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Effect of nonconservative forces on the neutralization of sputtered and other desorbed ions

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We discuss the effect of nonconservative forces on ions near surfaces and apply it to recent experimental work of Yu on the sputtering of O$^-$ from Nb and Va. These data displayed a significant deviation from the usual exponential dependence of yield on $1/v_\perp$. This deviation which occurs at low velocities was partially explained by Lang using a model in which the sputtered ion interacts with a single surface atom via a Morse potential. Although his model suggests that the effective velocity of the ion is larger than that observed it does not explain the full deviation of the effective velocity, which goes through a minimum and then turns up as the observed velocity goes to zero. In our paper we show that just by including a nonconservative force in the Lang model the full deviation can be explained nicely.

I. INTRODUCTION

Existing semiclassical theories on charge exchange between sputtered or desorbing ions and metal surfaces treat ions as classical particles, where the explicit time dependence of the electron hopping matrix element comes solely from the classical trajectory of the ions.[1-5] Thus the classical equations of motion of the ions play the important role in determining an analytical expression for the ion survival probability, and the energy dependence of the observed ion energy distribution will depend on the choice of ion-surface interaction forces.

Recent experimental data of Yu[6] on ion energy distributions of sputtered O$^-$ from vanadium and niobium surfaces display a significant deviation from the usual exponential dependence of the yield on the inverse of the normal component of the ion velocity. This deviation has been partially explained by Lang[1] with a suitable choice of ion trajectory, derived from a Morse potential. But it does not completely fit the experimental results. Sroubeck[7] introduces the effect of charge diffusion (back flow and buildup of holes in the metal). His model is based on an intuitive rate equation and seems to quantitatively explain the anomalous low-velocity effect observed in Yu's data; however, it does not have the "first-principle" appeal of Lang's approach which uses the Blandin, Nourtier, and Hone[8] method for calculating the neutralization probability. Since there are not enough experimental data available, it is not possible to come to any firm conclusion about the exact mechanism of ion reneutralization, but one can definitely explore various possibilities that may effect the rather complex processes of charge exchange. In this paper we would like to explore the effect of nonconservative forces on ion reneutralization and especially on the ion energy distribution. In the following sections we first review the various derivations of the nonconservative forces and discuss their application to ion reneutralization.

II. THE ORIGIN OF NONCONSERVATIVE FORCES IN QUANTUM MECHANICS

A. Green's-function approach to nonconservative forces

The time-dependent motion of an atom near the surface of a metal couples the affinity level to the Fermi sea. The result of the broadening of the level can be viewed as a nonconservative force acting on the trajectory of the atom. The level width can also be thought of as a slight departure from adiabaticity[9] where there is an exchange of energy between the electronic and atomic coordinates. The nonconservative forces can be derived from generalized correlation functions but can also be obtained from the time derivative of the expectation value of a time-dependent Hamiltonian. Following Blandin, Nourtier, and Hone,[9] the external time-dependent potential $V(t)$ is linearized about the value at some instant of time $t=0$, i.e., $\delta V(t)=V(t)-V(0)$. Therefore, the perturbed Green's function $\tilde{G}$ obeying Dyson's equation departs very little from the unperturbed $\tilde{G}$ corresponding to $\mathcal{H}=\mathcal{H}(0)$, that is,

$$\begin{aligned}\tilde{G}^{a}&=G^{a}+G^{a}\delta V\tilde{G}^{a}+O(\delta V^{2})\\&\simeq G^{a}+G^{a}\delta V G^{a}+O(\delta V^{2})\ ,\end{aligned}\tag{1}$$

where G^a denotes the advanced Green's function. Writing $\tilde{G}$ in terms of $\tilde{G}^{r}$ and $\tilde{G}^{a}$ yields

$$\tilde{G}=G+G^{a}\delta V G+G\delta V G^{r}-G^{a}\delta V G^{r}\ .\tag{2}$$

If $E(0)$ represents the expectation value of the Hamiltonian

$$\mathcal{H}(0),\quad \text{then } \dot{E}(0)=-\mathbf{v}\cdot\mathbf{F}\ ,\tag{3}$$

