

Comment on “Surface resistivity and vibrational damping in adsorbed layers”

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An analysis [Phys. Rev. B **44**, 3277 (1991)] linking surface resistivity, surface reflectance, adsorbate vibrational damping, and infrared antiabsorption resonances to the scattering of electrons by adsorbates overlooks a crucial distinction between elastic and inelastic scattering. When the proper distinction is made, the relation between resistivity and reflectance is preserved, but the connection to damping and antiabsorption resonances must be significantly modified.

Persson¹ has proposed the original and provocative idea that there is a simple relationship among four apparently disparate phenomena that occur when atoms or small molecules are adsorbed on metal surfaces: (1) an increase in the resistivity of the metal, (2) a reduction in the broadband infrared reflectance of the surface, (3) the damping of hindered translational modes of the adsorbate, and (4) the observation² of an antiabsorption resonance corresponding to the hindered rotation of CO on Cu(100). All four effects are attributed to the diffuse scattering of conduction electrons by the adsorbate. These ideas have been elaborated in a series of additional papers.³⁻⁹ There is considerable experimental and theoretical support for a linkage between electron scattering and the resistivity and reflectance of adsorbate-covered metal surfaces.^{1,10-16} The claim that vibrational damping and antiabsorption resonances are also directly connected to scattering and resistivity is, however, logically distinct and experimentally unverified. Here I point out that the argument for such a connection is incomplete because of the failure to distinguish between elastic and inelastic-scattering events.

The difficulty is the use of an “energy-loss” method for determining the adsorbate’s contribution to the resistivity. Adsorbates on the surface of a metal film induce a resistivity change $\Delta\rho$, and therefore a change ΔP in the power dissipated per unit volume, for a given current density J :

$$\Delta P = J^2 \Delta\rho . \tag{1}$$

Persson’s calculation of $\Delta\rho$ considers only the part of ΔP due to the direct transfer of energy from the electrons to vibrational or electronic excitations of the adsorbate (inelastic scattering). It is well established, however, that the resistivity due to static impurities (such as adsorbates) is dominated by elastic-scattering events, in which the electron energy is unchanged.¹⁷ The Joule heating that accompanies this resistivity occurs mostly in the bulk, via inelastic electron-phonon scattering, *not* by inelastic scattering from the static impurities or adsorbates themselves. (The Appendix gives a simple example to show how elastic scatterers indirectly give rise to Joule heating.) An energy-loss calculation that neglects this indirect heating mechanism reaches the clearly incorrect

conclusion that purely elastic scattering does not contribute to the resistivity.

Reference 1 presents both semiclassical and quantum-mechanical energy-loss calculations of the resistivity; subsequent publications³⁻⁶ emphasize the semiclassical argument, which in its simplest form attributes both Joule heating and vibrational damping to “friction” between the adsorbate and the electrons, analogous to the drag on a body moving through water.^{6,7} I will first summarize the semiclassical argument given in Sec. II of Ref. 1, and then argue that the same assumptions are embedded in the quantum-mechanical argument given in Sec. V.

First, we imagine the substrate and adsorbate at rest, but with a current density $\mathbf{J} = nev$ flowing parallel to the surface, as illustrated in Fig. 1(a). Here, n is the electron density, and v is the drift velocity. The Joule heating power dissipated in a unit volume of the substrate is

$$P_1 = J^2(\rho_0 + \Delta\rho) = (nev)^2(\rho_0 + \Delta\rho) , \tag{2}$$

where ρ_0 is the resistivity of the clean sample and $\Delta\rho$ is the adsorbate-induced increase in resistivity. The power $J^2\Delta\rho = \Delta P$ is the additional Joule heating caused (directly and indirectly) by the adsorbates.

Second, we assume the substrate is at rest, with no current flowing, while the adsorbate is oscillating parallel to the surface (hindered translation) at frequency Ω , as shown in Fig. 1(b). The average power per unit volume transferred from the adsorbate to the electrons is¹

$$P_2 = (n_a/t)\hbar\Omega/\tau_A \tag{3}$$

where n_a is the surface density of adsorbates, t is the thickness of the sample, and τ_A is the damping time of the oscillation.

