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Quantum size effects in transport properties of metallic films

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The confinement of electrons in small dimensions can lead to a discretization of energy levels. The associated quantum size effects in turn lead to an out-of-plane conductivity that shows nonanalytic behavior in the approach to the classical limit. The principal size dependence of the conductivity is $\sim 1/d$ for a film of thickness d; however, there is also a correction term that has an essential singularity in the small parameter l/d, where l is the mean free path in a bulk sample. Surface roughness in the film is introduced by establishing two physical length scales. Variations in d on length scales shorter than l are treated quantum mechanically by a suitable coordinate transformation. On the other hand, large-scale fluctuations which might reflect the presence of grains are incorporated classically by segmenting the film into independent units of length l. Impurity effects have also been included and in fact crossover behavior in the conductivity is found from a surface-dominated to an impurity-dominated regime. The transport coefficients—conductivity and thermopower—are found to show oscillations as a function of d with a period of half the Fermi wavelength.

I. INTRODUCTION

The behavior of electrons in systems having dimensions in the intermediate-length-scale or mesoscopic regime has been actively studied in the past few years.[1] In this regime the inelastic-scattering length can be much longer than the size of the system, and an electron can therefore maintain phase coherence as it travels the length of the system. In a disordered conductor this leads to a sensitivity of the response function to interference effects along different paths. The most important of these are time-reversed paths that "see" the same impurity configuration and which have the effect of reducing the conductivity because of weak-localization effects.[2] The latter have been observed in the magnetoconductance of films in a set of experiments by Bergmann.[3] Another distinguishing feature of the physics at these length scales is that it is possible to observe sample-specific "fingerprints" of the magnetoconductance which arise from the *non-self-averaging* nature of transport coefficients. This has led to a prediction of universal conductance fluctuations.[4]

In addition to the interference phenomena in disordered conductors, it is also possible to observe size effects in the response functions because of the confinement of electrons in systems of small spatial dimensions. The effect of the surface on the transport properties of films has been long studied in the classical-size-effect regime.[5-7] Classical size effects arise when the thickness of the film approaches the bulk mean free path, and have largely been interpreted according to the theories of Fuchs[8] and Sondheimer.[9] These theories are based on the Boltzmann equation in which the surface in incorporated via boundary conditions on the electron distribution function. In particular, the surface is characterized by a specularity parameter p according to the degree of scattering from the surface, with p lying between 0 (for completely diffuse) and 1 (for completely specular). Extensions of these theories to include angle-dependent specularity parameters have also been discussed.[10]

The Boltzmann equation is probably a reasonable starting point for film thicknesses $d \sim 500-1000$ Å, i.e., when $d > l$, where l is the mean free path. However, it must eventually fail when the energy-level spectrum is discrete and the corresponding quantum effects become important. This is expected when $d/\lambda \sim O(10^2)$, where λ is the wavelength of the electron. To be observable, it is necessary that the typical spacing between energy levels at the Fermi energy δE be much larger than the level broadening $\hbar/\tau$ arising from various scattering mechanisms (e.g., electron-electron, electron-impurity, etc.). Since $\delta E \sim \varepsilon_F/$(number of occupied levels), the condition for observing quantum size effects when translated in terms of lengths becomes $d < \pi l$ with $l = v_F \tau$. Transport coefficients in this quantum regime are then expected to show an oscillatory behavior[11] as a function of the film thickness, and with a period of half the Fermi wavelength. Experiments in this regime are overall much more difficult than in the classical size-effect regime since it is required that *continuous* films be grown and that these possess a high degree of uniformity in the thickness range 5–100 Å. However, data on Pt films are available[12] and these show oscillations in the resistivity as the thickness is scanned. Some interesting results have also been reported for CoSi$_2$ films[13] in the thickness range 60–1000 Å. It is claimed that these films are metallic with bulk mean free paths of about 1000 Å. Experiments on semimetallic films (e.g., bismuth) display quantum size effects under much less stringent conditions, since the wavelength of the important electron-hole pockets is larger by ~ 2 orders of magnitude as compared to the simple metals.[14]

Theoretically, quantum size effects in a film with perfect surfaces were first studied by Sandomirskiĭ[11] within an extension of the jellium model of a noninteracting electron system. Further extension of this theory to include surface roughness has followed a different route

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from the approaches in classical size-effect theories. The basic philosophy has been to incorporate variations in the confining potential of the rough surface as a *boundary condition* on the Hamiltonian. As there is no simple perturbation theory to treat arbitrary changes in the boundary conditions, the problem of a free-electron Hamiltonian with complicated boundary conditions is normally transformed by an appropriate coordinate transformation into a problem with simpler boundary conditions (e.g., in a perfect slab with flat surfaces). An expected consequence of this transformation is that additional terms are generated which play the role of potential coupling, i.e., it no longer remains a free-electron Hamiltonian. These are then treated by perturbative techniques which are valid if the surface roughness is small (for example, the rms variations in the thickness of the film are small compared to the thickness). The idea was suggested by Migdal[15] in the study of the deformation of nuclei. More recently, in the context of thin films such a coordinate transformation has been proposed by Tešanović *et al.*[16]

The purpose of the present work is to develop a theory for transport in small systems under conditions in which quantum size effects are manifestly important. On these length scales, it is necessary to go beyond the usual classical size-effect theories and to include from the start the effects of discreteness in the energy levels. We also extend the phenomenological descriptions of surface roughness of a conductor and give a microscopic quantum-mechanical description in which a boundary condition is imposed on the Hamiltonian. In addition, we analyze the behavior of the size-dependent conductivity and examine nonanalytic structure in the approach to the classical Drude limit. Towards this end, in Sec. II we introduce a simple model of a film with a perfect surface and then study the effects of quantization of the energy levels on the density of states. In Sec. III we evaluate the conductivity along the film and perpendicular to it, and discuss the inclusion of a finite inelastic broadening. We study the anisotropy in the dc conductivity components and show that in the approach to the Drude limit, the transverse conductivity is nonanalytic and has an essential singularity in l/d where l is the bulk mean free path and d is the film thickness. The effects of scattering on the static transport coefficients, from impurity centers embedded within the film and from surface roughness, is given in Sec. IV. Surface roughness is incorporated as a boundary condition on the Hamiltonian, and for sufficiently small variations in the thickness the problem is handled perturbatively. The role of grain-boundary scattering is also analyzed. We evaluate the crossover with film thickness from a surface-dominated regime to an impurity-dominated regime. In Sec. V we present a discussion of the thermopower, which being of derivative character is found to show very large variations as a function of d. We conclude in Sec. VI with some comments and suggestions for future directions.

II. SIMPLE MODEL OF A FILM

For a simple description of a film we take a particle-in-a-box model in which independent electrons are confined by a surface potential $U(\mathbf{r})$ of length scale d along the z direction. Assuming a jellium model for the ions, the free-particle Hamiltonian must be solved with boundary conditions dictated by the surface potential. We first consider the case of a film with perfect surfaces for which the eigenvalue spectrum is given by

$$\varepsilon_{kn}=\frac{\hbar^2k^2}{2m^*}+\varepsilon_0 n^2,\quad n=1,2,\ldots \tag{2.1}$$

i.e., described by a continuous quantum number k, the in-plane momentum, and a discrete subband index n. In (2.1), $\varepsilon_0=\hbar^2\pi^2/2m^*d^2$ is the zero-point energy of confinement in a film of thickness d. The thickness of the film is built directly into the eigenstates

$$\Psi_{kn}(\mathbf{r})=\sqrt{2/\Omega}\,\sin\left[\frac{n\pi z}{d}\right]e^{i\mathbf{k}\cdot\vec{\rho}}\,, \tag{2.2}$$

where $\vec{\rho}$ is a vector in the x-y plane and $\Omega=Ad$ is the volume of the film.