where $\mathbf{v}$ is the velocity of the atom and $\mathbf{F}$ represents all forces acting on the particle, (i.e., both conservative and nonconservative forces). E (0) can be written as

$$\begin{aligned}\dot{E}(0)&=\sum_{kk'}\dot{V}_{k'k}(0)\langle C_k^{+}(0)C_{k'}(0)\rangle\\&=\operatorname{Im}\operatorname{Tr}[\dot{V}(0)\tilde{G}(0,0^{+})]\ .\end{aligned}\tag{4}$$

If $\tilde{G}(0,0^{+})$ is replaced by G, then the first contribution to $\dot{E}(0)$ would be the conservative part of the force. Since for our problem we are interested in the nonconservative contribution to the force, we will look at the second contribution to $\dot{E}(0)$. The linear δV terms of Eq. (2) when substituted into Eq. (4) will give the nonconservative forces. Therefore, the frictional contribution to$\dot{E}(0)$ is

$$\dot{E}_f(0)=\mathrm{Im}\,\mathrm{Tr}\,\dot{V}(0)[G_0^a\delta V_0 G_0+G_0\delta V_0 G_0^r] \ . \tag{5}$$

If $\delta V(t)=\dot{V}(0)t$, then Eq. (5) yields

$$\dot{E}_f=\pi\,\mathrm{Tr}[\dot{V}\delta(\varepsilon_f-\mathcal{H})]^2 \ . \tag{6}$$

In the vector space spanned by the eigenfunctions of $\mathcal{H}$, i.e., $|\varepsilon,\nu\rangle$,

$$\dot{E}_f=\pi\sum_{\bar{\nu}\bar{\nu}'}|\langle\varepsilon_f\bar{\nu}|\dot{V}|\varepsilon_f\bar{\nu}'\rangle|^2 \ , \tag{7}$$

and the friction force is

$$F_f=-\pi\sum_{\bar{\nu},\bar{\nu}'}|\langle\varepsilon_f\nu|\nabla V|\varepsilon_f\nu'\rangle|^2\mathbf{v} \ . \tag{8}$$

The velocity dependence of the friction (nonconservative) force can also be obtained from the force-force correlation function as seen in Refs. 10 and 11. Equation (8) yields a nonconservative force that is dissipative in nature.

B. Nonconservative force from the optical potential

From the Born-Oppenheimer separability of the wave function, Brenig[12] has shown that the electronic level width function, which is proportional to the reneutralization or ionization rate, acts as a complex potential on the atom (or ion). Since we would like to consider the atom's trajectory as a classical one, first the time dependence of the expectation value of the momentum operator under the influence of the optical potential has to be examined, and then using the Erhenfest theorem the classical equation of motion can be obtained. Starting with the Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t}=H\psi=[H_H+H_A]\psi \ , \tag{9}$$

where $H_H=p_{\mathrm{can}}^2/2M$ is the Hermitian part of the Hamiltonian and H_A, which is equal to the optical potential, is the antihermitian part. (For simplicity we restrict ourselves to one dimension and ignore the conservative part of the potential). p_{can} represents the canonical momentum, namely $-i\hbar d/dZ$. We assume that H_A is explicitly dependent on time via the expectation value of the coordinate Z, i.e., $H(\langle Z\rangle)$. The time dependence of the expectation value of any operator O is given by

$$\frac{d}{dt}\int\psi^* O\psi dZ=\int\psi^*\left[\frac{i}{\hbar}[H_H,O]_-+\frac{\partial O}{\partial t}-\frac{i}{\hbar}[H_A,O]_+\right]\psi dZ \ , \tag{10}$$

where $[H_H,O]_{\mp}$ are the commutation and anticommutation of H_H and O, respectively.

