

Theory of the contribution to sliding friction from electronic excitations in the microbalance experiment

J. B. Sokoloff

Physics Department, Northeastern University, Boston, Massachusetts 02115

(Received 23 January 1995; revised manuscript received 17 April 1995)

The electronic contribution to the force of friction between a physisorbed film of atoms and the metallic substrate on which it is adsorbed in a microbalance experiment is calculated using time-dependent perturbation theory, and estimates of the experimentally observed slip time are made. The van der Waals interaction between an adsorbate and a substrate atom is also estimated. The connection between the adsorbate friction and the adsorbate contribution to the resistivity is also discussed on the basis of the perturbation theory calculations.

I. INTRODUCTION

In several publications, Persson calculated the electronic contribution to the force of friction between a layer of adsorbed atoms and a metallic substrate by making an analogy between the force of friction and the increased electrical resistivity due to this adsorbed layer.¹ This relationship has been questioned by Tobin² and his criticism has been answered by Persson.³ Despite this controversy over the theory of the electronic contribution to sliding friction, recent microbalance measurements of sliding friction support a picture in which the electronic contribution dominates in the case of a metallic substrate.⁴ In these experiments, an atomically smooth metallic layer is deposited on a quartz-crystal oscillator. When this layer is exposed to a gas, molecules are adsorbed on its surface, which are detected by a change in both the frequency and the damping of the oscillator. The observed frequency shift has been used for many years as a standard method to measure the number of molecules adsorbed on the metallic surface. The shift in the damping of the oscillator is used in Ref. 4 and in previous work by that group as a measure of the force of friction exerted on the adsorbate molecules as they slide on the surface. In order to provide additional theoretical support for the dominance of the electronic contribution to the friction in microbalances with metallic substrates, it would be useful to calculate the electronic contribution to the force of friction by a first-principles calculation of the force, due to the creation of excitations of the conduction electrons in the metal by the motion of the adsorbed layer over the metallic surface, using time-dependent perturbation theory. This is the subject of the

present paper. In the case of physisorption, the adsorbed atoms are neutral, and therefore, there is no direct electrostatic interaction or chemical bonding between the atoms and the conduction electrons, but only the van der Waals interaction, which only occurs in higher than first order in perturbation theory. (Xenon may actually be chemisorbed rather than physisorbed.)

II. CALCULATION OF THE SLIP TIME DUE TO THE van der WAALS INTERACTION

As a start, let us calculate the rate of energy absorption by the conduction electrons caused by an adsorbed hydrogen atom, because the energy levels and wave functions are exactly known for hydrogen. This result will then be used to estimate the rate of energy absorption for the rare-gas atoms, which were used in the microbalance experiment. Once the rate of energy absorption dE/dt is known, the force of friction f can be found from the relationship $f v = dE/dt$, where v is the velocity with which the adsorbed atoms are sliding on the surface. The conduction electrons in the metallic surface are modeled by a jellium model with a sharp cutoff at the surface, as a first approximation to the actual surface. The perturbation H' , which produces the energy absorption, is

$$H' = e^2 / |\mathbf{r} - \mathbf{r}_e - \mathbf{v}t| - e^2 / |\mathbf{r} - \mathbf{v}t|, \quad (1)$$

where \mathbf{r}_e is the location of the electron on the hydrogen atom, \mathbf{r} is the location of an electron in the metal (both relative to the nucleus), and e is the electronic charge. Using standard second-order time-dependent perturbation theory,⁵ we obtain