For the eigenvalues given in (2.1) the density of states per spin is

$$g(\varepsilon)=\frac{1}{\Omega}\sum_{(k,n)}\delta(\varepsilon-\varepsilon_{kn})=\frac{m^*}{2\pi\hbar^2 d}\mathrm{Int}[(\varepsilon/\varepsilon_0)^{1/2}]\,, \tag{2.3}$$

where Int denotes the integer part of a number. The behavior of $g(\varepsilon)$ is depicted in Fig. 1. The subbands in the eigenvalue spectrum lead to a step structure in the density of states with an envelope described by the three-dimensional density of states in the thermodynamic limit. In the ground state, the average density of electrons $n=\langle\hat{n}(\mathbf{r})\rangle$ is given by

$$n=\frac{2}{\Omega}\int_0^{\infty}d\varepsilon\, g(\varepsilon)f(\varepsilon)\,. \tag{2.4}$$

We assume that the film is connected to a particle bath (grand-canonical ensemble) with a fixed chemical potential so that as the thickness of the film is varied, the density of electrons in the film fluctuates to maintain a con-

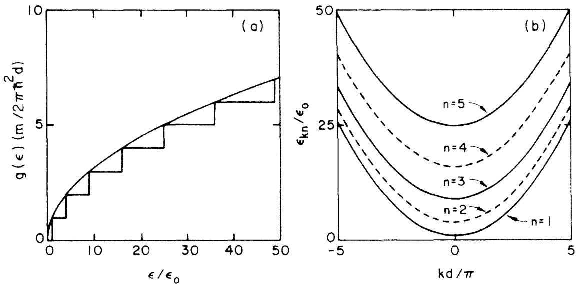

FIG. 1. (a) Density of states in units of $m^*/2\pi\hbar^2 d$ as a function of energy. The energy scale is set by $\varepsilon_0=\hbar^2\pi^2/2m^*d^2$, the zero-point energy because of confinement in a film of thickness d. The step structure arises from a discrete energy-level spectrum; the envelope is the density of states of a three-dimensional system in the thermodynamic limit. (b) Energy spectrum of a free-electron gas in a box. The eigenvalues are split into subbands and are parabolic within a band.

stant chemical potential. at $T=0$, (2.4) reduces to

$$\frac{n}{n_0}=\frac{3n_c}{2\kappa}\left[1-\frac{S(n_c)}{n_c\kappa^2}\right], \tag{2.5}$$

where $\kappa=k_F d/\pi$, $n_c=\mathrm{Int}[\kappa]$, and $S(n_c)=\sum_{n=1}^{n_c} n^2 = n_c(n_c+1)(2n_c+1)/6$. The Fermi energy is related to the wave vector k_F by $\varepsilon_F=\hbar^2 k_F^2/2m^*$ and $n_0=k_F^3/3\pi^2$ is the bulk density.

In Fig. 2 the thickness dependence of the density, obtained from (2.5), is plotted and is found to show oscillatory behavior and to have a period of half the Fermi wavelength. Notice that for metallic cesium, for example, with $k_F\sim 0.33a_0^{-1}$, the amplitude of the oscillation between $d=38a_0$ and $d=48a_0$ is about 5%, which is rather small. However, more significant is the depression in the *density* from its bulk value, which is approximately 20% at $d\sim 50a_0$. This observation leads us to an interesting suggestion that in response to the variation in the density, the lattice constant a of the metal might undergo a small expansion in order to maintain charge neutrality. The argument just presented is schematic and a more complete calculation is in fact required that evaluates the change in the density self-consistently by allowing for the adjustments in the surface potential as the thickness is varied. In addition, other contributions to the energy must also be taken into account, e.g., the Madelung energy and exchange and correlation effects. Proceeding with the simple picture of a noninteracting electron gas in a finite film, a 20% depression in the density will lead to anisotropy in the lattice constants, in which lattice parameters in the x and y directions remain practically unchanged, but that along z would increase by about 20%. For a bcc alkali metal with one electron donated per atom, (e.g., Cs) this implies an increase in a form 6.05 to 7.26 Å which ought to be detectable by glancing x-ray diffraction techniques. In the estimation given above, we have assumed that there is no surface reconstruction or rearrangement of atoms and that the lattice expands uniformly along z. We have also invoked *local* charge neutrality in the film which might in fact be violated because of the formation of a dipole layer at the surface that is energetically more favorable.

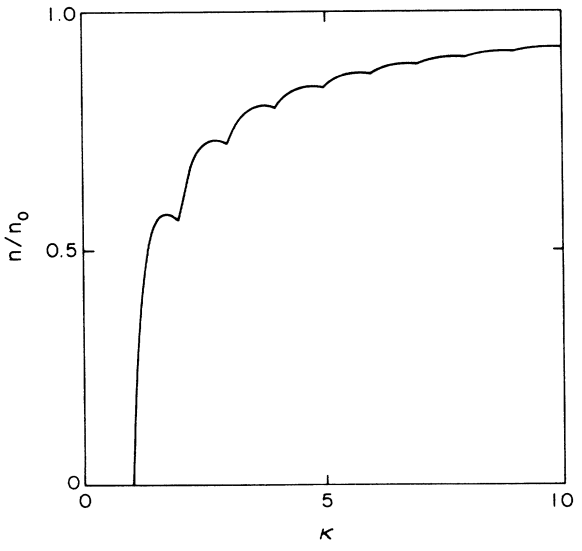

FIG. 2. Density of electrons (in units of $n_0=k_F^3/3\pi^3$) for a *fixed* chemical potential $\varepsilon_F=\hbar^2k_F^2/2m^*$ as a function of $\kappa=k_F d/\pi$. In the case of a film, k_F is fixed and the thickness d is varied; however, these oscillations can also be seen in MOSFET's, for example, as the chemical potential is changed at a fixed sample thickness.

In the limit of large κ, we find from (2.5) that $n/n_0=1-(3/4\kappa)-(1/4\kappa^2)$, which shows that the correction term is $\sim 1\%$ of the bulk density when $\kappa\sim 75$, or in the case of Cs, for example, when $d\sim 715a_0$. In this limit then, quantum size effects should no longer be visible since the discreteness in the eigenvalues is entirely washed out.

III. SIZE-DEPENDENT CONDUCTIVITY: APPROACH TO THE CLASSICAL LIMIT

A consequence of the discrete nature of eigenstates arising from the confinement in one dimension is that as d becomes much greater than the bulk mean free path l and the Drude limit is approached, the transverse conductivity is found to have a nonanalytic structure in the small parameter l/d. Quantum size effects also result in small oscillations in the conductivity as a function of the film thickness with a period of half the Fermi wavelength.

To see these effects, we first obtain an expression for the conductivity within the Kubo linear-response formalism by specifically including the discrete nature of the states in the system, as well as some coupling to a dissipative mechanism. In the independent-electron approximation, the Hamiltonian for an electron in the presence of an electromagnetic field characterized by a vector potential $\mathbf{A}(t)$ [and scalar potential $\phi(t)$ but set equal to 0 by choice of gauge] is

$$H=\frac{1}{2m^*}(\mathbf{p}-e\,\mathbf{A}/c)^2+V(\mathbf{r}) , \tag{3.1}$$

where $V(\mathbf{r})$ is the potential in the absence of an applied external potential and m^* is the effective mass of the electron arising from band-structure effects in the xy plane. We next treat $H_0=p^2/2m^*+V(\mathbf{r})$ as the unperturbed Hamiltonian which satisfies $H_0|\alpha\rangle=\varepsilon_\alpha|\alpha\rangle$ and evaluate the effects of the perturbation $H_1(t) = -(e/2m^*c)[\mathbf{p}\cdot\mathbf{A}(t)+\mathbf{A}(t)\cdot\mathbf{p}]$ to lowest order. In addition, we assume that the electrons are coupled to some source of dissipation, e.g., electron-electron interactions, phonons, etc., that is included to lowest order by introducing a relaxation rate γ. The equation of motion for the density matrix[17] of the electrons is

$$\frac{\partial\hat{\rho}(t)}{\partial t}+i[\hat{H}(t),\hat{\rho}(t)]=-\gamma[\hat{\rho}(t)-\hat{\rho}_{\mathrm{qe}}(t)] . \tag{3.2}$$

