \cdot \vec{X}}}{(2L^2 l)^{1/2}} \sin(kz). \quad (3.10)$$

Through the use of this set of wave functions, a number of interesting physical quantities of a rough metal film can be calculated. In the following section we shall describe the calculation of the electrical conductivity.

#### IV. MORI'S FORMALISM FOR THE ELECTRICAL CONDUCTIVITY

This section deals with the electrical conductivity of a metal thin film due to the scattering of conduction electrons with the rough surfaces and with a random distribution of static impurities within the bulk of the film. Effects due to electron-electron interaction will be left for a future study. However, effects due to electron screening of the impurities can be easily incorporated within the present approach, as discussed in Appendix A.

##### A. Model Hamiltonian

Within the film the electronic Hamiltonian can be written as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}',$$

where

$$\mathcal{H}' = \sum_{j=1}^N u(\vec{r}, \vec{r}_j), \quad (4.1)$$

and  $\vec{r}$  and  $\vec{r}_j$  denote the positions of the electron and the  $j$ th impurity, respectively. In terms of the fermion operators  $a_{\vec{p}}^\dagger$  and  $a_{\vec{p}}$ , which creates and annihilates, respectively, an electron with momentum  $\vec{p}$  within the film, we can write the impurity Hamiltonian as

$$\mathcal{H}' = \sum_j \sum_{\vec{p}, \vec{p}'} \int d^2X \times \int_{\xi_1(\vec{X})}^{\xi_2(\vec{X})} dz \psi_{\vec{p}}^*(\vec{r}) u(\vec{r}, \vec{r}_j) \psi_{\vec{p}'}(\vec{r}) a_{\vec{p}}^\dagger a_{\vec{p}'}, \quad (4.2)$$

Owing to the lack of translational invariance in the  $z$  direction, we shall use a Fourier cosine transform for  $z$ , but for  $\vec{X}$  we shall use the usual Fourier transform. Thus we have

$$u(\vec{r}, \vec{r}_j) = \sum_{\vec{Q}} \sum_{q, q'=1}^{\infty} \frac{e_q e_{q'}}{4} e^{-i\vec{Q} \cdot (\vec{X} - \vec{X}_j)} u(\vec{Q}, q, q') \times \cos(qz) \cos(q'z_j), \quad (4.3)$$

where  $q = \pi n / l$  ( $n = 0, 1, 2, \dots$ ), and  $e_q = 2$  when  $n = 0$  and  $e_q = 1$ , otherwise. Since we are interested in situations where the impurity concentration is low, and the small-roughness regime holds, we can neglect effects due to interferences between the scattering of an electron from the rough surface and from the impurities. Thus setting Eq. (4.3) into (4.2), we find

$$\mathcal{H}' = \sum_{\vec{p}, \vec{p}'} I(\vec{p}' - \vec{p}, p, p') a_{\vec{p}}^\dagger a_{\vec{p}'}, \quad (4.4)$$

where

$$I(\vec{p}' - \vec{p}, p, p') = V \sum_q \rho(\vec{p}' - \vec{p}, q) F(\vec{p}' - \vec{p}, p, p', q), \quad (4.5)$$

$$F(\vec{p}' - \vec{p}, p, p', q) = \frac{e_q}{4} [u(\vec{p}' - \vec{p}, |p - p'|, q) - u(\vec{p}' - \vec{p}, p + p', q)], \quad (4.6)$$

and  $\rho(\vec{Q}, q)$  is the Fourier transform of the electron density  $\rho(\vec{r}) = \sum_i \delta(\vec{r} - \vec{r}_i)$ .

### B. Current operators

We want to calculate the electrical conductivity for current flowing parallel to the surface. Now only the  $x$  component of the conductivity,  $\sigma_{xx}$ , needs to be con-

sidered since the corresponding results for the  $y$  component are rather similar. First we shall find the total current operator in second quantized form. The electrical conductivity is then related through Kubo's formula<sup>12</sup> to the current autorelaxation function. This latter quantity will be calculated through the use of the projection operator method developed by Mori.<sup>10</sup>

The  $x$  component of the current density operator can be written as

$$j_x(\vec{r}) = \frac{ie}{2m_e} \lim_{\vec{r}_1 \rightarrow \vec{r}} \sum_{\vec{p}, \vec{p}'} (\partial_{x_1} - \partial_x) \psi_{\vec{p}}^*(\vec{r}_1) \psi_{\vec{p}'}(\vec{r}) a_{\vec{p}}^\dagger a_{\vec{p}'}, \\ = j_x^0(\vec{r}) + j_x^s(\vec{r}), \quad (4.7)$$

where

$$j_x^0(\vec{r}) = \frac{ie}{2m_e} \lim_{\vec{r}_1 \rightarrow \vec{r}} \sum_{\vec{p}, \vec{p}'} (\partial_{x_1} - \partial_x) \psi_{\vec{p}}^{0*}(\vec{r}_1) \psi_{\vec{p}'}^0(\vec{r}) a_{\vec{p}}^\dagger a_{\vec{p}'}, \\ = \frac{e}{2m_e} \sum_{\vec{p}, \vec{p}'} (p_x + p'_x) \psi_{\vec{p}}^{0*}(\vec{r}) \psi_{\vec{p}'}^0(\vec{r}) a_{\vec{p}}^\dagger a_{\vec{p}'}, \quad (4.8)$$

is the unperturbed part of  $j_x(\vec{r})$ , and  $j_x^s(\vec{r})$ , the remaining part, results from the presence of the rough surfaces. The total current operator therefore has two parts,

$$j_x = j_x^0 + j_x^s, \quad (4.9)$$

where

$$j_x^0 = \frac{e}{m_e} \sum_{\vec{p}} p_x a_{\vec{p}}^\dagger a_{\vec{p}} \quad (4.10)$$

is the usual (unperturbed) current operator and  $j_x^s$  represents the surface contribution. To the lowest order in surface roughness, we find, by using Eqs. (3.11) and (4.7), that

$$j_x^s = \frac{e}{m_e} \sum_{\vec{p}, \vec{p}'} (p'_x - p_x) T(\vec{p}' - \vec{p}) a_{\vec{p}}^\dagger a_{\vec{p}'}, \quad (4.11)$$

where

$$T(\vec{p}' - \vec{p}) = \frac{2p'_x p_x}{l(|\vec{p}'|^2 - |\vec{p}|^2)} \{S(\vec{p}' - \vec{p}) \delta_{pp'} + (\delta_{pp'} - 1) [S_1(\vec{p}' - \vec{p}) + (-1)^{m_{p'} + m_p} S_2(\vec{p}' - \vec{p})]\}. \quad (4.12)$$

