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Sticking probability on metal surfaces: Temperature dependence of the electron-hole pair mechanism

K. Schönhammer
I. Institut für Theoretische Physik, Universität Hamburg, D-2000 Hamburg 36, Federal Republic of Germany

O. Gunnarsson
Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany

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We have studied how the sticking coefficient on metal surfaces depends on the substrate temperature T_s when the energy exchange is due to electron-hole pairs. A previously derived exact result for the energy-loss (-gain) probability in one round trip is generalized to finite substrate temperatures. This serves as the input for the stochastic equation which is used to describe the adparticle motion in the adsorption well. The solution of this equation shows that two competing effects can lead to a very weak dependence of the sticking probability on the substrate temperature.

I. INTRODUCTION

When an atom or a molecule hits a solid surface it can only stick at the surface if it can lose its kinetic energy. Two energy-loss mechanisms have been proposed, namely the coupling to the translational motion of the substrate atoms, i.e., excitation of phonons, and the energy loss to the low-energy electron-hole (*e-h*) pairs.[1] In a recent publication (I) we have presented calculations for the sticking probability focusing on the *e-h* pair mechanism for particles with thermal energies impinging on a *zero*-temperature metal substrate.[2] In this paper we discuss the additional effects that occur for finite substrate temperatures T_s.

Because of the large mass of the adsorbate compared to the electron mass, we assume, as in I, that the adsorbate nuclear motion can be treated classically. At zero substrate temperature the sticking coefficient is then given by the probability that the particle loses more than its initial kinetic energy in the *first round trip* in the metal-adsorbate potential well. A single (unperturbed) classical trajectory for the adparticle is a reasonable approximation if the energy loss during one round trip is small compared to the kinetic energy of the particle in the adsorption well given by the binding energy. At finite substrate temperatures the description of sticking is modified by the fact that excitations in the substrate are already present when the adparticle hits the surface. Thus, besides energy-loss processes, energy-gain processes are also possible.

We will show in the following that the (substrate-) temperature dependence of the probability of the adparticle to leave the surface after the first round trip strongly depends on the energy-loss distribution for a zero-temperature case: If at $T_s = 0$ the probability p_0 for elastic scattering is nonnegligible, this elastic scattering probability is strongly reduced due to stimulated emission of *e-h* pairs, and the probability of leaving after the first round trip is *decreased.* If on the other hand, the $T_s = 0$ elastic scattering probability p_0 is negligible, the probability of a loss event decreases with increasing T_s because of the gain events and the probability of leaving after the first round trip *increases.* At finite T_s the processes during the first round trip do not alone determine the sticking coefficient, because an adparticle which has lost more than its initial kinetic energy in the first round trip can gain enough energy from the excitations present in the substrate to leave the surface during the next few round trips before it has fallen deep into the potential well. One way to qualitatively describe this behavior is to assume that the different round trips in the adsorption well can be described as statistically independent. This leads to the master equation discussed by Iche and Nozières.[3] To obtain the sticking coefficient we first have to obtain a microscopic expression for the energy transfer per round trip and then solve the master equation.

As we are interested in adparticles chemisorbing on a metal surface [binding energies E_b in the eV range and surface temperatures on the order of room temperature or less ($kT_s << E_b$)], the question of sticking is decided near the top of the adsorption well. We therefore assume that the energy transfer per round trip is identical for all the relevant round trips, i.e., even a trajectory which corresponds to a situation where the particle is trapped near the top of the adsorption well is approximated by the elastic trajectory of the first round trip. In the next section we present a calculation of the spectrum of particle-hole pairs created (or absorbed) by the adparticle in the first round trip. This generalizes the results of I to finite surface temperatures.

II. DESCRIPTION OF THE ROUND TRIP

Before the adparticle hits the surface the substrate is in an electronic state $|E_m\rangle$ with a probability $p(E_m)=e^{-E_m/kT_s}/Z$, where Z is the partition function. We want to calculate the energy distribution in the substrate after one round trip. This is given by

$$P(\epsilon)=\sum_{m,n} |\langle E_n|U|E_m\rangle|^2 p(E_m)\delta(\epsilon-(E_n-E_m))$$
$$=p_0\delta(\epsilon)+\tilde{P}(\epsilon)\ , \qquad (1)$$

