PHYSICAL REVIEW B VOLUME 61, NUMBER 23 15 JUNE 2000-I

Ohmic damping of center-of-mass oscillations of a molecular monolayer

L. W. Bruch
Department of Physics, University of Wisconsin–Madison, Madison, Wisconsin 53706

(Received 10 January 2000)

The electrostatic moments on the atoms or molecules of a monolayer solid are the source of an electric field with spatial variation determined by the reciprocal-lattice vectors of the monolayer. Center-of-mass oscillations of the monolayer generate an oscillating electric field in a metallic substrate. The contribution of the resulting Ohmic loss to the damping of the oscillation on a normal metal is evaluated for adsorption dipole moments, with parameters for Xe/Ag(111), and for the molecular quadrupole moments in a monolayer herringbone lattice, with parameters for N_2/Pb and N_2/Ag(111). The analysis is very similar to the theory of the anomalous skin effect: the anomalous response arises because the spatial length scale of the driving field is small compared to the mean free path of electrons in the normal metal.

I. INTRODUCTION

In a recent experiment[1] there was an abrupt reduction of the sliding friction of a monolayer of nitrogen adsorbed on lead as the lead became superconducting. This was interpreted as clear evidence for the role of an electronic dissipation channel in the friction. Although that interpretation has been challenged,[2–4] recent modeling[5–7] has shown how the Ohmic heating in the substrate might be sharply reduced even for temperatures only slightly below the superconducting transition. A related experimental observation[1] is that there was no sharp reduction of the sliding friction at the superconducting transition for thin films of neon on the lead, although interpretation of the neon data was complicated by effects of migration of neon in the experimental cell.

At low temperatures, the molecular axes in incommensurate monolayer nitrogen solids are believed to form an orientationally ordered herringbone lattice,[8] with a net electrostatic field arising from the molecular quadrupole moments. On the other hand, the adsorption-induced dipole moments on light inert gas atoms have thus far been undetectably small.[9,10] Thus, the difference in the observations for N_2 and Ne may be related to differences in the electrostatic fields arising from the two adsorbates. The purpose of the present paper is to calculate the Ohmic loss in a normal metal driven by center-of-mass oscillations of a monolayer lattice of static moments. While the corresponding result for dilute adsorbates has been available for some time,[11] the calculation for the monolayer involves a new analysis similar to the calculations of the anomalous skin effect.[12] The distinction between the calculation of dissipation for a localized driving and a distributed coherent driving arises also[3,13] in evaluating the damping of monolayer vibrational modes by creation of substrate phonons.

The organization of this paper is as follows. Section II presents the Ohmic loss calculation for center-of-mass oscillations of a monolayer solid, with details of the Boltzmann equation theory relegated to Appendix A. Section III presents the results of applications to Xe/Ag(111), N_2/Pb, and N_2/Ag(111). In Sec. IV, concluding remarks, there is a discussion of the assumptions in the electrodynamic treatment of the normal metal and of the need for improved structural determinations of the monolayer solids in the sliding friction experiments.

II. OHMIC LOSS CALCULATION

A. Simplifying features

Some simplifying features of the N_2/Pb system enable quite compact forms for the Ohmic loss to be obtained. There are parameter combinations which are either very large or very small. While the values given here are specific to N_2/Pb, the magnitudes are expected to be similar for several other adsorbate and substrate combinations.

The conductivity measured on the 1500-Å-thick Pb film in the quartz-crystal microbalance experiments[1] is $\sigma_0 = 3 \times 10^{18}\ \mathrm{s}^{-1}$ near 10 K. Then the collision time is estimated to be $\tau_c \simeq 9 \times 10^{-14}$ s and the mean free path of electrons at the Fermi energy to be $l \simeq 1600$ Å. The 8-Mhz oscillator frequency gives $\Omega \tau_c < 5 \times 10^{-6}$ so that inertial terms may be neglected in the kinetic equation. The driving fields[14] from the adsorbate electric moments have wave numbers determined by the monolayer reciprocal-lattice vectors, $g \approx 2\ \text{Å}^{-1}$, so that the combination $Z \equiv gl = 3 \times 10^3$ is large. However (Sec. II B), the effective shielding parameter $\lambda = 3\pi\sigma_0/\Omega Z$ remains large (greater than 10^8).