If we now let $O=Z$, then

$$\frac{d}{dt}\langle Z\rangle=\frac{1}{M}\langle p_{\mathrm{can}}\rangle-\frac{2i}{\hbar}H_A\langle Z\rangle \ . \tag{11}$$

The mechanical-momentum operator can then be defined as

$$p_{\mathrm{can}}-\frac{2iM}{\hbar}H_A Z=p_m=Mv_m \ . \tag{12}$$

It is the expectation value of this mechanical momentum that is measurable and therefore translates into the classical momentum via the Erhenfest theorem. Substituting p_m into Eq. (10),

$$\begin{aligned}\frac{d}{dt}\langle p_m\rangle=&\frac{i}{\hbar}\left\langle\left[\frac{p_{\mathrm{can}}^2}{2M},\left(\frac{-2i}{\hbar}\right)H_A MZ\right]\right\rangle\\&-\left(\frac{2iM}{\hbar}\right)\frac{\partial}{\partial t}\langle Z\rangle\frac{\partial}{\partial\langle Z\rangle}H_A\\&-\frac{2i}{\hbar}H_A\langle p_{\mathrm{can}}\rangle+\left(\frac{-2i}{\hbar}\right)^2 H_A^2 M\langle Z\rangle \ .\end{aligned} \tag{13}$$

In the classical limit

$$\langle p_m\rangle=p(t)=M\frac{\partial}{\partial t}\langle Z\rangle=M\frac{\partial}{\partial t}Z(t) \ .$$

Therefore the classical force equation is

$$\begin{aligned}F=M&\left[-\frac{4i}{\hbar}H_A-\frac{2i}{\hbar}\frac{\partial H_A}{\partial Z(t)}Z(t)\right]v(t)\\&+\frac{4M}{\hbar^2}H_A^2 Z(t) \ .\end{aligned} \tag{14}$$

If H_A represents the explicit time-dependent level-width function, then the aforementioned expression for the force F represents the velocity-dependent nonconservative force arising due to the coupling of the electronic level of the desorbing atom with that of the continuum of the metal. If H_A is considered small then the last term of Eq. (14) can be neglected. It is again seen that a complex potential gives rise to a velocity-dependent dissipative force.

Specifically when $H_A=-i\Delta e^{-\alpha Z(t)}$ one can easily show that

$$v(Z)=v_{\perp}\left[1+\frac{2C}{\alpha v_{\perp}^2}\left(Z+\frac{1}{\alpha}\right)\right]^{1/2} \tag{15}$$

and

$$C=\frac{4}{\hbar^2}\Delta^2>0$$

with $v_{\perp}=v_{\infty}$. We will see in the next section that this velocity dependence serves to explain the sputtering data of Yu previously alluded to.

III. VELOCITY DEPENDENCE OF THE ION SURVIVAL PROBABILITY

A. Ion survival probability from time-dependent perturbation theory

The electron occupation number $n_a(t)$ of the affinity level of a desorbing ion is obtained from time-dependent perturbation theory[8] and can be written as

$$n_a(t)=\frac{1}{\pi}\int_{-\infty}^{\varepsilon_f}d\varepsilon\left|\int_{-\infty}^{t}d\tau U_{ak}(\tau)\exp\left[i\int_{\tau}^{t}[\varepsilon-\varepsilon_a(\tau')+i\Delta(\tau')]d\tau'\right]\right|^2 , \qquad (16)$$

where $U(t)$ is the electron hopping matrix element, Δ is the level width function and is proportional to the reneutralization rate, and $\varepsilon_0(t)$ corresponds to the electron energy level of the desorbing ion. The corresponding rate equation obtained by differentiating Eq. (16) is

$$\frac{dn_a(t)}{dt}=\frac{-2}{\pi}\Delta(t)n_a(t)+\frac{1}{\pi}\int_{-\infty}^{\varepsilon_f}d\varepsilon\, U_{ak}(t)A_0^*(t)+\text{c.c.} , \qquad (17)$$

