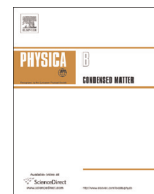




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Quantum theory of the effect of grain boundaries on the electrical conductivity of thin films and wires

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ABSTRACT

We calculate the electrical conductivity of a metallic sample under the effects of distributed impurities and a random distribution of grain boundaries by means of a quantum mechanical procedure based on Kubo formula. Grain boundaries are represented either by a one-dimensional regular array of Dirac delta potentials (Mayadas and Shatzkes model) or by its three-dimensional extension (Szczyrbowski and Schmalzbauer model). We give formulas expressing the conductivity of bulk samples, thin films and thin wires of rectangular cross-sections in the case when the samples are bounded by perfectly flat surfaces. We find that, even in the absence of surface roughness, the conductivity in thin samples is reduced from its bulk value. If there are too many grain boundaries per unit length, or their scattering strength is high enough, there is a critical value R_c of the reflectivity R of an individual boundary such that the electrical conductivity vanishes for $R > R_c$. Also, the conductivity of thin wires shows a stepwise dependence on R . The effect of weak random variations in the strength or separation of the grain boundaries is computed by means of the method of correlation length. Finally, the resistivity of nanometric polycrystalline tungsten films reported in Choi et al. J. Appl. Phys. (2014) 115 104308 is tentatively analyzed by means of the present formalism.

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1. Introduction

The continuous progress of modern semiconductor industry has resulted in a progressive shrinkage of the linear dimensions of the electronic components. The dimensions of the thin films and wires that constitute the building materials of the devices now reach nanoscale sizes, which are not only smaller than the electronic mean free path λ of the carriers but are such that quantum size effects begin to become important [1].

The electrical resistivity of large samples has been found to be independent of size and shape. But, when one of its linear dimensions becomes comparable with the mean free path of the conducting electrons, the resistivity increases over its bulk value. This effect has been explained by Fuchs [2] and Sondheimer [3] (FS) in terms of diffuse scattering occurring at the boundaries of the film. The theory is based on an appropriate solution of the Boltzmann transport equation and is, thus, semiclassical in nature. When data is interpreted in terms of this formalism, the only

unknown parameter is p – the fraction of electrons that are specularly scattered at the film surfaces. The FS formula for the conductivity σ_{FS} is

$$\frac{\sigma_{FS}}{\sigma_0} = 1 - \left(\frac{3\lambda}{2t}\right)(1-p) \int_1^\infty \left(\frac{1}{s^3} - \frac{1}{s^5}\right) \frac{1 - \exp(-ts/\lambda)}{1 - p \exp(-ts/\lambda)} ds, \quad (1)$$

where t is the thickness of the film and σ_0 is the conductivity of a bulk sample of identical composition.

Similar explanations have been found for the increase in the electric resistivities of thin wires of circular cross-section [4] and of square cross-section in case of completely diffuse surface scattering [5]. (For many years it was believed that the formalism of Chambers [6] – which is known to be equivalent to solving the Boltzmann transport equation – could be used for obtaining formulas expressing the resistivity of wires of arbitrary shapes and surface reflectivities. But this conjecture is now known to be erroneous [7].)

Further measurements on thin films and wires of increased purity did show that the electrical resistivity increases beyond the predictions of the FS theory. Mayadas and Shatzkes (MS) attributed this additional resistivity to scattering of electrons by grain boundaries [8]. According to this theory, the electrical conductivity σ_{MS} of a bulk sample with average grain diameter d and mean free

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path λ is (in units of σ_0 , the conductivity of an identical sample having no grain boundaries)

$$\frac{\sigma_{MS}}{\sigma_0} = 3 \left[\frac{1}{3} - \frac{1}{2}\alpha + \alpha^2 - \alpha^3 \ln(1 + \alpha^{-1}) \right]; \quad (2)$$

where

$$\alpha = \frac{\lambda}{d} \frac{R}{1 - R} \quad (3)$$

and where the parameter R denotes the reflection coefficient of a single grain boundary.

Furthermore, Mayadas and Shatzkes obtained a second formula describing the electrical conductivity of a polycrystalline thin film. This expression is similar in the form to FS formula, except that the unperturbed mean free path is incremented by an angle-dependent quantity that describes the additional scattering taking place at the grain boundaries. Again, the relevant parameter is the reflectivity R [8].

The conductivity σ_{MSS} predicted by this formula is

$$\sigma_{MSS} = \sigma_{MS} - \left(\frac{6\lambda\sigma_0}{\pi t} \right) (1 - p) \int_0^{\pi/2} d\phi \int_1^\infty ds \frac{\cos^2 \phi}{H^2} \times \left(\frac{1}{s^3} - \frac{1}{s^5} \right) \frac{1 - \exp(-tsH/\lambda)}{1 - p \exp(-tsH/\lambda)}, \quad (4)$$

where

$$H(s, \phi) = 1 + \frac{\alpha}{\sqrt{1 - s^{-2} \cos \phi}}. \quad (5)$$

For a long time, these formulas were the only tools possessing firm theoretical foundations that the experimenters could use in order to interpret their results. For lack of anything better, a number of semi-empirical formulas were also proposed and used [9–11]. Thus, the electrical conductivity of thin films of copper [12], gold [13] and tungsten [14] was measured, together with their respective thicknesses and grain diameters. It was found that the measurements of Cu films could be adequately interpreted by a combination of Eqs. (1) and (2), according to Matthiessens' rule [12]. On the other hand, it was determined that the dependence of the resistivity of Au films [13] on thickness and grain diameters was better explained by means of MS formula (4). Finally, Choi et al. tried to interpret the resistivities of thin W films by means of these methods, concluding that they were essentially equivalent in this case and that both resulted in systematic deviations from the experimental values [14].

The electrical conductivity of thin polycrystalline wires of gold [15], copper [10,11,16], and silver [7] was also measured for a number of thicknesses and grain diameters. Here, the lack of any formalism corresponding to (2) and (4) was most sorely felt. Josell et al. [7] noted that the many formulas employed in this connection were not equivalent. Furthermore, their purported justification in terms of Chambers' method [6] was shown to be erroneous [7].

Recently, a semi-numerical procedure for calculating the combined effects of surface roughness and grain boundaries on the conductivity of polycrystalline metallic films has been published [17]. The method is essentially equivalent to using an exact solution of the Boltzmann transport equation. By means of this formulation, it was possible to obtain tentative fits of the measurements of Steinghögl et al. of thin Cu films [16] and Josell et al. of thin Ag wires [7].

When solving the Boltzmann transport equation, the effects of the scattering by distributed impurities may be taken into account by fixing the time of relaxation, whilst those of diffuse surface scattering may be accounted by choosing appropriate boundary

conditions. However, the contribution of grain boundaries cannot be adequately described by either of these procedures. In the formalism of MS, grain boundary scattering is represented by the transition probability of scattering between two momentum states, calculated by first-order perturbation theory [8]. Thus, it appears that the theory can adequately describe the facts only for small enough values of R , the reflection coefficient of an individual grain boundary. Indeed, the analysis of thin film data made by Henriquez et al. [13] suggests that the corresponding MS formula is reasonably accurate only for values of R that do not exceed ≈ 0.3 .

Fortunately, the combined effects of distributed impurities and a regular array of grain boundaries can be accounted for at all orders of perturbation theory by means of a procedure that is quantum throughout. The purpose of the present work is to extend the ideas developed in Ref. [18]. In this paper we compute the effects of grain boundaries on the electrical conductivity of bulk samples and thin films and wires by means of the Kubo formula.

In the formalism of Kubo [19], the electrical conductivity σ is given by

$$\sigma = - \frac{2e^2 \hbar^3}{\pi m^2 V} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \left[\Im \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial x} \right] \left[\Im \frac{\partial G(\mathbf{r}', \mathbf{r})}{\partial x'} \right], \quad (6)$$

where $-e$ and m are the charge and mass of the carriers, respectively, V is the volume of the sample and $G(\mathbf{r}, \mathbf{r}')$ is Green's function appropriate for each case. For instance, it is customary to account for the effects of distributed impurities by adding an imaginary part to the Fermi energy – or to the Fermi wave vector k_F – as the quantum analogue of the mean free path λ [20]. By inserting into (6) Green's function for an infinite system

$$G_0(\mathbf{r}, \mathbf{r}') = - \frac{2m}{4\pi \hbar^2} \frac{e^{ik_F |\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}, \quad (7)$$

one obtains, for the conductivity of a bulk sample,

$$\sigma_0 = \frac{e^2}{6\pi^2 \hbar} \frac{(\Re k_F)^2}{\Im k_F}. \quad (8)$$

This coincides in the form with the well known Sommerfeld–Drude prescription [21]

$$\sigma_0 = \frac{e^2 \bar{k}_F^2}{3\pi^2 \hbar} \lambda \quad (9)$$

if we identify the real part of k_F with the observed value of the Fermi wave vector \bar{k}_F and its imaginary part as $\Im k_F = 1/2\lambda$ [22].