Through the use of Kubo's formula,<sup>12</sup> the dynamic conductivity can be written in terms of the frequency-transformed current autorelaxation function as

$$\sigma_{xx}(z) = \frac{1}{V} \int_0^\infty dt e^{izt} (j_x(t), j_x(0)) \\ = \frac{1}{V} (j_x, j_x)_z = \frac{i}{V} (j_x, (z - \mathcal{L})^{-1} j_x), \quad (4.13)$$

where  $z = \omega + i0$  denotes the complex frequency. We have also made use of Kubo's scalar product which is defined for arbitrary operators  $A$  and  $B$  by

$$(A, B) = \int_0^\beta d\lambda \langle e^{\lambda \mathcal{L}} A^\dagger B \rangle - \beta \langle A^\dagger \rangle \langle B \rangle, \quad (4.14)$$

where  $\mathcal{L}$  is the Liouville operator, so that  $j_x(t) = e^{i\mathcal{L}t} j_x(0)$  and  $\mathcal{L}A = [A, \mathcal{H}]$ .

### C. Mori's approach to the dynamic conductivity

The low-frequency dynamic conductivity of a bulk metal has been calculated in the past by summing up an infinite set of diagrams for the current correlation function,<sup>13</sup> or by truncating a hierarchy of equations of motion for the relevant Green's functions.<sup>14</sup> The basic difficulties in a calculation of the dynamic conductivity are caused by its resonance structures. The requirement of charge conservation implies the existence of a pole in  $\sigma(z)$  near  $z=0$ , and thus precludes any finite-order perturbative theories. Our present approach makes use of Mori's formalism,<sup>10</sup> which provides an explicit expression for the dynamic conductivity in terms of a holomorphic memory function  $M(z)$ .<sup>15</sup> This function has no resonance structure and can be calculated accurately by appropriate approximations. This method is quite analogous to expressing particle properties in terms of a self-energy, and corresponds to an infinite partial summation of diagrams including self-energy as well as vertex corrections. When applied to the bulk conductivity, this method readily reproduces all known results obtained by other methods.<sup>16</sup> However, the present approach has several distinct advantages. It can be extended straightforwardly to infinite as well as finite systems with arbitrary geometrical shapes. There is no need to invert any kind of integral equations for the two-particle Green's functions, which can be a difficult task due to the lack of translation invariance for inhomogeneous systems. The calculation here is manifestly gauge invariant, i.e., particle conservation has been built into the theory at the outset, and all other sum rules are obeyed at least to lowest order. Moreover, the results for the conductivity are valid not only in the hydrodynamic regime but in the entire frequency region,<sup>17</sup> although, of course, we are only interested here in the static limit.

We choose  $j_x$  as the dynamic variable in Mori's formalism. The dynamic conductivity can be expressed exactly by the equation<sup>10</sup>

$$\sigma_{xx}(z) = \frac{1}{V} \frac{i\chi}{z - M(z)/\chi}, \quad (4.15)$$

where

$$\chi = (j_x, j_x) \quad (4.16)$$

is the static susceptibility for the total current, and

$$M(z) = (\mathcal{D} \mathcal{L} j_x, (z - \mathcal{D} \mathcal{L} \mathcal{D})^{-1} \mathcal{D} \mathcal{L} j_x) \quad (4.17)$$

is the so-called memory function. In the above equation  $\mathcal{D} \equiv 1 - \mathcal{P}$  is a superoperator and  $\mathcal{P}$  is the projection superoperator which is defined so that for any operator  $A$  we have

$$\mathcal{P} A = (j_x, A) j_x / \chi. \quad (4.18)$$

The basic function of  $\mathcal{P}$  is to project out the secular part of an operator and thus  $\mathcal{D}$ , its complementary part, projects out the nonsecular part which describes damping effects. In Eq. (4.16)  $\chi$  can be calculated exactly by a sum rule as<sup>18</sup>

$$\chi = N_e e^2 / m_e, \quad (4.19)$$

where  $N_e$  is the total number of electrons. In deriving Eq. (4.15) we have made use of the fact that<sup>19</sup>

$$(\mathcal{L} j_x, j_x) = 0. \quad (4.20)$$

The problem now is to calculate the memory function  $M(z)$ .

To calculate  $M(z)$  we first note that because of Eq. (4.20) we have  $\mathcal{D} \mathcal{L} j_x = \mathcal{L} j_x$  and thus all the  $\mathcal{D}$ 's in Eq. (4.17) can be omitted. Next, since there is no resistivity in the absence of impurities and surface collisions, and so  $\mathcal{L}^0 j_x = [j_x, \mathcal{H}_0] = 0$ . Since the impurity concentration is low, in the small-roughness regime contributions due to electron scattering with the impurities and the rough surfaces are simply additive. We find through the use of Eqs. (4.1), (4.4), (4.9), (4.10) and (4.14) that

$$\begin{aligned} \mathcal{L} j_x &\cong \mathcal{L}' j_x^0 + \mathcal{L} \mathcal{O} j_x^s \\ &= \frac{e}{m_e} \sum_{\vec{p}, \vec{p}'} [(\epsilon_{\vec{p}} - \epsilon_{\vec{p}'}) T(\vec{p}', \vec{p}) - I(\vec{P}' - \vec{P}, p, p')] \\ &\quad \times (p_x - p'_x) a_{\vec{p}}^\dagger a_{\vec{p}'}. \end{aligned} \quad (4.21)$$

Thus within our assumptions we can write

$$M(z) = -i (\mathcal{L} j_x, \mathcal{L} j_x)_z^0, \quad (4.22)$$

where  $(, )_z^0$  means that the relaxation function is to be evaluated with the free-particle Liouville operator  $\mathcal{L}^0$  only. The evaluation of Eq. (4.22) with Eq. (4.21) requires computing free-particle relaxation functions involving four Fermion operators. The calculation is straightforward and details can be found in Appendix B.