where

$$A_0(t)=\int_{-\infty}^{t}dt'U_{ak}(t')\exp\left[i\int_{t'}^{t}dt''\right][\varepsilon-\varepsilon_a(t'')]P(t,t')$$

and

$$P(t,t')=\exp\left[-\int_{t'}^{t}\Delta(\tau)d\tau\right] .$$

The first term of Eq. (17) represents the electron survival rate on the atom and can be identified with the Menzel, Gomer, and Redhead (MGR) (Ref. 13) contribution to the ion survival probability. The second and third terms of Eq. (17) correspond to the rate at which the substrate states are replenished by the hopping back of the ionizing (neutralizing) electron. The MGR model does not take into account the effect of electrons tunneling back into the substrate. If in Eq. (17) the matrix element for tunneling back into the substrate is taken to be a δ function in time, i.e.,

$$U_{ak}(t)\propto U_{ak}\delta(t) ,$$

then the solution to Eq. (16) gives

$$n_a(\infty)\propto P(\infty,0)\propto\exp\left[-2\int_{0}^{\infty}\Delta(\tau)d\tau\right] , \qquad (18)$$

which is identical to the MGR result. The MGR model of ion survival probability is simple, and we will use it to calculate the reduction factor P for simple trajectories.

B. Ion survival probability with friction force proportional to the velocity

For simplicity of calculation we choose a hard wall conservative potential for the desorbing ion. The frictional force is chosen to be

$$F_f=Cv_Z(Z)e^{-Z/Z_c} , \qquad (19)$$

where C is constant either positive or negative depending on the nature of friction force (electronic transition or chemical plasma effect) and $v_Z(Z)$ is the surface-normal component of the ion velocity. The term e^{-Z/Z_d} is modeled into the equation to take care of the Z dependence of the level width function in the case of electronic excitations [Eq. (8)] or the Z dependence of the surface electron density in the case of the plasma polarization contribution to the energy change. The equation of motion of a particle under the influence of a friction force is then

$$v_Z(Z)=v_\perp+cZ_d\exp[-Z/Z_d] , \qquad (20)$$

$v_\perp$ being the normal component of the velocity of the detector. Usually the level width function $\Delta(\tau)$ is taken to be of the form $\Delta(\tau)=\Delta_0e^{-\gamma Z}$. If $\gamma\approx 1/Z_d$ then $P(\propto,0)$ becomes

$$P(\infty)=P(\infty,0)=\exp\left[-2\int_{Z_c}^{\infty}\frac{\Delta(Z)}{v_Z(Z)}dZ\right]=\exp\left[-\frac{2\Delta_0}{\gamma v_\perp C_0}\ln(1+C_0e^{-\gamma Z_c})\right] , \qquad (21)$$

where $C_0=C/\gamma v_\perp$. It is seen that $(-\ln P)^{-1}$ is not linear in $v_\perp$, as is often assumed. For $C\rightarrow 0$ one recovers the phenomenological exponent inverse velocity dependence.

C. Ion survival probability using an inverse velocity-dependent nonconservative force

In this section we investigate the nature of the velocity dependence of the ion survival probability for the case of the $v_{Z_1}^{-2}$-dependent nonconservative force. This model of the force is encountered in the case of fluctuations of the electric field in a plasma.[14]

The equation of motion is

$$v_Z\frac{dv_Z}{dZ}+a\frac{e^{-\alpha Z}}{v_Z^2}=0 ,$$

where a is the force constant and $e^{-\alpha Z}$ can be associated with the tailing of electron density with the surface-normal distance. The solution of the equation is

$$v_Z(Z)=\left[\frac{4a}{\alpha}e^{-\alpha Z}+v_\perp^4\right]^{1/4} .$$

Substituting the expression in the MGR model for the ion survival probability, we get for $\alpha=\gamma$

$$P(\infty)=\exp\left[\frac{-2\Delta_0}{\gamma v_\perp}\left\{\left[\left[1+\frac{4a}{\gamma v_\perp^4}e^{-\gamma Z_c}\right]^{3/4}-1\right]\Big/\left[\frac{4a}{\gamma v_\perp^4}\right]\right\}\right] . \qquad (22)$$