2. Grain boundaries and bulk conductivity

Excluding many-body effects, Green's function is the solution of the inhomogeneous Schrödinger equation

$$\left(\frac{\hbar^2}{2m} \nabla_{\mathbf{r}} + \mathcal{E}_F - V(\mathbf{r}) \right) G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r}, \mathbf{r}'), \quad (10)$$

that is symmetrical in its arguments $G(\mathbf{r}, \mathbf{r}') = G(\mathbf{r}', \mathbf{r})$ and satisfies appropriate conditions at the boundaries of the sample. Here $\mathcal{E}_F = \hbar^2 k_F^2 / (2m)$ is the Fermi energy (k_F is the Fermi wave vector) and $V(\mathbf{r})$ is an effective potential to be chosen in order to adequately model the effects of grain boundaries.

As a first approximation, Mayadas and Shatzkes noted that grain boundaries may be roughly classified as being oriented parallel or perpendicular to the applied electric field \mathbf{E} . Therefore, since the parallel barriers are encountered mainly at grazing incidences and, thus, do not contribute much to the scattering of the

carriers, it is plausible to neglect their effect entirely. The problem is thus reduced to the scattering from an array of plane barriers perpendicular to the direction of the electric field (which we take to be the x -axis). For simplicity, Mayadas and Shatzkes considered these barriers to be in the form of Dirac delta potentials with equal strengths $\hbar^2 S/2m$. Furthermore, the barriers were supposed to be uniformly distributed, with a separation equal to the average grain diameter d . This can be justified *a posteriori* since, as a result of Mayadas and Shatzkes procedure, the fluctuation s in the distribution of grain diameters contributes to the conductivity with terms of the order $\exp(-s^2 k_F^2)$ and is, thus, negligible for normal metals [8].

In this way, the quantum counterpart to the Mayadas and Shatzkes model is obtained by taking the potential $V(\mathbf{r})$ in (10) to be

$$V(x) = \sum_{n=-N/2}^{N/2} (\hbar^2 S/2m) \delta(x - nd). \quad (11)$$

In practice, N is a very large number. In the limit when N tends to infinity, this is an example of the well-known Kronig–Penney potential [23].

In the case of bulk samples, the system is uniform in the y - and z -directions, so we can write

$$G(\mathbf{r}, \mathbf{r}') = \frac{2m}{\hbar^2} \int \frac{d^2 \mathbf{k}_\perp}{(2\pi)^2} e^{i\mathbf{k}_\perp \cdot (\mathbf{r}_\perp - \mathbf{r}'_\perp)} g(k; x, x'); \quad (12)$$

where $\mathbf{r}_\perp = y\hat{\mathbf{y}} + z\hat{\mathbf{z}}$ and $g(k; x, x')$ is a one-dimensional Green's function, given by

$$\frac{\partial^2 g(k; x, x')}{\partial x^2} + \left[k^2 - S \sum_n \delta(x - nd) \right] g(k; x, x') = \delta(x - x'), \quad (13)$$

with

$$k = \sqrt{k_F^2 - k_\perp^2}. \quad (14)$$

The Kubo formula (6) simplifies considerably if written in terms of g . The result is

$$\sigma = - \frac{4e^2}{\pi^2 \hbar L} \int_{-L/2}^{L/2} dx \int_{-L/2}^{L/2} dx' \int_0^\infty k_\perp \left[\Im \frac{\partial g(k; x, x')}{\partial x} \right] \left[\Im \frac{\partial g(k; x', x)}{\partial x'} \right] dk_\perp, \quad (15)$$

where $L = Nd$.

Further simplifications depend on the specific form of Green's function for the Kronig–Penney potential $g(k; x, x')$. We find that

$$g(x, x') = \frac{1}{2ik \sin(kd) \sin \xi} \begin{cases} \psi(-\xi, x) \psi(\xi, x'); & x \leq x'; \\ \psi(-\xi, x') \psi(\xi, x); & x \geq x'; \end{cases} \\ = \frac{\psi(-\xi, x_<) \psi(\xi, x_>)}{2ik \sin(kd) \sin \xi}, \quad (16)$$

where $x_<$ is the smaller quantity between x and x' while $x_>$ is the greater of the two.

The (un-normalized) wave function $\psi(\xi; x)$ is

$$\psi(\xi, x) = \sum_{m=-\infty}^{\infty} \theta_m(x) e^{im\xi} \left[\sin k[x - (m+1)d] + e^{i\xi} \sin k(x - md) \right]; \quad (17)$$

where $\theta_m(x)$ is a function that is equal to one if $md < x < (m+1)d$ and zero otherwise. Finally, the relationship between k and the Kronig–Penney parameter ξ is

$$\cos \xi = \cos kd + \frac{S}{2k} \sin kd. \quad (18)$$

It is important to note that these formulas can be derived by means of a purely algebraic procedure that does not require that the hamiltonian be Hermitian. This is shown in detail in Appendix A of Ref. [18].

Inserting this into the Kubo formula, we find that in this case the electrical conductivity is

$$\sigma = \frac{e^2}{8\pi^2 \hbar d} \int_0^\infty \frac{I(k)}{|k \sin(kd) \sin \xi|^2} k_\perp dk_\perp \quad (19)$$

where

$$I(k) = \sinh(2\xi) \left[d \left(\frac{k_I^2}{k_R} \sin(2k_R d) - \frac{k_R^2}{k_I} \sinh(2k_I d) \right) + 2 \frac{k_R^2 - k_I^2}{k_R^2 + k_I^2} \right. \\ \left. | \sin(kd) |^2 \right] \\ + \sin(2\xi_R) \left[d \left(\frac{k_I^2}{k_R} \sinh(2k_I d) + \frac{k_R^2}{k_I} \sin(2k_R d) \right) \right. \\ \left. + 4 \frac{k_R k_I}{k_R^2 + k_I^2} | \sin(kd) |^2 \right] \\ - 4\Im \sin(\xi) \sin(kd) \left[d \left(\frac{k_I^2}{k_R} + i \frac{k_R^2}{k_I} \right) + \frac{k}{2k^*} \sin(2k^* d) \right]; \quad (20)$$

and where ξ_R and ξ are, respectively, the real and imaginary parts of the Kronig–Penney parameter ξ . Similarly, k_R and k_I are the real and imaginary parts of k . Appendix B of Ref. [18] contains the explicit derivation of this formula.

We note that the dependence on R of the conductivity described by the present formalism is qualitatively different from that prescribed by the MS theory [8]. This is shown in Fig. 1 for values of k_F appropriate for ordinary metals. We note further that the results of greatest interest occur at low enough values of k_{Fd} . An example of this is shown in Fig. 2. It is seen that the conductivity changes abruptly each time a band of allowed states becomes unavailable as the reflectivity R is increased. Finally, if no allowed state remains, the conductivity vanishes for all values of R greater than a critical value. Clearly, these are genuine quantum phenomena, quite beyond the predictive powers of a semiclassical theory.

3. Model of Szczyrbowski and Schmalzbauer

Assuming that the detailed shape of the individual grains that constitute a polycrystalline sample is less important than its volume and relative disposition, Szczyrbowski and Schmalzbauer (SS) generalized the model of Mayadas and Shatzkes by representing grain boundaries by three arrays of planar potentials perpendicular to the x -, y - and z -axes [24]. In a quantum treatment, this is equivalent to taking

$$V(\mathbf{r}) = \frac{\hbar^2 S}{2m} \sum_{n_x, n_y, n_z} [\delta(x - n_x d_x) + \delta(y - n_y d_y) + \delta(z - n_z d_z)], \quad (21)$$

as the potential in the Schrödinger equation (10), instead of Eq. (11).