With neglect of the inertial term in the kinetic equation, the electric field $\vec{E}$ and the current density $\vec{j}$ are both divergenceless fields,

$$\nabla \cdot \vec{E} = 0, \tag{2.1}$$

$$\nabla \cdot \vec{j} = 0. \tag{2.2}$$

B. Electrodynamics

Let the monolayer be at a perpendicular distance L_{ov} from the planar boundary of the metal at $z=0$, and choose a Cartesian coordinate system with $\hat{z}$ directed into an infinitely thick metal film. The electrostatic field from a monolayer lattice of electrostatic moments at $z_o = -L_{ov}$ has a lateral $(\vec{r})$

variation given in terms of the vectors of the monolayer reciprocal lattice. The z component of $\vec{E}$ can be written, with $\vec{g}\neq 0$,

$$E_z(\vec{r},z)=\sum_{\vec{g}} E(\vec{g},z)\exp(\imath\vec{g}\cdot\vec{r}), \tag{2.3}$$

while the parallel components, satisfying Eq. (2.1), are

$$\vec{E}_{\parallel}(\vec{r},z)=\sum_{\vec{g}} [\imath\vec{g}/g^2]\exp(\imath\vec{g}\cdot\vec{r})\partial E(\vec{g},z)/\partial z. \tag{2.4}$$

The corresponding decomposition for j_z has amplitudes $J(\vec{g},z)$; the parallel components of $\vec{j}$ are given in analogy to Eq. (2.4).

Specifically, the incident field at the metal from the 2-in herringbone monolayer lattice of quadrupoles has

$$E(\vec{g},z)=-\frac{\pi\theta}{a_c}\exp(-g[z-z_o])\sum_{\beta=1}^{2}\exp(-\imath\vec{g}\cdot\vec{\rho}_\beta)[\vec{g}\cdot\hat{l}_\beta]^2, \tag{2.5}$$

where θ is the molecular quadrupole moment, a_c is the area of the two-molecule unit cell, and the sum is over basis molecules at positions $\vec{\rho}_\beta$ and with unit vectors $\vec{l}_\beta$ for the molecular axis. The corresponding expression for the field component for a triangular lattice of dipoles μ oriented along $-\hat{z}$ is, with $a_c=\sqrt{3}L^2/2$,

$$E(\vec{g},z)=-\frac{2\pi g\mu}{a_c}\exp(-g[z-z_o]). \tag{2.6}$$

If there are driven lateral oscillations of the monolayer as a whole, with angular frequency Ω and vector amplitude $\vec{A}$, the field from the oscillating monolayer is constructed by the replacement

$$\exp(\imath\vec{g}\cdot\vec{r})\rightarrow\exp[\imath\vec{g}\cdot(\vec{r}-\vec{A}\cos\Omega t)] \tag{2.7}$$

in Eqs. (2.3) and (2.4). The time dependence thus is a sum of harmonics $\omega=K\Omega$, with Bessel function coefficients $J_K(\vec{g}\cdot\vec{A})$, and the solution for $E(\vec{g},z)$ is constructed from the Fourier amplitudes $\mathcal{E}(\vec{g},z,\omega)$. These amplitudes are determined by solving the Faraday-Ampere equation, omitting the displacement current,

$$\left[\frac{d^2}{dz^2}-g^2\right]\mathcal{E}=-\frac{\imath 4\pi\omega}{c^2}\mathcal{J}, \tag{2.8}$$

using a similar notation for the Fourier amplitude of the current density. The solution of Eq. (2.8) is treated in the Appendix.

The power dissipated in the metal is the volume integral of $\vec{j}\cdot\vec{E}$ and can be reduced using Eqs. (2.1), (2.2), and (2.8). The time-averaged power per unit area is

$$\mathcal{P}=-\sum_K\sum_{\vec{g}}\frac{1}{g^2}\left[\mathcal{J}^*\frac{\partial\mathcal{E}}{\partial z}+\mathcal{J}\frac{\partial\mathcal{E}^*}{\partial z}\right]\Bigg|_{z=0^+}. \tag{2.9}$$

