

Surface energy-loss function for the inelastic scattering of electrons from a metal substrate with an overlayer of adsorbed alkali-metal atoms

Adolfo G. Eguiluz and Dave A. Campbell

Department of Physics, University of California, Irvine, California 92717

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We investigate the spectrum of elementary excitations of the conduction electrons associated with an overlayer of sodium atoms adsorbed on a metal surface. We compute the surface energy-loss function for the small-angle backscattering of electrons as function of coverage (up to two full monolayers of sodium atoms are considered). The ground-state problem is dealt with by using Lang's uniform-background model of alkali-metal-atom-metal-surface chemisorption. The dynamical response of the electron gas is treated in the random-phase approximation. Previous theoretical work has, for the most part, assumed that an overlayer of atomic thickness responds as bulk matter. Our microscopic calculation reveals that for one-monolayer coverage the overlayer's response in fact deviates significantly from bulklike behavior. For two-monolayer coverage the response is bulklike, with a prominent collective (plasmon) mode. The quantum-mechanical nature of the overlayer response is displayed in detail. A case is made for the need that an angle-resolved electron-energy-loss experiment be performed, using an *s-p*-bonded metal, such as aluminum, as the substrate (instead of a transition metal).

I. INTRODUCTION

Electron-energy-loss spectroscopy (EELS) has been used extensively in recent years to study the vibrational¹ and electronic²⁻¹³ degrees of freedom of overlayers of atoms and molecules adsorbed on a metal surface. In particular, a system which has received considerable attention because of its technological interest and also because of the basic physics that is involved, is the alkali-metal-atom-metal-surface chemisorption system. EELS has been the tool of choice for probing the spectrum of collective and single-particle excitations in this system.

With few exceptions,^{9,10} the theoretical effort supporting the EELS measurements^{5,11-14} has not gone beyond the modeling of the overlayer by a thin slab characterized by a frequency-dependent dielectric constant $\epsilon_s(\omega)$,^{1,14} or semiclassical generalizations of it.¹⁵ However, when the overlayer is of atomic thickness the question of the legitimacy of the use of a bulk response property must be addressed. Furthermore, electron-hole pair excitations are absent from such a classical model, and there is evidence of their importance in some dynamical processes at surfaces.¹⁶ On the experimental side, while a number of papers have been published^{3,5-8} after some exciting (and controversial) seminal work on the detection of plasmons in an overlayer of alkali-metal atoms adsorbed on a transition-metal surface,^{2,3,11,12} some fundamental questions about the nature of the losses observed at monolayer coverage remain open.^{7,8} We hope that the results presented below will motivate further experimental work.

In this paper we present a fully microscopic theory of the dynamical response of the conduction electrons associated with an adsorbed alkali-metal-atom overlayer.

II. LANG'S MODEL OF ALKALI CHEMISORPTION

We proceed by solving first the ground-state chemisorption problem, and we do this using Lang's uniform-background model of alkali chemisorption.¹⁷ This simple model successfully explains the dramatic lowering of the substrate work function with alkali-metal-atom chemisorption and also the general work function trends for the alkali series. In Lang's model the ionic charge of each adsorbate layer is replaced by a jellium slab of thickness b , equal to the interplanar spacing of the most densely packed lattice planes in a bulk sample of the alkali metal. Full monolayer coverage is reached when the number of alkali atoms per unit area n_s is such that $n_s = bn_B$, where n_B is the bulk-alkali-metal density. Submonolayer coverage corresponds to values of $n_s < bn_B$.

We implement Lang's model of the ground state of the adsorbate-substrate system as follows. We adopt a recently introduced computational scheme¹⁸ based on the self-consistent solution of a matrix version of the Kohn-Sham equation¹⁹ for a jellium slab. A matrix eigenvalue problem is arrived at by expanding the Kohn-Sham wave functions for motion normal to the surface in a sine series. We generalize the procedure of Ref. 18 to our present problem by adding to the Hamiltonian matrix of the substrate the corresponding matrix for the overlayer. The self-consistent diagonalization of the Hamiltonian matrix proceeds in the same way as in the absence of the overlayer.¹⁸ (Exchange and correlation are included in the local-density functional approximation.¹⁹) Reflection symmetry about the midplane of the slab is preserved by introducing overlayers symmetrically on both sides of the substrate.

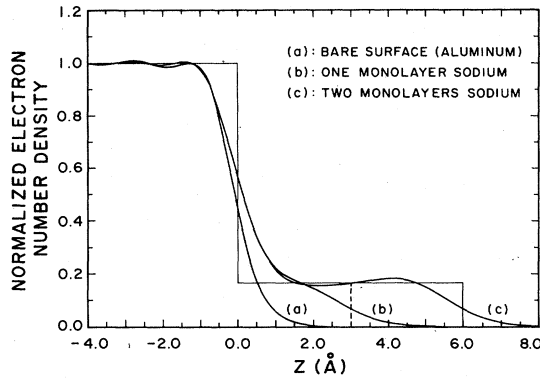


FIG. 1. Electron density profile in the Lang model of alkali adsorption (normalized to the bulk value of the substrate density). (a) Profile for a bare aluminum surface. (b) and (c) Profiles that result after the adsorption of one and two full monolayers of sodium atoms, respectively. The dashed line indicates the edge of the jellium for the first sodium layer. In all three cases the coordinate z is measured from the edge of the substrate jellium.