$$dE/dt = (2\pi/\hbar) \sum_{\mathbf{k}_f, \mathbf{k}_i} \left| \sum_{\mathbf{k}_I} \sum_{n=2}^{\infty} \frac{M_{\mathbf{k}_f, \mathbf{k}_I}^{0,n} M_{\mathbf{k}_I, \mathbf{k}_i}^{n,0}} {[(2m)^{-1} \hbar^2 k_i^2 - (2m)^{-1} \hbar^2 k_I^2 - (e^2/2a)(n^{-2} - 1)]} \right|^2 \\ \times [(2m)^{-1} \hbar^2 k_f^2 - (2m)^{-1} \hbar^2 k_i^2] [n_{\mathbf{k}_i} - n_{\mathbf{k}_f}] \delta[(2m)^{-1} \hbar^2 k_f^2 - (2m)^{-1} \hbar^2 k_i^2 - \hbar \mathbf{v} \cdot (\mathbf{k}_f - \mathbf{k}_i)], \quad (2)$$

where \mathbf{k}_i , \mathbf{k}_f , \mathbf{k}_I are the initial-, final-, and intermediate-state wave vectors of the conduction electron, a is the Bohr ra-

dius of the hydrogen atom, and $-(e^2/2a)(n^{-2}-1)$ is the difference between an excited atomic state of principle quantum number n and the ground-state hydrogen energy levels. In obtaining Eq. (2), the extreme adiabatic approximation was used for the hydrogen atom electronic wave functions [i.e., if $\phi(\mathbf{r}_e)$ is the wave function of a stationary hydrogen atom, $\phi(\mathbf{r}_e - \mathbf{v}t)$ is taken to be the wave function for one moving with speed \mathbf{v} in the adiabatic approximation]. This is a reasonable approximation, because v is quite small. Here, $n_{\mathbf{k}}$ is the Fermi function of wave vector \mathbf{k} , and the matrix element of the perturbation is given by

$$V^{-1} \int d^3r e^{-i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r} - v \cdot (\mathbf{k}_f - \mathbf{k}_i)t} \int d^3r_e \phi^*(\mathbf{r}_e) H' \phi_0(\mathbf{r}_e) = M_{\mathbf{k}_f, \mathbf{k}_i}^{0, n} e^{-v \cdot (\mathbf{k}_f - \mathbf{k}_i)t},$$

where V is the volume of the crystal. In this calculation, the perturbation H' is time dependent and the quantity $\hbar(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{v}$ in the argument of the δ function in Eq. (2) comes about because H' and the atomic wave functions depend on \mathbf{r} through $\mathbf{r} - \mathbf{v}t$. When we make the change of variables $\mathbf{r}' = \mathbf{r} - \mathbf{v}t$ in the expression for the matrix element, for example, we see that the time dependence of the matrix element is of the form $e^{-i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{v}t}$ (i.e., the matrix element is proportional to this factor), as seen above. When one includes this factor in the derivation of second-order time-dependent perturbation theory,⁵ we find that the argument of the δ function contains the energy $\hbar(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{v}$. We may expand H' to the first order in \mathbf{r}_e to a good approximation. It is found that by the time $(2m)^{-1} \hbar^2 k_f^2 - (2m)^{-1} \hbar^2 k_i^2$ becomes comparable to $(e^2/2a)$, the matrix elements have become quite small, and hence, it is a good approximation to neglect these kinetic-energy differences in the denominator compared to $(e^2/2a)(n^{-2}-1)$. Then, using the completeness of the intermediate conduction-electron states, equation (2) becomes

$$dE/dt = (2\pi/\hbar) \sum_{\mathbf{k}_f, \mathbf{k}_i} \left| V^{-1} \int d^3r e^{-i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r}} (\hbar^2/2m)(k_f^2 - k_i^2) \sum_{n=2}^{\infty} \frac{|M_{0, n}(\mathbf{r})|^2}{(e^2/2a)(n^{-2}-1)} \right|^2 \times \delta[(2m)^{-1} \hbar^2 k_f^2 - (2m)^{-1} \hbar^2 k_i^2 - \hbar \mathbf{v} \cdot \mathbf{K}] [n_{\mathbf{k}_i} - n_{\mathbf{k}_f}], \quad (3)$$

where $M_{0, n}(\mathbf{r}) = \int d^3r_e \phi_n^*(\mathbf{r}_e) [e^2 \mathbf{r} \cdot \mathbf{r}_e / r^2] \phi_0(\mathbf{r}_e)$ and $\mathbf{K} = \mathbf{k}_f - \mathbf{k}_i$. In Merzbacher's book,⁶ it is shown that

$$\sum_n \frac{|\mathbf{r} \cdot \langle n | \mathbf{r}_e | 0 \rangle|^2}{(e^2/2a)(n^{-2}-1)} = -(\frac{9}{4})(ma^4/\hbar^2)r^2.$$