Under the assumption that a fraction p $[1-p]$ of the conduction electrons are specularly [diffusely] reflected at the $z=0$ interface, the analysis in the Appendix gives, in leading approximation,

$$\mathcal{J}(\vec{g},0^+,\omega)=\sigma_g\mathcal{E}(\vec{g},0^+,\omega),\quad \sigma_g=\frac{3\sigma_0(1-p)}{4gl} \tag{2.10}$$

and

$$\frac{\partial\mathcal{E}}{\partial z}=-g\mathcal{E}\big|_{z=0^+}. \tag{2.11}$$

Then the power per unit area is

$$\mathcal{P}=2\sum_K\sum_{\vec{g}}\frac{\sigma_g}{g}|\mathcal{E}(\vec{g},0^+,K\Omega)|^2. \tag{2.12}$$

The final step is to satisfy the continuity requirements for the incident, reflected, and transmitted fields at $z=0$ and thus to express the field in the metal in terms of the incident field constructed from Eqs. (2.5) and (2.6),

$$\mathcal{E}(0^+)=\mathcal{E}(0^-)\frac{2}{1+\imath\lambda_g/K},\qquad \lambda_g=3\pi\sigma_0(1-p)/[\Omega gl]. \tag{2.13}$$

The resulting expression for the power is, after using Neumann's addition theorem to sum the harmonics,

$$\mathcal{P}=2\sum_{\vec{g}}\frac{\sigma_g}{g\lambda_g^2}|E(\vec{g},0^-)|^2(\vec{g}\cdot\vec{A})^2. \tag{2.14}$$

In Eq. (2.14) many parameters of the adsorbate and substrate combination, such as the electrostatic moments and static conductivity, enter as factors and the summation over $\vec{g}$ is rapidly convergent.

III. APPLICATIONS

The power loss can be characterized by a decay time t_d for the energy of the oscillating monolayer. For the algebraically simpler case of a monatomic triangular lattice of dipoles, with one atom of mass M in the unit cell of area a_c, the decay of the oscillator energy is

$$\frac{d}{dt}\frac{1}{2}M\Omega^2A^2=-a_c\mathcal{P}. \tag{3.1}$$

Using Eq. (2.6) in Eq. (2.14) and the sixfold rotation symmetry of the lattice for one further reduction, the decay time can be evaluated from

$$1/t_d\equiv-\frac{1}{A^2}\frac{dA^2}{dt}=\frac{2\mu^2 l}{3Ma_c\sigma_0(1-p)}\sum_{\vec{g}} g^4\exp(-2gL_{ov}). \tag{3.2}$$

Because of the symmetry of the triangular lattice, t_d is the same for all orientations of $\vec{A}$ relative to the adlayer axes.

For the herringbone lattice with two identical molecules, each of mass M and quadrupole moment θ, in the unit cell of area a_c, the decay time depends on the axis of the oscillation $\hat{A}$ and is written

$$1/t_d(\hat{A}) = \frac{\theta^2 l}{6M\sigma_0(1-p)}\Sigma(\hat{A}), \tag{3.3}$$

where the structural properties of the lattice are contained in the sum

$$\Sigma(\hat{A}) \equiv \frac{1}{a_c}\sum_{\vec{g}} (\vec{g}\cdot\hat{A})^2 \exp(-2gL_{ov}) \times \left|\sum_{\beta=1}^{2} \exp(-\imath\vec{g}\cdot\vec{\rho}_\beta)[\vec{g}\cdot\hat{l}_\beta]^2\right|^2. \tag{3.4}$$

Some typical magnitudes for the moments demonstrate why the quadrupole moment of N_2 is so significant. [10] Molecular quadrupole moments are on the scale of 1×10^{-26} esu cm^2 while a large adsorption dipole moment, as for xenon strongly bound to some metals, is on the scale of 0.5 debye $=0.5\times10^{-18}$ esu cm. Thus, because $g\approx2$ Å^{-1}, the quadrupole factor $(g\theta)^2$ for molecules is much larger than μ^2 for most adatoms. The numerical estimates here show the Ohmic damping is larger for N_2/Pb than for Xe/Ag(111). The electrostatic effects for Ne/Pb should be much smaller than those for N_2/Pb.