Figure 1 shows first the electron density profile $n_0(z)$ for a bare jellium surface with the bulk density of aluminum (z is the coordinate normal to the surface). In this work the thickness of the substrate corresponds to 15 atomic layers of aluminum in the [100] direction (≈ 30.4 Å). For the rather large two-dimensional wavevector transfers considered in this paper the substrate film effects are small; these effects will be noted below. (It was verified that our results for the overlayer response are not changed in any significant way if somewhat thicker slabs are used.) We note that the bare-surface profile shown in Fig. 1 agrees to high accuracy (better than 1%) with the Lang-Kohn density profile that obtains for a semi-infinite substrate with the bulk density of aluminum.²⁰ Figure 1 also shows the electron density profile that obtains upon chemisorbing one and two full monolayers of sodium, respectively. The main feature to be noted in Fig. 1 is that the two-layer profile looks substantially more bulk-like throughout the overlayer than the one-layer profile does. This feature of $n_0(z)$ has repercussions in the response of the overlayer to an external electron, as we shall see.

III. LOSS FUNCTION FOR THE REFLECTION OF AN ELECTRON

In the first Born approximation the scattering efficiency for a process in which an incoming electron is reflected from a metal surface with a two-dimensional momentum transfer $\hbar q_{\parallel}$ and energy loss $\hbar\omega$ is, for $q_{\parallel} \ll k_F$, proportional to the loss function $P(q_{\parallel}, \omega)$, given at $T=0$ K by the equation¹

$$P(q_{\parallel}, \omega) = -2\hbar e^2 \int_0^d dz \int_0^d dz' e^{-q_{\parallel}(z+z')} \times \text{Im}\chi(q_{\parallel}; \omega + i0^+ | z, z'). \quad (1)$$

In Eq. (1) we have introduced the density response function $\chi(q_{\parallel}; \omega + i0^+ | z, z')$, giving the electron density response to an external longitudinal field²¹ (in the present case, the field of the incoming electron). The length d is the spatial extent of the electronic system along the z axis.^{18,21} The response function χ vanishes for $z, z' > d$ and $z, z' < 0$ (i.e., outside the electron gas). Note that the full scattering cross section includes a kinematic multiplicative factor¹ that must be included in a complete analysis of the cross section. (It is in this factor that the kinetic energy of the incoming electron enters.)

From the f -sum rule for the inhomogeneous electron gas satisfied by $\text{Im}\chi(q_{\parallel}; \omega + i0^+ | z, z')$,²² we can readily establish the result that

$$\int_0^{\infty} d\omega \omega P(q_{\parallel}, \omega) = \frac{\pi \hbar e^2}{m} q_{\parallel} \int_0^d dz e^{-2q_{\parallel}z} \frac{d}{dz} n_0(z), \quad (2)$$

which relates the first-frequency moment of $P(q_{\parallel}, \omega)$ to an integral over the first derivative of the electron density profile.²³ Equation (2) is an exact result for $P(q_{\parallel}, \omega)$ that must be verified by our numerical results.

For comparison purposes we recall that if both substrate and overlayer are described by frequency-dependent dielectric constants $\epsilon_b(\omega)$ and $\epsilon_s(\omega)$, respectively, the energy-loss function $P(q_{\parallel}, \omega)$ defined by Eq. (1) can be shown to reduce to the following simple expression:^{1,14}

$$P(q_{\parallel}, \omega) = \frac{2\hbar q_{\parallel}}{\pi} \text{Im} \left[\frac{-1}{1 + \tilde{\epsilon}(q_{\parallel}, \omega)} \right], \quad (3)$$

where the substrate has been assumed to be semi-infinite, and the effective dielectric constant of the adsorbate-substrate system, $\tilde{\epsilon}(q_{\parallel}, \omega)$, is defined by the equation

$$\tilde{\epsilon}(q_{\parallel}, \omega) = \epsilon_s(\omega) \frac{1 + \Delta(\omega) e^{-2q_{\parallel}b}}{1 - \Delta(\omega) e^{-2q_{\parallel}b}}, \quad (4)$$

where b is the thickness of the overlayer, and

$$\Delta(\omega) = \frac{\epsilon_b(\omega) - \epsilon_s(\omega)}{\epsilon_b(\omega) + \epsilon_s(\omega)}. \quad (5)$$

Note that for $b=0$ we have that $\tilde{\epsilon}(q_{\parallel}, \omega) = \epsilon_b(\omega)$, and the surface energy-loss function given by Eq. (3) takes on the well-known form

$$P(q_{\parallel}, \omega) = \frac{2\hbar q_{\parallel}}{\pi} \text{Im} \left[\frac{-1}{1 + \epsilon_b(\omega)} \right], \quad (6)$$

which corresponds to an energy-loss peak at the surface-plasmon frequency of the substrate. For finite b the denominator of Eq. (3) has two zeroes.¹¹ One zero corresponds to a high-frequency mode whose frequency equals the surface-plasmon frequency of the substrate for $q_{\parallel}b \ll 1$ and the substrate-adsorbate plasma frequency for $q_{\parallel}b \gg 1$. The other zero corresponds to a mode which is, in the case that the substrate density is much larger than that of the adsorbate, very similar to the antisymmetric surface mode of a free-standing film; its frequency equals the bulk (surface) plasmon frequency of the adsorbate for $q_{\parallel}b \ll 1$ ($q_{\parallel}b \gg 1$).