Then, Eq. (3) becomes

$$dE/dt = (2\pi/\hbar)(\frac{9}{2})^2 e^8 (ma^4/\hbar^2)^2 V^{-2} (2\pi)^2 \times \sum_{\mathbf{k}_f, \mathbf{k}_i} n_{\mathbf{k}_i} \left| \int_a^{\infty} dr [\sin(Kr)/Kr^3] \right|^2 \hbar \mathbf{v} \cdot \mathbf{K} \times \delta[(2m)^{-1} \hbar^2 k_f^2 - (2m)^{-1} \hbar^2 k_i^2 - \hbar \mathbf{v} \cdot \mathbf{K}], \quad (4)$$

where $\mathbf{K} = \mathbf{k}_f - \mathbf{k}_i$.

The lower limit of the integral over r was taken to be a because the nucleus of the adsorbed atom must lie outside the region containing the conduction electrons. Here, it was assumed to lie a Bohr radius above the surface of the metal. The largest value of this integral occurs when $Ka \ll 1$, when it becomes $1/a$. For larger values of K , it is much smaller. For example, a numerical integration of this integral gives 0.378 58/ a for $Ka = 1$ and 0.053 867/ a for $Ka = 2$. Then in order to obtain an upper bound to dE/dt , let us set the integral equal to $1/a$ and perform the summations over \mathbf{k}_f and \mathbf{k}_i in Eq. (4) by converting the summations to integrals in the usual way,⁷ to obtain

$$dE/dt = (2\pi/\hbar)(\frac{9}{2})^2 e^8 (ma^4/\hbar^2)^2 (4m^2/\hbar^4) (2\pi)^{-4} a^{-2} \times \frac{mk_i}{\hbar} \int d^3k_i n_{\mathbf{k}_i} k_i [v^2 + (\mathbf{v} \cdot \mathbf{k}_i / k_i)^2], \quad (5)$$

which becomes when the integral over k_i is carried out at zero temperature, where $n_{\mathbf{k}_i}$ is equal to unity for k_i

within the Fermi sphere and zero otherwise,

$$dE/dt = (13.5/\pi) \hbar^{-1} (ma^2/\hbar^2)^3 e^8 k_F^4 m v^2. \quad (6)$$

Since dE/dt is proportional to v^2 and since the force of friction is defined by $f v = dE/dt$, we conclude that f is proportional to v .

Since the adsorbed atoms are many-electron atoms rather than hydrogen, which was used in the present calculations, it is necessary to estimate how these results would be modified if one were to redo the calculations with more realistic many-electron atoms. The perturbation term in this case is given by

$$H' = Z e^2 / |\mathbf{r} - \mathbf{v}t| - e^2 \sum_{j=1}^Z 1 / |\mathbf{r} - \mathbf{r}_j^e - \mathbf{v}t| \approx e^2 \sum_j \mathbf{r}_{ej} \cdot (\mathbf{r} - \mathbf{v}t) / |\mathbf{r} - \mathbf{v}t|^3, \quad (7)$$