For small a, we expand

$$\left[1+\frac{a}{\gamma v_{\perp}^{4}}e^{-\gamma Z_c}\right]^{3/4}$$

to second order in a

$$P(\infty)=\exp\left[-\tfrac{3}{2}\frac{\Delta_0}{\gamma v_{\perp}}e^{-aZ_c}\left[1-\tfrac{1}{2}\frac{ae^{-aZ}}{\gamma v_{\perp}^{4}}\right]\right] . \qquad (23)$$

A plot of $-[\ln P(\infty)]^{-1}$ versus $v_{\perp}$, using Eq. (23) will deviate from linearity at the low-velocity regime. If a is negative, i.e., the nonconservative force is such that the ion gains energy from the system,[14] then the plot will deviate upward similar to that observed by Yu.[4]

IV. APPLICATION TO SPUTTERING OF O^- FROM Va/Nb SURFACES

In this section we review the results of time-dependent perturbation theory for the ionization or reneutralization probability by Blandin, Nourtier, and Hone,[9] Norskov and Lundquist,[2] and Brako and Newn.[15] This theory was applied to the sputtering of oxygen from vanadium and niobium surfaces by Lang[1] which we will extend to include dissipative or optical potentials. The metal is treated as a noninteracting Fermi gas. The electronic state $|a\rangle$ of the desorbing atom interacts with the state $|k\rangle$ of the metal via the matrix element $U_{ak}=\langle a|U|k\rangle$ where U is the time-dependent perturbing potential representing the atom-surface interaction. The charge transfer between the broadened level $|a\rangle$ and the level $|k\rangle$ is assumed to be essentially resonant. Following previous workers we approximate the level broadening function $\Delta(t)$ with an exponential dependence, namely,

$$\begin{aligned}\Delta(t)&=\Delta_0\exp[-\gamma Z(t)] \quad t>0 ,\\ &=0 \quad t<0 , \qquad (24)\end{aligned}$$

$Z(t)$ being the normal component of the classical trajectory of the atom. Using Eq. (24) the ionization probability, derived in Ref. 9 is,

$$P(\infty)\propto\exp[-(\phi-A)/\varepsilon_0(v_{\perp})] , \qquad (25)$$

where ϕ is the work function of the metal, and A the affinity level of the atom and $\varepsilon_0\propto v_{\perp}$, where $v_{\perp}$ is the normal component of the velocity of the desorbing particle. The derivation of Eq. (25) assumes $Z_1=v_{\perp}t$ and terms $O(e^{-\Delta_0/\gamma v_{\perp}})$ are neglected.

From the experimental viewpoint the validity of Eq. (25) has been tested by Ming Yu[4] for O^- from Va and Nb surfaces. The metal work function is changed by depositing a sublayer of lithium. Changes in the work function up to 3 eV are achieved by the method. Experimental extraction of ε_0 entails measuring $\Delta(\ln P)/\Delta\phi$, and therefore,

$$\varepsilon_0=-(\Delta\ln P/\Delta\phi)^{-1}\approx-\left[\frac{d\ln P}{d\phi}\right]^{-1} . \qquad (26)$$

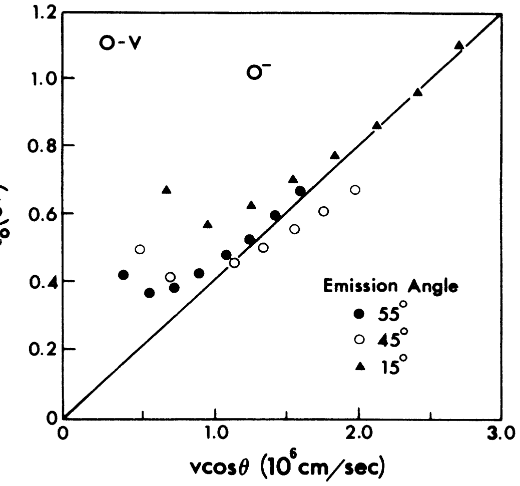

FIG. 1. Dependence of ε_0 [for O^- sputtered from oxygenated (1 L) vanadium surface] on the normal component $v_{\perp}$ of the emission velocity as measured by Yu.