In this case, we find that Green's function is given by

$$G(\mathbf{r}, \mathbf{r}') = \frac{2m}{\hbar^2} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \int_0^{2\pi} \frac{d\xi_y}{2\pi} \int_0^{2\pi} \frac{d\xi_z}{2\pi} Fg(k_{n_y, n_z}; x, x') \quad \text{where} \\ F = A_{n_y}^2 A_{n_z}^2 \psi_{n_y}(-\xi_y; y) \psi_{n_y}(\xi_y; y') \psi_{n_z}(-\xi_z; z) \psi_{n_z}(\xi_z; z'); \quad (22)$$

instead of (12). The coefficients A_n are

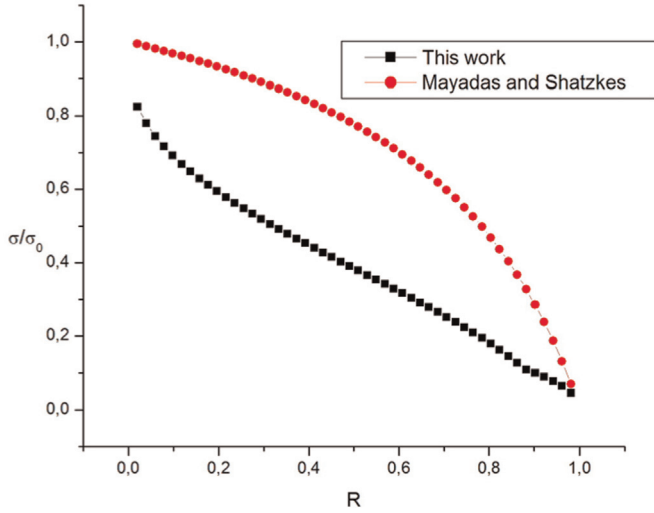


Fig. 1. The electrical conductivity of a bulk sample with grain boundaries represented by a one-dimensional regular array of Dirac deltas with separation d , in units of the conductivity of an identical sample having no grain boundaries, according to the quantum theory [Eq. (19) of this paper] compared to Mayadas and Shatzkes semiclassical expression – Eq. (10) of Ref. [8]. In both cases $k_F d = 15 + 2.5i$.

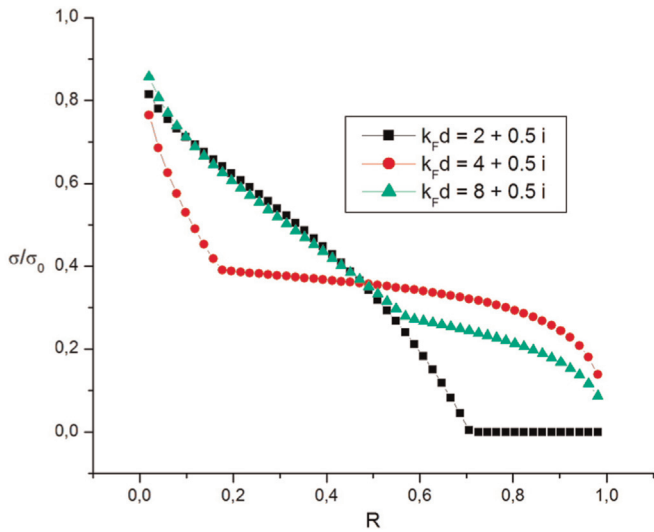


Fig. 2. The electrical conductivity of a bulk sample with grain boundaries represented by a one-dimensional regular array of Dirac deltas with separation d , in units of the conductivity of an identical sample having no grain boundaries according to the quantum theory [Eq. (19) of this paper].

$$A_n^{-2} = d \sin(k_{\xi,n} d) \left[\left(1 + \frac{S}{2k_{\xi,n}^2 d} \right) \sin(k_{\xi,n} d) - \frac{S}{2k_{\xi,n}} \cos(k_{\xi,n} d) \right]; \quad (23)$$

and

$$k_{ny,nz} = \sqrt{k_F^2 - k_{\xi,y}^2 - k_{\xi,z}^2}, \quad (24)$$

where $k_{\xi,n}$ are the solutions of the condition

$$\cos \xi = \cos k_{\xi,n} d + \frac{S}{2k_{\xi,n}} \sin k_{\xi,n} d, \quad (25)$$

for a given ξ . (For simplicity, we assume in this paper that $d_x = d_y = d_z = d$. The extension to the general case may be obtained without difficulty.)

Proceeding as before, we find that in the SS model the electrical

conductivity is given by

$$\sigma = \frac{e^2}{4\pi\hbar d^2} \sum_{ny,nz} \int_0^{2\pi} \frac{d\xi_y}{2\pi} \int_0^{2\pi} \frac{d\xi_z}{2\pi} \frac{I(k_{ny,nz})}{|D(k_{ny,nz})|^2}, \quad (26)$$

instead of (19). Here, due to the separability of the problem, I is still given by Eq. (20). Also, as before, the sums should be computed only over those values of $k_{ny,nz}$ that lie inside an allowed band and such that $\sqrt{k_{\xi,y}^2 + k_{\xi,z}^2} \leq \bar{k}_F$.

In Fig. 3 we show some examples of evaluating Eq. (26). It is seen that, at equal values of all the relevant parameters, the conductivity prescribed by this model is (apart from some differences in shape) smaller than the corresponding value obtained from Eq. (19). This is expected because, as a consequence of the additional confinement, the number of states available at a given energy in the SS model is smaller than in the model of MS. Since this will be the case for any treatment that is more realistic than Mayadas and Shatzkes' model, any data that is interpreted by means of MS formalism will result in a value of R that is smaller than the true one.

4. Thin films with smooth surfaces

In this section we consider the effects of grain boundaries in the electrical conductivity of a thin film of thickness t . In order to disentangle these effects from those arising from surface roughness or other surface defects, we shall treat here only the case of perfectly smooth boundaries. Usually, it is assumed that perfect surfaces scatter carriers elastically and, thus, do not change the conductivity from its bulk's value [2]. But, at the scales where quantum effects are important, the added effects of confinement limit the number of states available when performing the integral in Eq. (6), resulting in a further reduction of the electrical conductivity.

This can be shown as follows. Let us suppose that the sample extends from $z=0$ to $z=t$ and is of indefinite extent in the x - and y -directions. As in Mayadas and Shatzkes model, grain boundaries are represented by a regular array of barriers oriented perpendicularly to the x -axis. Thus, Green's function for this case is

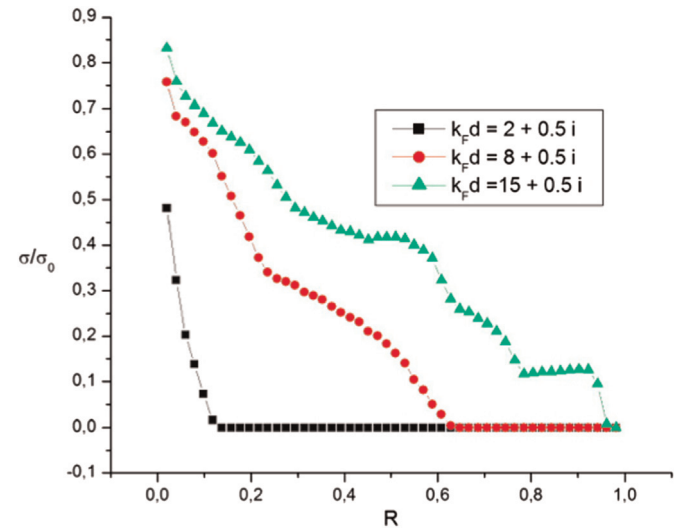


Fig. 3. The electrical conductivity of a bulk sample with grain boundaries represented by a three-dimensional regular array of Dirac deltas with separation d , in units of the conductivity of an identical sample having no grain boundaries, according to the quantum theory [Eq. (26) of this paper].

$$G(\mathbf{r}, \mathbf{r}') = \frac{2m}{\hbar^2} \sum_{n=1}^{\infty} \int_{-\infty}^{\infty} \frac{dk_y}{2\pi} e^{iky(y-y')} \phi_n(z) \phi_n(z') g(k_n; x, x'), \quad (27)$$

where

$$\phi_n(z) = \sqrt{\frac{2}{t}} \sin\left(\frac{n\pi z}{t}\right), \quad (28)$$

and

$$k_n = \sqrt{k_F^2 - k_y^2 - \left(\frac{n\pi}{t}\right)^2}, \quad (29)$$

instead of (12) and (14). As a consequence of the separability of this problem, Green's function is still given by Eq. (16).

