Boundary Conditions for Electron Distributions at Crystal Surfaces

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(Received 12 August 1965)

We derive a boundary condition (b.c.), differing significantly from the well-known Fuchs' b.c., for the distribution function for conduction electrons at a crystal surface. The new b.c. reduces to the simple Fuchs' form under physical conditions which are not fulfilled in certain important cases. The Fuchs' reflectivity parameter is shown to differ in physical significance and in magnitude from the kinetic specularity, with which it is commonly associated. The connection between the b.c. and surface-scattering models is clarified.

I. INTRODUCTION

THE effect of a physical surface on electron transport in metals and semiconductors is usually treated[1] by assuming Fuchs' simple boundary condition (b.c.)[2] on the distribution function $f=f_e+f_1$ at the surface:

$$f_1(\mu_+,\phi_+)=p(\mu_+,\phi_+)f_1(-\mu_+,\phi_+);\quad 0\leq p\leq 1\,, \quad (1)$$

where μ_+,ϕ_+ are the angular coordinates of an electron leaving the surface $z=0$ ($\mu=\cos(\mathbf{k},z)$, $\cos\phi=k_x/(k^2-k_z^2)^{1/2}$), and where p is a parameter which interpolates between the assumption of complete specularity, $p=1$, and complete diffuseness, $p=0$. It has commonly been considered that p is simply the probability that an electron undergo a specular reflection without scattering.

There does not seem to be in the literature,[3] however, any critical discussion of how such a b.c. might arise, and when it would need revision. Furthermore, a derivation of the correct b.c. is needed in order to make clear the connection with specific scattering mechanisms. We, therefore, derive a b.c. for f_1 valid for a wide class of metal, semimetal, and semiconductor surfaces. The new b.c. has an integral form which reduces to the simple Fuchs' form only in certain cases: e.g., for metal surfaces, but not for strong accumulation layers at semiconductor surfaces. When the Fuchs' form is valid, the reflectivity parameter p can be expressed in terms of scattering probabilities, and is shown to be physically and numerically distinct from the kinetic probability W_0 of specular reflection. The status of the Fuchs' reflectivity p for different kinds of surface scattering is discussed.

II. NEW SURFACE-SCATTERING BOUNDARY CONDITION

We will assume that each electron striking the surface with direction $\mu_-\phi_-$, say, immediately leaves the surface within some range of direction $d\mu_+d\phi_+$, with probability $w(\mu_-,\phi_-|\mu_+\phi_+)d\mu_+d\phi_+$. There are $v\mu_+f(\mu_+\phi_+)$ electrons leaving the surface in direction $\mu_+\phi_+$ (v=velocity, and we are assuming a scalar electron mass). The conservation of these electrons is expressed by

$$\mu_+f(\mu_+\phi_+)=\int_{-1}^{0}d\mu_-\int_0^{2\pi}d\phi_-(-\mu_-f(\mu_-\phi_-))\times w(\mu_-,\phi_-|\mu_+,\phi_+)\,, \quad (2)$$

assuming elastic processes only at the surface. Since (2) must hold for thermodynamic equilibrium also, one has (if $|f_1|\ll|f_e|$)

$$f_1(\mu_+\phi_+)=\int_{-1}^{0}d\mu_-\int_0^{2\pi}d\phi_-\left(\frac{-\mu_-}{\mu_+}\right)\times\{f_1(\mu_-\phi_-)w_e(-|+)+f_e(\mu_-\phi_-)(w-w_e)\}\,, \quad (3)$$

$$1=\int_{-1}^{0}d\mu_-\int_0^{2\pi}d\phi_-(-\mu_-/\mu_+)w_e(-|+)\,. \quad (4)$$

Since w is a probability, one must also have

$$1=\int_0^1 d\mu_+\int_0^{2\pi}d\phi_+ w(-|+)\,. \quad (5)$$

These equations were given by Moliner and Simons[4,5] without, however, any distinction being made between w and its equilibrium form w_e [see Eq. (8) below]. The same authors have also proposed a [4,5] relation based on microscopic reversibility and symmetry considerations which, in our notation, is

$$-\mu_-w_e(\mu_-\phi_-|\mu_+\phi_+)=\mu_+w_e(-\mu_+,\pi+\phi_+|-\mu_-,\pi+\phi_-)\,, \quad (6)$$

and which can be used to simplify some of the relations given below.