Important features of the experimental data in Figs. 1 and 2 are (a) $\ln P$ is linear in ϕ, (b) ε_0 is linear in $v_{\perp}$ for velocities greater than 1×10^6 cm/sec, (c) ε_0 versus $v_{\perp}$ has a positive intercept, (d) ε_0 versus $v_{\perp}$ shows a minimum for $v_{\perp}$ around 0.5×10^6 cm/sec, (e) both the intercept and the minimum have polar angle dependence. Lang[1] attempts to explain the anomalous behavior of ε_0 for low velocities by correcting the classical ion trajectories for potential effects. He models the sputtering of O^- using a two-body Morse potential existing between the oxygen atom and the Nb or Va atom. Numerical calculation of ε_0 would extrapolate to a $v_{\perp}=0$ intercept and there is also a slight appearance of a minimum, Fig. (3). The problem of this model is the presence of a cutoff in the velocity so that the low-velocity features are obscured, as well as the lack of significant turn up of the ε_0 versus $v_{\perp}$ curve.

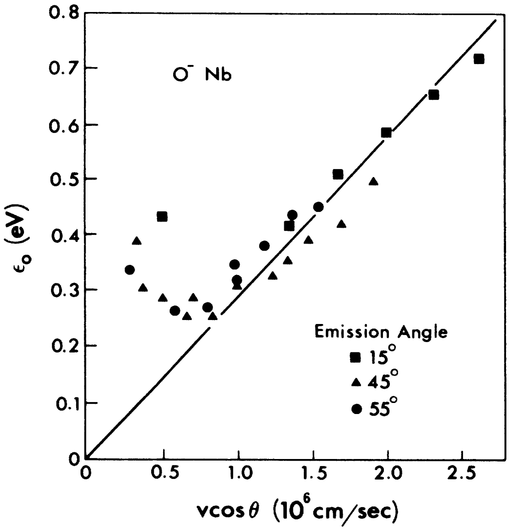

FIG. 2. Dependence of ε_0 [for O sputtered from oxygenated (1 L) niobium surface] on the normal component $v_{\perp}$ of the emission velocity as measured by Yu.

In our previous work on this problem[5] it was shown

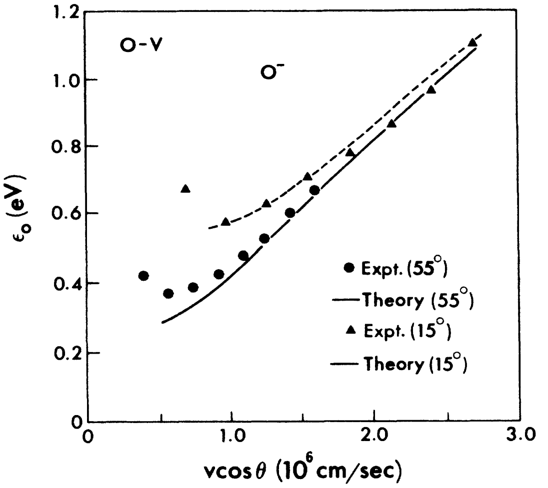

FIG. 3. Lang's theoretical values of ε_0 compared to Yu's experimental ε_0 values for O^- from vanadium.

that if $v_\perp$ in Eq. (25) is replaced by the quantum expectation value of the velocity operator, a good fit to the experimental data of Yu is obtained. In order to explain the nonlinearity of ε_0 versus $v_\perp$, however, a large unrealistic optical force was required. The necessity of a quantum model for the trajectory was therefore viewed as questionable. However, the existence of a classical nonconservative force remains a possibility.