Proceeding as before, we find that in this case that the electrical conductivity is given by

$$\sigma = \frac{e^2}{2\pi^2 \hbar t} \sum_n \int_0^{\infty} \frac{I(k_n)}{|k_n \sin(k_n d) \sin \xi|^2} dk_y, \quad (30)$$

instead of (19). Here, I is given by Eq. (20). In Appendix A we give an alternative proof, in which this formula is obtained in the limit of zero roughness amplitude.

Typical conductivity versus reflectivity curves are shown in Fig. 4 for the case when film thicknesses coincide with their respective grain diameter. It is seen that, as a general rule, the conductivity of a thin film is smaller than the bulk value at equal k_F , λ and R . This is the case even if the film's surfaces are perfectly smooth.

It is further observed that the derivative of this function changes discontinuously when an allowed band is suppressed as R increases. This phenomenon is best illustrated at low enough values of $k_F d$. (Of course, this effect would be scarcely visible in simple metals, which have Fermi wavelengths λ_F of the order of 0.5 nm.)

5. Thin wire of rectangular cross-section

We consider now a wire of rectangular cross-section $0 \leq y \leq D_y$, $0 \leq z \leq D_z$ and very long in the x -direction. The effect of grain boundaries is again described by means of the Mayadas and

Shatzkes model. Again, we consider here only the case of perfectly smooth surfaces. It is seen that the appropriate Green's function is

$$G(\mathbf{r}, \mathbf{r}') = \frac{2m}{\hbar^2} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} Y_n(y) Y_n(y') Z_m(z) Z_m(z') g(k_{n,m}; x, x'), \quad (31)$$

where

$$Y_n(y) = \sqrt{\frac{2}{D_y}} \sin\left(\frac{n\pi y}{D_y}\right), \quad (32)$$

$$Z_n(z) = \sqrt{\frac{2}{D_z}} \sin\left(\frac{n\pi z}{D_z}\right).$$

Here

$$k_{n,m} = \sqrt{k_F^2 - \left(\frac{n\pi}{D_y}\right)^2 - \left(\frac{m\pi}{D_z}\right)^2}. \quad (33)$$

The electrical conductivity is given by

$$\sigma = \frac{e^2}{2\pi^2 \hbar D_y D_z} \sum_{n,m} \frac{I(k_{n,m})}{|k_{n,m} \sin(k_{n,m} d) \sin \xi|^2}. \quad (34)$$

Here, the sum is performed only over those values of n and m such that $k_{n,m}$ do not exceed k_F .

As before, the interesting phenomena tend to occur at somewhat extreme values of $k_F d$. Thus, in Fig. 5 we show some results of using Eq. (34), in the particular case when $D_y = D_z = d$. It is well known that the electrical conductivity of a quantum conductor is a stepwise function of the bias voltage [25]. We see here, in a somewhat different connection, that the electrical conductivity of a thin wire is a stepwise function of the reflectivity R . Furthermore, it is known that there exists a critical amount of impurity scattering beyond which the conduction electrons are localized and the conductivity vanishes [26]. In the present case we find a similar phenomenon. For wires that are thin enough, there is a critical value R_c such that the conductivity is equal to zero for $R > R_c$.

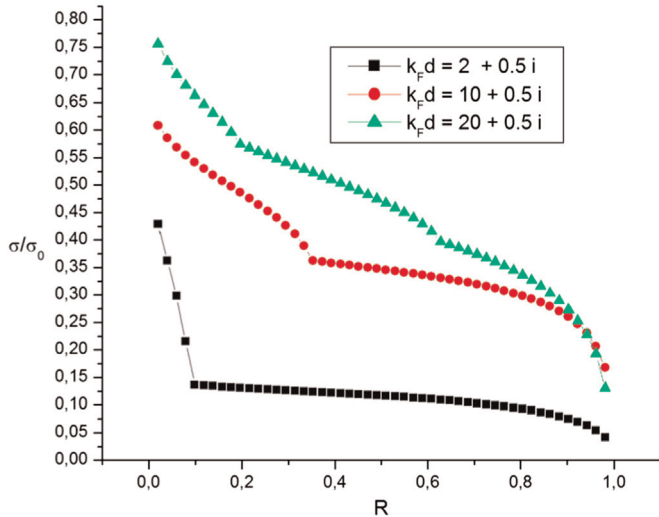


Fig. 4. The electrical conductivity of a thin film of thickness t with grain boundaries represented by a one-dimensional regular array of Dirac deltas with separation d , in units of the conductivity of a bulk sample having no grain boundaries, according to the quantum theory [Eq. (30) of this paper]. In this figure, thickness t is assumed to be equal to d .

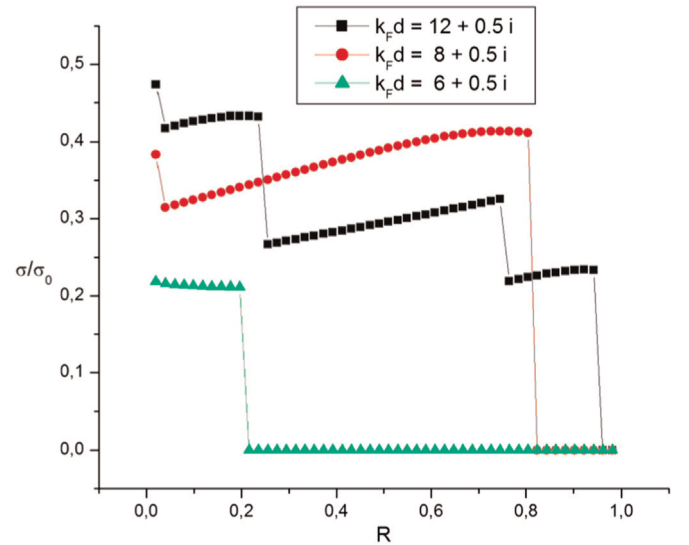


Fig. 5. The electrical conductivity of a thin wire of square cross-section of width d with grain boundaries represented by a one-dimensional regular array of Dirac deltas also separated by d , in units of the conductivity of a bulk sample having no grain boundaries, according to the quantum theory [Eq. (34) of this paper].

6. Effects of weak compositional and structural disorder

We consider now a version of the potential (11) that incorporates disorder

$$V(x) = \sum_n (\hbar^2 S_n / 2m) \delta(x - x_n); \quad (35)$$

describing an aperiodic array of delta barriers of random strength. We set $S_n = S(1 + s_n)$ and $d_n = x_{n+1} - x_n = d + \Delta_n$, defining the random fluctuations in fractional strength s_n around its mean value S and the random departure Δ_n from perfect periodicity of the average crystal. We shall suppose that s_n and Δ_n are random processes with mean zero and standard deviations s^2 and Δ^2 . Also, they may be correlated with correlation χ . Thus,

$$\begin{aligned} \langle s_n \rangle &= 0; & \langle s_n^2 \rangle &= s^2; \\ \langle \Delta_n \rangle &= 0; & \langle \Delta_n^2 \rangle &= \Delta^2; \\ \langle s_n \Delta_n \rangle &= \chi. \end{aligned} \quad (36)$$

Since we assume that the disorder is weak ($s_n \hat{a} \ll 1$ and $k_F \Delta_n \hat{a} \ll 1$), it will not be necessary to specify higher moments.

It is known that the transmission T_N through N identical cells is

$$T_N = \exp(-l_{loc}^{-1}), \quad (37)$$

where l_{loc} is the rescaled (or adimensional) localization length [27].

Thus, the effect of weak disorder both in grain diameters and in the scattering strength of grain boundaries can be incorporated in a conductivity formula. For instance, in the case of a bulk sample traversed by N grain boundaries, we find that according to the MS model (19) the conductivity is

$$\sigma_N = \frac{e^2}{8\pi^2 \hbar} \int_0^\infty \frac{T_N I(k)}{|k \sin(kd) \sin \xi|^2} k_\perp dk_\perp, \quad (38)$$

where $I(k)$ and T_N are given by (20) and (37) and where, in the present case, the localization length is found to be

$$\begin{aligned} \frac{1}{l_{loc}} &= \frac{N}{2 \sin^2 \xi} \left[k^2 \Delta^2 \left(\sin^2 \xi + \frac{S^2}{4k^2} \right) \right. \\ &\quad \left. - \chi S \sin kd \left(\sin kd - \frac{S}{2k} \cos kd \right) + \frac{s^2 S^2}{4k^2} \right]. \end{aligned} \quad (39)$$

This is shown in Appendix B.