We must now average  $M(z)$  over a random distribution of impurities with concentration  $c$ . By denoting these averages by  $\langle \rangle_c$ , we find

$$\begin{aligned} \langle \rho(\vec{q}) \rangle_c &= \prod_{j=1}^N \left[ \frac{1}{V} \int d^2 X_j \int dz_j \right] \sum_{i=1}^N e^{i \vec{Q} \cdot \vec{X}_i} \cos q z_i \\ &= N \delta(\vec{Q}) \delta_{n_q, 0}. \end{aligned} \quad (4.23)$$

However, from Eqs. (4.22) and (4.21) we see that the  $\vec{Q}=0$  and  $n_q=0$  part does not contribute to  $\langle M(z) \rangle_c$ . Next we find that

$$\langle \rho^*(\vec{q}_1) \rho(\vec{q}_2) \rangle_c = \frac{N}{V^2} \delta(\vec{Q}_1 - \vec{Q}_2) \delta_{n_{q_1} n_{q_2}} e_{q_1}^{-1}. \quad (4.24)$$

The zero-frequency conductivity is given by Eq. (4.15) by allowing  $\omega \rightarrow 0$ . By combining Eqs. (4.15), (4.22), (4.21), (4.23), and (B4), the dc conductivity is given by

$$\sigma_{xx} = \frac{\chi^2}{VM''}, \quad (4.25)$$

where  $M''$ , the imaginary part of the zero-frequency limit of  $M(z)$ , has two separate contributions:

$$M'' = M_S'' + M_I'' \quad (4.26)$$

The first term, which is due to the rough surfaces, is given by<sup>20</sup>

$$M_S'' = \frac{\pi \hbar e^2}{m_e^2} \sum_{\vec{p}, \vec{p}'} (\epsilon_{\vec{p}} - \epsilon_{\vec{p}'})^2 |T(\vec{p}', \vec{p})|^2 (p_x - p'_x)^2 \times \delta(\epsilon_F - \epsilon_{\vec{p}}) \delta(\epsilon_F - \epsilon_{\vec{p}'}) , \quad (4.27)$$

and the second term, which represents the impurity contribution, is given by

$$M_I'' = \frac{\pi \hbar e^2}{m_e} \sum_{\vec{p}, \vec{p}'} \langle |I(\vec{P}' - \vec{P}, p, p')|^2 \rangle_c (p_x - p'_x)^2 \times \delta(\epsilon_F - \epsilon_{\vec{p}}) \delta(\epsilon_F - \epsilon_{\vec{p}'}) . \quad (4.28)$$

By utilizing Eq. (4.24) with Eqs. (4.5) and (4.6), we find that

$$\begin{aligned} \langle |I(\vec{P}' - \vec{P}, p, p')|^2 \rangle_c &= N \sum_q e_{n_q}^{-1} |F(\vec{P}' - \vec{P}, p, p', q)|^2 \\ &= \frac{N}{16} \sum_q e_{n_q} |u(\vec{P}' - \vec{P}, |p - p'|, q) \\ &\quad - u(\vec{P}' - \vec{P}, p + p', q)|^2 . \end{aligned} \quad (4.29)$$

$$\begin{aligned} \langle |S_i(\vec{Q})|^2 \rangle_S &= (4L^2)^{-2} \int d^2X \int d^2X' e^{-i\vec{Q} \cdot (\vec{X} - \vec{X}')} \langle S_i(\vec{X}) S_i(\vec{X}') \rangle_S \\ &= (4L^2)^{-2} \int d^2X \int d^2X' e^{-i\vec{Q} \cdot \vec{X}'} \langle S_i(\vec{X}) S_i(\vec{X} - \vec{X}') \rangle_S \equiv F_i(\vec{Q}) , \end{aligned} \quad (4.31)$$

where  $F_i(\vec{Q})$  is the two-dimensional Fourier transform of the surface-profile autocorrelation function

$$F_i(\vec{X}) = \int \frac{d^2X'}{4L^2} \langle S_i(\vec{X}') S_i(\vec{X}' - \vec{X}) \rangle_S . \quad (4.32)$$

For a randomly rough surface we expect that  $F_i(\vec{X})$  has a Gaussian form<sup>21</sup>

$$F_i(\vec{X}) = \eta_i^2 \exp \left[ - \left| \frac{\vec{X}}{2\xi_i} \right|^2 \right] , \quad (4.33)$$

where  $\eta_i^2$  is the rms deviation in the height and  $2\xi_i$  is the correlation distance along the surface.  $F(\vec{Q})$  is easily found to be

$$F_i(\vec{Q}) = \frac{\pi \eta_i^2}{L^2} e^{-Q^2 \xi_i^2} . \quad (4.34)$$

Now, through the use of Eq. (4.30), we find from (4.12) that

$$\begin{aligned} (\epsilon_{\vec{p}} - \epsilon_{\vec{p}'})^2 \langle |T(\vec{p}' - \vec{p})|^2 \rangle_S \\ = \frac{p'^2 p^2}{m_e^2} [ \langle |S_1(\vec{P}' - \vec{P})|^2 \rangle_S + \langle |S_2(\vec{P}' - \vec{P})|^2 \rangle_S ] , \end{aligned} \quad (4.35)$$

and obviously the two surfaces contribute independently to the resistivity. If the two surfaces can be characterized

Thus once the form of the electron-impurity interaction potential is known, one can readily obtain from Eqs. (4.19), (4.28), and (4.29) the impurity contribution to the electrical resistivity  $R_I = VM_I''/\chi^2$ . The corresponding contribution due to electron scattering from the rough surfaces  $R_S = VM_S''/\chi^2$  can be obtained from Eqs. (4.19), (4.27), and (4.12) if the surface-profile functions  $\xi_1(\vec{X})$  and  $\xi_2(\vec{X})$  are known. Thus a great deal of information on the morphology of the film surfaces may be extracted from resistivity measurements.