In this section we would like to focus on the effect of a velocity-dependent friction force on $P(\infty)$. From Eq. (20) the equation for the velocity is given by

$$v_Z(Z)=v_\perp+c/\gamma e^{-\gamma Z} ,$$

where $v_\perp=v_Z(\infty)$ or the velocity measured by Yu. The above equation assumes a hard wall for the surface potential. Any image correction to the potentials are ignored on the ground that most of the ionization occurs very close to the surface within a characteristic time of 10^{-13} sec and therefore effects of all long-ranged potentials in the calculation of $P(\infty)$ are small.

As has been shown by Brako and Newn[15] and Lang,[1] if

$$E_a(Z)=E_f+b(Z-Z_c) , \tag{27}$$

then

$$P(\infty)=\exp[-2\Delta_0\exp(-\gamma Z_0)/\gamma v_\perp] , \tag{28}$$

where Z_c is the distance and where $E_\infty(Z)$ crosses the Fermi energy. This expression is no different than that obtained for the MGR model provided the trajectory is written as $Z(t)=Z_c+v_\perp t$, or the effective distance at which most of ionization occurs is the Fermi cross-over point. We can thus introduce the velocity correction to this model and obtain a new expression for $P(\infty)$, i.e., that of Eq. (21).

If the work function dependence $(E=-\phi)$ of $P(\infty)$ comes from $Z_c(\phi)$ then ε_0 can be written as

$$\varepsilon_0=(-v_\perp Z'/2\Delta_0)[1+(c/\gamma v_\perp)c^{-\gamma Z_c}]/e^{-\gamma Z_c} , \tag{29}$$

where $Z'=dZ_c/d\phi$ and is negative. As seen Eq. (29) will give an intercept for the ε_0 versus $v_\perp$plot but will not produce the observed nonlinearity.

$P(\infty)$ calculated earlier is an approximate way of introducing the velocity correction to the ionization probability. One can obtain a better expression for $P(\infty)$ from the Blandin, Nourtier, and Hone expression for $n_a(\infty)$. Knowing $v_Z(Z)$ a trajectory expression for $Z(t)$ can be obtained. Neglecting terms of $O(e^{-\Lambda})$ or higher[1] and after some calculation we obtain the expression for $P(\infty)$

$$P(\infty)\propto \exp[-(2\Delta(Z_c)/\gamma v_\perp)(1+C_1/v_\perp)] , \tag{30}$$

where

$$C_1=c/\gamma,\quad \Lambda=\Delta_0/\gamma v_\perp .$$

In order to obtain Z_c we take the same route of Lang, namely,

$$E_f-E_a(Z_c)=(\phi-A+E_0)e^{-\alpha Z_c}-(\phi-A) , \tag{31}$$

where A is the affinity level of O at $z=\infty$ and is equal to 1.5 eV. The above expression assumes that $E_c(Z)$ follows the surface barrier potential. The inverse decay length α for the potential is calculated for a high-density metal substrate as being equal to 0.4 bohr^{-1} and photoemission data gives the value of $E_f=E_a(0)=E_0$ for O as 6 eV.[16,17] From Eq. (31) the Fermi crossover distance is given as