7. The resistivity of thin tungsten films

Recently, Choi et al. measured the electrical resistivity at 4.2 and 293 K of eight polycrystalline tungsten films, ranging in thicknesses from 10 to 310 nm and lateral grain size from 74 to 133 nm [14]. They analyzed their results by means of two different methods. First they tried a combination of Fuchs–Sondheimer (1) and Mayadas–Shatzkes (2) models, where the resistivities $\rho_{FS} = 1/\sigma_{FS}$ and $\rho_{MS} = 1/\sigma_{MS}$ are combined according to Matthiessen's rule $\rho = \rho_{FS} + \rho_{MS}$. The second model is the Mayadas and Shatzkes equation for polycrystalline films equation (4). In order to interpret the measurements, both the surface specularity p and the grain boundary reflectivity R were considered as parameters and varied so as to best fit the data. The bulk mean free paths at 4.2 and 293 K were prescribed and fixed at $\lambda_{4.2} = 77.7$ nm and $\lambda_{293} = 16.1$ nm, respectively.

As a result, both methods gave values that were essentially

equivalent. However, there appeared “systematic errors in the fit that suggest that these models cannot be used with confidence to describe scaling of the resistivity with film thickness. This (they found) is specially true for film thicknesses below ~ 20 nm.” (Ref. [14].) Thus, Choi et al. concluded that semiclassical models fail to describe the resistivity of these nanometric polycrystalline tungsten films.

Of course, any formalism based on the Boltzmann transport equation is an approximation to a reality that should be truly described only by a quantum mechanical procedure. Thus, both models assayed by Choi et al. are in fact approximations to an approximation. In order to test the importance of this fact, we analyzed this data by a recent formalism that computes the resistivity by a method essentially equivalent to an exact solution Boltzmann equation [17]. For instance, this procedure takes into account trajectories of electrons that undergo multiple interface or grain-boundary scattering events. Furthermore, the method succeeded in providing fits to the resistivity versus width of thin Cu [16] and Ag [7] wires. However, the result of this analysis coincides with that of Choi et al. We found that, assuming the aforesaid restrictions, no possible combination of p and R could accurately describe the low values of the resistivity ratio in this case.

We will now describe a full quantum mechanical treatment of the data of Choi et al. First, we slightly generalized the treatment in this paper in order to account both for the effects of the scattering by grain boundaries and that of surface roughness. A perturbative calculation shows that surface roughness changes the quantum reflectivity A of the potential barrier describing the surface from the value $A=1$, appropriate for a perfectly smooth surface, to

$$A = \frac{1 - k_z Q}{1 + k_z Q}, \quad (40)$$

where k_z is the component of the wave vector perpendicular to the surface and the distance Q is a known function of the surface roughness amplitude and its lateral correlation length [28–30,18]. As a result, the wave vector characterizing the sub-bands changes from $k_n = n\pi/t$ to other (usually complex) value.

Since the details of the surface profile are unknown in this case, we did assume that Q is a parameter that could be varied freely in order to find the best fit of data. The other parameter is the scattering strength S of an individual grain boundary. These are the quantum counterpart of p and R of the semiclassical treatment.

The result of the fit is shown in Fig. 6. The values of the resulting parameters are listed in Table 1.

It is the case that the quantum and semiclassical descriptions of the dependence of the conductivity on the mean free path (or the resistivity on temperature) are qualitatively similar at small values of the scattering strength of the surface or grain boundaries, but differ in form in the opposite case. It is this change in form that causes the quantum treatment to successfully describe – in contradistinction to the semiclassical one – the low value of the resistivity ratio $\rho_{293}/\rho_{4.2}$ that characterizes the experiment of Choi et al. [14]

On the other hand, both Q and S represent entities that have physical existence and can, in principle, be measured. Furthermore, the dependence of the resistivity on temperature for values of T intermediate between 4.2 and 293 K may be measured in detail. Thus, there is room for further comparison between the present theory and reality [18].

8. Conclusions

In this paper we have calculated the conductivity σ of

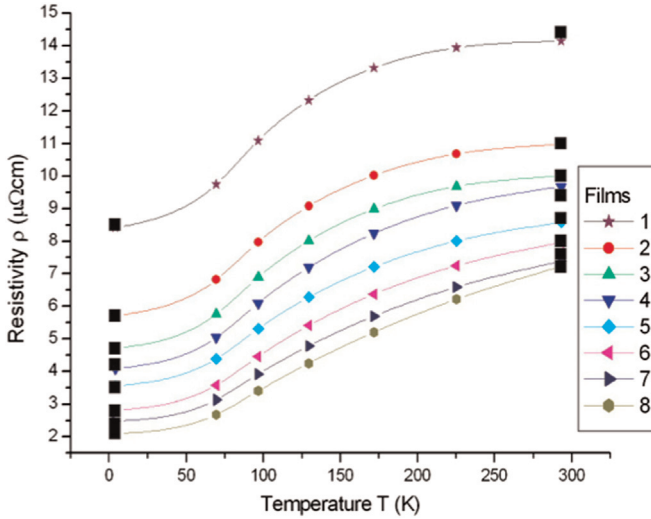


Fig. 6. A tentative fit of the resistivity data of eight thin W films reported by Choi et al. [14]. Black squares depict experimental data. Colored lines show the values obtained from the present theory equation (A.12) for values of the parameters S and Q that best fit the data. The values of these parameters are listed in Table 1. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

Table 1

Thicknesses t , lateral grain sizes d , resistivities $\rho_{4,2}$ and ρ_{293} at 4.2 K and 293 K, respectively, of the eight tungsten films reported by Choi et al. [14]. S and Q are the values of the parameters defining the scattering strength of the grain boundaries and the surface roughness used in the fits of Fig. 6. We also assume an effective value of the Fermi wave vector $k_F = 15.5 \times 10^9 \text{ m}^{-1}$. Following Choi et al., the values of the mean free path λ and bulk resistivity ρ_0 are related by $\rho_0 \lambda = 1.01 \times 10^{-15} \Omega \text{ m}^2$. The relation between ρ_0 and temperature for W is taken from Ref. [31].

Film	t (nm)	d (nm)	ρ ($\mu\Omega\text{cm}$)		S (10^9 m^{-1})	Q (nm)
			$\rho_{4,2}$	ρ_{293}		
1	10.3	74	8.5	14.4	3	$9.2 + i$
2	20.6	90	5.7	11.0	2	$13.8 + 6i$
3	30.8	83	4.7	10.0	2.34	$17 + 6i$
4	41.4	84	4.2	9.4	2.34	$18 + 6i$
5	61.7	95	3.5	8.7	2.34	$21 + 6i$
6	123.4	106	2.8	8.0	7	$50 + 6i$
7	185.1	133	2.4	7.6	7	$23 + 6i$
8	310.2	119	2.1	7.2	7	$21 + 6i$

polycrystalline metallic samples as a function of the mean grain diameter d and grain boundary reflectivity R . We have found explicit formulae for σ – Eqs. (19) and (26) for bulk samples, Eq. (30) for thin films and Eq. (34) for thin wires of rectangular cross-sections. It is seen that these formulae are only slightly more involved than the well known equations of Fuchs [2] or Dingle [4] that describe the conductivity of thin films and wires in the absence of grain boundary scattering. In contradistinction with former treatments, our calculations are a direct consequence of Schrödinger equation, by means of Kubo formula [19].

By an extension of this procedure that takes into account the quantum effects of surface roughness, we attempted also a fit to the resistivity measurements performed by Choi et al. on thin W films [14]. However, the result may be objected in two accounts: First, it is difficult to see why the parameters Q and S would show such large and unsystematic variation as a function of film thickness as appears in the present Table 1. Furthermore, the calculated resistivities in Fig. 6 show a distinctly non-linear variation with temperature. This non-linearity does not agree with the

experimental results shown in p. 76 of Choi's thesis [37]. Clearly, there remain a number of open issues left for future studies.