where Z is the atomic number. The off-diagonal matrix elements of \mathbf{r}_{ej} cannot be more than a small numerical factor larger in this case than for the hydrogen atom. Although there are now Z electrons rather than only one (for hydrogen) to make transitions to higher-energy states, since most of them are core electrons for which the energy denominator $E_i - E_l$ is very large compared to the values for the hydrogen atom, the overwhelming majority of these transitions will not contribute significantly in Eq. (3). Thus, one can get a rough estimate for the slip time by using dE/dt calculated for hydrogen. Since the equation of motion for the sliding adsorbed atom has the form $M dv/dt = f = -(M/\tau)v$, where τ is defined by $\tau = Mv/f$, where M is the mass of the atom, whose solution is $v = v_0 e^{-t/\tau}$, the slip time τ may be easily calculated from Eq. (6),

$$\tau^{-1} = (13.5/\pi)\hbar^{-1}(ma^2/\hbar^2)^3 e^8 k_F^4 (m/M). \quad (8)$$

Taking $a = 0.5 \times 10^{-8}$ cm, $k_F = 10^8$ cm $^{-1}$, and $M = 10^{-22}$ g (which is the approximate value for the mass of Krypton), we obtain $\tau \approx 10^{-11}$ s. As mentioned earlier, this is a lower bound to τ since the integral over r in Eq. (4) was evaluated for $K=0$, which gives the maximum value of this integral. A more realistic value of Ka would be 1, which gives a value of the integral one order of magnitude smaller, and hence a value for τ a factor of two orders of magnitude larger, i.e., a value for τ of about 10^{-9} s. It is easily shown that if we take K to be nonzero in the integral over r in Eq. (4) and expand to lowest non-vanishing order in v , the result for dE/dt will still be quadratic in v .

Except for extremely low concentrations, the adsorbed atoms will form clusters, rather than individual atoms, on the surface. As we shall see, this could easily increase the slip time over what it would be for individual atoms. Let us assume that the adsorbate atoms form a periodic cluster on the surface. Then the perturbation that they produce is obtained by replacing \mathbf{r} in Eq. (1) by $\mathbf{r} - \mathbf{R}$, where \mathbf{R} is the location of an adsorbate atom nucleus and summing the resulting potential over \mathbf{R} . Similarly, the atomic wave function for the \mathbf{R} th site will have $\mathbf{r}_e - \mathbf{R}$ as its argument. Including only matrix elements between atomic wave functions on the same site as each successive term in the summation over \mathbf{R} in Eq. (1) in the calculation of the matrix elements in Eq. (2), we find that each matrix element will contain a factor $e^{-i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}}$. Then, equations (3) and (4) will be multiplied by the square of the absolute value of the sum of this quantity. Since these expressions must then be summed over \mathbf{R} (i.e., the locations of the various adsorbed atoms), Eqs. (3) and (4), displayed in the text will now be multiplied by a factor $|\sum_{\mathbf{R}} e^{-i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{R}}|^2$. If \mathbf{R} runs over a periodic cluster, this factor will be of order unity unless $\mathbf{k}_f - \mathbf{k}_i$ is equal to a reciprocal-lattice vector of the cluster, when it will be equal to the square of the number of atoms in the cluster. In the calculation of τ in Eq. (8), the mass of a single atom M will now get multiplied by the number of atoms in the cluster, which will increase τ by this number.

III. CALCULATION OF THE CONTRIBUTION TO THE SLIP TIME FROM THE HARD CORE INTERACTION

As pointed out by Persson in his discussion of the damping of surface-atom vibrations,¹ there should also be a contribution to the damping of the motion of surface atoms from the interaction of the conduction electrons with the repulsive hard core of an adsorbate atom. Let us now estimate the magnitude of this contribution to the friction. In order to determine this contribution, let us first determine the t matrix for the scattering of electrons from an infinite spherical repulsive potential by setting the expression for the scattering rate,

$$(2\pi/\hbar) \sum_{\mathbf{k}_j} |T_{\mathbf{k}_f, \mathbf{k}_i}|^2 \delta[(\hbar^2/2m)(k_f^2 - k_i^2)],$$