The results to be given below will expose the limitations of Eq. (3) (which will be referred to as the "classical" loss function) when applied to the case of an overlayer of atomic thickness.

In this work we evaluate $P(q_{\parallel}, \omega)$ using in Eq. (1) the density response function $\chi(q_{\parallel}; \omega + i0^+ | z, z')$ obtained recently by one of us^{21,24} within the random-phase approximation (RPA). The integral equation for $\chi(q_{\parallel}; \omega + i0^+ | z, z')$ is formally the same in the presence of the overlayer as in its absence, and the method of solution set forth in Ref. 21 applies equally well in either case. The presence of the sodium overlayer is brought into the RPA integral equation via the irreducible response

$$\chi^{(0)}(q_{\parallel}; \omega + i0^+ | z, z')$$

(the response function for noninteracting electrons), which is defined in terms of the electron wave functions and energy eigenvalues obtained self-consistently with the adsorbate-substrate density profiles depicted in Fig. 1.

Now, the conceptual objection may be posed^{25,26} that while exchange and correlation effects are absent from the kernel of the RPA integral equation for χ , these effects are present in Lang's chemisorption model (within the local-density functional approximation); thus, they are included in the wave functions used to compute $\chi^{(0)}$. However, we have verified that our results for the loss function are not changed qualitatively if we exclude the contribution from exchange and correlation to the effective potential of the Kohn-Sham equation for the electron wave functions. (The response function computed on the basis of the Hartree wave functions is the "true" RPA response function.) Basically, only the widths of the collective-mode losses to be described below change, but their frequencies remain essentially unchanged. We note that if exchange and correlation effects are excluded from the chemisorption calculation the electron work function is lowered. This enhances the leaking out of the electrons through the nominal surface. Thus, the RPA (or Hartree) electron density profile at the surface has a relatively longer tail than the Lang-Kohn profile. This gives rise to an enhancement of the electron-hole pair damping mechanism, which translates into somewhat broader plasmon losses,²⁷ but it does not affect significantly the energies of the collective modes (or their *existence*). Since the Hartree ground state is not very "realistic," we have opted to present our results for the Lang-Kohn-type profiles shown in Fig. 1.

For completeness, and as an exploratory assessment of the effects of exchange and correlation in χ (and thus in the loss function), we have introduced these effects in the kernel of the integral equation satisfied by χ within the local-density functional approximation.²⁴ This procedure is strictly valid for $\omega=0$ only. The results so obtained agree qualitatively with the RPA results. (Again, the widths of the losses are affected.)

Before presenting our results for $P(Q_{\parallel}, \omega)$ we would like to note that the response function is obtained without the introduction of phenomenological damping (i.e., χ is obtained for $\omega + i0^+$, as indicated by our notation). Thus the finite width of the collective-mode losses to be investi-

gated below is strictly due to collisionless (or Landau) damping (decay into electron-hole pairs).

IV. RESULTS AND DISCUSSION

Figures 2 through 4 give representative results for $P(q_{\parallel}, \omega)$. The units of $P(q_{\parallel}, \omega)$ are chosen such that the right-hand side of Eq. (2) equals unity. Numerically this sum rule is verified to better than 1%, which serves as a global check of the accuracy of our numerical work. The frequency ω is given in units of the Fermi frequency of the system ω_F (which is equal to that of the aluminum substrate), and the wave-vector transfer q_{\parallel} is given in units of the Fermi wave vector k_F . It is noteworthy that ω_F defines the only scale of frequencies that is available before performing the response computation. The collective mode frequencies are obtained from the solution to the integral equation for χ .

Consider first the bottom panel of Fig. 2, showing the aluminum surface-plasmon energy-loss peak for $k_{\parallel} \equiv q_{\parallel}/k_F = 0.06$. We note that for $k_{\parallel} \lesssim 0.06$ the aluminum surface plasmon splits into the two surface plasmons of a thin film. Thus our 15-layer substrate can be used to approximate the surface-plasmon energy loss of a semi-