#### D. Application to randomly rough surfaces

In some situations the roughness on the surface of a thin film is found to be rather random.<sup>21</sup> We shall compute the surface contribution to the electrical resistivity for this case in more detail here. We need to take some kind of average  $\langle \rangle_S$  over the surface-profile functions in Eq. (4.27). If the structures on the top and the bottom surfaces are uncorrelated with each other, then we can write

$$\langle S_i^*(\vec{Q}) S_j(\vec{Q}) \rangle_S = \delta_{ij} \langle |S_i(\vec{Q})|^2 \rangle_S , \quad (4.30)$$

where  $i = 1$  or  $2$ , respectively, for the top and the bottom surfaces. We can set  $\langle |S_i(\vec{Q})|^2 \rangle_S$  in a slightly different form,

by the same Gaussian distribution function, then we can use Eqs. (4.27), (4.35), (4.31), and (4.34) to obtain

$$\begin{aligned} M_S'' &= \frac{\pi^2 \hbar e^2 \eta^2 \xi^2}{m_e^4 L^2} \sum_{\vec{p}, \vec{p}'} p'^2 p^2 (p_x - p'_x)^2 e^{-|\vec{P} - \vec{P}'|^2 \xi^2} \\ &\quad \times \delta(\epsilon_F - \epsilon_{\vec{p}}) \delta(\epsilon_F - \epsilon_{\vec{p}'}) \end{aligned} \quad (4.36)$$

Before the wave-vector sums in the above equation can be performed one must investigate the Fermi-level structures of a thin metal film. The results are derived in Appendix C. We find that the occupied states at  $T=0$  K are confined within a stack of flat circular disks whose sizes are bounded by an effective Fermi sphere with an effective Fermi wave vector which depends on the thickness parameter  $t$ . The angular part (within the  $p_x$ - $p_y$  plane) of the sums in Eq. (4.36) can be carried out easily. The surface-roughness contribution to the electrical resistivity is found to be given by

$$R_S = \frac{VM_S''}{\chi} = \frac{q \pi \hbar k_F \eta^2}{e^2} \tilde{R}_S , \quad (4.37)$$

where  $\tilde{R}_S$  can be expressed in terms of dimensionless quantities as

$$\begin{aligned} \tilde{R}_S = \frac{\tilde{\xi}^2}{t^7} & \left[ \sum_{m=1}^{m_f} m^4 a_m^2 e^{-2a_m^2 \tilde{\xi}^2} [I_0(2a_m^2 \tilde{\xi}^2) - I_1(2a_m^2 \tilde{\xi}^2)] \right. \\ & \left. + \sum_{m=1}^{m_f} \sum_{m'=m+1}^{m_f} m^2 m'^2 e^{-(a_m^2 + a_{m'}^2) \tilde{\xi}^2} [(a_m^2 + a_{m'}^2) I_0(2a_m a_{m'} \tilde{\xi}^2) - 2a_m a_{m'} I_1(2a_m a_{m'} \tilde{\xi}^2)] \right], \end{aligned} \quad (4.38)$$

and

$$\begin{aligned} a_m^2 & \equiv \tilde{k}_F^2 - (m/t)^2, \quad \tilde{k}_F \equiv k_F(l)/k_F, \\ \tilde{\xi} & \equiv k_F \xi, \quad t \equiv k_F l / \pi. \end{aligned}$$

There are a few points that deserve comment here. (1) The surface-roughness contribution to the electrical resistivity is in fact a purely quantum-mechanical effect since it is proportional to  $\hbar$ . (2) It is independent of the mass of charge carrier. (3) For randomly rough surfaces it is proportional to the mean-square height of the roughness, and also increases rapidly as the correlation distance along the surface decreases. (4) As a function of  $t$ , due to the underlying structure of the Fermi levels, discontinuous jumps are expected to occur for  $t$  less than about 30, if broadening effects are sufficiently weak.

From the usual electron mean-free-path argument it is clear that the resistivity has to increase as  $t$  is decreased. However, we see from Eqs. (4.37) and (4.38) that there is an abrupt drop in  $R_S$  as  $t$  is decreased across each  $t_{m_f}$  values. (See Fig. 1.) The reason for this behavior is rather simple. We can see from Appendix C that as  $t$  is decreased, the distance between adjacent  $k_z$  levels increases. At the moment  $t$  decreases across  $t_{m_f}$ , the  $m = m_f$  level shrinks to nothing and is pushed out of the effective Fer-

mi sphere. This leads to a sudden decrease in the fraction of electrons near the Fermi surface and thus a corresponding decrease in the resistivity. These jumps are enormous for small values of  $m_f$ . This kind of anomaly reflects the discrete nature of the Fermi surface, and similar effects can be expected in almost all the electronic properties of ultrathin metal films, as long as level-broadening effects are not overwhelmingly large.

The behavior of  $R_S$  for different values of the surface autocorrelation distance  $2\xi$  is also shown in Fig. 1. As is expected,  $\tilde{R}_S$  decreases as  $\tilde{\xi}$  is increased. In Fig. 2 we plot  $\tilde{R}_S$  versus  $t^{-1}$  in order to show that  $R_S$  is approximately inversely proportional to the thickness of the film.