In (3.2), $\hat{\rho}_{\mathrm{qe}}$ is the quasiequilibrium density matrix given by $(\exp\{\beta[\hat{H}_0+\hat{H}_1(t)-\mu_0]\}+1)^{-1}$ and μ_0 is the chemical potential. Note that the quasiequilibrium state is determined by the total Hamiltonian. Additional comments on the choice of quasiequilibrium distribution function are given in Appendix B. Within linear-response theory, the density matrix can be approximated by $\hat{\rho}=\hat{\rho}_0+\delta\hat{\rho}$, where the deviation from equilibrium $\delta\hat{\rho}$ is linear in the perturbation. Expanding the quasiequilibrium density matrix, we find that to lowest order it is given by

$$\langle\alpha|\hat{\rho}_{qe}|\beta\rangle=f_\alpha\delta_{\alpha\beta}-\frac{f_\alpha-f_\beta}{\varepsilon_{\alpha\beta}}\langle\alpha|\hat{H}_1|\beta\rangle\ , \qquad (3.3)$$

where $\varepsilon_{\alpha\beta}=\varepsilon_\alpha-\varepsilon_\beta$, $\hat{\rho}_0|\alpha\rangle=f_\alpha|\alpha\rangle$, and $f_\alpha=\{\exp[\beta(\varepsilon_\alpha-\mu_0)]+1\}^{-1}$ is the Fermi distribution function. The off-diagonal components of the density matrix from (3.2) are of the form

$$\langle\alpha|\delta\hat{\rho}|\beta\rangle=\frac{f_\alpha-f_\beta}{\varepsilon_{\alpha\beta}}\frac{\varepsilon_{\alpha\beta}-i\gamma}{\varepsilon_{\alpha\beta}-\omega-i\gamma}\langle\alpha|\hat{H}_1|\beta\rangle\ . \qquad (3.4)$$

We can now calculate the induced current J_{ind} which is given by $\text{Tr}\{\hat{J}\hat{\rho}\}$; in general, the induced current is composed of two parts, namely (i) a diamagnetic contribution arising from the change in the current operator due to the vector potential, and (ii) a paramagnetic term from the off-diagonal element in the density matrix. We find the conductivity defined as $J_{\text{ind}}=\sigma E=\sigma(i\omega/c)\delta A$ to be given by

$$\sigma_{\mu\mu}(\omega)=\frac{i}{\omega\Omega}\left[\frac{ne^2}{m^*}+\frac{e^2}{(m^*)^2}\sum_{\alpha\neq\beta}\frac{f_\alpha-f_\beta}{\varepsilon_{\alpha\beta}}\frac{\varepsilon_{\alpha\beta}-i\gamma}{\varepsilon_{\alpha\beta}-\omega-i\gamma}\times|\langle\alpha|\hat{p}_\mu|\beta\rangle|^2\right]\ , \qquad (3.5)$$

where $\langle\alpha|\hat{p}_\mu|\beta\rangle$ is the matrix element of the momentum operator along the direction μ. We emphasize once again that the broadening γ of the energy levels arises from bulk scattering processes, e.g., electron-impurity or electron-electron scattering, and does *not* include any effects of the surface. The surface potential is in fact directly incorporated as a boundary condition on the eigenfunctions, as will be shown presently. Initially we will assume that the scattering rate is constant; however, later we will comment on an energy-dependent γ.

The real part of the conductivity in (3.5) now becomes

$$\text{Re}\sigma_{\mu\mu}(\omega)=\frac{e^2}{(m^*)^2\Omega}\sum_{\alpha\neq\beta}\frac{f_\alpha-f_\beta}{\varepsilon_\beta-\varepsilon_\alpha}|\langle\alpha|\hat{p}_\mu|\beta\rangle|^2\times\frac{\gamma}{(\varepsilon_{\alpha\beta}-\omega)^2+\gamma^2}\ . \qquad (3.6)$$

The diamagnetic term in this case (for discrete energy levels with no dispersion) is exactly canceled by a piece from the paramagnetic term. This can be shown by invoking the f-sum rule[18] which states that independent of the choice of α,

$$\frac{2}{m^*}\sum_\beta\frac{|p^\mu_{\alpha\beta}|^2}{\varepsilon_{\alpha\beta}}=-1\ . \qquad (3.7)$$

The matrix elements of the momentum operator can next be evaluated between states $|\alpha\rangle\equiv|\mathbf{k},n\rangle$ and $|\beta\rangle\equiv|\mathbf{k}',n'\rangle$. We obtain for the momentum operators along the x and z directions, respectively,

$$\langle\alpha|\hat{p}_x|\beta\rangle=(-i\hbar)k_x\delta_{\mathbf{k},\mathbf{k}'}\delta_{n,n'}$$

and

$$\langle\alpha|\hat{p}_z|\beta\rangle=(-i\hbar)\frac{2}{d}\frac{nn'}{n^2-n'^2}[1-(-1)^{n+n'}]\delta_{\mathbf{k},\mathbf{k}'}\ . \qquad (3.8)$$

The difference in the momentum matrix elements arises primarily from the loss of translational invariance along the z direction because of the presence of surfaces. If we restrict ourselves to zero temperature, the dc conductivity along the film is, using (3.8),

$$\sigma_{xx}(\omega\rightarrow 0)=n(d)e^2\tau/m^*\ , \qquad (3.9)$$

where $\tau=1/\gamma$. The in-plane conductivity, therefore, essentially follows the size dependence of the density as given in (2.5). However the intersubband coupling given in (3.8) leads to a very different out-of-plane conductivity which is given by

$$\frac{\sigma_{zz}(\omega\rightarrow 0)}{\sigma_0}=\frac{n(d)}{n_0}-\frac{48}{\pi^2\Gamma^2 n_c^3}\text{Re}\sum_{n=1}^{n_c}n^2(n_c^2-n^2)\times\begin{cases}-v\tan v & \text{if } m \text{ is even}\\ v\cot v & \text{if } m \text{ is odd}\end{cases} \qquad (3.10)$$

where $\Gamma=\gamma/\varepsilon_0$ is the level broadening in units of the zero-point energy, $\sigma_0=n_0e^2\tau/m^*$ is the Drude conductivity, and $v=(\pi n/2)(1-i\Gamma/n^2)^{1/2}$. Equation (3.10) is obtained by first performing the integrals over $\mathbf{k}$ and $\mathbf{k}'$, which leaves a double summation over n and n'. The summation over n' is evaluated exactly[17] by exploiting the fact that the function $\cot(\pi z)$ has poles at $z=n$ for $n=0,\pm1,\pm2,\ldots$. The second term in (3.10), denoted by Δ, is the anisotropy between the in-plane and out-of-plane responses and is shown in Fig. 3.

We are interested in the conductivity for large d, or equivalently for $n_c\gg 1$, in which case the summation over n in (3.10) is approximated by an integral using the Euler-Maclaurin summation formula.[19] The end-point corrections for even n are zero and those for odd n can be neglected when $d\gg a_0$. We next study the behavior of Δ as the Drude limit is approached, that is, in the limit when for a fixed thickness of the film, the broadening of the energy levels increases to become comparable to the spacing *between* levels. Alternatively, the width of energy levels can be fixed but d increased, which has the equivalent effect of reducing the level spacing. For $x\equiv l/d\ll 1$, an approximate evaluation of the real part of the summation in (3.10) yields (neglecting corrections to the integral approximation involving Bernoulli numbers)[20]

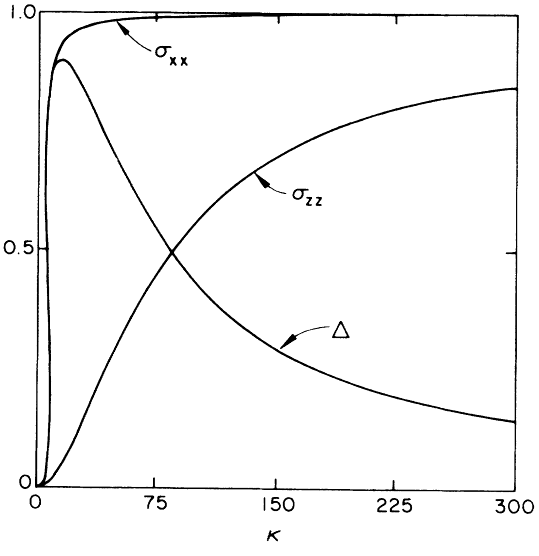

FIG. 3. Anisotropy between the in-plane σ_{xx} and out-of-plane σ_{zz} conductivity in units of the Drude conductivity as a function of κ. The difference between the two conductivity components is denoted by Δ. The dominant behavior is $\sim 1/d$, but there is also a weak essential singularity in the small parameter l/d (see text).