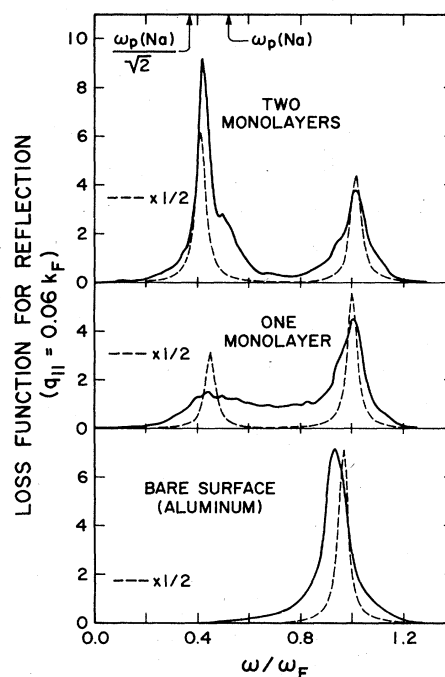


FIG. 2. Energy-loss function $P(q_{\parallel}, \omega)$ for $q_{\parallel} = 0.06k_F$ as function of the reduced frequency ω/ω_F , where k_F and ω_F are, respectively, the Fermi wave vector and frequency for aluminum ($k_F = 1.75 \text{ \AA}^{-1}$ and $\hbar\omega_F = 11.65 \text{ eV}$). Each panel gives $P(q_{\parallel}, \omega)$ for the corresponding profile shown in Fig. 1. The units of $P(q_{\parallel}, \omega)$ have been chosen such that the right-hand side of Eq. (2) equals unity. The dashed lines show the "classical" energy-loss function given by Eq. (3), reduced by a factor of 2. [The dielectric constants $\epsilon_s(\omega)$ and $\epsilon_F(\omega)$ that enter Eq. (5) were taken to be Drude-like; we used a phenomenological collision frequency $\omega_c = 0.045\omega_F$.]

infinite bare aluminum slab for $k_{\parallel} \geq 0.06$ only. For smaller values of k_{\parallel} the *overlayer* response can still be studied, however, provided the lower surface plasmon of our finite-width substrate does not lie in the frequency range in which the overlayer responds (cf. Figs. 3 and 4). We remark that the aluminum surface plasmon is shifted down in frequency from its half-space value $\nu = \omega/\omega_F \cong 0.96$ ($=\omega_p/\sqrt{2}$ for aluminum, ω_p being the plasma frequency) to $\nu \cong 0.93$. This is a substrate film effect.

The central panel of Fig. 2 shows the energy-loss spectrum that obtains upon chemisorbing a full monolayer of sodium atoms. The loss structure induced by the presence of the overlayer is very broad: it extends from frequencies below $\omega_p(\text{Na})/\sqrt{2}$ to frequencies well above $\omega_p(\text{Na})$. Its spectral weight reaches a maximum between those two frequencies, but the response can hardly be described as showing a well-defined plasmon mode. Rather, it is dominated by electron-hole pair excitations. As for the aluminum surface plasmon, note its upward shift due to coverage and its increased Landau damping. We note that for $k_{\parallel} = 0$ the shift of the aluminum surface-plasmon peak with coverage vanishes, since in the RPA the surface-plasmon frequency does not depend on the form of $n_0(z)$ for $k_{\parallel} = 0$.²⁸ [This can be easily verified with the classical loss function given by Eq. (3).]

Figure 2 finally shows $P(q_{\parallel}, \omega)$ after the adsorption of a second full monolayer of sodium atoms. The low-frequency loss is now unmistakably due to the excitation of a collective mode (plasmon) of the sodium overlayer. The plasmon has gained spectral weight at the expense of both the incoherent background of electron-hole pairs (which dominated the one-monolayer response for the same wave-vector transfer) and of the aluminum surface plasmon. Note that the latter has shifted very little with the adsorption of the second sodium layer. The coverage dependence of the substrate surface plasmon will be not discussed any further in the remainder of this paper. This has been discussed at length by Feibelman.²⁸

The dashed lines in Fig. 2 show the classical loss function given by Eq. (3). We used Drude dielectric constants for both substrate and overlayer, and broadened the otherwise delta-function peaks by introducing a phenomenological collision frequency ω_c . (We chose $\omega_c = 0.045\omega_F$; for simplicity we used the same value for both substrate and overlayer.) For the wave-vector transfer considered in Fig. 2 the classical loss calculation could be said to be qualitatively valid for two-monolayer coverage (except, of course, that the classical broadening mechanism is not the decay into electron-hole pairs). For one-monolayer coverage, however, the sharp classical loss bears little resemblance to the microscopic loss spectrum of the overlayer.

Now, Eq. (3) refers to a semi-infinite substrate, whereas our microscopic calculation was performed for a slab. A comparison of the two sets of results given in Fig. 2 confirms that our use of a slab of finite width to study the overlayer response is a good approximation. (The small relative shift in the position of the bare substrate surface plasmon is, as alluded to above, a thin-film effect.)