where U is the unitary operator that describes the time evolution of the electronic wave function under the action of the perturbation presented by the adparticle motion. Thus $U|E_m\rangle=|\phi_m(\infty)\rangle$ is the solution of the time-dependent Schrödinger equation with the full Hamiltonian $H_t=H_0+V_t$ including the perturbation due to the adsorbate

$$i\frac{\partial}{\partial t}|\phi_m(t)\rangle=H_t|\phi_m(t)\rangle \qquad (2)$$

with the initial condition $|\phi_m(-\infty)\rangle=|E_m\rangle$. The probability of elastic scattering is given by p_0. In Eq. (1) the thermal average over the possible initial states has been performed. In I we have calculated $P(\epsilon)$ for a model of noninteracting electrons at $T_s=0$, describing the low-lying e-h pairs as bosons. It is straightforward to generalize the calculations in I to finite temperatures. To show the connection of our boson approach to standard quantum-mechanical techniques we describe here an alternative way to calculate $P(\epsilon)$, which like the approach in I uses the fact that a thermal adparticle presents a slow perturbation to the substrate electrons. We therefore introduce the adiabatic eigenstates $|E_m^t\rangle$:

$$H_t|E_m^t\rangle=E_m^t|E_m^t\rangle\ . \qquad (3)$$

The time evolution of the initial state $|E_m\rangle$ can be described in terms of the amplitudes $c_{n,m}(t)$ defined as

$$c_{n,m}(t)\equiv\exp\left[i\int_{-\infty}^{t}E_n^{t'}dt'\right]\langle E_n^t|\phi_m(t)\rangle\ . \qquad (4)$$

Differentiating with respect to time yields

$$\frac{\partial c_{n,m}(t)}{\partial t}=\sum_{n'}\left\langle\frac{\partial}{\partial t}E_n^t\middle|E_{n'}^t\right\rangle\exp\left[i\int_{-\infty}^{t}(E_n^{t'}-E_{n'}^{t'})dt'\right]c_{n',m}(t)\ . \qquad (5)$$

As in time-dependent perturbation theory we can write the equation for the $c_{n,m}(t)$ as an integral equation. In the case of weak inelasticity we can iterate this equation to obtain the transition amplitudes (for $n\neq m$)

$$c_{n,m}(t)=\int_{-\infty}^{t}\left\langle\frac{\partial}{\partial t'}E_n^{t'}\middle|E_m^{t'}\right\rangle\exp\left[i\int_{-\infty}^{t'}(E_n^{t''}-E_m^{t''})dt''\right]dt'+\cdots\ . \qquad (6)$$

If we differentiate $\langle E_n^t|(H_t-E_n^t)=0$ with respect to time and multiply from the right by $|E_m^t\rangle$ we can use the resulting relation to rewrite (6) (for $n\neq m$) as

$$c_{n,m}(\infty)=\int_{-\infty}^{\infty}\frac{\left\langle E_n^t\middle|\frac{\partial H_t}{\partial t}\middle|E_m^t\right\rangle}{E_n^t-E_m^t}\exp\left[i\int_{-\infty}^{t}(E_n^{t'}-E_m^{t'})dt'\right]dt\ . \qquad (7)$$

In terms of the $c_{n,m}(\infty)$, $P(\epsilon)$ is given as

$$P(\epsilon)=\sum_{m,n}|c_{n,m}(\infty)|^2 p(E_m)\delta(\epsilon-(E_n-E_m))\ . \qquad (8)$$

As in I we assume that $\dot{H}_t=\partial H_t/\partial t$ is a one-particle operator. We express this operator in terms of the creation and annihilation operators $\psi_{\alpha,t}^{\dagger}$ and $\psi_{\alpha,t}$ of the adiabatic one-particle states $H_t|\epsilon_\alpha^t\rangle=\epsilon_\alpha|\epsilon_\alpha^t\rangle$. Note that in the limit of a semi-infinite substrate the energy of an extended one-particle state is not changed by the presence of a localized perturbation, i.e., ϵ_α is independent of time:

$$\dot{H}_t=\sum_{\alpha,\alpha'}\langle\epsilon_\alpha^t\,|\,\dot{H}_t\,|\,\epsilon_{\alpha'}^t\rangle\psi_{\alpha,t}^\dagger\psi_{\alpha',t}\ . \tag{9}$$