As an example of the dipole moment case, consider the Ohmic loss for a monolayer solid of Xe/Ag(111) at 77 K. The Xe/Ag(111) solid is very well-characterized experimentally[9,15,16] and a slip time of ≈2 ns has been measured[17] in sliding friction experiments at 77 K. The static conductivity of bulk Ag at 77 K is $\sigma_0\approx3\times10^{18}$ s^{-1}, giving a collision time $\tau_c=2\times10^{-13}$ s and a mean free path $l=2800$ Å. For a triangular lattice with nearest-neighbor spacing 4.40 Å, the leading reciprocal-lattice vector has magnitude $g=1.65$ Å^{-1} so that $Z=4600$. The dipole moment per atom in the monolayer solid is[16] $\mu=0.2$ debye, reflecting large depolarization effects. The measured[15] Xe-Ag spacing corresponds[18] to $L_{ov}=2.0$ Å. Then, with $p=0$, the estimated decay time for the Ohmic loss mechanism is $t_d=200$ ns, about 10^2 times the observed slip time. Thus this is not an important loss mechanism for the Xe/Ag(111) sliding friction.

The incommensurate monolayer N_2 solid on Ag(111) was shown[19] to be a physically adsorbed system, although herringbone ordering was not observed at the temperatures of the experiments. Calculations[8] indicate the ordering temperature is approximately 20 K, using an effective[20] quadrupole moment of the molecule of $\theta=-1.17\times10^{-26}$ esu cm^2. The herringbone unit cell is rectangular $L_1\hat{x}\times L_2\hat{y}$ and the unit vectors of the molecular axes are denoted $\hat{l}=\cos\chi\hat{x}\pm\sin\chi\hat{y}$. Two cases of the N_2/Ag(111) monolayer herringbone solid at very low temperatures, taken from the model calculations,[8] are treated here: the zero-spreading-pressure lattice which minimizes the free energy of the N_2/Ag(111) model[8] at 10 K [$L_1=7.14$ Å, $L_2=4.50$ Å, $L_{ov}=2.0$ Å, and $\chi=0.96$ radian] and a lattice with a triangular arrangement of the molecular centers of mass and nearest-neighbor spacing comparable to the smallest spacings observed in experiments[19] on N_2/Ag(111) at temperatures above 25 K [$L_1=7.19$ Å, $L_2=4.15$ Å, $L_{ov}=2.0$ Å, and χ=0.84 radian]. For both cases the overlayer height is $L_{ov}=2.0$ Å. Finally, the choice $p=0$ is made, as for the Xe/Ag(111) estimate. To estimate the decay time for Ohmic damping of the ordered layer, the conductivity[21] of silver at 20 K, $\sigma_0\approx2\times10^{20}$ s^{-1}, is used. The average of t_d along the x and y directions then is 6 ns. The only measurements[22] of the slip times of N_2 monolayers on noble metals are at 77 K for a monolayer state which is orientationally disordered and may be a liquid. There, the slip time is approximately 3 ns. That is, the time scale from the Ohmic damping calculation is comparable to experimental data for N_2 taken under very different conditions, suggesting this is a process to be considered in extensions of those experiments.