The nature of the overlayer response is further elucidated in Figs. 3 and 4, where we show the loss function in the

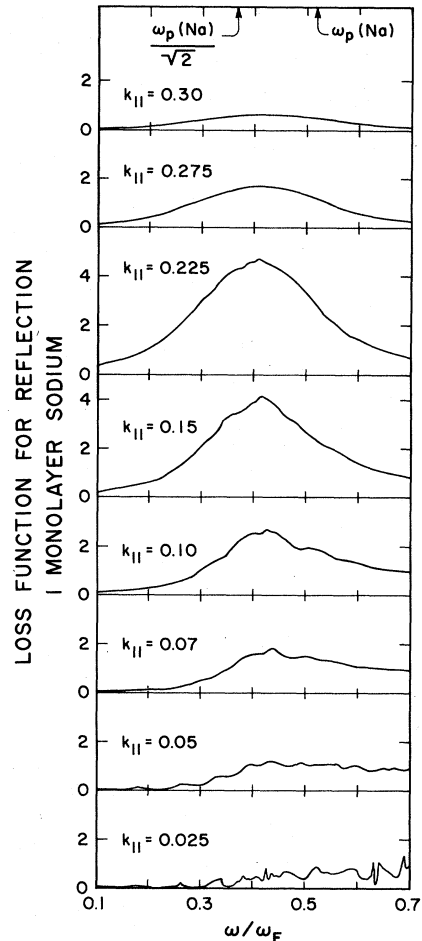


FIG. 3. Energy-loss function $P(q_{\parallel}, \omega)$ for one monolayer coverage of sodium on an aluminum substrate, for increasing values of the wave-vector transfer $k_{\parallel} \equiv q_{\parallel}/k_F$. The units of $P(q_{\parallel}, \omega)$ are chosen as in Fig. 2.

low-frequency region (i.e., below the surface plasmon of the aluminum substrate) for one- and two-layer coverage, respectively, for increasing values of the two-dimensional wave-vector transfer.

Consider Fig. 3 first. For the smallest wave vector considered,²⁹ $k_{\parallel} = 0.025$, the response is clearly due to the incoherent excitation of electron-hole pairs.³⁰ As the wave-vector transfer is increased the spectral weight of the overlayer-induced loss increases. For $k_{\parallel} \geq 0.07$ the spectral weight is relatively more localized between $\omega_p(\text{Na})/\sqrt{2}$ and $\omega_p(\text{Na})$. We interpret this broad loss structure as corresponding to the formation of a highly-damped overlayer plasmon. For large wave vectors ($k_{\parallel} \geq 0.225$) the spectral weight of the loss rapidly decreases, and for $k_{\parallel} \geq 0.30$ the loss disappears. For the purposes of the discussion to be given below it is important to note that for one-monolayer coverage the loss peak shifts very little in frequency as the wave vector is increased beyond $k_{\parallel} \geq 0.15$.

The contrast between the one-monolayer results shown in Fig. 3 and the results shown in Fig. 4 for two-monolayer coverage is striking. For $k_{\parallel} = 0.025$ the two-

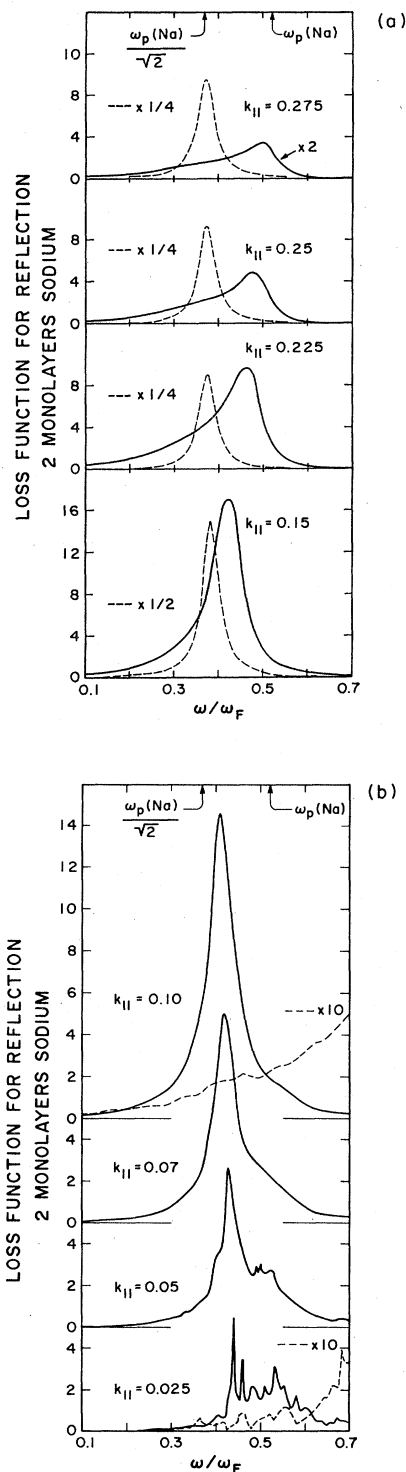


FIG. 4. Energy-loss function $P(q_{\parallel}, \omega)$ for two-monolayer coverage of sodium on an aluminum substrate for increasing values of the wave-vector transfer $k_{\parallel} \equiv q_{\parallel}/k_F$. The units of $P(q_{\parallel}, \omega)$ are chosen as in Fig. 2. In Fig. 4(b) the dashed lines show the energy-loss function $P(q_{\parallel}, \omega)$ (magnified by a factor of 10) for the bare aluminum substrate for $k_{\parallel}=0.025$ and $k_{\parallel}=0.10$, respectively. In Fig. 4(a) the dashed lines show the classical energy-loss function given by Eq. (3) (reduced by the factor shown in each panel).