It is clear, however, that the present change in outlook has deeper consequences than a mere improvement in calculating tools. In the semiclassical picture each grain boundary contributes to the electrical resistance by scattering a certain fraction of the incoming electrons. In the quantum conception, there is no such thing as a partial scattering. There are states (in the allowed bands) that transmit electrons essentially unhindered, whilst the electrons in the remaining states (the forbidden bands) are localized. Thus, changes in the size of the sample, or in the diameter or reflectivity of grains, can add or remove complete bands; a fact reflected in the discontinuities in the slope of the conductivity versus R in the case of thin films, or the stepwise change of the same function in the case of thin wires. Furthermore, in the case of thin enough samples and for large enough values of R , all the electrons become localized and the conductivity drops to zero. As in other well known cases, this insulating character is due to a quantum-mechanical mechanism and is not a result of successive semiclassical encounters in an infinite one-dimensional system [25,26].

All conductivity formulae interpolate between $\sigma/\sigma_0 = 1$ for $R=0$ and $\sigma/\sigma_0 = 0$ for $R=1$. However, we have found (Fig. 1) that the shape of the interpolation curve can differ greatly according to the use of a semiclassical or a quantum-mechanical treatment. There are a number of further general conclusions that disagree with previous findings. First, we see that the effects of grain boundaries that run parallel to the current are far from negligible. Also, the effects on the conductivity of disorder in the scattering strength or separation between grain boundaries are not small, in contradiction with the conclusions of Mayadas and Shtazkes [8]. And, finally, the electrical conductivity of a given sample depends on its shape and size, even if it is bounded by perfectly smooth surfaces (the case $p=1$ of the semiclassical treatment).

Recently, a number of important works have been published that employ a complementary procedure. Instead of using the methods of mathematical physics [32] – as was done in the past [2–5,8] and also in this work – the procedure consists in numerical investigations of the detailed structure of surface roughness or grain boundaries, made of atoms of a specified nature. Once these structures are determined, the dependence on angle and energy of the scattering power of the lattice defects can be accurately calculated and their contributions to the electrical resistivity can be ascertained [33–36]. In this way, this research program functions as a powerful microscope that allows the determination of the true properties of these nanometric structures, which are otherwise so difficult to be put under direct observation.

Physics is a science so vast and rich that there are many tools available for treating a given problem; and these can be combined in a variety of proportions. Since atomic-scale modeling are limited by material constraints to calculations covering around a dozen atomic layers, probably its principal contribution will be the determination of the small-scale characteristics of the conduction processes – for instance, the setting-up of accurate pseudopotentials representing the scattering power of an individual grain boundary. We note that the Kronig–Penney procedure [23] can be easily generalized to treat the infinite repetition of any individual potential. Thus, it is conceivable that the present procedure could be extended in order to capture the larger-scale quantum mechanical effects of these realistic surface and grain boundary structures [34].

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Appendix A. Thin films limited by rough surfaces

We present here an explicit derivation of the formula for the electrical conductivity σ of a thin polycrystalline film of thickness t bounded by rough surfaces. The case of perfectly flat surfaces has been described in Appendix C of Ref. [18]. In the present case, Green's function is

$$G(\mathbf{r}, \mathbf{r}') = \frac{2m}{\hbar^2} \sum_{n,m=1}^{\infty} \int_0^{2\pi} \frac{d\xi}{2\pi} g(k_{nm}; x, x') A_n^2 \psi_n(-\xi; y) \psi_n(\xi; y') \times C_m^2 \sin(k_n z + \delta_{0m}) \sin(k_n z' + \delta_{0m}); \quad (\text{A.1})$$

where $g(k; x, x')$ is the one-dimensional Green's function for the Kronig–Penney potential $V(x) = \sum_n (\hbar^2 S/2m) \delta(x - nd)$, that is

$$g(k; x, x') = \sum_{n=1}^{\infty} \int_0^{2\pi} \frac{d\xi}{2\pi} \frac{A_n^2 \psi_n(-\xi; x) \psi_n(\xi; x')}{k^2 - k_{\xi,n}^2}; \quad (\text{A.2})$$

with $\psi_n(\xi; x)$ being the un-normalized wave function for the same potential equation (17). The normalization constant A_n is given by Eq. (23). Also $k_{\xi,n}$ is given by (25).

It is known that these wave functions form an orthogonal and complete set

$$\int_{-\infty}^{\infty} A_n A_m \psi_n(-\xi; x) \psi_m(\xi'; x) dx = 2\pi \delta(\xi - \xi') \delta_{n,m}; \quad (\text{A.3})$$

$$\sum_{n=1}^{\infty} \int_0^{2\pi} \frac{d\xi}{2\pi} A_n^2 \psi_n(-\xi; x) \psi_n(\xi; x') = \delta(x - x'). \quad (\text{A.4})$$

Finally, the wave numbers k_{nm} are given by

$$k_{nm} = \sqrt{k_F^2 - k_{\xi,n}^2 - k_m^2}; \quad (\text{A.5})$$

where the meaning of the numbers k_m will be explained presently.

The wave functions that depend on x and y account for the effects of grain boundaries. We describe as follows the effect of roughness at the film's surfaces. First, we assume that the film has thickness t ; so that the range of z is $0 \leq z \leq t$. We suppose, further, that each electron propagates essentially as a free particle in the z -direction, except in the immediate neighborhood of the rough surfaces situated at $z=0$ and $z=t$; where it is scattered in a way described by the respective reflectivity amplitudes A_0 and A_t – and where these amplitudes are chosen in such a way that $A_0 = A_t = 1$ describe the specular scattering produced by a plane potential barrier of infinite strength. Shen et al. [28] have calculated these amplitudes. They are, in the present notation,

$$A_0 = \frac{1 - k_z Q_0}{1 + k_z Q_0}; \quad A_t = \frac{1 - k_z Q_t}{1 + k_z Q_t}; \quad (\text{A.6})$$

where the lengths Q_0 and Q_t are known functions of the respective roughness profiles [28–30,18].

Alternatively, these scattering properties may be represented by phase shifts δ_0 and δ_t , defined in terms of the amplitudes by $A_0 = \exp(2i\delta_0)$ and $A_t = \exp(2i\delta_t)$. In this way, it is found that the eigenfunctions are

$$\phi_m(z) = C_m \sin(k_m z + \delta_{0m}); \quad (\text{A.7})$$

and the energy eigenvalues are determined by

$$k_m t = m\pi - \delta_{0m} - \delta_{tm}; \quad m = 1, 2, \dots \quad (\text{A.8})$$

where δ_{0m} and δ_{tm} are the values taken by δ_0 and δ_t when k_z is replaced by k_m . The normalization constant is found to be

$$C_m^{-2} = \frac{1}{2}(t + \delta_{0m} + \delta_{tm}). \quad (\text{A.9})$$

Here $\delta_{0m} = \partial\delta_0/\partial k_{k=k_m}$ and $\delta_{tm} = \partial\delta_t/\partial k_{k=k_m}$. Finally, it is found that the following completeness and normalization condition are valid:

$$\sum_{n=1}^{\infty} C_n^2 \sin(k_n z + \delta_{0n}) \sin(k_n z' + \delta_{0n}) = \delta(z - z'); \quad (\text{A.10})$$

$$\int_0^t C_n C_m \sin(k_n z + \delta_{0n}) \sin(k_m z + \delta_{0m}) dz = \delta_{n,m}. \quad (\text{A.11})$$

By replacing the appropriate form of Green's function (A.1) into the Kubo formula (6), we find that

$$\sigma = \frac{4e^2}{\pi\hbar} \mathfrak{A}(I_1 - I_2), \quad (\text{A.12})$$

where

$$I_1 = \sum_{m,n,\mu,\nu=1}^{\infty} \int_0^{2\pi} \frac{d\xi d\xi'}{(2\pi)^2} \frac{1}{L} \int_{-L/2}^{L/2} dx dx' \frac{\partial g(k_{nm}; x, x')}{\partial x} \frac{\partial g(k_{\mu\nu}; x', x)}{\partial x'} \times \frac{1}{L} \int_{-L/2}^{L/2} dy dy' A_n^2 A_{\nu}^2 \psi_n(-\xi; y) \psi_{\nu}(\xi'; y) \psi_n(\xi; y') \psi_{\nu}(-\xi'; y') \times \frac{1}{t} \int_0^t dz dz' \phi_m(z) \phi_{\mu}(z) \phi_{\nu}(z') \phi_n(z') \quad (\text{A.13})$$

and

$$I_2 = \sum_{m,n,\mu,\nu=1}^{\infty} \int_0^{2\pi} \frac{d\xi d\xi'}{(2\pi)^2} \frac{1}{L} \int_{-L/2}^{L/2} dx dx' \frac{\partial g(k_{nm}; x, x')}{\partial x} \frac{\partial g(k_{\nu\mu}; x', x)}{\partial x'} \times \frac{1}{L} \int_{-L/2}^{L/2} dy dy' A_n^2 A_{\nu}^2 \psi_n(-\xi; y) \psi_{\nu}(\xi'; y) \psi_n(\xi; y') \psi_{\nu}^*(-\xi'; y') \times \frac{1}{t} \int_0^t dz dz' \phi_m(z) \phi_{\nu}(z) \phi_{\mu}^*(z') \phi_n(z'). \quad (\text{A.14})$$