In order to make some kind of contact with classical SET's, which clearly cannot predict the above-mentioned quantum size oscillations, and to describe experiments which are performed on somewhat thicker films, we now neglect the thickness dependence of the Fermi wave vector by setting  $k_f(t) = k_f$ . Moreover, we convert all wave-vector sums into integrals. We then obtain from Eq. (4.38)

$$\tilde{R}_S = \frac{\tilde{\xi}^2}{2t} I(\tilde{\xi}^2), \quad (4.39a)$$

where

$$I(\tilde{\xi}^2) \equiv \int_0^1 dx x(1-x^2)^{1/2} \int_0^1 dx' x'(1-x'^2)^{1/2} e^{-(x^2+x'^2)\tilde{\xi}^2} [(x^2+x'^2)I_0(2\tilde{\xi}^2 xx') - 2xx'I_1(2\tilde{\xi}^2 xx')], \quad (4.39b)$$

and  $I_0$  and  $I_1$  are, respectively, the modified Bessel function of the zeroth and first order. Thus we see that for sufficiently thick films the surface-roughness contribution to the resistivity is inversely proportional to the film thickness. Such a behavior has been seen in the pioneer-

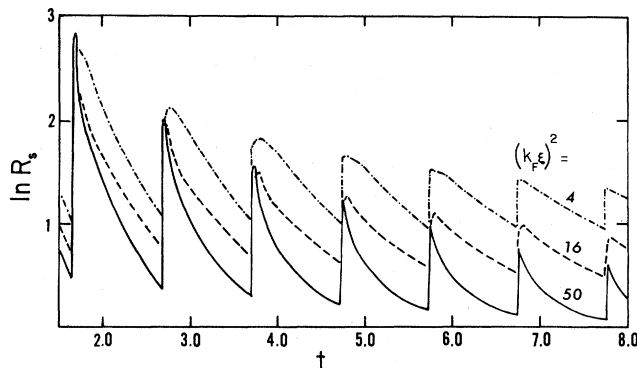


FIG. 1. Surface-roughness resistivities for various values of the surface correlation distance  $\tilde{\xi} = k_F \xi$  are plotted as a function of the thickness parameter  $t = k_F l / \pi$ .

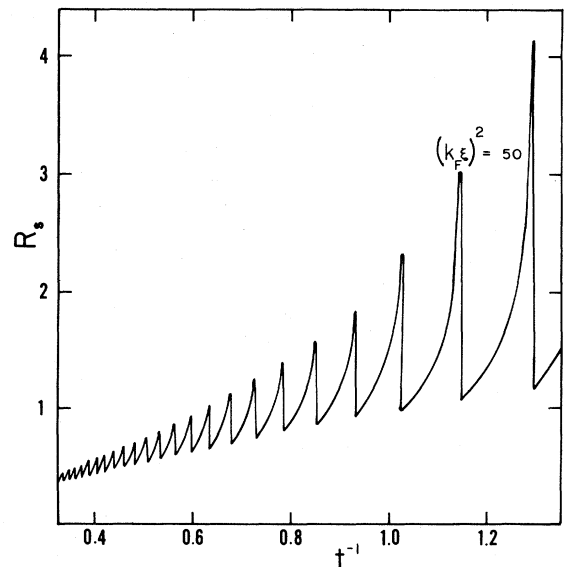


FIG. 2. Surface-roughness resistivities are plotted as a function of  $t^{-1}$ .



ing works of Appleyard and Lovell<sup>22</sup> on alkali-metal films, which have also been repeated and verified by Nossek.<sup>23</sup>

Now according to Fuchs's theory<sup>1</sup> the ratio of the resistivity of a thin film to that of the bulk material can be written in the thick-film limit (i.e.,  $l_0/l \ll 1$ ) as

$$\frac{R_F}{R_B} = 1 + \frac{3l_0}{8l}(1 - P_0), \quad (4.40)$$

where  $l_0$  is the electron mean free path and  $P_0$  is Fuch's specular factor. If we identify the excess resistivity  $R_F - R_B$  as the surface contribution of the resistivity, Fuchs's result can be rewritten as

$$R_S = \frac{3m_e v_F}{8\rho_e e^2 l}(1 - P_0). \quad (4.41)$$

Now if one tries to compare this classical result with our result in Eq. (4.38) in order to extract the specular factor, one would conclude that

$$1 - P_0 = 4k_F^4 \eta^2 \xi^2 I(\xi^2). \quad (4.42)$$

In the limit where  $\eta^2 \rightarrow 0$  and  $\xi^2 \rightarrow \infty$  the right-hand side of Eq. (4.42) vanishes, and this is consistent with the fact that  $P_0$  should be 1 if the surfaces are perfectly flat. However, in the limit of large  $\eta^2$  and small  $\xi^2$  (i.e., extremely rough surfaces) it can be shown that our result becomes very large but does not saturate. On the other hand, the classical result has a maximum value of 1 when  $P_0 \rightarrow 0$  (totally diffuse surface scattering). This may explain why it is sometimes necessary to use unphysical negative values of  $P_0$  in order to fit experimental data to these classical theories.

## V. DISCUSSION

In this section we shall point out a few limitations of our results, and discuss some possible areas for future studies. Despite the exactness of the coordinate transformation discussed in Sec. II, the results of Sec. III and IV rely on the assumption of small roughness and thus cannot be applied, for example, to surfaces with steps on the atomic scale.<sup>24</sup> However, one can certainly extend the present theory to metals with anisotropic Fermi surfaces,<sup>25</sup> and adopt a more realistic model than the infinite-barrier model used here. A more accurate treatment of the effects due to electron-electron interactions than what is discussed in Appendix A can be accomplished within the random-phase approximation using the bosonization method developed recently for inhomogeneous electron systems.<sup>26</sup> These effects may be rather important for our problem due to the loss of translational invariance in the direction perpendicular to the surfaces of the film. Evidence for such behavior has been reported in recent experiments on the low-temperature resistivity of ultrathin metal wires.<sup>27</sup> Calculations along these lines will be left for the future.