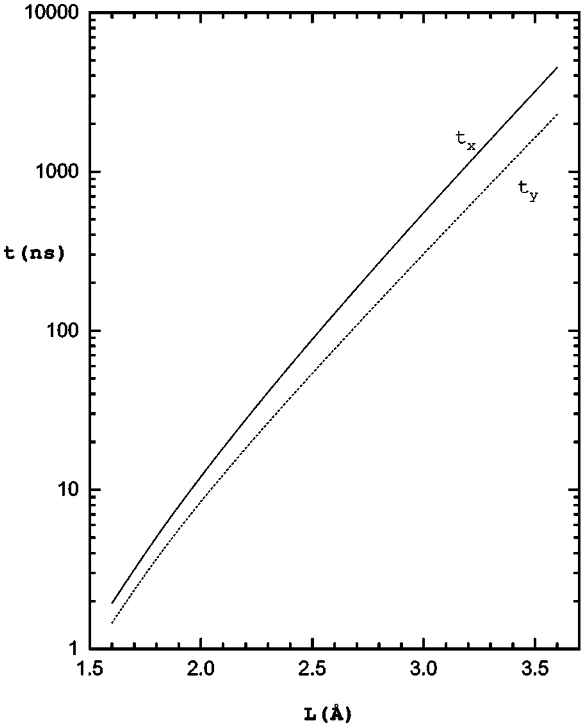

FIG. 1. Ohmic damping time t_d for the oscillating N_2/Pb monolayer solid. The decay time (in ns) defined by Eq. (3.3) of the text is plotted as a function of the distance L_{ov} (in Å) from the monolayer to the electrodynamic edge of the metal for orientations of the oscillation amplitude parallel to the long (t_x) and short (t_y) sides of the herringbone unit cell. Parameters of the calculation are given in Sec. III. The overlayer height expected from calculations for N_2/Ag(111) is $L_{ov}\simeq2.0$ Å. The slip time measured for N_2 on normal Pb near 10 K is (Ref. 1) $t_s\approx10$ ns.

There are no structural measurements for the N_2/Pb monolayer, so the structural parameters for estimating the Ohmic loss rate of N_2/Pb are taken to be those of the N_2/Ag(111) system just discussed. The results for t_d for the first of these cases, with $p=0$ and the minimum free energy structure at 10 K, are shown in Fig. 1 for a range of values of L_{ov} and for two orientations of $\hat{A}$, along $\hat{x}$ and along $\hat{y}$. For L_{ov} in 1.6–3.0 Å, the values of t_d for the two orientations differ by less than a factor of 2. The compressed structure gives very similar results to those shown in the figure. The t_d for the N_2/Ag(111) model are obtained by dividing the times shown in Fig. 1 by a factor 1.7.

It is noteworthy that for values of L_{ov} near the value 2.0 Å used for N_2/Ag(111) the decay times are in the range 2–20 ns and thus are in the range of slip times observed[1] for the N_2/Pb monolayer at about 10 K where the metal is normal. The damping is much reduced, and t_d is much larger, for larger N_2-metal distances. In particular, if there were a 3-Å insulating oxide layer in the N_2/Pb experiments,[1,3] the Ohmic damping time in the normal metal would be longer than 300 ns and hence would be a negligible contribution to the effective slip time measured in the experiments.

IV. CONCLUDING REMARKS

Although the evaluation of the Ohmic damping has used simplifying approximations to a complex electrodynamic problem, the role of this mechanism in frictional losses can be confirmed by comparative studies of adsorbates with qualitatively different electrostatic moments. Molecular nitrogen has some advantages relative to inert-gas adsorbates because the quadrupole moment of the N_2 can be treated as a source external to the metal, while the spatial structure of the adsorption-induced dipole moments on xenon is still not known. Thermal effects on the ordering of the N_2 moment may provide qualitative tests. The N_2 monolayer at 10 K is believed[8] to be quite well ordered and the effect of the mean-square librations of the molecular axes on the net electrostatic field could be evaluated with an extension of methods used[23] for N_2 on graphite. A larger effect is the great reduction of the effective electric field for the orientationally disordered N_2 monolayer above the plastic-crystal phase transition expected[8] to be near 20 K.

In the Appendix the continuum description of the metal response is applied close to plausible limits of validity, using wave vectors of the same magnitude as the Fermi wave number of the metal and assuming a sharp electrodynamic boundary. The present theory does not determine the fraction p of conduction electrons specularly reflected at the surface. Although it was taken to be $p=0$, values in the range 0–0.5 would not disrupt the estimates of this paper. An improved treatment of the substrate electrodynamics, including an account of the surface scattering, will be necessary if comparisons more detailed than orders of magnitude are to be given. The fact that the conduction electron mean free path is close to the metal film thickness [7] does not seem to be a serious complication in the present analysis, and this might be confirmed in a more complete theory.

Thin physisorbed layers of small closed-shell molecules and inert-gas atoms are quite promising subjects for fundamental studies of sliding friction, but quantitative modeling requires much more detailed structural data than are available for most adsorbate and substrate combinations. Properties such as the structure of the monolayer unit cell and the overlayer spacing relative to the metal are required. The energy from the Ohmic damping of the oscillating adlayer is mostly deposited in the first few angstroms of the metal. For cases where it is appreciable more detailed accounts of the electronic structure of the metal surface will be needed. It may be that extensions of the sliding friction experiments with molecular adsorbates will provide significant tests of the application of continuum electrodynamics at surfaces.