The orthogonality conditions (A.3) and (A.10) allow a considerable simplification of the integral I_1 . It is readily seen that

$$I_1 = \frac{1}{L^2 t} \sum_{m,n=1}^{\infty} \int_0^{2\pi} \frac{d\xi}{2\pi} \int_{-L/2}^{L/2} dx dx' \frac{\partial g(k_{nm}; x, x')}{\partial x} \frac{\partial g(k_{\mu\nu}; x', x)}{\partial x'} = \frac{1}{4iLt} \sum_{m,n=1}^{\infty} \int_0^{2\pi} \frac{d\xi}{2\pi} \frac{1}{k_{nm} \sin \xi} \left[\left(1 + \frac{S}{2k_{nm}^2 d} \right) \sin(k_{nm} d) - \frac{S}{2k_{nm}} \cos(k_{nm} d) \right]. \quad (\text{A.15})$$

The explicit form of the integral I_2 is much more involved. We find that

$$I_2 = \sum_{m,\mu,n=1}^{\infty} \frac{H_{m,\mu}^2}{4Lt} \int_0^{2\pi} \frac{d\xi}{2\pi} \int_{-L/2}^{L/2} dx dx' \frac{\partial g(k_{nm}; x, x')}{\partial x} \frac{\partial g^*(k_{\mu\nu}; x', x)}{\partial x'}, \quad (\text{A.16})$$

where

$$H_{m,\mu} = C_m C_{\mu}^* \left\{ \frac{\sin[(k_m - k_{\mu}^*)t + \delta_{0,m} - \delta_{\mu}^*] - \sin(\delta_{0,m} - \delta_{\mu}^*)}{k_m - k_{\mu}^*} - \frac{\sin[(k_m + k_{\mu}^*)t + \delta_{0,m} + \delta_{\mu}^*] - \sin(\delta_{0,m} + \delta_{\mu}^*)}{k_m + k_{\mu}^*} \right\} \quad (\text{A.17})$$

It is interesting to calculate the last factor of (A.16) in detail. It is seen that

$$\begin{aligned} & \frac{1}{L} \int_{-L/2}^{L/2} dx dx' \frac{\partial g(k; x, x')}{\partial x} \frac{\partial g^*(q; x', x)}{\partial x'} \\ &= \frac{1}{D_k D_q^* L} \int_{-L/2}^{L/2} dx \left\{ f_{kq}^{(+)*}(x) \int_{-L/2}^x f_{kq}^{(-)}(x') \right. \\ & \quad \left. x dx' + f_{kq}^{(-)*}(x) \int_x^{L/2} f_{kq}^{(+)}(x') dx' \right\} \end{aligned} \quad (\text{A.18})$$

where

$$f_{kq}^{(\pm)}(x) = \psi(\pm \xi_k; x) \frac{\partial \psi^*(\pm \xi_q; x)}{\partial x} = \frac{1}{2} \left[\frac{dF_{kq}^{(\pm)}(x)}{dx} + W_{kq}^{(\pm)}(x) \right], \quad (\text{A.19})$$

where

$$F_{kq}^{(\pm)}(x) = \psi(\pm \xi_k; x) \psi^*(\pm \xi_q; x) \quad (\text{A.20})$$

and

$$W_{kq}^{(\pm)}(x) = W\{\psi(\pm \xi_k; x), \psi^*(\pm \xi_q; x)\}; \quad (\text{A.21})$$

and where $W\{f(x), g(x)\} = f(x) dg(x)/dx - g(x) df(x)/dx$ denotes the Wronskian of f and g . It is seen that

$$F_{kq}^{(\pm)*}(x) = F_{kq}^{(\pm)}(x), \quad W_{kq}^{(\pm)*}(x) = -W_{kq}^{(\pm)}(x). \quad (\text{A.22})$$

If we neglect terms of order L^{-1} , we find that

$$\begin{aligned} & \frac{1}{L} \int_{-L/2}^{L/2} dx dx' \frac{\partial g(k; x, x')}{\partial x} \frac{\partial g^*(q; x', x)}{\partial x'} \\ &= \frac{1}{4D_k D_q^* L} \int_{-L/2}^{L/2} dx [W\{F_{kq}^{(-)}(x), F_{kq}^{(+)}(x)\} - W\{Z_{kq}^{(-)}(x), Z_{kq}^{(+)}(x)\}], \end{aligned} \quad (\text{A.23})$$

where $Z_{kq}^{(\pm)}$ is any function such that

$$\frac{dZ_{kq}^{(\pm)}(x)}{dx} = W_{kq}^{(\pm)}(x). \quad (\text{A.24})$$

The first integral gives

$$\begin{aligned} & \frac{1}{4D_k D_q^* L} \int_{-L/2}^{L/2} W\{F_{kq}^{(-)}(x), F_{kq}^{(+)}(x)\} dx, \\ &= \frac{1}{4D_k d} \int_0^d \psi(-\xi_k; x) \psi(\xi_k; x) \\ & \quad dx + \frac{1}{4D_q^* d} \int_0^d \psi^*(-\xi_q; x) \psi^*(\xi_q; x) dx. \end{aligned} \quad (\text{A.25})$$

The integrand of the second integral also is periodic with period d . Thus

$$\begin{aligned} & -\frac{1}{4D_k D_q^* L} \int_{-L/2}^{L/2} W\{Z_{kq}^{(-)}(x), Z_{kq}^{(+)}(x)\} dx \\ &= -\frac{1}{4D_k D_q^* d} \int_0^d W\{z_{kq}^{(-)}(x), z_{kq}^{(+)}(x)\} dx, \end{aligned} \quad (\text{A.26})$$

with

$$\begin{aligned} z_{kq}^{(\pm)}(x) &= \frac{1}{2} \left\{ \frac{k-q^*}{k+q^*} \cos(k+q^*)(x-d) - \frac{k+q^*}{k-q^*} \cos(k-q^*)(x-d) \right. \\ & \quad \left. + e^{\pm i(\xi_k - \xi_q)} \left[\frac{k-q^*}{k+q^*} \cos(k+q^*)x - \frac{k+q^*}{k-q^*} \cos(k-q^*)x \right] \right. \\ & \quad \left. - e^{\mp i\xi_q} \left[\frac{k-q^*}{k+q^*} \cos[(k+q^*)x - kd] - \frac{k+q^*}{k-q^*} \cos[(k-q^*)x - kd] \right] \right. \\ & \quad \left. - e^{\pm i\xi_k} \left[\frac{k-q^*}{k+q^*} \cos[(k+q^*)x - q^*d] - \frac{k+q^*}{k-q^*} \cos[(k-q^*)x + q^*d] \right] \right\} \end{aligned} \quad (\text{A.27})$$

The Wronskian $W\{z_{kq}^{(-)}(x), z_{kq}^{(+)}(x)\}$ and the integral over x can be readily calculated by hand. The result is

$$\begin{aligned} & -\frac{1}{4D_k D_q^* L} \int_{-L/2}^{L/2} W\{z_{kq}^{(-)}(x), z_{kq}^{(+)}(x)\} dx \\ &= \frac{i}{4D_k D_q^* d} \{w_1 \sin(\xi_k + \xi_q^*) + w_2 \sin(\xi_k - \xi_q^*) - w_3(k, q^*) \\ & \quad \sin \xi_k + w_3(q^*, k) \sin \xi_q^*\}, \end{aligned} \quad (\text{A.28})$$

where

$$\begin{aligned} w_1 &= \frac{d}{2} \left\{ \frac{(k-q^*)^2}{k+q^*} \sin[(k-q^*)d] + \frac{(k+q^*)^2}{k-q^*} \sin[(k+q^*)d] \right\} \\ & \quad + \left(\frac{q^*}{k} - \frac{k}{q^*} \right) \sin(kd) \sin(q^*d); \end{aligned} \quad (\text{A.29})$$

$$\begin{aligned} w_2 &= \frac{d}{2} \left\{ \frac{(k-q^*)^2}{k+q^*} \sin[(k+q^*)d] + \frac{(k+q^*)^2}{k-q^*} \sin[(k-q^*)d] \right\} \\ & \quad - \left(\frac{q^*}{k} + \frac{k}{q^*} \right) \sin(kd) \sin(q^*d); \end{aligned} \quad (\text{A.30})$$

$$\begin{aligned} w_3(k, q^*) &= d \left[\frac{(k-q^*)^2}{k+q^*} + \frac{(k+q^*)^2}{k-q^*} \right] \sin(kd) \\ & \quad - \frac{k}{q^*} \sin(kd) \sin(2q^*d). \end{aligned} \quad (\text{A.31})$$

In the limit of perfectly smooth surfaces, $Q_0 = Q_t = 0$ and Eq. (A.8) simplifies to $k_m = m\pi/t$. Also $H_{m,\mu} = \delta_{m,\mu}$ and only the diagonal terms with $k=q$ occur in Eq. (A.28). It can be seen that, in this case, the conductivity (A.12) reduces to the formula (34).