The matrix element occurring in the transition amplitude in (7) can be expressed in terms of the unperturbed substrate eigenstates and the unperturbed creation and annihilation operators $\psi_\alpha^\dagger$ and $\psi_{\alpha'}$,

$$\begin{aligned}&\langle E_n^t\,|\,\psi_{\alpha,t}^\dagger\psi_{\alpha',t}\,|\,E_m^t\rangle u(E_n^t-E_m^t)\\&\quad=\langle E_n\,|\,\psi_\alpha^\dagger\psi_{\alpha'}\,|\,E_m\rangle u(\epsilon_\alpha-\epsilon_{\alpha'})\ ,\end{aligned} \tag{10}$$

where $u(x)$ is an arbitrary function. The equality of the first factors follows from the fact that the $|\,E_m^t\rangle$ are built from the $\psi_{\alpha,t}^\dagger$ in identically the same way as the $|\,E_m\rangle$ are built from the $\psi_\alpha^\dagger$. The argument $E_m^t-E_n^t$ in the function u can be replaced by $\epsilon_\alpha-\epsilon_{\alpha'}$ because $\langle E_n^t\,|\,\psi_{\alpha,t}^\dagger\psi_{\alpha,t}\,|\,E_m^t\rangle$ vanishes unless $E_n^t-E_m^t=\epsilon_\alpha-\epsilon_{\alpha'}$. From this argument we conclude that while the individual energies E_n^t depend on time, the energy difference of two adiabatic eigenstates connected by a nonvanishing matrix element with respect to $\dot{H}_t$ are *independent* of time, which allows us to simplify the exponents in (7). Inserting (7) together with (10) in (8) yields

$$\begin{aligned}\widetilde{P}(\epsilon)&=\sum_{m,n}p\left|(E_m)\left\langle E_m\left|\sum_{\alpha_1\alpha_2}v_{\alpha_1\alpha_2}\psi_{\alpha_1}^\dagger\psi_{\alpha_2}\right|E_n\right\rangle\right\langle E_n\left|\sum_{\alpha_3\alpha_4}v_{\alpha_3\alpha_4}\delta(\epsilon-(\epsilon_{\alpha_3}-\epsilon_{\alpha_4}))\psi_{\alpha_3}^\dagger\psi_{\alpha_4}\right|E_m\right\rangle\\&=\sum_{\alpha_1\alpha_2}\sum_{\alpha_3\alpha_4}v_{\alpha_1\alpha_2}v_{\alpha_3\alpha_4}\delta(\epsilon-(\epsilon_{\alpha_3}-\epsilon_{\alpha_4}))\langle\psi_{\alpha_1}^\dagger\psi_{\alpha_2}\psi_{\alpha_3}^\dagger\psi_{\alpha_4}\rangle\ ,\end{aligned} \tag{11}$$

where $\langle\ \rangle$ denotes the thermal average and

$$v_{\alpha_1\alpha_2}=\int_{-\infty}^{\infty}\frac{\langle\epsilon_{\alpha_1}^t\,|\,\dot{H}_t\,|\,\epsilon_{\alpha_2}^t\rangle}{\epsilon_{\alpha_1}-\epsilon_{\alpha_2}}e^{i(\epsilon_{\alpha_1}-\epsilon_{\alpha_2})t}dt\ . \tag{12}$$

For $\alpha_3\neq\alpha_4$ the expectation value can be expressed in terms of Fermi functions as

$$\langle\psi_{\alpha_1}^\dagger\psi_{\alpha_2}\psi_{\alpha_3}^\dagger\psi_{\alpha_4}\rangle=f(\epsilon_{\alpha_1})[1-f(\epsilon_{\alpha_2})]\delta_{\alpha_1\alpha_4}\delta_{\alpha_2\alpha_3} \tag{13}$$

and we obtain for the inelastic part of $P(\epsilon)$

$$\widetilde{P}(\epsilon)=\sum_{\alpha_1\alpha_2}|\,v_{\alpha_1\alpha_2}\,|^2f(\epsilon_{\alpha_1})[1-f(\epsilon_{\alpha_2})]\delta(\epsilon-(\epsilon_{\alpha_2}-\epsilon_{\alpha_1}))\ . \tag{14}$$

The elastic scattering probability p_0 follows from the sum rule $\int P(\epsilon)d\epsilon=1$:

$$p_0=1-\int_{-\infty}^{\infty}\widetilde{P}(\epsilon)d\epsilon=1-\sum_{\alpha_1\alpha_2}|\,v_{\alpha_1\alpha_2}\,|^2f(\epsilon_{\alpha_1})[1-f(\epsilon_{\alpha_2})]\ . \tag{15}$$

