Relation between Dynamical Processes at Surfaces and Electron-Energy-Loss Measurements

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(Received 11 January 1983)

The surface response function $d_\perp(\omega)$ (the frequency-dependent centroid of the induced charge density) determines the influence of a metal surface on all dynamical processes occurring well outside of it. It is shown that this function can be measured directly by use of electron-energy-loss spectroscopy.

PACS numbers: 73.20.Cw, 79.20.Kz

There has been a steadily increasing interest in dynamical processes at surfaces. Processes involving chemisorbed molecules, such as dissociation reactions[1] or vibrational damping,[2] are interesting but complicated. Processes involving molecules not in direct contact with the surface are simpler because such molecules can interact with the metal only through the electromagnetic field. Interesting examples of this type include the van der Waals interaction between a molecule and a metal, and the fluorescence decay of an excited molecule studied as a function of the distance to the surface. The influence of the metal surface on the latter type of processes is entirely contained in the linear response function $g(q_\parallel, \omega)$ which is defined as follows: Let the metal occupy the half space $z<0$ and consider an arbitrary electric current density located in the half space $z>d$ (>0). Assume for simplicity that retardation effects can be neglected. Thus, the electric field from the external current density can be written as $\vec{E}_{\text{ext}} = -\nabla\varphi_{\text{ext}}$. Since $\nabla^2\varphi_{\text{ext}}=0$ for $z<d$, φ_{ext} can in this region of space be written as a superposition of evanescent plane waves,

$$\varphi_{\text{ext}}(\vec{x}, t) = \int d^2q_\parallel\, d\omega\, \tilde{\varphi}_{\text{ext}}(q_\parallel, \omega)\exp(i\vec{q}_\parallel \cdot \vec{x}_\parallel - q_\parallel|z-d| - i\omega t). \tag{1}$$

This external potential induces a current density in the metal which gives rise to an induced potential $\varphi_{\text{ind}}(\vec{x}, t)$. Assume that φ_{ext} is so weak that the metal responds linearly to φ_{ext}. For $z>0$, where $\nabla^2\varphi_{\text{ind}}=0$, we can then write

$$\varphi_{\text{ind}}(\vec{x}, t) = \int d^2q_\parallel\, d\omega\, g(q_\parallel, \omega)\tilde{\varphi}_{\text{ext}}(\vec{q}_\parallel, \omega)\exp(-q_\parallel d)\exp(i\vec{q}_\parallel \cdot \vec{x}_\parallel - q_\parallel|z| - i\omega t). \tag{2}$$

This equation defines $g(q_\parallel, \omega)$. It is implicitly understood that the metal can be treated as translationally invariant parallel to the surface. Equation (2) shows that the response of the metal to an external probe is entirely contained in $g(q_\parallel, \omega)$ as long as we are only interested in the induced potential outside the metal.

It is convenient to write

$$g(q_\parallel, \omega) = \frac{\epsilon(\omega) - 1 - A(q_\parallel, \omega)}{\epsilon(\omega) + 1 + A(q_\parallel, \omega)}, \tag{3}$$

where $\epsilon(\omega)$ is the bulk dielectric function. As $q_\parallel \to 0$, $g(q_\parallel, \omega)$ must reduce to the Fresnel formula for p-polarized light evaluated in the nonretarded limit (i.e., $c\to\infty$). Thus we must have $A(q_\parallel, \omega) \to 0$ as $q_\parallel \to 0$. Now assume that $q_\parallel$ is finite but small ($q_\parallel/k_F \ll 1$, where k_F is the Fermi wave number of the metal). We can then expand $A(q_\parallel, \omega)$ to first order in $q_\parallel$ and write

$$A(q_\parallel, \omega) \simeq [\epsilon(\omega) - 1]d_\perp(\omega)q_\parallel. \tag{4}$$

This formula defines $d_\perp(\omega)$. It has been shown previously by Feibelman[3] that $d_\perp(\omega)$ is the centroid