Appendix B. Localization length

Since the particle propagates freely between successive barriers the wave function, subjected to the potential (35), has the form

$$\psi(x) = \sum_{n=-\infty}^{\infty} \theta_n(x) [A_n^+ e^{ik(x-x_n)} + A_n^- e^{-ik(x-x_n)}]; \quad (\text{B.1})$$

where $\theta_n(x)$ is equal to one if $x_n < x < x_{n+1}$ and zero otherwise. We determine the amplitudes A_n by imposing that the wave function be continuous at each point x_n and that its derivative has a discontinuity of magnitude $S_n \psi(x_n)/ik$ there. This is expressed by the recurrence relation

$$\begin{pmatrix} A_{n+1}^+ \\ A_{n+1}^- \end{pmatrix} = \begin{pmatrix} u_n & v_n^* \\ v_n & u_n^* \end{pmatrix} \begin{pmatrix} A_n^+ \\ A_n^- \end{pmatrix}; \quad \text{or} \\ \begin{pmatrix} A_{n+1}^+ \\ A_{n+1}^- \end{pmatrix} = Q_n \begin{pmatrix} A_n^+ \\ A_n^- \end{pmatrix} \quad (\text{B.2})$$

where

$$u_n = \left(1 + \frac{S_n}{2ik}\right) e^{ikd_n}; \quad v_n = -\frac{S_n}{2ik} e^{ikd_n}; \quad (\text{B.3})$$

and $d_n = x_{n+1} - x_n$.

The wave function of a particle propagating in a definite direction (right to left, or left to right) have amplitudes \tilde{A}_n^+ and \tilde{A}_n^- , respectively. These are obtained by a canonical transformation

$$\begin{pmatrix} \tilde{A}_n^+ \\ \tilde{A}_n^- \end{pmatrix} = P \begin{pmatrix} A_n^+ \\ A_n^- \end{pmatrix}. \quad (\text{B.4})$$

Thus, the recurrence relation is

$$\begin{pmatrix} \tilde{A}_{n+1}^+ \\ \tilde{A}_{n+1}^- \end{pmatrix} = P Q_n P^{-1} \begin{pmatrix} \tilde{A}_n^+ \\ \tilde{A}_n^- \end{pmatrix}. \quad (\text{B.5})$$

The matrix P is such that diagonalizes the unperturbed transfer matrix. Luna-Acosta et al. [27] have shown that

$$P = \begin{pmatrix} |v|\beta_+^{-1} & -iv^*\beta_-^{-1} \\ iv\beta_-^{-1} & |v|\beta_+^{-1} \end{pmatrix}; \quad (\text{B.6})$$

where

$$u = \left(1 + \frac{S}{2ik}\right) e^{ikd}; \quad v = -\frac{S}{2ik} e^{ikd}; \quad (\text{B.7})$$

$$\beta_{\pm}^2 = 2\sqrt{1 - u_R^2} [u_I \mp \sqrt{1 - u_R^2}] = 2\sin\xi [u_I \mp \sin\xi]. \quad (\text{B.8})$$

and u_R , u_I , v_R , v_I denote the real and imaginary parts of u and v , respectively.

We now set $S_n = S(1 + s_n)$ and $d_n = d + \Delta_n$; and expand u_n and v_n up to second order on the small departures s_n and Δ_n from perfect periodicity. We find that

$$u_n = u(1 + ik\Delta_n - \frac{1}{2}k^2\Delta_n^2) - s_n v(1 + ik\Delta_n); \\ v_n = v(1 + ik\Delta_n - \frac{1}{2}k^2\Delta_n^2) + s_n v(1 + ik\Delta_n).$$

Thus,

$$P Q_n P^{-1} = \begin{pmatrix} 1 - \frac{1}{2}k^2\Delta_n^2 & e^{i\xi} & 0 \\ 0 & e^{-i\xi} & 0 \end{pmatrix} \\ + i \frac{k\Delta_n}{\sin\xi} \begin{pmatrix} u_I e^{i\xi} & iv^* e^{i\xi} \\ ive^{-i\xi} & -u_I e^{-i\xi} \end{pmatrix} \\ + \frac{s_n}{\sin\xi} \begin{pmatrix} iv_R e^{i\xi} & v^* \sin kd \\ v \sin kd & -iv_R e^{-i\xi} \end{pmatrix} \\ + \frac{ks_n}{\sin\xi} \Delta_n \begin{pmatrix} -iu_I v_R + v_I \sin\xi & v^*(v_R - i \sin\xi) \\ v(v_R + i \sin\xi) & iu_I v_R + v_I \sin\xi \end{pmatrix}. \quad (\text{B.9})$$

If we define $A_n^{\pm} = R_n e^{\pm i\theta_n}$, and use (B.5) keeping terms up to second order in the small quantities $k\Delta_n$ and s_n , we find that

$$\ln \left(\frac{R_{n+1}^2}{R_n^2} \right) = \frac{2}{\sin\xi} [-k\Delta_n \Re(v e^{2i\theta_n}) + s_n \sin(kd) \Re(v e^{i(\xi+2\theta_n)})] \\ + \frac{1}{\sin^2\xi} \{ k^2\Delta_n^2 [u_I^2 + |v|^2 - 2\Re(v e^{2i\theta_n})^2] \\ + s_n^2 [v_R^2 + |v|^2 \sin^2 kd + 2v_R \sin(kd) \Re(ive^{i(\xi+2\theta_n)}) \\ - 2\sin^2(kd) \Re(v e^{i(\xi+2\theta_n)})^2] \\ + 2k\Delta_n s_n [\sin\xi \Re(v(v_R + i \sin\xi) e^{i(\xi+2\theta_n)}) + u_I v_R \\ + u_I \sin(kd) \Re(ive^{2i\theta_n}) \\ - |v|^2 \sin(kd) \cos\xi + 2\sin(kd) \Re(v e^{2i\theta_n}) \\ \Re(v e^{i(\xi+2\theta_n)})] \}. \quad (\text{B.10})$$

We calculate now the double average $\langle ab \rangle$ over the random departures from perfect periodicity s_n and Δ_n and \overline{ab} over the rapidly changing phase θ_n . We perform the first by using (36). In order to do the average over the random phases we assume – as usual in a first approximation in cases of spatially uncorrelated weak disorder – that the underlying probability distribution is uniform [27]. Thus, for instance,

$$\overline{\Re(v e^{2i\theta_n})} = 0;$$

but

$$\overline{[\Re(v e^{2i\theta_n})]^2} = \frac{1}{2}|v|^2.$$

Proceeding in this way, we find that

$$\left\langle \ln \left(\frac{R_{n+1}}{R_n} \right)^2 \right\rangle = \frac{1}{\sin^2\xi} (k^2\Delta^2 u_I^2 + s^2 v_R^2 + 2k\chi u_I v_R). \quad (\text{B.11})$$

The localization length L_{loc} is given by [27]

$$L_{loc}^{-1} = \frac{1}{2d} \left\langle \ln \left(\frac{R_{n+1}}{R_n} \right)^2 \right\rangle. \quad (\text{B.12})$$

Finally, the rescaled localization length l_{loc} is [27]

$$l_{loc}^{-1} = L/L_{loc}. \quad (\text{B.13})$$

The explicit form of this formula is Eq. (39).

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