Let us now consider the kinetics of electrons at surfaces a little more closely. Some of the electrons leaving the surface in direction $\mu_+\phi_+$ have been specularly re-

[1] R. F. Greene, Surface Sci. **2**, 101 (1964).
[2] K. Fuchs, Proc. Cambridge Phil. Soc. **34**, 100 (1938).
[3] Ziman gives an equation [Ziman, Ref. 7, (Eq. 11.2.6)] similar to (2), but this subsequent development of (1) appears incorrect to us. Ziman's treatment of p is concerned with physical roughness, while ours is concerned with surfaces whose scale of roughness is smaller than the electron wavelength.
[4] F. G. Moliner and S. Simons, Proc. Cambridge Phil. Soc. **53**, 848 (1957).
[5] S. Simons, Phil. Trans. Roy. Soc. London **253A**, 1024, 137 (1961).

flected from the "image direction" $-\mu_+\phi_+$ with some finite probability W_0, which we may call the kinetic specularity. There must be a corresponding singularity in w:

$$w(\mu_-\phi_-|\mu_+\phi_+)=W_0(\mu_+\phi_+)\delta(\mu_-+\mu_-)\delta(\phi_--\phi_+)+(1-f(\mu_+\phi_+))w_s(\mu_-\phi_-|\mu_+\phi_+), \quad (7a)$$

$$0\leq W_0\leq 1. \quad (7b)$$

Here w_s describes scattering processes, which should disappear at $T=0°$K for ideal surfaces, and $(1-f)$ accounts roughly for the exclusion principle. No $(1-f)$ factor accompanies W_0 explicitly, because this term does not describe transitions into possibly filled states. Of course, the normalization condition (4) will impose exclusion-principle effects implicitly on W_0.

The idea underlying (7) is that the unperturbed electron states of a crystal with an ideal physical surface, composed of a crystallographic plane, are really standing-wave states: suitably phased combinations of incident and specularly reflected Bloch waves $|\mathbf{k}\rangle$ and $|\hat{k}\rangle$. Scattering mechanisms provide perturbations which induce transitions, described by w_s, but do not, in general, completely randomize the relative phase of $|\mathbf{k}\rangle$ and $|\hat{k}\rangle$. Therefore, the W_0 term is, in general, present. [A discussion of the development of (7) from a specific surface-scattering model will be given in a forthcoming publication.[6]]

We can apply (7) to (3) and (4), making use of

$$w(\mu_-\phi_-|\mu_+\phi_+)-w_e(\mu_-\phi_-|\mu_+\phi_+)=-f_1(\mu_+\phi_+)w_s(\mu_-\phi_-|\mu_+\phi_+), \quad (8)$$

to get

$$f_1(\mu_+\phi_+)=(1+f_eW_s(\mu_+\phi_+))^{-1}\{W_0(\mu_+\phi_+)f_1(-\mu_+\phi_+)+(1-W_0(\mu_+\phi_+))\langle f_1(\mu_-\phi_-)\rangle\} \quad (9)$$

and

$$1=W_0(\mu_+\phi_+)+(1-f_e)W_s(\mu_+\phi_+), \quad (10)$$

where

$$W_s(\mu_+\phi_+)=\int_{-1}^{0}d\mu_-\int_0^{2\pi}d\phi_- \times(-\mu_-/\mu_+)w_s(\mu_-\phi_-|\mu_+\phi_+), \quad (11)$$

and

$$\langle f_1(\mu_-\phi_-)\rangle\equiv W_s(\mu_+\phi_+)^{-1}\times\int_{-1}^{0}d\mu_-\int_0^{2\pi}d\phi_-\left(\frac{-\mu_-}{\mu_+}\right)w_s(-|+)f_1(\mu_-\phi_-). \quad (12)$$