equal to the product of incident flux of particle, $(k_i/m)/V$, and the total scattering cross section for the hard core,⁹ $4\pi a^2$. The resulting t -matrix magnitude is given by $|T_{\mathbf{k}_i, \mathbf{k}_f}| = 2^{1/2} \pi \hbar^2 a / mV$. In order to calculate the rate of energy loss, due to scattering of the conduction electrons by the hard core of a moving adsorbate atom, let us consider the problem in a coordinate system in which the adsorbate atom is stationary and the metallic substrate is moving. The rate of scattering of electrons is given by

$$(2\pi/\hbar) \sum_{\mathbf{k}_f, \mathbf{k}_i} (n_{\mathbf{k}_i - m\mathbf{v}/\hbar} - n_{\mathbf{k}_f - m\mathbf{v}/\hbar}) |T_{\mathbf{k}_f, \mathbf{k}_i}|^2 \times \delta[(\hbar^2/2m)(k_f^2 - k_i^2)].$$

Transforming to the coordinate system in which the metal is stationary (i.e., letting $\mathbf{k}' = \mathbf{k} - m\mathbf{v}/\hbar$ and substituting for k_i and k_f in terms of k'_i and k'_f), we obtain

$$(2\pi/\hbar) \sum_{\mathbf{k}'_f, \mathbf{k}'_i} (n_{\mathbf{k}'_i} - n_{\mathbf{k}'_f}) |T_{\mathbf{k}'_f, \mathbf{k}'_i}| \delta[(\hbar^2/2m)(k_f'^2 - k_i'^2) - \mathbf{v} \cdot (\mathbf{k}'_f - \mathbf{k}'_i)].$$

In order to obtain an expression for the rate of energy dissipation, due to creation of electronic excitation in the metal, we simply insert the energy change, which occurs in the scattering process $(\hbar^2/2m)(k_f'^2 - k_i'^2)$ in the above summation, giving

$$dE/dt = (2\pi/\hbar) \sum_{\mathbf{k}'_f, \mathbf{k}'_i} (n_{\mathbf{k}'_i} - n_{\mathbf{k}'_f}) |T_{\mathbf{k}'_f, \mathbf{k}'_i}|^2 \times [(\hbar^2/2m)(k_f'^2 - k_i'^2)] \times \delta[(\hbar^2/2m)(k_f'^2 - k_i'^2) - \mathbf{v} \cdot (\mathbf{k}'_f - \mathbf{k}'_i)]. \quad (9)$$

The question that we must now ask is how this contribution compares to that given in Eqs. (3) or (4). Then, we must compare the quantity,

$$\left(\frac{v}{2}\right) (e^4 m a^4 / \hbar^2) (2\pi/V) \int_a^\infty dr \sin(Kr) / Kr^3,$$

from Eq. (4) to $(2)^{1/2} (\pi \hbar^2 / m) (a/V)$ from Eq. (9). The maximum value of this ratio, which occurs when we set $K=0$ in the integral over r , is about 250, implying that the contribution calculated from Eq. (4) dominates. When one takes more realistic values of K , as discussed previously, the two contributions become comparable.

IV. EFFECTS OF METALLIC SCREENING ON THE INTERATOM van der WAALS INTERACTION

In addition to the electronic contribution to the friction, there is expected to be a contribution from the phonon excitations, which are created by the van der Waals interaction between the adsorbate and substrate atoms. In the case of a metallic substrate, the electrostatic in-

teraction between the atoms is screened by the conduction electrons, which will result in a reduced van der Waals interaction. In order to estimate this reduction, let us consider the derivation of the interatomic van der Waals interaction using second-order perturbation theory. Let the screened electrostatic interaction be denoted by $V(|\mathbf{R} + \mathbf{r}_{e1} - \mathbf{r}_{e2}|)$, where \mathbf{R} is the distance between the atomic nuclei, and \mathbf{r}_{e1} and \mathbf{r}_{e2} are the positions of the electrons of atom 1 and atom 2, respectively, relative to their respective nuclei. V can be expanded in \mathbf{r}_{e1} and \mathbf{r}_{e2} . The van der Waals interaction comes from the second-order term in this expansion, because this is the lowest-order term in the expansion, which is able to cause transitions between states on the two atoms simultaneously. This second-order term under consideration is

$$R^{-1} \partial / \partial (R^{-1} \partial V / \partial R) (\mathbf{R} \cdot \mathbf{r}_{e1}) (\mathbf{R} \cdot \mathbf{r}_{e2}) + R^{-1} \partial V / \partial R (\mathbf{r}_{e1} \cdot \mathbf{r}_{e2}). \quad (10)$$