monolayer plasmon appears as a distinct peak at the bottom edge of a "band" of electron-hole pair excitations.³⁰ It seems worth noting in passing that in the frequency region $\omega_p(\text{Na})/\sqrt{2} < \omega < \omega_p(\text{Na})$ the loss function of the bare substrate (corresponding to the excitation of electron-hole pairs) has negligible spectral weight. This loss function is shown in Fig. 4(b) by the dashed lines for $k_{\parallel}=0.025$ and $k_{\parallel}=0.10$; note that it has been magnified by a factor of 10.

As the wave-vector transfer is increased, Fig. 4(b) vividly shows a well-defined overlayer plasmon loss, whose spectral weight increases with k_{\parallel} , and whose frequency shifts downward toward $\omega_p(\text{Na})/\sqrt{2}$. For larger wave vectors [Fig. 4(a)], the plasmon loss eventually shifts to higher frequencies and, at the same time, it becomes progressively more Landau damped, until for $\omega \sim \omega_p(\text{Na})$ it ceases to exist.²¹ Both features of the two-monolayer plasmon found here at large wave vectors (upward shift and increased damping) are also present in the case of the surface plasmon of a semi-infinite slab;³² they are manifestations of spatial dispersion (or nonlocal) effects, which are built into the RPA response function. It is clear that if we were to increase the overlayer's thickness (i.e., if we were to repeat the calculation for three or more adsorbed layers) the two-monolayer loss peak would change smoothly into the surface-plasmon loss peak of a thick sodium slab. With the adsorption of more layers the wave-vector interval in which the loss peak shifts downward [Fig. 4(b)] would shrink, until eventually the peak would occur at $\omega_p(\text{Na})/\sqrt{2}$ for $k_{\parallel} \rightarrow 0$; at large wave vectors the loss function would be qualitatively described by the results of Fig. 4(a).

We note that the inherently microscopic behavior of the two-monolayer plasmon shown in Fig. 4(a) is absent from the classical calculation [shown by the dashed lines in Fig. 4(a)], which yields a symmetric peak whose position [$\omega \sim \omega_p(\text{Na})/\sqrt{2}$] and spectral weight are independent of k_{\parallel} .

The above discussion is concisely highlighted in Fig. 5, where we show the dispersion relation of the overlayer plasmon, obtained from the position of the loss peak as

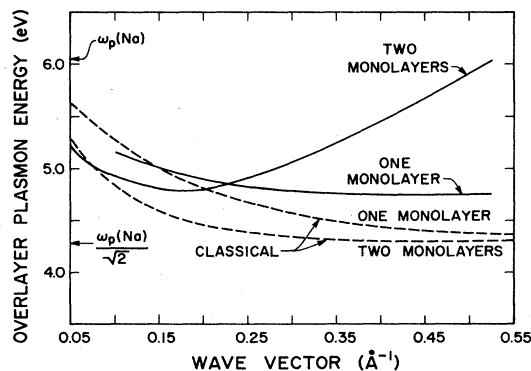


FIG. 5. Dispersion relation of the overlayer plasmon for one- and two-monolayer coverage of sodium on an aluminum substrate. The dashed lines show the corresponding classical dispersion relations, obtained from Eq. (3).

k_{\parallel} is varied.³³ Note that for one-monolayer coverage the dispersion relation terminates not only at large wave vectors (as it does for two-monolayer coverage) but also at small wave vectors, since, as noted above, the one-monolayer response is not collective in nature for small k_{\parallel} . The dashed lines in Fig. 5 show the corresponding classical dispersion relations;¹¹ the poor agreement with our microscopic quantum-mechanical results is apparent.

The feature of Fig. 5 that we would like to emphasize is that the dispersion relations for one- and two-monolayer coverage are qualitatively different. This result can be viewed as signaling a transition from nonbulk response to quasibulk response; from the shape of the two-monolayer plasmon dispersion relation it is rather obvious that further increase of the overlayer's thickness will turn that dispersion relation smoothly into the surface-plasmon dispersion relation of a semi-infinite sodium slab³² [which starts out at $\omega_p(\text{Na})/\sqrt{2}$ for $k_{\parallel}=0$].

Note that there is no such transition in the classical response theory: in that case there is no qualitative difference between the response of a one-monolayer film and that of a thick film. A related statement is that the classical loss function, unlike our microscopic theory, and contrary to experiment (see below) predicts a plasmon loss for small wave vectors for arbitrarily small coverages (its oscillator strength does, however, decrease with the coverage).