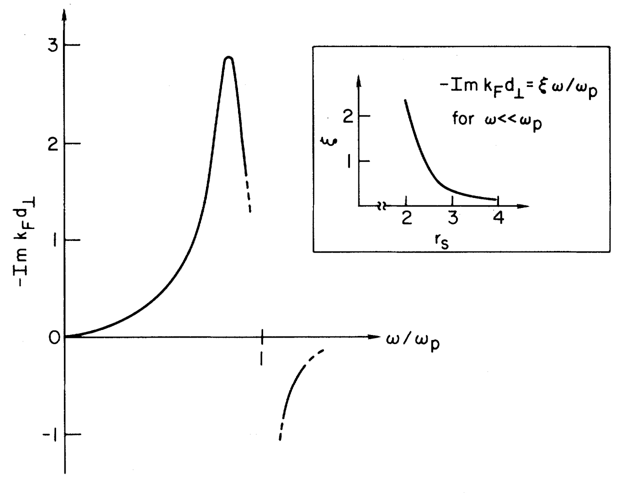

FIG. 1. Within the jellium model, $d_\perp(\omega)$ has been calculated for $\omega > \omega_p/2$ by Feibelman and for $\omega \ll \omega_p$ by Persson and Lang. The figure shows the result for $r_s = 3$. For $\omega \ll \omega_p$, $\mathrm{Im}\, d_\perp(\omega)$ depends linearly on ω, i.e., $-\mathrm{Im}\, k_F d_\perp(\omega) = \xi\omega/\omega_p$. ξ depends only on the electron gas density parameter r_s as shown in the inset.

of the induced charge density which in general is a complex number because of loss processes (i.e., electron-hole pairs). Figure 1 shows the structure of $\mathrm{Im}\,d_\perp(\omega)$ as obtained for a jellium description of the metal. The real part of $d_\perp(\omega)$ is obtained directly from $\mathrm{Im}\,d_\perp(\omega)$ via a Kramers-Kronig formula.[4]

The spatial variation parallel to the metal surface of the electric field from a point charge located at a distance d above a metal surface contains wave-vector components up to $q_\parallel \sim 1/d$. Thus the small-$q_\parallel$ expansion of $A(q_\parallel, \omega)$ given by Eq. (4) can be used to determine the response of the metal when the external probe is located well above the surface ($k_\mathrm{F} d \gg 1$). Consider, for example, the lifetime of an excited molecule located a distance d above a metal surface. When the molecule is close to the surface (typically $d \lesssim 100$ Å) the dominant damping is due to nonradiative transfer of the excitation energy to the metal. The damping rate is then given by[5]

$$\tau^{-1} = (2\mu^2/\hbar)\int_0^\infty dq_\parallel\, q_\parallel^2\, \mathrm{Im}\, g(q_\parallel, \omega)\exp(-2q_\parallel d), \tag{5}$$

where $\mu = |\langle B|\hat{\mu}|A\rangle|$ is the dynamic dipole moment for the transition $|B\rangle \rightarrow |A\rangle$ between the excited molecular state $|B\rangle$ and the ground state $|A\rangle$. Substituting Eq. (3) into (5) and assuming that d is so large that Eq. (4) is valid, we obtain[3, 6, 7]

$$\frac{1}{\tau} = \frac{\mu^2}{2\hbar d^3}\left\{\mathrm{Im}\,\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1} - 3\,\mathrm{Re}\,\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\,\mathrm{Im}\,d_{\mathrm{IP}}(\omega)/d\right\}, \tag{6}$$

where $d_{\mathrm{IP}}(\omega) = d_\perp(\omega)\epsilon(\omega)/[1+\epsilon(\omega)]$ is the frequency-dependent image-plane position.[3] We note that the damping rate $1/\tau$ has two contributions—one which is proportional to $1/d^3$ and only depends on the bulk dielectric function $\epsilon(\omega)$, and a second term proportional to $1/d^4$ which depends on the surface response function $d_\perp(\omega)$. The first term is the "bulk damping" and is caused by "Ohmic losses," i.e., by scattering of metal electrons from phonons, impurities, and the bulk crystal potential. The second term is the "surface damping" where the momentum needed for the excitation of the metal electrons arises from the surface potential.

It should be clear from the discussion above that a good knowledge of $g(q_\parallel, \omega)$ as a function of both $q_\parallel$ and ω is crucial for the understanding of dynamical processes occurring above metal surfaces. In this Letter it will be shown that this function can be measured directly with electron-energy-loss spectroscopy (EELS). We will focus on the small-$q_\parallel$ limit where the expansion (4) is valid, but this limitation is easily removed.