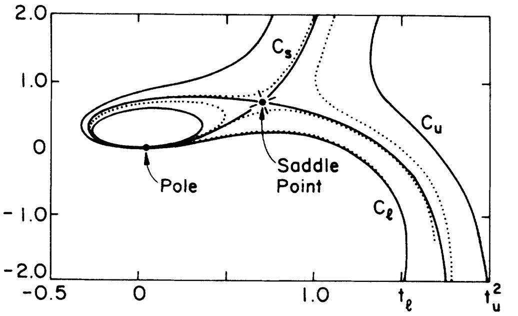

FIG. 4. Paths of constant $\text{Im}\rho(t)$ in the complex t plane for $\beta=2/k_Fl=1$. The integration contour begins at the lower end point along a path of constant phase in a direction of steepest descent, denoted by C_l. It switches at the pole of the function ρ to a path with a different value of the phase but still along a path of steepest descent C_s. It the passes through the saddle point of ρ out to infinity and then approaches the upper end point along C_u. Note that the presence of the pole allows paths with different values of the phase to intersect. The intergration contour shown is the unique contour such that one always moves in the direction of steepest descent along sections having a constant value of the phase of ρ.

$$\Delta=6\sqrt{2}x\beta\int_0^1 dy\, y^2(1-y^2) \times\left[\frac{\beta}{t}+2e^{-2\sqrt{2}/xt} \times\left[t\sin(xt)+\frac{\beta}{t}\cos(xt)\right]\right], \tag{3.11}$$

where $t=[y^2+(y^4+\beta^2)^{1/2}]^{1/2}$ and $\beta=\hbar/\varepsilon_F\tau=2/k_Fl$. The first term within the outer large square brackets is analytic and is the dominant contribution to Δ. But there is also nonanalytic structure in the second term in (3.11) which we now examine. The analysis is facilitated by choosing t as the variable of intergration; then the nonanalytic part of the second term Δ_{na} is

$$\Delta_{\text{na}}=12\sqrt{2}x\beta\,\text{Im}\int_{\sqrt{\beta}}^{t_u} dt\, g(t)e^{2\sqrt{2}\rho(t)/x}, \tag{3.12}$$

where

$$t_u=[1+(1+\beta^2)^{1/2}]^{1/2}\sim\sqrt{2}$$

and

$$g(t)=(-\tfrac{1}{4}\sqrt{2}t^5)(t^4+\beta^2)(t^4-\beta^2)^{1/2}(t^4-\beta^2-2t^2).$$

The function $\rho(t)$ given by $\rho(t)=-1/t+it/\beta$ has saddle points at $t=\pm\sqrt{i\beta}$ and the integration can be performed by deforming the original contour in the complex t plane along paths of constant $\text{Im}\rho(t)$ as shown in Fig. 4. A detailed analysis of the integration along these paths by the method of steepest descent is presented in Appendix A. An interesting feature of this saddle-point intergration is the presence of a pole of the function ρ which transforms paths of steepest descent into steepest-ascent paths. There is thus a *unique* contour from the lower to the upper end point in the complex t plane such that one always moves along paths of steepest descent. The integral is dominated by the local contribution from the end points and the saddle point. Explicit expressions for this are provided in Appendix A, and it is seen there that the most important piece arises from the path through the upper end point. The observation that the dominant contribution is from the upper end point is perfectly plausible since this implies that only energies near the Fermi level are important in the dc conductivity. This also suggests that if τ is energy dependent, only its value at ε_F is required.

The final result is

$$\sigma_{zz}=\sigma_0\left[\frac{n(d)}{n_0}-\frac{A}{d}-Bx^2\frac{1}{k_Fd}e^{-\alpha/x}\sin(\alpha k_Fd/2)\right], \tag{3.13}$$

where $B=6(1+\beta^2)^{1/2}t_u^3/[\sqrt{2}(t_u^2+\beta^2)]$, $\alpha=2\sqrt{2}t_u$, and t_u is the position of the upper end point defined previously. From a mathematical standpoint the term evaluated by saddle-point methods has an essential singularity[21] in the small-parameter x; however, from an experimental point of view the magnitude of this term is probably too small to be observable. If the Drude limit is approached by keeping l fixed and increasing d, (3.13) shows that the correction term vanishes exponentially, an expected result. On the other hand, if d is fixed and the amount of scattering is increased then there is indeed an essential singularity in l/d. It is rather surprising that such a nonperturbative result should have emerged from this simple model of a particle in a box. It could be argued that in the limit of very small l the Drude theory, which is based on independent scattering events, should break down. This is certainly true. However, our claim here is that even after we have accounted for weak-localization effects, etc., there is an additional contribution from quantum size effects that has a nonanalytic structure. The nonanalytic behavior exists only in the out-of-plane conductivity and arises because of the possibility of intersubband scattering. In this sense it is a purely quantum-mechanical result.

IV. EFFECTS OF IMPURITY POTENTIALS AND SURFACE ROUGHNESS

In Sec. III, the effect of scattering within the film was included via a phenomenological relaxation time τ (taken as constant). In this section we treat by first principles the case of impurity scattering within the film, which is the dominant mechanism at low temperatures. To include the effect of impurity potentials, the Hamiltonian studied in Sec. III is augmented by an additional term given by

$$V_I(\mathbf{r})=\sum_{j=1}^{N_i} U(\mathbf{r}-\mathbf{R}_j) \tag{4.1}$$

which can lead to transitions between the unperturbed eigenstates. Within the Born approximation the transition rate W is

$$\langle \mathbf{k}'n'|W_I|\mathbf{k}n\rangle=\frac{2\pi}{\hbar}\left[\frac{U_0}{\Omega}\right]^2 |F_{nn'}(\mathbf{q})|^2\delta(\varepsilon_{k'n'}-\varepsilon_{kn}) , \tag{4.2}$$

where

$$F_{nn'}(\mathbf{q})=\sum_{j=1}^{N_i} 2\sin\left[\frac{n\pi z_j}{d}\right]\sin\left[\frac{n'\pi z_j}{d}\right]e^{-i\mathbf{q}\cdot\boldsymbol{\rho}_j} \tag{4.3}$$

and for simplicity the impurity scattering potential is described by a δ function of strength U_0. The scattering rate for an electron in the state $|\mathbf{k}n\rangle$ is

$$\begin{aligned}\frac{1}{\tau_{kn}^I}&=\sum_{(\mathbf{k}',n')}\overline{\langle \mathbf{k}'n'|W|\mathbf{k}n\rangle}\\ &=\frac{1}{\tau_0(\varepsilon_F)}\frac{m+\frac{1}{2}}{\kappa} ,\end{aligned} \tag{4.4}$$

where the overbar denotes an average over disorder, furthermore, $1/\tau_0=2\pi U_0^2 n_i g(\varepsilon_F)$ is the scattering rate in a bulk system with an impurity density n_i, and $m=\mathrm{Int}[(\varepsilon_{kn}/\varepsilon_0)^{1/2}]$. In (4.4), interference between scattering events into different channels, i.e., between the processes $[(\mathbf{k},n)\rightarrow(\mathbf{k}',n')$ and $(\mathbf{k},n)\rightarrow(\mathbf{k}'',n'')]$, where the two final states are different, has been neglected. It is known experimentally that impurities typically migrate to the surfaces and may form clusters; however, in this analysis we have taken them to be uniformly distributed in the film.