Figures 2 and 3 were drawn under the assumption that the Gaussian nature of the surfaces does not vary with the film thickness. This may not be true in reality, depending on the procedures under which the films are deposited. The quantum size oscillations depicted in Fig. 1 may be

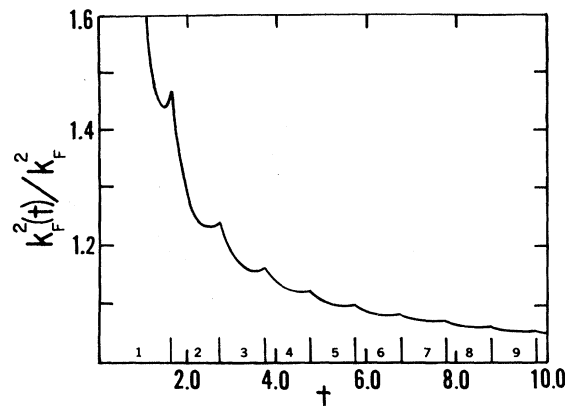


FIG. 3. Square of the effective Fermi wave vector is plotted versus the thickness parameter  $t = k_F l / \pi$ . The number of occupied  $k_z$  levels for a given thickness is also known.

difficult to be observed experimentally due to various level broadening effects and because rather thin films must be used. The Fermi-level structures used in our calculation were derived only for ideal films with flat surfaces. Effects due to the smearing of the electron levels resulting from scattering with impurities may be studied employing a method similar to that used by Rytova.<sup>28</sup> For semiconductor films, due to the low electron density, these oscillations should happen even for much thicker films. Moreover, the thickness parameter  $t$  can also be varied by changing the carrier concentration via doping, or by changing the temperature.<sup>29</sup>

The relative simplicity of the experimental arrangement and the high degree of accuracy make resistivity studies an important tool to gain insight into the electrical and structural properties of metallic films. When other experiments<sup>4-6</sup> such as the temperature coefficient of the resistivity, the anomalous skin effect, the metallic field effect,<sup>30</sup> optical-reflectivity, and light absorption,<sup>31</sup> can be performed on the same specimen even more detailed information may be obtained.

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## APPENDIX A: ELECTRON SCREENING OF IMPURITIES

Impurities within a metal are screened by the conduction electrons. Such effects can be easily incorporated within our formalism by using the dielectric function for

the electron system,  $\epsilon^{-1}(\vec{r}, \vec{r}', \omega)$ . The Hamiltonian describing the scattering of an electron with the screened impurities may be written, in the static limit, as

$$\mathcal{H}'_{sc} = \int d\vec{r}' \epsilon^{-1}(\vec{r}, \vec{r}') \sum_j u(\vec{r}' - \vec{r}_j) = \sum_j u_{sc}(\vec{r}, \vec{r}_j), \quad (\text{A1})$$

where

$$u_{sc}(\vec{r}, \vec{r}_j) \equiv \int d\vec{r}' \epsilon^{-1}(\vec{r}, \vec{r}') u(\vec{r}' - \vec{r}_j) \quad (\text{A2})$$

is the screened electron-impurity interaction. For a film with flat surfaces perpendicular to the  $z$  axis, we have

$$\epsilon(\vec{r}, \vec{r}') = \epsilon(\vec{X} - \vec{X}', z, z'), \quad (\text{A3})$$

and so

$$\begin{aligned} u_{sc}(\vec{r}, \vec{r}_j) &= u_{sc}(\vec{X} - \vec{X}_j, z, z_j) \\ &= \int dz' \int d^2X' \epsilon^{-1}(\vec{X} - \vec{X}_j - \vec{X}', z, z') \\ &\quad \times u(\vec{X}', z' - z_j). \end{aligned} \quad (\text{A4})$$

Thus certain effects due to screening may be taken into account by replacing  $u(\vec{Q}, q, q')$  in Eq. (4.6) by  $u_{sc}(\vec{Q}, q, q')$  which is the Fourier transform of  $u_{sc}(\vec{X}, z, z')$ . Note that although the unscreened interaction  $u(\vec{r} - \vec{r}')$  depends only on  $z - z'$ , the screened interaction  $u_{sc}(\vec{r}, \vec{r}')$  depends separately on  $z$  and  $z'$ . The screening electron cloud around an impurity is no longer spherical, especially so for those impurities near the surface. Thus besides the contribution due to the rough surfaces, this aspherical scattering will also lead to some kind of angular-dependent scattering of conduction electrons near a metal surface.

## APPENDIX B: EVALUATION OF FREE-PARTICLE RELAXATION FUNCTIONS

The evaluation of free-particle relaxation functions such as  $(a_1^\dagger a_2, a_{\alpha\beta}^\dagger)_z^0$  is quite straightforward. By definition we can write

$$(a_1^\dagger a_2, a_{\alpha\beta}^\dagger)_z^0 = \int_0^\infty dt e^{izt} (a_1^\dagger(t) a_2(t), a_{\alpha\beta}^\dagger) = \int_0^\infty dt e^{izt} \int_0^\beta d\lambda \langle [a_1^\dagger(t - i\lambda) a_2(t - i\lambda)]^\dagger a_{\alpha\beta}^\dagger \rangle - \frac{i\beta}{z} \langle a_1^\dagger a_2 \rangle^* \langle a_{\alpha\beta}^\dagger \rangle. \quad (\text{B1})$$

From the fact that for free particles

$$a_{\vec{p}}(t) = e^{i\epsilon_{\vec{p}} t} a_{\vec{p}}(0), \quad a_{\vec{p}}^\dagger(t) = e^{i\epsilon_{\vec{p}} t} a_{\vec{p}}^\dagger(0), \quad (\text{B2})$$

we readily obtain

$$\begin{aligned} (a_1^\dagger a_2, a_{\alpha\beta}^\dagger)_z^0 &= \frac{i(1 - e^{-\beta\epsilon_{12}})}{\epsilon_{12}(z - \epsilon_{12})} \langle (a_1^\dagger a_2)^\dagger a_{\alpha\beta}^\dagger \rangle \\ &\quad - \frac{i\beta}{z} \langle a_1^\dagger a_2 \rangle^* \langle a_{\alpha\beta}^\dagger \rangle, \end{aligned} \quad (\text{B3})$$

where  $\epsilon_{12} \equiv \epsilon_1 - \epsilon_2$ . The thermal averages can be evaluated using Wick's theorem developed by Gaudin<sup>32</sup> to finally obtain

$$(a_1^\dagger a_2, a_{\alpha\beta}^\dagger)_z^0 = \frac{-i\delta_{1\alpha}\delta_{2\beta}f_{12}}{\epsilon_{12}(z - \epsilon_{12}/\hbar)}, \quad (\text{B4})$$

where  $f_{12} \equiv f_1 - f_2$ ,  $f_1 = (e^{\beta(\epsilon_1 - \epsilon_f)} + 1)^{-1}$  is the Fermi function, and an  $\hbar$  has been retrieved.