Finally, we consider this last situation as viewed from a reference frame moving with the adsorbate, as shown in Fig. 1(c). In this frame the electrons have a nonzero average velocity and are therefore said to be equivalent to an oscillating current. Persson argues that the dissipated power can be calculated from Eq. (2) with ρ_0 set to zero, since the electrons are (on average) at rest relative to the substrate. If this argument were correct, the power dissipated per unit volume would be

$$P_3 = (ne\delta x\Omega)^2(\Delta\rho)/2 , \tag{4}$$

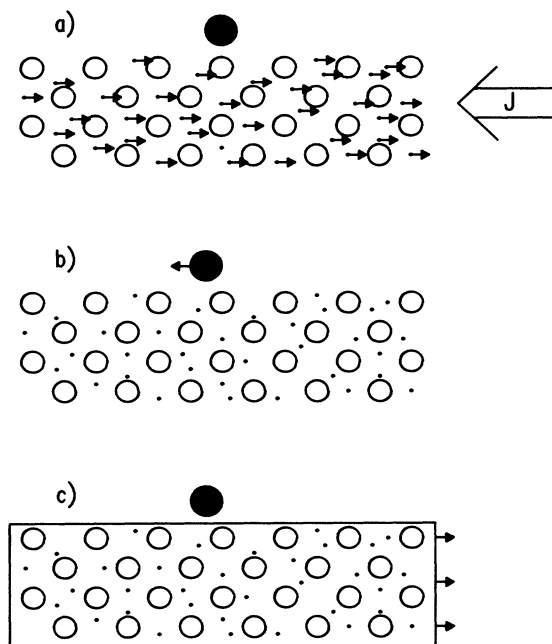


FIG. 1. The three situations used in the derivation of Eq. (5). The open circles represent lattice ions, the filled circle represents the adsorbate, and the small dots represent conduction electrons. (a) The adsorbate is at rest and a current density \mathbf{J} is flowing; the arrows represent the drift velocity of the electrons. (b) No current flows, but the adsorbate is vibrating parallel to the surface. The arrow represents the instantaneous velocity of the adsorbate. (c) The same situation as (b), but viewed from the frame of reference of the adsorbate; the electrons and lattice are moving together relative to the adsorbate.

where $\delta x = (2\hbar/M\Omega)^{1/2}$ is the amplitude of the adsorbate's motion and M is the mass of the adsorbate.¹ Since this is exactly the same physical situation that resulted in Eq. (3), the power dissipated must be the same. Equating P_2 [Eq. (3)] and P_3 [Eq. (4)], for low adsorbate coverage, leads immediately to a relationship between τ_A and the resistivity

$$\frac{1}{\tau_A} = \frac{n^2 e^2}{M} t \left. \frac{\partial \rho}{\partial n_a} \right|_{n_a=0}. \quad (5)$$

This relation is the basis for most of the proposed applications of surface resistivity.^{1,3-9}

But the situation in Fig. 1(a), in which an electric field and a real current flow are present, is *not* comparable to that in Figs. 1(b) and 1(c), with an oscillating adsorbate and no electric field. In the absence of the field the only source of energy is the vibrational energy of the adsorbate, and the only energy transfer mechanism is direct inelastic electron-adsorbate scattering. With a field present [Fig. 1(a)] the inelastic mechanism remains, but the indirect contribution of elastic electron-adsorbate scattering to bulk Joule heating must also be considered. Because the indirect channel is neglected, Eqs. (4) and (5) are incomplete.

My comments to this point have addressed the semi-

classical argument put forward in Sec. II of Ref. 1; the more complex quantum-mechanical calculation of Sec. V, however, is subject to the same criticisms. The energy-loss method is again used to calculate the power absorbed from an oscillating electric field, and that power is equated with the Joule heating term $J^2 \Delta \rho$ to obtain a generalized form of Eq. (5). Since only transitions *directly* mediated by the adsorbate potential are considered (and indeed the substrate is assumed to be lossless), this calculation, like the semiclassical version, ignores the dominant contribution of elastic scattering to $\Delta \rho$.