ACKNOWLEDGMENTS

It is a pleasure to thank A. V. Chubukov for helpful discussions and J. Krim for providing additional information on her experiments. This work has been partially supported by NSF-DMR9807410.

APPENDIX: KINETIC THEORY

The semiclassical relaxation-time Boltzmann equation for the distribution function $F(\vec{r},\vec{v},t)$ of charges $-|e|$ moving in an electric field $\vec{E}$ is

$$\frac{\partial f}{\partial t} + \vec{v}\cdot\nabla f + [-|e|\vec{E}/m]\cdot\nabla_v f = -\frac{f-f_0}{\tau_c}, \qquad \text{(A1)}$$

where f_0 denotes the equilibrium distribution. This paper treats the case of a degenerate Fermi gas (low temperatures) with spherical Fermi surface and isotropic scattering time τ_c. More complex geometries are included in the theory of the anomalous skin effect.[12]

As it stands, Eq. (A1) assures that the equation of continuity for charge and current density is satisfied. However, the time-derivative term is omitted here, because $\omega\tau_c \ll 1$, so that the driven currents are divergenceless and satisfy Eq. (2.2).

The equation is linearized according to

$$f = f_0 - [-|e| v_F \tau_c \Psi]\partial f_0/\partial\epsilon, \qquad \text{(A2)}$$

where ϵ denotes the single-partial energy, f_0 is approximated as a unit step at the Fermi energy, and v_F is the speed of electrons at the Fermi energy. Then the current density is given in terms of an integral over the solid angle of the Fermi surface by

$$\vec{j}(\vec{r},t) = \frac{3\sigma_0}{4\pi}\int d\Omega\,\hat{n}(\Omega)\Psi(\Omega,\vec{r},t), \quad \sigma_0 = ne^2\tau_c/m, \qquad \text{(A3)}$$

where n is the number density and σ_0 is the static long-wavelength conductivity of the metal.

The linearized Boltzmann equation is, for the amplitudes with space and time variation $\exp[\imath(\vec{g}\cdot\vec{r}-\omega t)]$ and mean free path $l = v_F\tau_c$,

$$\left(1 + l\left[\cos\theta\frac{\partial}{\partial z} + \imath g\sin\theta\cos\phi\right]\right)\Psi(\cos\theta,\phi,z)$$

$$= \cos\theta\,\mathcal{E}(g,z) - (\imath/g)\sin\theta\cos\phi\frac{\partial\mathcal{E}}{\partial z}, \qquad \text{(A4)}$$

where the reference axes of the spherical polar coordinates, polar angle θ, and azimuthal angle ϕ are $\hat{z}$ and $\hat{g}$, respectively. Following the theory of the anomalous skin effect,[12] the boundary condition on Ψ at the surface is taken to be

$$\Psi(|\cos\theta|,\phi,0^+) = p\Psi(-|\cos\theta|,\phi,0^+), \qquad \text{(A5)}$$

where p is the fraction $(0<p<1)$ of incident electrons which are specularly reflected, the remainder $1-p$ being assumed to be diffusely scattered. The field and the current density are related by the Faraday-Ampere equation, Eq. (2.8).

The solution for $0<z<\infty$ is constructed by analogy with a treatment of Reuter and Sondheimer.[12] The semi-infinite slab is replaced by a symmetric infinite slab with discontinuous $\mathcal{E}$ at $z=0$. Then $\mathcal{E}(g,z)$ is an odd function of z, $d\mathcal{E}/dz$ is an even function of z, and the amplitude $\epsilon(q)$ in the Fourier decomposition

$$\mathcal{E}(g,z)=\int_{-\infty}^{\infty}dq\,\epsilon(q)\exp(\imath qgz) \tag{A6}$$

is an odd function of q. The Fourier amplitudes $J(q)$ and $\psi(q)$ are defined by transforms of $\mathcal{J}$ and Ψ analogous to Eq. (A6).