Note that the above results can be readily extended to calculate relaxation functions and static susceptibilities for any number of  $a$ 's and  $a^\dagger$ 's. The extension to the case for bosons is also straightforward.

## APPENDIX C: FERMI-LEVEL STRUCTURES OF THIN-METAL FILMS

We consider here the Fermi-level structures of a free-electron gas confined within an ideal thin film of thickness  $l$ . For bulk systems one can define a Fermi wave vector  $k_F$  such that at  $T=0$  states labeled by  $k \leq k_F$  are

all filled, and those with  $k > k_F$  are all empty. The bulk Fermi wave vector depends only on the density of electrons,

$$\rho_e = \frac{k_F^3}{3\pi^2}, \quad (\text{C1})$$

which characterizes a given material.

In the thin-film geometry  $k_z$  becomes discrete and the allowed states at  $T=0$  are confined within a stack of very thin circular disks lying perpendicular to the  $z$  axis. The distance between adjacent levels is  $\pi/l$ . There are two basic quantities of concern here for a film with given values of  $l$  and  $\rho_e$ . First, we want to know the maximum number of nonempty  $k_z$  levels, which we shall denote by  $m_f$ . Second, for a given occupied level labeled by some  $m \leq m_f$ , we need to find the radius  $K_f(m)$  such that states with  $K \leq K_f(m)$  are all filled. Note that  $m_f$  must be a positive integer while  $K_f(m)$  can assume any real value.

To proceed, first note that because the total number of occupied states must be  $N_e$ , the total number of electrons, thus instead of Eq. (C1) for the bulk we have

$$\begin{aligned} \rho_e &= \frac{2}{V} \sum_{\vec{k}} \Theta(m_f - m) \Theta(K_f^2(m) - |\vec{K}|^2) \\ &= \frac{1}{2\pi l} \sum_{m=1}^{m_f} K_f^2(m). \end{aligned} \quad (\text{C2})$$

Next, we must fill up the states in such a way that the total energy is lowest. At  $T=0$ , the total energy is given by

$$\sum_{\substack{\text{occupied} \\ \vec{k}}} \epsilon_{\vec{k}} = 2\pi \sum_{m=1}^{m_f} \int_0^{K_f(m)} dK K \frac{\hbar^2}{2m_e} \left[ K^2 + \left( \frac{m\pi}{l} \right)^2 \right] \\ = \frac{\pi \hbar^2}{4m_e} \sum_{m=1}^{m_f} [K_f^4(m) + 2\pi^2 m^2 K_f^2(m) l^{-2}]. \quad (\text{C3})$$

Thus in terms of the reduced variables

$$t \equiv k_F l / \pi, \quad \tilde{K}_f(m) \equiv K_f(m) / k_F, \quad (\text{C4})$$

our task is to minimize the quantity

$$\sum_{m=1}^{m_f} [\tilde{K}_f^4(m) + 2m^2 \tilde{K}_f^2(m) t^{-2}] \quad (\text{C5})$$

subject to the constraint that

$$\frac{2}{3}t = \sum_{m=1}^{m_f} \tilde{K}_f^2(m). \quad (\text{C6})$$

Now it is important to note that for a given thickness parameter  $t$ , there exist two numbers  $t_{m_f}$  and  $t_{m_{f+1}}$  such that as long as  $t$  lies between them (i.e.,  $t_{m_f} \leq t < t_{m_{f+1}}$ ) the total number of occupied  $k_z$  levels is  $m_f$ . But as  $t$  is increased above  $t_{m_{f+1}}$ , the total number of occupied levels increases by one, until  $t$  is above  $t_{m_{f+2}}$ , etc. Thus if we restrict  $t$  such that  $t_{m_f} \leq t < t_{m_{f+1}}$  then  $m_f$  remains unchanged, and we can use Lagrange undetermined multiplier method and consider the minimization of the quantity

$$\sum_{m=1}^{m_f} \left[ \tilde{K}_f^4(m) + \frac{2m^2}{t^2} \tilde{K}_f^2(m) \right] + \lambda \left[ \frac{2}{3}t - \sum_{m=1}^{m_f} \tilde{K}_f^2(m) \right]. \quad (\text{C7})$$

This yields the set of equations

$$2\tilde{K}_f^2(m) + \frac{2m^2}{t^2} - \lambda = 0, \quad m = 1, 2, \dots, m_f. \quad (\text{C8})$$

By summing over these equations and using Eq. (C6), we find the Lagrange multiplier to be

$$\lambda = \frac{4t}{3m_f} + \frac{(m_f+1)(2m_f+1)}{3t^2}. \quad (\text{C9})$$

By substituting  $\lambda$  back in Eq. (C8) we obtain

$$\tilde{K}_f^2(m) = \frac{2t}{3m_f} + \frac{(m_f+1)(2m_f+1)}{6t^2} - \frac{m^2}{t^2}. \quad (\text{C10})$$

This equation shows that the occupied  $k_z$  levels are bounded by an effective Fermi sphere which is characterized by a thickness-dependent Fermi wave vector defined by

$$k_f(t) = k_f \left[ \frac{4t^3 + m_f(m_f+1)(2m_f+1)}{6m_f t^2} \right]^{1/2}. \quad (\text{C11})$$

Thus we can rewrite Eq. (C10) as

$$\tilde{K}_f^2(m) = \tilde{k}_f^2(t) - (m/t)^2, \quad (\text{C12})$$

where

$$\tilde{k}_f(t) = k_f(t) / k_f.$$

Now to determine  $m_f$ , note that at the moment when a new level is opening up its radius  $K_f(m)$  must be zero [i.e.,  $K_f^2(m_f) = 0$ ]. Thus we obtain the equation

$$t_{m_f} = [m_f(m_f-1)(m_f+\frac{1}{4})]^{1/3}. \quad (\text{C13})$$

So, for a given value of  $t$ ,  $m_f$  can be determined from the self-consistency equation

$$m_f = \left[ \frac{l}{\pi} k_f(t) \right] \\ = \left[ \left[ \frac{2t^3}{3m_f} + \frac{m_f}{6} (m_f+1)(2m_f+1) \right]^{1/2} \right], \quad (\text{C14})$$

where the square brackets denote the integer value, or better yet,  $m_f$  can be determined from Table I.