The in-plane conductivity is obtained from the Boltzmann equation as

$$\sigma_{xx}^I=2e^2\frac{1}{\Omega}\sum_{(k,n)} v_x^2\tau_{kn}\delta(\varepsilon_F-\varepsilon_{kn}) , \tag{4.5}$$

where v_x is the velocity along $\hat{x}$. Note that the $\cos\theta$ piece in the usual $1-\cos\theta$ term in the conductivity that weights backscattering processes averages to zero for δ-function potentials. The integral over k and the sum over the discrete index n are both straightforward and reduce to

$$\frac{\sigma_{xx}^I}{\sigma_0}=\frac{n(d)\tau(d)}{n_0\tau_0} , \tag{4.6}$$

where $\sigma_0=n_0e^2\tau_0/m^*$ is the Drude conductivity, $n(d)$ is defined in (2.5), and $\tau(d)$ in (4.4) with $m=n_c$. This result has also been obtained by Sandomirskiĭ.[11] The behavior of σ_{xx} as a function of d is shown in Fig. 5(a) and in comparison to Fig. 2 it is seen that the additional size dependence in the scattering rate produces much larger oscillations in the response function. In previous work[22] it has been asserted that the oscillations in the density of states as a function of film thickness is the primary source of oscillations in the transport coefficients. However, as can be seen from this simple exercise of impurity scattering (summarized in Fig. 5), the dominant source of oscillations is in the matrix element of the transition probability and not the density of states.

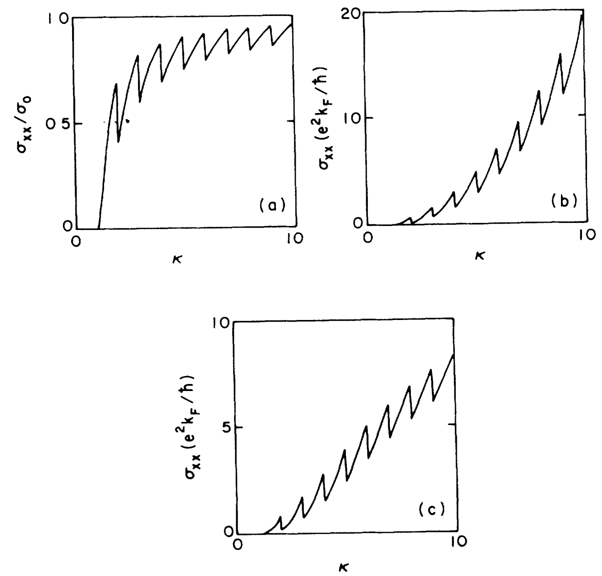

FIG. 5. Oscillations in the in-plane conductivity as a function of $\kappa=k_Fd/\pi$. (a) Effect of impurity scattering from Eq. (4.6). (b) Effect of surface roughness from Eq. (4.12). The rms variation in the thickness $\delta d=2.5$ Å and $k_Fa_0=1$. (c) Effect of both impurity and roughness from Eq. (4.13). The bulk mean free path from impurities $l_0=500$ Å, $\delta d=2.5$ Å, and $k_Fa_0=1$. Note the crossover from the impurity-dominated to the surface-dominated regime. Finite-temperature effects ($k_BT\sim\delta E$, the typical energy-level spacing) and large-scale roughness tend to smooth out the oscillations.

The next level of complexity is to introduce surface roughness. In this context the inelastic length scale l_i, over which an electron loses phase coherence, plays an important role. Typically, electron-electron interactions or electron-phonon interactions are both sources of inelastic scattering. Grain-boundary scattering can also contribute to the scrambling of the phase of the electron wave function, in which case l_i is of the order of the size of a grain. The problem of surface roughness is handled here in two parts. (i) The effect of roughness existing *on the scale of the mean free path* is included by evaluating the conductivity of the ith segment having small variations in the thickness d_i about an average value. A quantum-mechanical treatment of the problem is required in this regime since the electron motion is coherent over length scales of order the size of a grain, or over length scales of order the inelastic mean free path. (ii) Large-scale fluctuations in the film thickness are subsequently treated by recognizing that as the electron travels from one segment of length larger than the mean free path to another, it loses phase coherence and the propagation of the electron on this length scale can therefore be described semiclassically. The segments are treated as independent units and the total resistance of the film is then a sum of the resistances of the individual segments labeled by i, of average thickness d_i and length l_i, as shown in Fig. 6. Large-scale fluctuations in a film can arise because of the formation of grains or crystallites of different sizes. Such a separation of length scales was first proposed by Namba[23] in the context of size effects in rough films. However, in that treatment the surface roughness at short wavelengths was included within a classical theory. An alternative approach is to handle these two scales on the same footing by looking at the behavior of the two different Fourier components in the surface profile.

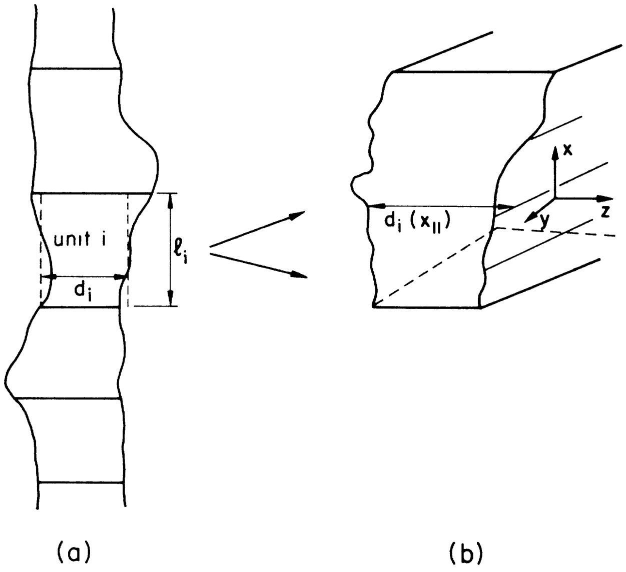

FIG. 6. (a) Large-scale fluctuations in the film thickness. The film is divided into segments i, of length l_i and thickness d_i. The electron motion between segments is treated classically. (b) Expanded view of the ith segment showing the presence of small-scale fluctuations in the thickness. Since the electron wave function is coherent over this region, surface roughness is included quantum mechanically as a boundary condition on the Hamiltonian.

A. Small-scale roughness

The description of roughness on small scales requires solving the Hamiltonian given in Sec. III with rather complicated boundary conditions such as arise naturally for a rough surface. As shown in Fig. 6(b), the confining potential V is a function of z only; however, it depends on a thickness scale $d(\boldsymbol{\rho})$ defined at each point $\boldsymbol{\rho}$ on the surface of the film. The full Hamiltonian we wish to solve is

$$H=\frac{p_z^2}{2m^*}+V(z)\ , \tag{4.7}$$

i.e., we want to evaluate the eigenstates and eigenvalues $H|\Psi\rangle=E|\Psi\rangle$ given that the problem of a film with a perfect surface $H_0|\Psi_0\rangle=E_0|\Psi_0\rangle$ can be solved. The Hamiltonian that can be solved is given by $H_0=p_z^2/(2m^*)+V_0$ where V_0 is the confining potential corresponding to a constant thickness $d(\boldsymbol{\rho})=d_0$ and was discussed in Sec. II. The average thickness d_0 is chosen by requiring that the volume of the original film with rough surfaces remain unchanged after it is transformed to one with flat surfaces. Following Tešanović *et al.*[16] the eigenstates for the full problem can be obtained by a unitary transformation as $|\Psi\rangle=U|\Psi_0\rangle$ where U is a dilation operator that stretches or compresses the eigenfunctions of H_0 by amounts that are sufficient to obtain the eigenstates of H that fit in a box with the rough surface. It may be helpful to think of the rough surface as a corrugated potential, which under the action of the dilation operator is transformed to yield a flat surface. The required unitary operator $U=e^{S_0}$ is given by

$$S_0=\frac{i}{2\hbar}\eta(\boldsymbol{\rho})(zp_z+p_zz)\ , \tag{4.8}$$

where $\eta=\delta d(\boldsymbol{\rho})/d_0$ is small provided the film thickness does not deviate appreciably from the average value. In addition a nonunitary transformation is found to relate the Hamiltonian of the smooth and the rough problems by $H=e^{2\eta}UH_0U^{-1}$. To lowest order in η the perturbation is

$$V_S(\mathbf{r})=\frac{i}{2\hbar}\eta[(zp_z+p_zz)H_0-\text{c.c.}]+2\eta H_0\ . \tag{4.9}$$