(Note that our convention is to label p, W_0, and W_s with the direction of the *rebounding* electron.) We regard (9), together with (10), (11), and (12), as the basic boundary condition to be used with the Boltzmann equation to describe electron transport near a surface. The two terms on the right-hand side of (9) represent, of course, the two contributions to the outgoing flux in a particular direction: the particles provided by specular reflection, and the particles provided by scattering processes from all incident directions.

It may be noted that (6) now becomes

$$-\mu_-w_s(\mu_-\phi_-|\mu_+\phi_+)=\mu_+w_s(-\mu_+,\pi+\phi_+|-\mu_-,\pi+\phi_-), \quad (13a)$$

using the symmetry condition

$$W_0(\mu_+\phi_+)=W_0(\mu_+,\pi+\phi_+) \quad (13b)$$

which appears to be implicit in the derivation also of (6).

III. RELATION TO FUCHS' BOUNDARY CONDITION: REFLECTIVITY AND SPECULARITY

The new b.c. (9) has a rather complicated form. Worse than that, it has to be reevaluated for each distinct surface transport problem because each array of external fields produces its own distinct incident distribution function. Thus, there is really no single Fuchs' reflectivity p which characterizes a surface precisely for all surface transport phenomena. We shall see, however, that the Fuchs' b.c. does result from a certain approximation.

Specifically, the Fuchs' form (1) is regained from the general form (9) to the extent that the incident distribution function may be approximated by

$$f_1{}^0=g(v^2)\cos\phi_-(1-\mu_-{}^2)^{1/2}. \quad (14)$$

This is exactly the form of the bulk solution[7]

$$e\tau\mathbf{p}\cdot\mathbf{E}(\partial f_0/\partial e)$$

of the Boltzmann equation in the relaxation time approximation, and in the absence of a magnetic field. It is also the exact form[8] of $f_1(\mu_-\phi_-)$ at a surface where, in addition, the bands are flat, and the bulk relaxation time is used right up to the surface. (Under these conditions the Boltzmann equation has a single space derivation so $f_1(\mu_-\phi_-)$ is obtained by integrating from the bulk toward the surface.[8] These incident electrons, one might say, are still "unaware" of the surface and still have a bulk distribution.) On the other hand, $f_1(\mu_-\phi_-)$ usually does not have the simple form $f_1{}^0$: e.g., when there is a magnetic field,[9] when the bands are not flat,[8] and when the surface-scattering process affects the bulk scattering rate of the incident electrons.[10–12]

If we approximate $f_1(\mu_-\phi_-)$ by $f_1{}^0$, and note that w_s

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[6] R. F. Greene and R. W. O'Donnell (to be published).

[7] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960).

[8] R. F. Greene, D. R. Frankl, and J. N. Zemel, Phys. Rev. **118**, 967 (1960).

[9] E. H. Sondheimer, Advan. Physics **1**, 1 (1952).

[10] F. S. Ham and D. C. Mattis, University of Illinois Technical Report No. 4, 1955 (unpublished).

[11] M. J. Baines, Proc. Cambridge Phil. Soc. **57**, 606 (1960).

[12] F. J. Blatt and H. G. Satz, Helv. Phys. Acta **33**, 1007 (1960).

must be an even function of $\Delta\phi=\phi_- - \phi_+$, then (9) reduces to the Fuchs' form (1), with

$$p(\mu_+\phi_+)=(1+f_eW_s)^{-1}\{1-(1-W_0)\times\langle 1-\cos\Delta\phi(1-\mu_-^2)^{1/2}/(1-\mu_+^2)^{1/2}\rangle\}. \quad (15)$$

This we regard as the best form for the reflectivity p in terms of the specularity W_0. Clearly, p and W_0 are physically distinct, and the distinction comes primarily from the extra weighting factor $(1-\cos\Delta\phi\sqrt{\cdots})$, which causes low-angle scattering events (measured from the specular direction) to contribute relatively little to p.