In the derivation of the "golden-rule-type" expression (14) we have assumed weak inelasticity and have, therefore, iterated the integral version of Eq. (5). The breakdown of this assumption is signaled when $\int\widetilde{P}(\epsilon)d\epsilon$ becomes larger than one, which would lead via (15) to a negative p_0. A method to avoid this difficulty without going beyond the first iteration of Eq. (5) suggests itself if we write the expressions (14) and (15) in the form

$$P(\epsilon)=\int_{-\infty}^{\infty}\left[1-\sum_{\alpha_1\alpha_2}|\,v_{\alpha_1\alpha_2}\,|^2f(\epsilon_{\alpha_1})[1-f(\epsilon_{\alpha_2})](1-e^{-i(\epsilon_{\alpha_2}-\epsilon_{\alpha_1})t})\right]e^{i\epsilon t}\frac{dt}{2\pi}\ . \tag{16}$$

If we now consider the expression in the large parentheses as the first two terms of the expansion of an exponential, we obtain

$$P(\epsilon)=\int_{-\infty}^{\infty}\exp\left[-\sum_{\alpha_1\alpha_2}|\,v_{\alpha_1\alpha_2}\,|^2f(\epsilon_{\alpha_1})[1-f(\epsilon_{\alpha_2})](1-e^{-i(\epsilon_{\alpha_1}-\epsilon_{\alpha_2})t})\right]e^{i\epsilon t}\frac{dt}{2\pi}\ . \tag{17}$$

To evaluate the sums in the exponent we again use the fact that the adparticle presents a *slow* perturbation to the electronic system. The adiabatic one-particle states $|\epsilon_\alpha^t\rangle$ can generally be characterized by the energy ϵ and additional quantum numbers σ, i.e., we replace the summation over α by an integration over ϵ and a summation over σ $[\alpha\rightarrow(\epsilon,\sigma)]$ and write the states in the following as $|\epsilon,\sigma\rangle^t$. With this notation Eq. (12) reads

$$v_{\alpha_1\alpha_2}=\frac{1}{\epsilon_1-\epsilon_2}\int_{-\infty}^{\infty}{}^t\langle\epsilon_1,\sigma_1|\dot{H}_t|\epsilon_2,\sigma_2\rangle^t e^{i(\epsilon_1-\epsilon_2)t}dt\ . \tag{18}$$

We now assume that the perturbation is slow on a time scale $h/\bar{\epsilon}$, where $\bar{\epsilon}$ is the energy range over which the matrix element in (18) varies appreciably. If, in addition, the substrate temperature T_s is small compared to characteristic electronic energies, the energies in ${}^t\langle\epsilon_1,\sigma_1|\dot{H}_t|\epsilon_2,\sigma_2\rangle^t$ can both be replaced by the Fermi energy because of the Fermi functions in (17). With the definition

$$\lambda_{\sigma_1\sigma_2}(\epsilon)=\int_{-\infty}^{\infty}{}^t\langle\epsilon_f,\sigma_1|\dot{H}_t|\epsilon_f,\sigma_2\rangle^t e^{i\epsilon t}dt\ , \tag{19}$$

the exponent in (17) reads

$$\begin{aligned}(\cdots)&=-\sum_{\sigma_1\sigma_2}\int\int\frac{|\lambda_{\sigma_1\sigma_2}(\epsilon_1-\epsilon_2)|^2}{(\epsilon_1-\epsilon_2)^2}f(\epsilon_1)[1-f(\epsilon_2)](1-e^{-i(\epsilon_2-\epsilon_1)t})d\epsilon_1 d\epsilon_2\\ &=-\int d\epsilon'\sum_{\sigma_1\sigma_2}\frac{|\lambda_{\sigma_1\sigma_2}(\epsilon')|^2}{\epsilon'^2}A(\epsilon')(1-e^{-i\epsilon' t})d\epsilon'\ ,\end{aligned} \tag{20}$$

with

$$A(\epsilon)=\int d\epsilon_1 d\epsilon_2 f(\epsilon_1)[1-f(\epsilon_2)]\delta(\epsilon-(\epsilon_2-\epsilon_1))$$

describing the "excitation density" of the *e-h* pairs. Straightforward integration yields

$$A(\epsilon)=\epsilon\left[1+\frac{1}{e^{\epsilon/kT_S}-1}\right]=\epsilon[1+n(\epsilon)]\ , \tag{21}$$