Following the lines of our previous analysis for the impurity case, we find that the surface roughness scatters electrons between different subbands. The corresponding scattering rate from $\mathbf{k}$ to $\mathbf{k}'$ ($\mathbf{k}'-\mathbf{k}=\mathbf{q}$) obtained by a golden-rule calculation is then

$$\frac{1}{\tau_{kn}^S}=\langle\eta(\mathbf{q})\eta(-\mathbf{q})\rangle(2\varepsilon_0)^2\frac{Am^*}{\hbar^2}S(m)n^2\ , \tag{4.10}$$

where m and $S(m)$ are defined following Eqs. (4.4) and (2.5), respectively. The angular brackets in (4.10) indicate an average over all surface profiles. Using the central-limit theorem the spatial correlation function between two points $\boldsymbol{\rho}$ and $\boldsymbol{\rho}'$ on the surface of the film can be described in terms of a surface correlation length ξ as

$$\langle \eta(\boldsymbol{\rho})\eta(\boldsymbol{\rho}')\rangle \sim \frac{A}{\sqrt{2\pi}\xi^2} e^{-|\rho-\rho'|^2/2\xi^2} \langle \eta(\boldsymbol{\rho})\eta(\boldsymbol{\rho}')\rangle \ . \tag{4.11}$$

For simplicity we assume here that only short-range correlations are present and replace the Gaussian by a δ function. We next obtain an average over all surface profiles with the assumption that the film thickness is distributed uniformly with a root-mean-square deviation δd; then $\langle \eta(\mathbf{q})\eta(-\mathbf{q})\rangle \sim (\delta d/d_0)^2$. The conductivity in the presence of a rough surface alone is given by

$$\sigma_{xx}^{S} = \frac{1}{2}\frac{e^2 k_F}{\hbar}\left[\frac{d_0}{\delta d}\right]^2 \frac{f(n_c)}{s(n_c)}\left[1-\frac{6n_c}{f(n_c)(\pi\kappa)^2}\right] , \tag{4.12}$$

where $f(n_c)=[\sum_{n=1}^{n_c}(1/n^2)]/(\pi^2/6)$ and $s(n_c)=3S(n_c)/n_c^3$, are both of order 1. The conductivity attributable to surface roughness rises as d^2, and this behavior is displayed in Fig. 5(b). This dependence on d arises primarily from the cost in kinetic energy to change the curvature of the electron wave function so that after the coordinate transformation it fits in a box with smooth surfaces. The oscillatory behavior of the conductivity is important for sufficiently thin films with $\kappa=k_F d/\pi \approx 20-30$.

In the presence of both impurity and roughness the total scattering rate is given by the sum of (4.4) and (4.10) and the conductivity in the plane is

$$\sigma_{xx}^{I+S} = \frac{e^2 k_F}{\hbar\pi^2}\frac{1}{\kappa}\sum_{n=1}^{n_c}\frac{1-n^2/\kappa^2}{\left[\dfrac{2n_c+1}{k_F l_0 \kappa}+\left[\dfrac{\delta d}{d_0}\right]^2\dfrac{s(n_c)n^2}{3\kappa}\right]} , \tag{4.13}$$

where $l_0=v_F\tau_0$ is the impurity mean free path. This result is plotted in Fig. 5(c) and it can be seen that the conductivity crosses over from the surface-dominated regime to the regime where impurity scattering is important at a point where the thickness of the film is of the order of the bulk mean free path. More precisely, from (4.13) the crossover occurs when $d \sim [\pi(\delta d)^2 l_0/6]^{1/3}$. As noted above, the averaging over impurities in the film and averaging over surface roughness are independent processes and, therefore, the *total rate* is additive. However, an important distinction between the impurity and surface scattering rates is that the latter depends explicitly on the subband index n and, as a consequence, the total resistivity is not given by a sum of the impurity and surface resistivities; i.e., Mattheissen's rule is not obeyed.

We next address a somewhat subtle point. Our approach in this section has been to describe surface roughness as a boundary condition on the Hamiltonian $H_0=p^2/2m^*$, which is then shown to be equivalent to a problem with different (usually simpler) boundary conditions on H_0 plus additional terms in the Hamiltonian introduced from the transformation. These additional terms are treated as a scattering potential for the electrons and contribute to resistance in the film. On the other hand, H_0 with the original boundary conditions can be diagonalized in principle, and when this is done there ought to be no resistance in a Hamiltonian system. The resolution of this apparent paradox is that in the presence of any potential, for example, as might arise from impurities or surfaces in this problem, the current operator J no longer commutes with the Hamiltonian. In general, J possesses off-diagonal elements that can be interpreted *within linear-response theory* as current arising from scattered electrons. However, since the electron retains phase coherence in elastic collisions the system is still completely reversible. To produce dissipation, the system must then be coupled to an external dissipative bath, albeit weakly. This destroys the phase coherence of the electron on length scales of the order of the inelastic length. The electron samples different configurations of impurities and surface profiles and it is this averaging effect that leads to resistance. If the total rate is given by the sum of an elastic rate and an inelastic rate as $\tau^{-1}=\tau_{\text{el}}^{-1}+\tau_{\text{inel}}^{-1}$, such that $\tau_{\text{inel}}^{-1} \ll \tau_{\text{el}}^{-1}$, then, even though the dynamics is determined by the elastic rate, it is the presence of a small inelastic rate that is essential to the introduction of dissipation. It is within this interpretation that we assign resistance to surface or impurity potentials.

B. Large-scale fluctuations

The effect of fluctuations in the thickness of the film on a scale larger than the mean free path is included by breaking up the film into units of length l_i and thickness d_i. The resistance of this unit is $R_i=\rho(d_i)l_i/wd_i$. If the total resistance is defined as $R=\bar{\rho}L/w\bar{d}$, then

$$\bar{\rho}_{xx} = \sum_{i=1}^{N}\frac{\rho_{xx}(d_i)l_i\bar{d}}{Ld_i} = \bar{d}\int dz \frac{P_1(z)\rho_{xx}(z)}{z} \ . \tag{4.14}$$

In obtaining the above expression it has been assumed that the probability P of finding a segment (l_i,d_i) can be factored into disjoint probabilities in the two variables $P_1(d)$ and $P_2(l)$, since l_i and d_i are treated as independent random variables. The probability distribution of the thickness of a film $P_1(d)$ is taken to be a Gaussian with a mean $\bar{d}$ and a rms deviation δD. The quantity $\rho_{xx}(d_i)$ is given in (4.13).