The Fourier transform of Eq. (A4) is, with a large parameter $Z=gl$,

$$\begin{aligned}&[1+\imath Z(q\cos\theta+\sin\theta\cos\phi)]\psi(q,\Omega)\\&\quad+\frac{Z\cos\theta}{2\pi}\{\Psi(-\cos\theta,\phi,0^{+})-\Psi(\cos\theta,\phi,0^{+})\}\\&=(\cos\theta-q\sin\theta\cos\phi)\epsilon(q)-\frac{\imath}{\pi}\sin\theta\cos\phi\,\mathcal{E}(0^{+}),\end{aligned} \tag{A7}$$

while the Faraday-Ampere equation transforms to

$$(q^{2}+1)\epsilon(q)+\frac{\imath q}{\pi}\mathcal{E}(0^{+})=\frac{\imath 4\pi\omega}{g^{2}c^{2}}J(q). \tag{A8}$$

A self-consistency equation obtained from Eq. (A7) is

$$\Psi(\Omega,0^{+})=\int_{-\infty}^{\infty}dq\,\psi(q,\Omega)\exp(\imath q0^{+}), \tag{A9}$$

and for $\cos\theta>0$ this gives

$$\begin{aligned}\Psi(-\cos\theta,\phi,0^{+})=&-\frac{2\imath\tan\theta\cos\phi}{Z}\mathcal{E}(0^{+})\\&+\int_{-\infty}^{\infty}dq\,\epsilon(q)\exp(\imath q0^{+})\\&\times\frac{\cos\theta-q\sin\theta\cos\phi}{1+iZ(q\cos\theta+\sin\theta\cos\phi)}.\end{aligned} \tag{A10}$$

The current density at the surface is obtained by combining Eqs. (A3) and (A10). The solid angle integration simplifies greatly for $Z\gg 1$ and the result for the z component of the current density is

$$\begin{aligned}\mathcal{J}(0^{+})=&\frac{\imath 3\sigma_{0}(1-p)}{4Z}\int_{-\infty}^{\infty}dq\,\epsilon(q)\exp(\imath q0^{+})\\&\times\left[-\frac{\imath\pi}{2\sqrt{1+q^{2}}}+\frac{\ln(\sqrt{1+q^{2}}+q)}{\sqrt{1+q^{2}}}\right].\end{aligned} \tag{A11}$$

The current term $J(q)$ in Eq. (A8) can also be simplified considerably for $Z\gg 1$ and formally Eq. (A8) becomes an integral equation for $\epsilon(q)$. However, the current term then has a very small dimensionless parameter $\Gamma=3\omega\sigma_{0}/g^{2}c^{2}Z$. For the N_2/Pb case, $\Gamma<10^{-14}$ and the electric field calculation reduces to

$$(q^{2}+1)\epsilon(q)+\frac{\imath q}{\pi}E(0^{+})\simeq 0. \tag{A12}$$

Then the electric field at $z>0$ is given by

$$\mathcal{E}(g,z)=\mathcal{E}(g,0^{+})\exp(-gz), \tag{A13}$$

and Eq. (A11) becomes

$$\mathcal{J}(0^{+})=\frac{3\sigma_{0}(1-p)}{4Z}\mathcal{E}(0^{+}). \tag{A14}$$

These are the results used at Eqs. (2.10) and (2.11).

As in the theory of the anomalous skin effect, the combination σ_{0}/l arises because the field changes over distances significantly smaller than the mean free path, here $Z=gl\gg 1$. Although the collision time τ_c cancels from the formalism, there still is dissipation and the free-electron response term in the kinetic equation, proportional to $\omega\tau_c$, remains negligible. However, the length scale associated with g is only a few angstroms so that the validity of two approximations implicit in the skin effect theory is no longer evident: (1) the semiclassical Boltzmann equation may be an inadequate starting point for such large wave vectors, which are on the scale of the Fermi wave number of the metal; (2) the diffuseness of the electron distribution at the metal surface may play a significant role here. The latter effect is also discussed[14,18] as part of the problem of determining the distance L_{ov} of the monolayer from the effective electrodynamic boundary of the metal.

---

[1] A. Dayo, W. Alnasrallah, and J. Krim, Phys. Rev. Lett. **80**, 1690 (1998); A. G. J. V. Dayo, Ph.D. thesis, Northeastern University, 1998.

[2] B. N. J. Persson and E. Tosatti, Surf. Sci. **411**, 855 (1998).

[3] B. N. J. Persson, E. Tosatti, D. Fuhrmann, G. Witte, and Ch. Wöll, Phys. Rev. B **59**, 11 777 (1999).