Finally, we note that what we could refer to here as quasi-two-dimensional electronic behavior, namely the behavior of the conduction electrons for monolayer coverage, is qualitatively different from the behavior of the electrons in a free-standing thin film of atomic thickness, or of the electrons in an inversion layer at a semiconductor surface. In the latter two systems there exist a well-defined two-dimensional plasmon mode whose dispersion relation is of the form $\omega \sim q_{\parallel}^{1/2}$ for $q_{\parallel} \rightarrow 0$.

V. RELATION TO EXPERIMENT

Our results for the loss function give a clear physical picture of the spectrum of elementary excitations of the conduction electrons of a sodium overlayer of atomic thickness. Of course, these results have been obtained on the basis of a simple model of alkali-metal-atom-metal-surface chemisorption. However, this model is expected to be adequate for monolayer coverage. The supporting evidence for this expectation is Lang's own successful study of work-function changes with alkali-metal-atom adsorption,¹⁷ and the fact that single-particle $ns \rightarrow np$ transitions in the overlayer (which are entirely absent from the model) are thought to be important for coverages less than monolayer coverage.⁵⁻⁷ In fact, for monolayer coverage the evidence seems to be that the overlayer has completed its transition from the ionic behavior that characterizes the low-coverage regime to metallic behavior.^{6,7,34}

Given the proportionality relation that exists between the loss function $P(q_{\parallel}, \omega)$ and the differential electron back-scattering cross section for small momentum transfers,¹ our results could be probed rather directly by performing an angle-resolved loss experiment on an

alkali-metal-atom overlayer adsorbed on an s - p -bonded metal such as aluminum. Unfortunately, all but one⁵ of the experiments have been performed by integrating the inelastic electron current over a large scattering angle. Furthermore, only transition metals^{2,5,7,8} (W, Ni, Mo, and Pt, respectively) and noble metals⁶ (Cu) have been used as substrates. However, despite this lack of direct experimental information on the loss function that we have computed, some overall features of the experiments can be addressed in the light of our results, and we shall do so. We hope to stimulate further experimental work.

We recall that the interpretation of the experimental (angle-integrated) loss found at monolayer coverage in terms of an overlayer plasmon⁶ is based on the smooth shift of that loss into the alkali-metal surface plasmon that is observed when more layers are adsorbed (by cooling). As indicated above, the loss peak that we obtained for two-monolayer coverage will also change smoothly into the sodium surface-plasmon peak as the overlayer becomes thicker.

Now it seems fair to state that some aspects of the experimental findings at monolayer coverage are controversial. On the one hand, Lindgren and Walldén⁶ have concluded that the substrate plays little role in the observed losses. This conclusion originates on the observation that the energy of the loss for monolayer coverage is approximately the same for Cs on W(100) (Ref. 2) and for Cs on Cu(111) (Ref. 6). On the other hand, recent loss experiments by Soukiassian *et al.*⁷ for Cs on Mo(100), and also for Cs on W(100) have been interpreted as showing no plasmon excitation in the cesium at monolayer coverage. The loss observed in Ref. 7 is interpreted as being due to a single-particle transition with initial and final states "probably" belonging to the adsorbate.⁷ The reason that the plasmon interpretation is ruled out in these experiments is that the observed loss does not shift with coverage, as a plasmon loss would. (Coverages up to a full monolayer are considered in Ref. 7.)

The results of Ref. 7 seem to pose a serious question on the previously-accepted interpretation of the observed loss at monolayer coverage. In effect, being a collective mode, a plasmon is a global property of the conduction electrons of the alkali overlayer, and one would expect that if the mode exists for monolayer coverage of Cs on Cu, it would also exist for Cs on Mo or W.

At this point we note that our results for the loss function indicate that the loss observed at monolayer coverage will not correspond to collective-mode excitation unless rather large wave vectors contribute to that loss. We hope to make this statement more quantitative in the future by carrying out a full cross-section calculation that integrates the loss function over the solid angle of the detector in a near-specular scattering configuration.¹

With the above comments as background let us briefly refer to the magnitude of the observed losses. Ever since the first experiment dealing with the formation of a plasmon in an alkali-metal overlayer was reported by MacRae *et al.*,² there has been a puzzling (and important) quantitative discrepancy between theory and experiment, namely the energy loss observed at monolayer coverage is much too small. For example, in the case of Na on

Ni(100) the loss occurs at 3.1 eV (Ref. 3). Previous attempts at explaining this loss were based mostly on the classical model discussed above.¹¹ Since for sodium $\hbar\omega_p = 6.04$ eV and $\hbar\omega_p = \sqrt{2} = 4.27$ eV (assuming free-electron values of the charge and mass) the quantitative discrepancy with experiment is apparent. This discrepancy is not alleviated significantly in the "box model" of Newns.³⁵ Obviously, it subsists in the rather elaborate calculation that we have done, since the dispersion relation of the broad loss peak that we obtained for monolayer coverage lies at about 5 eV.