Consider an electron with a few electronvolts energy, incident upon a clean metal surface. Let $\vec{k}$ and $\vec{k}'$ denote the wave vectors of an incident and an inelastically scattered electron, respectively. Thus $\hbar\vec{q}_\parallel$, where $\vec{q}_\parallel = \vec{k}_\parallel - \vec{k}_\parallel'$, is the momentum transfer (parallel to the surface) to the excitation in the metal and $\hbar\omega = \hbar^2(k^2 - k'^2)/2m$ is the energy transfer. Let $P(\vec{k}, \vec{k}')d\Omega_{k'}\, d(\hbar\omega)$ be the probability that an incident electron is scattered into the range of energy losses between $\hbar\omega$ and $\hbar(\omega + d\omega)$ and into the solid angle $d\Omega_{k'}$ around the direction of $\vec{k}'$. For small momentum transfer, $q_\parallel \ll k$, one has from standard dipole scattering theory[8]

$$P = 2\left(\frac{me}{\hbar^2\pi}\right)^2 \frac{1}{\cos\alpha}\,\frac{k'}{k}\,\frac{q_\parallel}{[q_\parallel^{\,2} + q_\perp^{\,2}]^2}\,\mathrm{Im}\, g(q_\parallel, \omega), \tag{7}$$

where $q_\perp = k_z - k_z'$ and where α is the angle of incidence. Substituting (4) into (3) gives to first order in $q_\parallel$

$$\mathrm{Im}\, g(q_\parallel, \omega) = \mathrm{Im}\,\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1} - 2\,\mathrm{Re}\,\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\,\mathrm{Im}\,d_{\mathrm{IP}}(\omega)q_\parallel. \tag{8}$$

Assume that $\hbar\omega$ is small (say $\hbar\omega \lesssim 1$ eV) and that $\epsilon(\omega)$ is well approximated with a Drude dielectric function, i.e., $\epsilon(\omega) = 1 - \omega_p^{\,2}/\omega(\omega + i/\tau')$. Under these conditions, Eq. (8) reduces to

$$\mathrm{Im}\, g(q_\parallel, \omega) \simeq \frac{\omega}{\omega_p}\,\frac{1}{k_\mathrm{F} l}\left(4\frac{\omega_\mathrm{F}}{\omega_p}\right) - 2\,\mathrm{Im}\,d_\perp(\omega)q_\parallel,$$

where l is the mean free path for an electron in the bulk. For small ω it has been shown[7] that $\mathrm{Im}\,d_\perp(\omega)$ is linear in ω, i.e., $\mathrm{Im}\,k_\mathrm{F} d_\perp = -\xi\omega/\omega_p$ for $\omega \ll \omega_p$, where ξ is independent of ω. Thus

$$\mathrm{Im}\, g(q_\parallel, \omega) \simeq \frac{\omega}{\omega_p}\left(\frac{a}{k_\mathrm{F} l} + b\frac{q_\parallel}{k_\mathrm{F}}\right),$$

where $a = 4\omega_\mathrm{F}/\omega_p$ and $b = 2\xi$. In the jellium model ξ is only a function of the electron-gas density parameter r_s, as shown by the inset in Fig. 1. For the noble metals copper, silver, and gold one gets

$$a(\mathrm{Cu}) \approx 2.6, \quad a(\mathrm{Ag}) \approx a(\mathrm{Au}) \approx 2.4,$$

$$b(\mathrm{Cu}) \approx 1.13, \quad b(\mathrm{Ag}) \approx b(\mathrm{Au}) \approx 0.6.$$

The inelastically scattered electrons, as described by Eq. (7), form a narrow lobe centered close to the specular direction. A typical momentum loss of an inelastically scattered electron is[8] $q_\parallel \sim k\hbar\omega/(2E_0)$ where E_0 is the energy of the incident electrons. For $E_0 \sim 3$ eV and $\hbar\omega \sim 0.3$ eV this gives $q_\parallel \sim 0.04$ Å^{-1} and thus $bq_\parallel/k_F \sim 0.03$ for Cu. For Cu, at room temperature, $l \sim 400$ Å and therefore $a/k_F l \sim 0.007$. The surface contribution to Img is therefore already at room temperature nearly 1 order of magnitude larger than the bulk contribution. At lower termperatures the difference is even larger because $l \to \infty$ as $T \to 0$. By study of the intensity of the inelastically scattered electrons as a function of temperature, it is possible to separate the volume contribution to Img from the surface contribution.

In EELS one does not measure $P(\vec{k}, \vec{k}')$ directly but rather P integrated over the solid angle of detection, $\Delta\Omega$:

$$\Delta P = \int_{\Delta\Omega} P\, d\Omega.$$

Figure 2 shows ΔP as a function of the excitation energy $\hbar\omega$. In this calculation P [as given by Eq. (7)] was integrated over a circular aperture of half angle 1° centered around the specular direction (angle of incidence $\alpha = 65°$). The two solid curves show the surface contribution to ΔP for Cu ($a = 0$, $b = 1.13$) for two different energies of the incident electrons ($E_0 = 3$ and 5 eV). The dashed curves in the same figure show the bulk contribution to ΔP for Cu ($a = 2.6$, $b = 0$) at room temperature ($l \sim 400$ Å) and at $T = 80$ K ($l \sim 4400$ Å). It is obvious that the surface contribution dominates already at room temperature.