[4] R. L. Renner, J. E. Rutledge, and P. Taborek, Phys. Rev. Lett. **83**, 1261 (1999); J. Krim, *ibid.* **83**, 1262 (1999).

[5] J. B. Sokoloff, M. S. Tomassone, and A. Widom, Phys. Rev. Lett. **84**, 515 (2000).

[6] T. Novotný and B. Velický, Phys. Rev. Lett. **83**, 4112 (1999).

[7] V. Popov, Pis'ma Zh. Eksp. Teor. Fiz. **69**, 520 (1999) [JETP Lett. **69**, 3277 (1991)].

[8] L. W. Bruch and F. Y. Hansen, Phys. Rev. B **57**, 9285 (1998).

[9] P. Zeppenfeld (unpublished). See also T.-C. Chiang, G. Kaindl, and D. E. Eastman, Solid State Commun. **41**, 661 (1982); Y. C. Chen, J. E. Cunningham, and C. P. Flynn, Phys. Rev. B **30**, 7317 (1984).

[10] In the present paper it is implicitly assumed that N_2 is physically adsorbed with exceedingly small adsorption dipole moment, although this has not been confirmed experimentally for N_2/Pb. It is known that there is also a state of

weak chemisorption for N_2 on some metals. For $N_2/\mathrm{Ni}(111)$ the chemisorbed and physisorbed states were distinguished by desorption experiments, M. Breitschafter, E. Umbach, and D. Menzel, Surf. Sci. **178**, 725 (1986). $N_2/\mathrm{Al}(111)$ and $N_2/\mathrm{Ag}(111)$ are believed to be pure physisorption cases, M. Bertolo and K. Jacobi, *ibid.* **265**, 1 (1992) and references contained therein.

[11] T. H. Boyer, Phys. Rev. A **9**, 68 (1974); M. S. Tomassone and A. Widom, Am. J. Phys. **65**, 1181 (1997).

[12] G. E. H. Reuter and E. H. Sondheimer, Proc. R. Soc. London, Ser. A **195**, 336 (1948); E. M. Lifshitz and L. P. Pitaevskii, *Physical Kinetics* (Pergamon, New York, 1981), Sec. 86.

[13] M. V. Pykhtin, S. P. Lewis, E. J. Mele, and A. M. Rappe, Phys. Rev. Lett. **81**, 5940 (1998).

[14] L. W. Bruch, M. W. Cole, and E. Zaremba, *Physical Adsorption: Forces and Phenomena* (Oxford University Press, Oxford, 1997).

[15] J. Unguris, L. W. Bruch, E. R. Moog, and M. B. Webb, Surf. Sci. **87**, 415 (1979).

[16] R. J. Behm, C. R. Brundle, and K. Wandelt, J. Chem. Phys. **85**, 1061 (1986).

[17] C. Daly and J. Krim, Phys. Rev. Lett. **76**, 803 (1996).

[18] L. W. Bruch, P. I. Cohen, and M. B. Webb, Surf. Sci. **59**, 1 (1976).

[19] G. S. Leatherman and R. D. Diehl, Langmuir **13**, 7063 (1997).

[20] C. Graham, J. Pierrus, and R. E. Raab, Mol. Phys. **93**, 49 (1998), report $\theta=-1.40\times10^{-26}\,\mathrm{esu\,cm}^2$ for an isolated molecule. Dense phase models generally use a smaller, effective, quadrupole moment to mimic the effects of the finite extent of the charge distribution in the molecule.

[21] G. K. White and S. B. Woods, Philos. Trans. R. Soc. London, Ser. A **251**, 273 (1959). Although the silver films in the quartz microbalance experiments have smaller conductivity, this is not crucial for the estimates of the present paper because the conductivity enters Eq. (3.3) through the combination σ_0/l.

[22] J. Krim, E. T. Watts, and J. Digel, J. Vac. Sci. Technol. A **8**, 3417 (1990); V. Panella, R. Chiarello, and J. Krim, Phys. Rev. Lett. **76**, 3606 (1996).

[23] D. Marx, O. Opitz, P. Nielaba, and K. Binder, Phys. Rev. Lett. **70**, 2908 (1993).