For the sake of obtaining an upper bound on the effect of the screening, we will take the adsorbate atom to lie inside the region containing the conduction electrons, even though we know that it is most likely outside this region. Then using Thomas-Fermi screening $V(R) = e^2 \exp(-k_s R) / R$, where k_s is the inverse Thomas-Fermi screening length, and from Eq. (10), we have for the perturbation

$$e^2 [(3 + 3k_s R + k_s^2 R^2) / R^5 - (1 + k_s R) / R^3] \exp(-k_s R), \quad (11)$$

which for $k_s = 0$, reduces to the dipole-dipole interaction, which is the perturbation, which gives the usual van der Waals interaction in the absence of screening.⁸ Since at metallic densities k_s is of the order of one reciprocal angstrom, this interaction is reduced by about a factor of e and since the van der Waals interaction occurs in second order in perturbation theory, this means that the screening reduces the van der Waals interaction by at most a factor of about 7. Previous estimates show that the van der Waals interaction should be reduced by an order of magnitude.¹⁰ Theoretical treatments of friction due to phonon excitations assume that the free space van der Waals interaction is reduced by the latter factor.¹¹ The present calculations indicate that this factor is reasonable, but the interaction should be a little larger.

V. RELATIONSHIP BETWEEN THE RESISTIVITY DUE TO THE ADSORBATE AND THE FORCE OF FRICTION

In order to complete the discussion, I would now like to discuss the relationship suggested by Persson between the resistivity contribution of the metallic substrate, due to the adsorbed atom and the electronic contribution to the force of friction acting on the adsorbate atoms as they slide over the surface. It was shown by Ziman,¹² on the basis of an approximate solution of the Boltzmann equation, that the effect of an applied dc electric field on the conduction electrons in a metal is to shift the origin of

the distribution of electron wave vectors by $-m\mathbf{v}/\hbar$, where \mathbf{v} is the drift velocity. Therefore, the inverse scattering time for the electrons in the metallic substrate in an applied dc field, due to scattering from a stationary adsorbate atom, is given by

$$\tau^{-1} = (2\pi/\hbar) \sum_{\mathbf{k}_i, \mathbf{k}_f} |M'_{\mathbf{k}_i, \mathbf{k}_f}|^2 (n_{\mathbf{k}_i - (m\mathbf{v}/\hbar)} - n_{\mathbf{k}_f - (m\mathbf{v}/\hbar)}) \times \delta[(\hbar^2/2m)(k_f^2 - k_i^2)], \quad (12)$$

where

$$M'_{\mathbf{k}_i, \mathbf{k}_f} = V^{-1} \int d^3r e^{-i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r}} \times \sum_{n=2}^{\infty} \frac{|M_{0,n}(\mathbf{r})|^2}{(e^2/2a)(n^{-2} - 1)}.$$