In Fig. 7 data on the size dependence of platinum films taken by Hoffmann and Fischer[12] are displayed. As can be seen the fit to the data according to the classical size-effect theory does rather poorly at small thicknesses, of order 100 Å. Much better agreement is obtained by incorporating quantum size effects. Several points emerge from the comparison of the experimental data with theory in (4.13). The films possess small-scale roughness on the order of 5 Å. In addition, the resistivity is sensitive to variations in d. This can be seen by comparing the resistivity of a specular film with $\delta d=0$ and a rough film with $\delta d=5$ Å. Within the classical size-effect theory the resistivity of a specular film is independent of the thick-

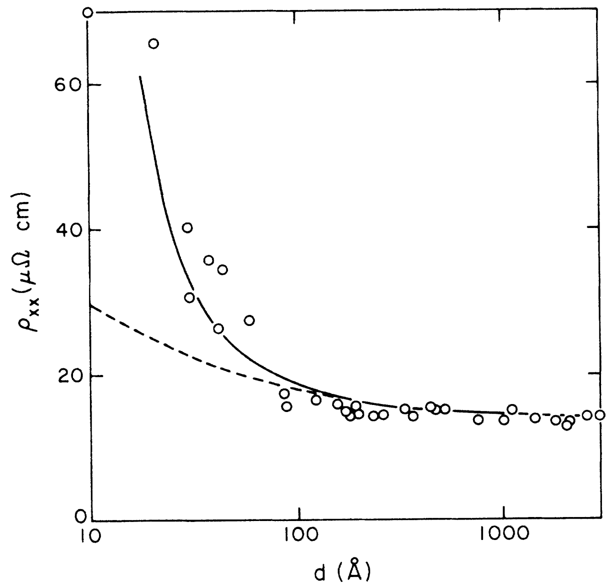

FIG. 7. Comparison with data on size dependence of resistivity of Pt films (Ref. 12). The dotted line is a fit according to the classical size-effect theories. The solid line is a fit according to (4.13) with $\delta d \sim 5$ Å. A value of $k_F = 0.53$ Å^{-1} is assumed in the above fits and is deduced from additional data in Ref. 12 showing oscillations in the conductivity.

ness of the film; however, quantum mechanically the size dependence in the states and in the density of states leads to a rise in the resistivity above the Drude value as the thickness is reduced, even in a specular film. Oscillations in the conductivity as a function of thickness have been presented in Ref. 12 and from these data a value of $k_F = 0.53$ Å^{-1} is deduced. The amplitude of the oscillations is, however, much smaller than that predicted by our theory including only atomic-scale roughness [Fig. 5(c)]. If large-scale fluctuations δD are also included as discussed above, these lead to a reduction in the amplitude of the oscillations while leaving the period unchanged.

V. THERMOPOWER

The thermopower is defined as the electrostatic potential developed across a system in a unit thermal gradient, when no current is allowed to flow. It is given by[24]

$$Q_{\mu\mu} = \frac{-\pi^2 k_B^2 T}{3|e|\varepsilon_F} \left[\varepsilon \frac{\partial \ln \sigma_{\mu\mu}(\varepsilon)}{\partial \varepsilon} \right]_{\varepsilon=\varepsilon_F} \tag{5.1}$$

and is related to the variation of a function $\sigma(\varepsilon)$ which, when evaluated at the Fermi surface, is the physically measurable conductivity. With respect to measurements on size dependence in films thermoelectric effects can be an important source of information. As seen in Figs. 2 and 5, the in-plane conductivity shows cusps or discontinuities when $k_F d/\pi$ is an integer. These singularities should be enhanced in the thermopower as suggested by (5.1).

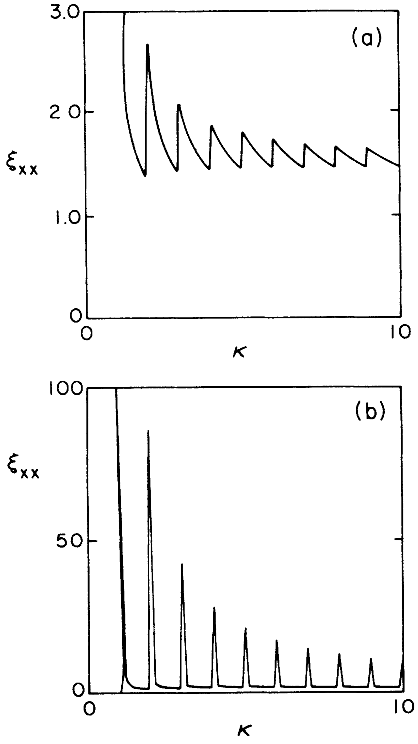

FIG. 8. Thermopower in units of $-\pi^2 k_B^2 T/3|e|\varepsilon_F$ as a function of $\kappa = k_F d/\pi$. (a) Consequence of oscillations in the density of states. The cusps in the conductivity (Fig. 2) get enhanced in the thermopower and appear as discontinuities. (b) Behavior in the presence of impurity scattering. In this case discontinuities in the conductivity lead to singularities in the thermopower.

For the simple case discussed in (3.9), where the size dependence arises solely from the density of states, the dimensionless thermopower given by the term in large parentheses in (5.1) is

$$\xi_{xx} = \frac{n_c \kappa^2}{n_c \kappa^2 - S(n_c)} \; . \tag{5.2}$$

This is shown in Fig. 8(a), and note that while the amplitude of oscillation between $\kappa = 4$ and 5 in the conductivity is only $\sim 5\%$, the thermopower varies by $\sim 20\%$. If we next consider the effect of impurity scattering on the thermopower, we find that there is a spectacular enhancement when κ approaches an integer. The height of these peaks decreases inversely with κ [see Fig. 8(b)]. It can be seen that the large variations in the thermopower require the thickness to be rather sensitively tuned. Fabrication of films with small increments in the thickness ~ 0.6 Å has been demonstrated in experiments[25] on tin films.

VI. DISCUSSION AND CONCLUSIONS

We have investigated quantum size effects on the transport properties of thin metallic films. Other systems that may show such effects are quasi-two-dimensional semiconductor systems, e.g., MOSFET's and quantum wells and semimetallic films. The problem with semiconductor systems from the standpoint of the present picture is that typical doping densities and temperatures are so low that only the lowest subband is occupied and intersubband scattering is not observed. These systems, however, have an advantage over metallic systems, in that the wave vector k_F can be varied by tuning the gate voltage for a fixed thickness of the sample. Semimetallic systems also are very favorable since they have small values of k_F ($\sim 0.01 a_0^{-1}$) and this implies that typical d values for observing quantum size effects[14] are $d \sim 10^3$ Å. A simple theory for these semimetallic systems has been developed[11] which includes the effects of both electron and hole bands. However, for a more complete description, roughness at the surfaces must also be included, as has been discussed here for metallic films. It would also be interesting to examine quasi-one-dimensional channels in which the $\varepsilon^{-1/2}$ singularity in the density of states leads to more structure in the transport coefficients.

The small sizes of films and quantum wells also provide an opportunity to study the interplay between size effects and quantum-interference effects. For instance, in the average over disorder or over different thickness profiles studied in Sec. IV, it was assumed that the resistance can be written as an average of resistances of samples with slightly different impurity configurations. Using the central-limit theorem it can be shown that the relative variance of the conductance g is given by $\mathrm{var}(g)/\langle g\rangle^2 \approx L^{-d}$ where $\mathrm{var}(g) = (g - \langle g\rangle)^2$ and d is the dimensionality. Thus, as the thermodynamic limit is approached, the relative variance goes to zero, i.e., g is a self-averaging quantity. This is justified, for example, in a 1-μm^2 sample of thickness ~ 100 Å which contains $\sim 10^3$ impurities at a density of 1 part per million. However, the naive assumption of the self-averaging nature of the conductance can break down as the thickness becomes smaller and the inelastic length is much longer than the sample dimensions. The conductance can then become sensitive to the precise microscopic configurations of impurities which can produce large fluctuations in the conductance such that the $\mathrm{var}(g)$ is of order unity in all dimensions less than 4.[4] Since by Ohm's law $\langle g\rangle \approx \sigma L^{d-2}$, this implies that the relative variance goes as $L^{2(2-d)}$. Therefore in quasi-two- or lower dimensions the conductance no longer self-averages.

Here we have shown that the approach of the transverse conductivity to the Drude limit is predominantly $\propto l/d$, but also possesses a weak essential singularity in l/d where l/d is the ratio of the mean free path to the film thickness. The nonanalytic structure of the correction term is a purely quantum-mechanical result and arises from the discreteness of the energy-level spectrum. We find that in addition to the size dependence of the density of states, the matrix elements are also a strong function of the thickness of the film; both lead to oscillations in the transport coefficients. In the quantum regime where the electron wave function is coherent on length scales of the thickness of the film (i.e., $d < l$), the surface profile must be included as a boundary condition on the Hamiltonian. This is in contrast to the classical size-effect theories that provide a phenomenological treatment of surface scattering. The method described can be extended to include effects of finite temperature of the film and the effects of correlation in the surface profile. It would also be interesting to consider the interplay between weak-localization effects or conductance fluctuations (that arise because of quantum-interference effects) and quantum size effects.