Scattering by localized surface charges[6] produces, e.g., mostly small-angle scattering events, so that w_s is appreciable only for small values of $\Delta\phi$ and of $\Delta\mu=\mu_-+\mu_+=\Delta\cos\theta$. Then

$$p=(1+f_eW_s)^{-1}\left\{1-(1-f_e)\int d\Delta\mu \times\int\frac{d\Delta\phi w_s(-|+)(\Delta\phi^2+3\Delta\theta^2)}{2}\right\}, \quad (16a)$$

$$W_0=1-(1-f_s)\int d\Delta\mu\int d\Delta\phi w_s(-|+). \quad (16b)$$

The weight factor in (16a) is reminiscent of the $(1-\cos\xi)\sim\frac{1}{2}\xi^2$ weight factor which is important for the bulk momentum relaxation time against charged impurity scattering. There, for a somewhat different reason, small-angle scattering events are also low-weighted.

As a further example, we may consider the case of scattering which is isotropic with respect to the exit direction. Then p and W_0 are equal, provided that the statistics are nondegenerate. Then we find, using (13), (10), and (15),

$$W_0(\mu_+\phi_+)=1-(1-f_e)2\pi w_s(-\mu_+,\pi+\phi_+|\cdots), \quad (17a)$$

$$p(\mu_+\phi_+)=(1+f_eW_s)^{-1}W_0(\mu_+\phi_+). \quad (17b)$$

IV. CONCLUSIONS

A general transport-theory boundary condition, for the electron distribution function at a wide class of crystal surfaces, has been derived from simple considerations of flux conservation and of properties of wave functions at a surface. The new b.c. is of integral form and does not, in general, reduce to the simple familiar Fuchs' b.c. The conditions under which the new b.c. reduces to the Fuchs' form are given and discussed.

The connection of the new b.c. with perturbation-theory treatments of surface scattering is discussed. It is shown that, when the Fuchs' b.c. is valid, the Fuchs' reflectivity parameter p is physically and numerically quite distinct from the kinetic specularity probability W_0, contrary to previous ideas. Comparison of p and W_0 is made for different kinds of surface scattering.

ACKNOWLEDGMENT

It is a pleasure to thank R. W. O'Donnell for many stimulating and valuable discussions of surface scattering.

APPENDIX: WHEN IS $p>W_0$?

In the nondegenerate statistics case, (9) can be written

$$p-W_0=\int_{-1}^{0}d\mu_-\left(\frac{-\mu_-}{+\mu_+}\right)\left(\frac{1-\mu_-^2}{1-\mu_+^2}\right)^{1/2}\times\int_0^{2\pi}d\Delta\phi\cos\Delta\phi w_s(\mu_-,\Delta\phi|\mu_+,\phi_+). \quad (A1)$$

When the medium and the scattering mechanism are isotropic in the plane of the surface

$$w_s(\mu_-,\Delta\phi|\mu_+\phi_+)=w_s(\mu_-,2\pi-\Delta\phi|\mu_+), \quad (A2)$$

so that, after some manipulation,

$$p-W_0=2\int_{-1}^{0}d\mu_-\left(\frac{-\mu_-}{+\mu_+}\right)\left(\frac{1-\mu_-^2}{1-\mu_+^2}\right)^{1/2}\times\int_0^{\pi/2}d\Delta\phi\cos\Delta\phi\{w_s(\mu_-,\Delta\phi|\mu_+)-w_s(\mu_-,\pi-\Delta\phi|\mu_+)\}. \quad (A3)$$

Thus, a sufficient (but not necessary) condition for $p>W_0$ is that $w_s(\mu_-,\Delta\phi|\mu_+)$ decrease monotonically with increasing $\Delta\phi$.