If we make the change of variables $\mathbf{k}' = \mathbf{k} - m\mathbf{v}/\hbar$, where \mathbf{k} represents \mathbf{k}_i and \mathbf{k}_f , we obtain

$$\tau^{-1} = (2\pi/\hbar) \sum_{\mathbf{k}'_i, \mathbf{k}'_f} |M'_{\mathbf{k}'_i, \mathbf{k}'_f}|^2 n_{\mathbf{k}'_i} \delta\{(\hbar^2/2m)[(k'_f)^2 - (k'_i)^2] - \hbar\mathbf{v} \cdot \mathbf{K}'\}, \quad (13)$$

which is identical to the inverse of the scattering time for an electron scattering off an adsorbate atom moving with velocity \mathbf{v} over the surface, with no applied dc field. This can easily be seen because the latter quantity is equal to the expression in Eq. (3) with the factor $\hbar\mathbf{K} \cdot \mathbf{v}$ removed from the summation over \mathbf{k}_i , and the resulting expression is identical to Eq. (13). The same expression is obtained when we consider the scattering of the electrons by the adsorbate atom when there is no electric field applied to the metal, but when the metal is viewed from a coordinate system in which the adsorbate is stationary and the metal is moving with velocity \mathbf{v} . In this case, the conduction electron wave functions are given by

$$e^{i\mathbf{k}_i \cdot (\mathbf{r} - \mathbf{v}t)} e^{-i(\hbar\mathbf{k}_i^2/2m)t},$$

which implies that the conduction electron energy changes from $\hbar k_i^2/2m$ to $\hbar k_i^2/2m + \hbar\mathbf{v} \cdot \mathbf{k}_i$, but the electron distribution is still $n_{\mathbf{k}_i}$, since the fact that the metal is moving will not change the electron wave-vector distribution. Then second-order time-dependent perturbation theory will yield an expression identical to Eq. (13). Because of the δ function in Eq. (3), and since $n_{\mathbf{k}_i}$ is an even function of \mathbf{k}_i , we find from Eq. (3) that $dE/dt = mv^2/\tau$, the rate of energy loss for a single electron, which implies that the power lost by the moving adsorbate atom is given by $P = nmv^2/\tau$, where n is the number of electrons per unit volume. The power loss due to Joule heating is given by $P = J^2/\sigma$, where σ is given by $ne^2\tau/m$ in the present model. Combining these, we find $P = nmv^2/\tau$, which seems to support Persson's contention for the case

of a physisorbed atom. This is only an approximate result, however, because expression (13) is not the correct expression for the inverse scattering time for conductivity. Rather, the summation should contain a factor of $1 - \cos\theta$, where θ is the angle between \mathbf{k}_f and \mathbf{k}_i .¹³

ACKNOWLEDGMENTS

I wish to thank the Office of Naval Research for their support during the time that this work was performed. I also wish to thank J. Krim, C. Daly, and R. Tobin for discussions of this work.

¹B. N. J. Persson, *J. Chem. Phys.* **98**, 1695 (1993); *Phys. Rev. B* **44**, 3277 (1991); *Surf. Sci.* **269/270**, 103 (1992).

²R. G. Tobin, *Phys. Rev. B* **48**, 15 468 (1993).

³B. N. J. Persson, *Phys. Rev. B* **48**, 15 471 (1993).

⁴C. Mak, C. Daly, and J. Krim, *Thin Solid Films* **253**, 190 (1994).

⁵E. Merzbacher, *Quantum Mechanics* (Wiley, New York, 1964), pp. 463, 470, 471.

⁶E. Merzbacher, *Quantum Mechanics* (Ref. 5), pp. 384–385.

⁷N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College, Philadelphia, 1976), p. 37.

⁸N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Ref. 7),

p. 393.

⁹A. Messiah, *Quantum Mechanics* (Wiley, New York, 1961), pp. 393–934.

¹⁰L. W. Bruch and J. M. Phillips, *Surf. Sci.* **91**, 1 (1980).

¹¹M. Cieplak, E. D. Smith, and M. O. Robbins, *Surf. Sci.* **265**, 1209 (1994); J. B. Sokoloff, *Phys. Rev. B* **42**, 760 (1990), **42**, 6745(E) (1990).

¹²J. M. Ziman, *Principles of the Theory of Solids*, 2nd ed. (Cambridge University Press, Cambridge, England, 1972), p. 217.

¹³J. M. Ziman, *Principles of the Theory of Solids* (Ref. 12), p. 220.