Let us now compare the theoretical predictions for ΔP with experiment. Very few EEL spectra have been reported for *clean* metal surfaces. For copper we know of only one such measurement.[9] At $T = 25$ K and with $E_0 = 2$ eV and $\alpha = 50°$ Andersson and Harris obtain $\Delta P \simeq (2 \pm 1) \times 10^{-6}$ meV^{-1} at $\hbar\omega = 0.08$ eV while we predict[10] $\Delta P(\text{surface}) = 1 \times 10^{-6}$ meV^{-1}. The volume contribution to ΔP at $T = 25$ K is extremely small, $\Delta P(\text{volume}) < 10^{-7}$ meV^{-1}.

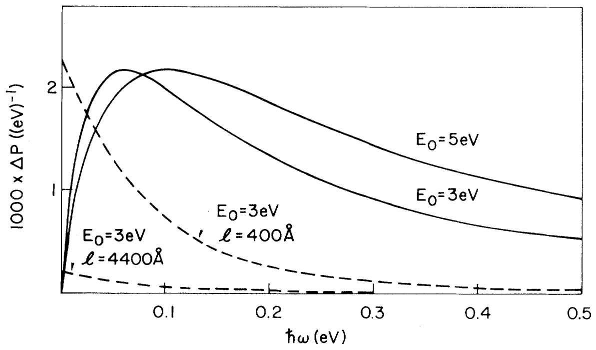

FIG. 2. The relative loss intensity, ΔP, as a function of the loss energy $\hbar\omega$. The solid curves show ΔP (surface) for $E_0 = 2$ and 5 eV. The dashed curves show the volume contribution to ΔP at room temperature ($l \approx 400$ Å) and at $T = 80$ K ($l \approx 4400$ Å). Angle of incidence $\alpha = 65°$ and half angle of the analyzer $\theta_1 = 1°$.

The results presented above suggest that the surface response function $d_\perp(\omega)$ can be measured directly with inelastic electron scattering. If so, this would be very important since $d_\perp(\omega)$ has the same central role in the description of dynamical processes at surfaces as the bulk dielectric function $\epsilon(\omega)$ has for the description of dynamical processes in the bulk.[11]

I would like to thank Ph. Avouris, J. E. Demuth, N. D. Lang, and A. R. Williams for useful discussions.

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[1] J. E. Demuth, H. Ibach, and S. Lehwald, Phys. Rev. Lett. 40, 1044 (1978).

[2] B. N. J. Persson and R. Ryberg, Phys. Rev. Lett. 48, 549 (1982).

[3] P. J. Feibelman, Phys. Rev. B 22, 3654 (1980). See also the review work by P. J. Feibelman, to be published.

[4] B. N. J. Persson and P. Apell, Phys. Rev. B (to be published).

[5] H. Morawitz, Phys. Rev. 187, 1792 (1969); R. R. Chance, A. Prock, and R. Silbey, Adv. Chem. Phys. 37, 1 (1978); B. N. J. Persson, J. Phys. C 11, 4251 (1978).

[6] P. Apell, Phys. Scr. 24, 795 (1981).

[7] B. N. J. Persson and N. D. Lang, Phys. Rev. B 26, 5409 (1982).

[8] H. Ibach and D. L. Mills, in *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1982); D. L. Mills, Surf. Sci. 48, 59 (1975); E. Evans and D. L. Mills, Phys. Rev. B 5, 4126 (1972); D. M. Newns, Phys. Lett. 60A, 461 (1977); F. Delanaye, A. Lucas, and G. D. Mahan, Surf. Sci. 70, 629 (1978); B. N. J. Persson, Solid State Commun. 24, 573 (1977). D. Sokcevic, Z. Lenac, R. Brako, and M. Sunjic, Z. Phys. B 28, 677 (1977).

[9] S. Andersson and J. Harris, Phys. Rev. Lett. 48, 545 (1982).

[10] In this calculation we have used an improved dipole scattering theory which accounts for the force on the incident electron from its own image [B. N. J. Persson, Surf. Sci. 92, 265 (1980)].

[11] The review work by Feibelman (Ref. 3) contains many illustrative applications of $d_\perp(\omega)$, for example to the surface plasmon damping and dispersion, the surface photoelectric effect, the friction force on a charged particle, the position of the effective image plane, surface power absorption, etc. See also P. Apell and A. Ljungbert, Phys. Scr. 26, 113 (1982), for application to small metallic particles.