ACKNOWLEDGMENTS

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APPENDIX A: EVALUATION OF INTEGRAL BY METHOD OF STEEPEST DESCENT

We evaluate the contribution of the nonanalytic term in the transverse conductivity given in (3.12). The integral in (3.12) is defined as

$$I(x) = \int_{\sqrt{\beta}}^{t_u} dt\, g(t) e^{x\rho(t)} , \qquad \text{(A1)}$$

where $g(t)$ is given following (3.12), $t_u = [1 + (1+\beta^2)^{1/2}]^{1/2}$, $x = 2\sqrt{2}/x$, and $\beta = 2/k_F l \ll 1$. Consider I for $x \gg 1$. The function $\rho(t) = -\beta/t + it$ has a saddle point at $t = \pm\sqrt{i\beta}$. We deform the integration contour in the complex t plane along paths on which $\mathrm{Im}\rho(t)$ is constant to eliminate rapid oscillations of the integrand when x is large. These paths are shown in Fig. 4. A contour plot of constant $e^{x\rho(t)}$ is identical with curves of constant real part of $\rho(t)$ [which are orthogonal to the paths on which $\mathrm{Im}\rho(t)$ is constant]. Note that since $\rho(t)$ has a pole at $t=0$, it becomes possible for curves with different values of the phase to intersect. Given the form of $\rho(t)$, it is easy to see that for t near zero the integral will converge only along a path such that $\mathrm{Re}t > 0$, given that x is large and positive. Thus if we move along C_l, a path of constant phase through the lower end point of integration, in a direction such that $\mathrm{Re}\rho$ is decreasing as shown, this path encounters the singularity of $\rho(t)$ at $t=0$. Beyond this the path around $t \sim 0$ must be chosen such that $\mathrm{Re}t > 0$. It is therefore evident that the only possible path is through the saddle point in the first quadrant along C_s. This is a path of steepest descent, as will be demonstrated presently, with a value of the phase distinct from that along C_l. The contour is completed by approaching the upper end point along C_u, a path of constant phase in a direction such that $\mathrm{Re}\rho$ is increasing.

The contribution to the integral along C_l, C_s, and C_u is dominated by the behavior near the end points and the saddle point. We perform a local analysis near these points of interest. A linearized solution of $\mathrm{Im}\rho = t_u$ yields $v = -\delta t_u^2/\beta$, where $t = u + iv$ and $\delta = u - t_u$ is the deviation in $\mathrm{Re}(t)$ from the end point denoted by t_u. Further, the real part of $\rho(t)$ along this path is given by

$\mathrm{Re}\rho=-\beta/t_u+(\beta/t_u^2+t_u^2/\beta)\delta+\cdots$, which establishes the sense in which the path of constant phase must be traversed.

At the saddle point $t=\sqrt{i\beta}$, a local analysis of $\mathrm{Im}\rho=\sqrt{2\beta}$ yields $\delta^2-\eta^2+2\delta\eta=0$ where $\delta=u-\sqrt{\beta/2}$ and $\eta=v-\sqrt{\beta/2}$. As expected, the equation of the path of constant phase is second order in the deviations around the saddle point, unlike the path through the end points. In addition,

$$\mathrm{Re}\rho=-\sqrt{\beta/2}[2+(1/\beta)(\eta^2-\delta^2+2\delta\eta)]$$

indicates that $\delta=\eta(-1+\sqrt{2})$ is the path of steepest descent. The other path $\delta=-\eta(1+\sqrt{2})$ is a path of steepest ascent. Notice how the path of steepest descent through the saddle point becomes a path of steepest ascent after passing through $t=0$ in Fig. 4. This is only possible because of the singularity at $t=0$.

Knowing the behavior of the paths locally, we can next evaluate the integral along C_l, C_s, and C_u. It is found that the dominant contribution arises from the region around the upper end point $t_u=[1+(1+\beta^2)^{1/2}]^{1/2}$. The integral along C_u is evaluated along the path $v=-t_u^2\delta/\beta$ and this yields

$$\int_{C_u} dt\, g(t)e^{x\rho(t)}=(-1+i)e^{-xt_u(1-i)}\int_0^{\varepsilon} dv\, g(v)e^{-2xv}\,. \tag{A2}$$

The behavior of $g(t)$ locally around the lower end point and along C_u is found to be

$$g(v)=-pv(1-t_u^2)(t_u^4+\beta^2)/t_u^2$$

where $p=(\beta/t_u^2-i)/t_u$. Since the maximum of the integral in (A2) occurs at $v=0$, for large x it decreases very rapidly, therefore an exponentially small error is made by extending the upper limit to infinity. The integral over v can easily be performed in terms of Γ functions and gives

$$\int_{C_u}=\left[1-\frac{\beta^2}{t_u^4}+2i\frac{\beta}{t_u^2}\right]\frac{t_u^5(1-t_u^2)}{t_u^4+\beta^2}\frac{1}{x^2}e^{-x(\beta/t_u-it_u)}\,. \tag{A3}$$

The contribution from the saddle point is smaller than (A3) since the exponential term is replaced by $\exp(-x\sqrt{\beta})$; therefore for $\beta\ll 1$ this term can be neglected. Using the expression in (A3) we find the conductivity given by (3.13).

APPENDIX B: INCLUSION OF INELASTIC SCATTERING

We discuss some points with regard to the inclusion of inelastic scattering in a way that the equation of continuity is satisifed.

(i) In the problem of transport in a film considered here, we have assumed that the fields are uniform in space and only time-dependent perturbations have been considered. In the event that spatial variations are important, the analysis given in Sec. III would need to be modified. In particular, it can be shown[26] that if the effects of scattering are treated within a relaxation-time approximation, the equation of continuity is violated. To rectify this, it then becomes necessary to introduce a shift in the chemical potential.

(ii) Within the context of only time-dependent fields, the density matrix must satisfy $\mathrm{Tr}\rho=1$. Since the trace of the unperturbed density operator is unity, this implies that within linear-response theory the trace of perturbed density operator $\delta\rho$ must be zero. This condition is trivially satisfied by the problem at hand because the diagonal matrix element of the current $\langle\alpha|J|\alpha\rangle$ which is related to trace of $\delta\rho$ is zero. It is therefore not necessary to introduce any shift in chemical potential for this case.

(iii) However, notice that we have introduced a quasiequilibrium density operator

$$\rho_{\mathrm{qe}}=(\exp\{\beta[H_0+H_1(t)-\mu_0]+1\})$$

that is different from the equilibrium density operator ρ_0 in that it is governed by the total Hamiltonian. What are the consequences of using ρ_{qe} or ρ_0 as the state to which the system is assumed to relax to, in the presence of some damping? This has been discussed in detail by Trivedi and Browne.[27] Here we only quote the results: when the system relaxes to ρ_0 the real part of the conductivity is given by

$$\mathrm{Re}\sigma_{\mu\mu}(\omega)=\frac{e^2}{\Omega(m^*)^2}\sum_{\alpha\neq\beta}\frac{f_\alpha-f_\beta}{\varepsilon_{\beta\alpha}}|p_{\alpha\beta}^{\mu}|^2\frac{\gamma}{(\varepsilon_{\alpha\beta}-\omega)^2+\gamma^2}\times\left[\frac{2(\varepsilon_{\alpha\beta})^2}{(\varepsilon_{\alpha\beta}+\omega)^2+\gamma^2}\right]. \tag{B1}$$

On the other hand, if the system relaxes to ρ_{qe}, the conductivity is given by (3.6), which differs from that in (B1) by the absence of the term in large parentheses. Thus, to obtain the correct expression (3.6) for the conductivity in a metal in the presence of only time-dependent fields, it is necessary that the quasiequilibrium state be described by the *total* Hamiltonian including the perturbation.

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[21] The nonanalytic structure in the conductivity is rather subtle and arises because of the discreteness of states in a small system. It is crucial that the sum over n' be performed exactly. In case it is approximated by an integral using the Euler-Maclaurin summation formula, only an analytic contribution that is $\sim 1/d$ is found in the second term in (3.10).

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