$$Z_c=\left[\frac{1}{\alpha}\right]\ln[(\phi-A+E_0)/(\phi-A)] . \tag{32}$$

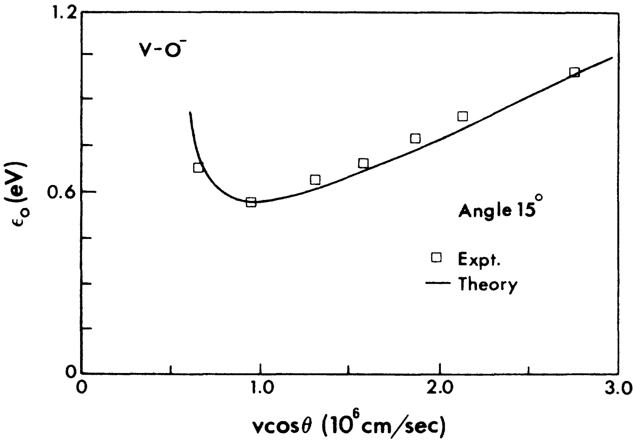

FIG. 4. Theoretical fit to the sputtering data of O^- from vanadium surface. $\phi=5.2$ eV, $E_0=6.0$ eV, $A=1.5$ eV, $\alpha=0.4$ bohr^{-1}, $\gamma=0.5$ bohr^{-1}, $\Delta_0=1.59$ eV, $c_1=0.0146\times10^6$ cm/sec.

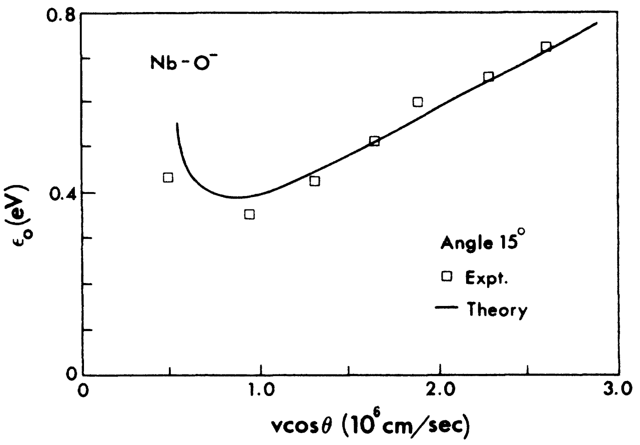

FIG. 5. Theoretical fit to the sputtering data of O from niobium surface. $\phi=4.4$ eV, $E_0=6.0$ eV, $A=1.5$ eV, $\alpha=0.4$ bohr^{-1}, $\gamma=0.5$ bohr^{-1}, $\Delta_0=1.7$ eV, $c_1=0.007\times10^6$ cm/sec.

Equation (31) is linearized around Z_c and substituted into the expression for $P(\infty)$. From Eq. (30) and Eq. (26)

$$\varepsilon_0=\frac{\alpha}{2\Delta_0}\frac{(\phi-A+E_0)^{\gamma/\alpha+}}{E_0(\phi-A)^{\gamma/\alpha-1}}v_\perp[1+C_1/v_\perp]^{-1}\,, \tag{33}$$

which is seen to be nonlinear in $v_\perp$.

In order to fit the experimental data ϕ and γ need to be known. The work function of polycrystalline vanadium and niobium is 4.3 eV (Ref. 9) but the change in ϕ introduced by 1 L of oxygen is 0.9 eV for vanadium and 0.1 eV for niobium.[9] Therefore $\phi=5.2$ eV for Va and 4.4 eV for Nb are taken. In Ref. (18) and (19), Δ_0 is of the order of 1.5 eV and $\gamma\approx0.5$ bohr^{-1}. For the purpose of fitting the data we use $\Delta_0=1.59$ eV for vanadium and 1.7 eV for niobium. In our model C_1 is an experimental fitting parameter and $C_1=-0.0146\times10^6$ cm/sec for Va and -0.007×10^6 cm/sec for Nb. The theoretical fit to the experimental curves are shown in Figs. 4 and 5.

An interesting point to note is that C_1 which is required to reproduce Yu's data must be negative. This implies that the nonconservative force is one in which an ion gains energy from the substrate (similar to the contribution from polarization of a plasma). One may therefore conclude that our model of n_a including a nonconservative force may well be the cause of the nonlinear behavior of ε_0 versus $v_\perp$. This model can also augment that of Lang, where the occurrence of a minimum in the potential leads to an effective increase in the kinetic energy of the ion near the surface at the expense of the Morse well. More experimental data in the low-velocity regime is required for a better understanding of the ionization probability.

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