We believe that our evaluation of the loss function contains the basic physics of the response of the simple metal-alkali-metal chemisorption system. Thus, if we accept the plasmon interpretation of the loss observed at monolayer coverage, we are led to the conclusion that the quantitative disagreement with experiment must be a reflection of the fact that the substrate used in Ref. 3 is a transition metal. It is indeed possible that the measured loss could be shifted, relative to its free-electron value, in much the same way that the bulk and surface plasmons of transition metals are shifted by interband transitions. Since our objective in this paper (and in much of the related literature) is the physics of the response of the conduction electrons of the overlayer, and not the response of the transition-metal substrate (an outstanding problem), we would like to suggest that an EELS experiment be performed using aluminum as the substrate. This should provide a stringent quantitative test of the validity of electron-gas theory for monolayer coverage.

It is interesting to note that our electron-gas theory provides a consistent qualitative interpretation of the behavior of the linewidth of the observed loss as function of coverage. This aspect of the experiment has up to now lacked an explanation based on a theory of the dielectric response of the overlayer. Clearly, the behavior of the linewidth is beyond the scope of the classical theory. What is observed is that the width of the loss, quite broad for coverages near threshold for plasmon formation, becomes sharper with further deposition, all the way to saturation coverage. (Threshold corresponds roughly to the coverage for which the work function reaches its minimum—about half monolayer.) Conversely, when the alkali-metal atoms are desorbed, the loss line broadens and eventually disappears at the threshold coverage. MacRae *et al.*² originally suggested that this gave evidence for a metal-insulator transition, an interpretation strongly challenged by Powell.¹² The picture that quite naturally emerges from our electron-gas results is that the broadening and finite-coverage disappearance of the plasmon as the coverage is reduced, is simply a manifestation of Landau damping and the f -sum rule at work. This is illustrated in Fig. 6, where we show the loss function for two-, one-, and half-monolayer coverage, for a wave-vector transfer ($k_{||} = 0.15$) for which the spectral weight of the overlayer-induced loss at low coverage is finite.

Finally, as alluded to above, an angle-resolved EELS experiment has been reported by Jostell⁵ for Na adsorbed on Ni(100). Interestingly, he presented results for one- and two-monolayer coverage. Two features of Jostell's re-

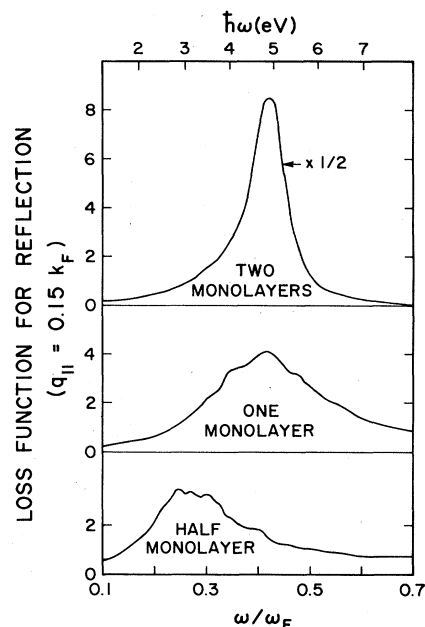


FIG. 6. Energy-loss function $P(q_{||}, \omega)$ for half-, one-, and two-monolayer coverage of sodium on an aluminum substrate for $k_{||} = q_{||}/k_F = 0.15$. The units of $P(q_{||}, \omega)$ are chosen as in Fig. 2. (Note that the two-monolayer loss peak has been reduced by a factor of 2.)

sults that agree qualitatively with ours are the large enhancement of the spectral weight of the loss that results from the adsorption of the second layer, and the upward shift of the frequency of this loss with increasing deflection angles. The main quantitative disagreement between our results and Jostell's experiments is that for two-layer coverage the measured dispersion relation ranges from $\hbar\omega \cong 3.9$ eV for $q_{||} \cong 0.1$ Å to $\hbar\omega \cong 4.3$ eV for $q_{||} \cong 0.5$ Å, while from Fig. 5 we have $\hbar\omega \cong 4.9$ and 5.9 eV, respectively. It would be very useful if Jostell's angle-resolved experiment were repeated, but using aluminum as the substrate (cf. above discussion).

VI. SUMMARY

We have presented the first study of the dynamical response of the conduction electrons of an adsorbed alkali-metal-atom overlayer that is based on a microscopic model of the adsorption process.³⁶ Our quantum-mechanical response calculation shows that for monolayer coverage (or less) the response differs qualitatively from the bulklike response that pertains to thicker films (and which is well described by macroscopic models at small wave vectors). For two-monolayer coverage the overlayer behaves qualitatively like a thicker (adsorbed) film does, with a well-defined plasmon peak that shows spatial dispersion effects at large wave vectors.

We have given a qualitative interpretation of the behavior of the linewidth of the energy-loss peak as function of coverage that is observed experimentally. We have advocated the need that an angle-resolved loss experiment be carried out on an alkali-metal-atom/aluminum chem-

isorption system. That experiment should help elucidate the physics behind the quantitative discrepancy that exists between theory and experiment with regard to the energy of the collective mode for one- and two-monolayer coverage. Such work could provide additional insight into alkali-metal-atom chemisorption and also into electronic behavior in systems of reduced dimensionality.

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