Despite the fact that as  $t$  varies across each value of  $t_{m_{f+1}}$  ( $m_f = 1, 2, \dots$ )  $m_f$  changes discontinuously by one, one can show that  $k_f(t)$  as given in (C11) is in fact a continuous function of  $t$  for all  $t > 0$ . The slope, however, has a finite jump across each value of  $t_{m_{f+1}}$ . It can also be shown that  $k_f(t)$  is always larger than  $k_F$ , its bulk value. This is of course expected from the uncertainty principle. It approaches  $k_f$  as  $t \rightarrow \infty$ , as it should. However, it is not exactly a monotonically decreasing function of  $t$ . (See Fig. 3.) Oscillation in the value of  $k_f(t)$  is a direct consequence of the discreteness in the energies of the system. In addition we also note from Eq. (C13) that there is a critical value for the thickness parameter

$$t_c = \left( \frac{9}{2} \right)^{1/3} \quad (\text{C15})$$

below which only the lowest  $k_z$  level can be occupied at  $T=0$ . And if the levels are not broadened significantly compared with the energy

TABLE I. For a given value of  $t = k_F l / \pi$  such that  $t_{m_f} \leq t < t_{m_{f+1}}$ , the number of nonempty  $k_z$  levels,  $m_f$ , is as shown.

$m_f$	2	3	4	5	6	7	8
$t_{m_f}$	1.651	2.692	3.708	4.718	5.724	6.728	7.731
$m_f$	9	10	11	12	13	14	
$t_{m_f}$	8.733	9.735	10.736	11.737	12.738	13.739	

$$\frac{\hbar^2}{2m_e} \left[ \frac{4\pi^2}{l^2} - k_F^2(t) \right] = \frac{2}{3} t \epsilon_f \left[ \left( \frac{t_c}{t} \right)^3 - 1 \right],$$

then the electronic properties will be basically those for a two-dimensional object. This regime can almost never be met experimentally for metal films. However, for semimetal or semiconductor films, due to the low values of the electron density, one can easily be in this regime.

From Eq. (C13) we see that for sufficiently thick films, i.e.,  $m_f \gg 1$ , we have

$$t_{m_f} \cong m_f - \frac{1}{4} + \mathcal{O}(m_f^{-1}). \quad (\text{C16})$$

Moreover, within each  $m_f - \frac{1}{4} \leq t < m_f + \frac{3}{4}$  interval,  $k_f(t)$  has a local minimum at  $t = m_f - \frac{1}{2}$ .

Through the use of the results derived in this appendix, sums over the occupied states will be carried out as follows:

$$\sum_{\vec{k}} \Theta(\epsilon_f - \epsilon_{\vec{k}}) \rightarrow \left( \frac{L}{2\pi} \right)^2 \sum_{m=1}^{m_f} \int_0^{2\pi} d\theta \int_0^{K_f(m)} dK K. \quad (\text{C17})$$

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<sup>5</sup>D. C. Larson, in *Physics of Thin Films*, edited by G. Hess and R. E. Thun (Academic, New York, 1971).

<sup>6</sup>T. J. Coutts, *Electrical Conduction in Thin Metal Films* (Elsevier, Amsterdam, 1974).

<sup>7</sup>P. Wissmann and K. Müller, in *Surface Physics*, Vol. 77 of *Springer Tracts in Modern Physics* (Springer, New York, 1975), Chap. 1.

<sup>8</sup>However, a calculation for  $P_0$  due to the scattering of conduction electrons by localized surface charges has been reported by R. F. Greene and R. W. O'Donnell using the Boltzmann equation approach [Phys. Rev. **147**, 599 (1968)].

<sup>9</sup>A preliminary account of this work has appeared in K. M. Leung, Bull. Am. Phys. Soc. **27**, 217 (1982).

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<sup>11</sup>The basic idea follows from the work of P. A. Fedders [Phys. Rev. **165**, 580 (1968)] where the coupling of photons to the surface plasmon via surface roughness is studied for a semi-infinite medium. The transformation in Eq. (2.2) reduces to his result [Eq. (2) in his paper] in the limit  $l \rightarrow \infty$ , and is a natural generalization to the present thin-film geometry.

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<sup>15</sup>A similar method has been discussed by W. Götze and P. Wölfle, Phys. Rev. B **6**, 1226 (1972).

<sup>16</sup>See Ref. 15 and K. M. Leung (unpublished).

<sup>17</sup>Application to the absorption of light by small metal particles has been studied by K. M. Leung, Bull. Am. Phys. Soc. **28**,

286 (1983).

<sup>18</sup>This exact relation can be derived easily as follows. From the fact that

$$j_x = e \sum_i \dot{X}_i = \frac{e}{m_e} \sum_i P_{xi}$$

we have

$$\begin{aligned} X = (j_x, j_x) &= \frac{e^2}{m_e} \sum_{i,j} (\dot{X}_i, P_{xi}) = -\frac{ie^2}{m_e} \sum_{i,j} (\mathcal{L} X_i, P_{xi}) \\ &= -\frac{ie^2}{\hbar m_e} \sum_{i,j} \langle [X_i, P_{xj}] \rangle = \frac{N_e e^2}{m_e}, \end{aligned}$$

where we have made use of Kubo's identity which states that

$$(\mathcal{L} A, B) = \frac{1}{\hbar} \langle [A^\dagger, B] \rangle$$

for arbitrary operators  $A$  and  $B$ .

<sup>19</sup>Equation (4.20) holds because of time-reversal invariance, and follows immediately also from Kubo's identity (cf. Ref. 18).

<sup>20</sup>We have already taken the zero-temperature limit in writing Eqs. (4.27) and (4.28).

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