A secondary objection is that both the semiclassical and quantum calculations depend upon the assumption that the lattice can be ignored; through the jellium approximation they assume that the change in the electron-scattering probability due to a displacement of the adsorbate is the same as that due to the imposition of a drift velocity on the electrons. Since the dominant adsorbate-electron interaction is assumed to arise from an electronic state near the Fermi level, the width and position of which are likely to be very sensitive to the adsorbate position—but insensitive to the presence of a current—this assumption seems highly questionable.

Since the adsorbate-induced resistivity arises predominantly from elastic scattering, while vibrational damping is related to inelastic scattering, there is not likely to be any simple and general relationship between the two. Nevertheless there will be some correlation; a chemisorbed molecule with orbitals that interact strongly with electrons near the Fermi level is likely to have a large cross section for elastic scattering, and will also exhibit strongly damped vibrations.^{1,18} The correlation between adsorbate electronic structure and $\Delta \rho$ is apparent in Table I of Ref. 1, but does not in itself provide evidence for Eq. (5).

One of the most attractive aspects of the model given in Ref. 1 is that it provides an explanation for the infrared antiabsorption resonance observed for the hindered rotation of CO on Cu(100).² Persson's analysis shows that at the vibrational frequency, the applied field does not excite any direct adsorbate-mediated electronic transitions, so the reflectance is predicted to rise back to its zero-adsorbate value. I have argued, however, that such direct inelastic events are responsible for only a fraction of the adsorbate-induced resistivity change, and therefore of the reflectance change. It is to be expected, therefore, that the effect will be much smaller than predicted. This in fact is what is observed; the amplitude of the resonance is $\sim 16\%$ of the broadband reflectance change.² Possibly this provides some measure of the relative significance of elastic and inelastic scattering for this system.

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APPENDIX

I present here an extremely simple classical model to illustrate how elastic scattering can dominate the resistivity and determine the rate of Joule heating, even though the heating actually occurs in independent inelastic events. The derivation treats the case of fixed electric field E ; the generalization to fixed current density J is straightforward.

Consider charged particles propagating through a medium under the influence of an applied electric field E in the x direction. They can undergo two types of scattering events. Elastic events, which occur at mean intervals τ_{el} , randomize the direction of motion but result in no loss of energy. Inelastic events, which occur at mean intervals τ_{in} , cause the particles to lose all energy acquired from the field since the last inelastic collision. For simplicity, I assume $\tau_{in} \gg \tau_{el}$. This will be the case only for very disordered metals or at very low temperature, but it is not an essential restriction.

Between collisions each particle is uniformly accelerated by the field. The average work done by the field on a particle between two elastic collisions is $\langle W_{el} \rangle = eE \langle \Delta x \rangle$, where $\langle \Delta x \rangle$ is the average distance traveled

in the x direction between the collisions. Since the velocity after each collision is on average zero,

$$\langle \Delta x \rangle = a \langle \tau^2 \rangle / 2 = (eE/m) \tau_{el}^2, \quad (\text{A1})$$

where $a = eE/m$ and I have used the fact that for an exponential distribution $\langle \tau^2 \rangle = 2 \langle \tau \rangle^2$. There are τ_{in}/τ_{el} elastic collisions per inelastic collision, so the average work done on a particle between *inelastic* collisions is

$$\langle W_{in} \rangle = (\tau_{in}/\tau_{el}) \langle W_{el} \rangle = \tau_{in} E^2 (e^2 \tau_{el} / m) \quad (\text{A2})$$

and the power dissipated per unit volume is given by

$$P = n \langle W_{in} \rangle / \tau_{in} = E^2 (n e^2 \tau_{el} / m) = E^2 / \rho, \quad (\text{A3})$$

where n is the carrier density and ρ is the dc resistivity.

While this example is obviously crude, it illustrates the essential point that the rate of *elastic* scattering can determine the resistivity and the rate of Joule heating. Impurities (such as adsorbates) can and do contribute to the resistivity even if there is no direct energy transfer between the impurity and the electrons. This conclusion is not changed if $\tau_{in} < \tau_{el}$; τ_{el} is simply replaced throughout the argument by a total scattering time τ_T , where $\tau_T^{-1} = \tau_{in}^{-1} + \tau_{el}^{-1}$.

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