with $n(\epsilon)$ the Bose function. If we use the fact that $\sum_{\sigma_1\sigma_2}|\lambda_{\sigma_1\sigma_2}(\epsilon')\,^2$ is an even function of ϵ' we can replace the integral over all ϵ' in (20) by an integral over positive ϵ only. Then the result for $P(\epsilon)$ reads

$$P(\epsilon)=\int_{-\infty}^{\infty}\exp\left[-\int_0^{\infty}\sum_{\sigma_1\sigma_2}\frac{|\lambda_{\sigma_1\sigma_2}(\epsilon')|^2}{\epsilon'}\{1+2n(\epsilon')-[1+n(\epsilon')]e^{-i\epsilon' t}-n(\epsilon')e^{i\epsilon' t}\}d\epsilon'\right]e^{i\epsilon t}\frac{dt}{2\pi}\ . \tag{22}$$

We could also have obtained this result more directly by a $T_s\neq 0$ version of our boson approach of I. It is instructive to compare (22) with the corresponding $T_s=0$ result which is obtained by putting $n(\epsilon')\equiv 0$. The term in the exponent which is proportional to $e^{-i\epsilon' t}$ describes the energy-loss processes. The $T_s\neq 0$ generalization is to replace $e^{-i\epsilon' t}$ by $[1+n(\epsilon')]e^{-i\epsilon' t}$, i.e., in addition to the spontaneous creation of excitations stimulated emission of *e-h* pairs occurs. The term with $e^{i\epsilon' t}$, on the other hand, describes the gain processes and has the number of bosons present as a proportionality factor. To maintain unitarity the constant 1 in the exponent has to be replaced by $1+2n(\epsilon')$.

The step from (16) to (17) in our derivation, where we put the result of (16) in the exponent, may look like an uncontrolled approximation. This is actually not the case: In I we have shown that for the case when the one-particle eigenstates are labeled by the *energy only* (no σ's), coherent superpositions of low-energy *e-h* pairs first considered by Tomonaga,[4] in the presence of a slowly varying perturbation *exactly* behave as bosons. For that case (22) therefore presents the *exact result for* $P(\epsilon)$ if kT_s is small compared to the bandwidth and $\sum_{\sigma_1\sigma_2}|\lambda_{\sigma_1\sigma_2}(\epsilon)|^2$ can be replaced by the Fourier transform of the time derivative $\dot{\delta}_{\epsilon_f}(t)$ of the phase shift at the Fermi energy.[2,5] When the one-particle states are labeled by additional quantum numbers

σ, (22) in the general case does *not* give the exact result for a slow perturbation. It is, however, possible to show that the first two moments of $P(\epsilon)$ are given exactly. The expression (17) for $P(\epsilon)$, which still contains the Fermi functions, also correctly describes the limit of a *weak* perturbation with an *arbitrary* time dependence. This result for $P(\epsilon)$, which cannot be obtained by a boson description, has therefore, a wider range of applicability than the expression (22) containing the Bose functions, which should only be used for slow perturbations. The nonzero temperature version of the weak-coupling boson approach of Müller-Hartman *et al.*[6] is, therefore, valid only for weak *and* slow perturbations.

All the information about the perturbation in the "slow case," Eq. (22), is contained in $\sum_{\sigma_1\sigma_2} |\lambda_{\sigma_1\sigma_2}(\epsilon)|^2$. In I we have considered only the perpendicular incidence of the adparticle and have described the interaction of the adsorbate and the metal surface by a coupling between the adsorbate affinity level and the metal band states. If the affinity level couples, with a time-dependent coupling constant, to the *same* linear combination of metal band states at all times, the calculation of $P(\epsilon)$ is simplified considerably. These assumptions lead to an effective one-dimensional coupling (no σ's) and the sum over the $|\lambda_{\sigma_1\sigma_2}|^2$ is replaced by

$$\sum_{\sigma_1\sigma_2} |\lambda_{\sigma_1\sigma_2}(\epsilon)|^2 \to \left| \int_{-\infty}^{\infty} \frac{\dot{\delta}_{\epsilon_F}(t)}{\pi} e^{i\epsilon t} dt \right|^2 = |\lambda(\epsilon)|^2 , \tag{23}$$

where $\delta_{\epsilon_F}(t)$ is the phase shift at the Fermi level produced by the perturbation presented by the adatom. The time derivative $\dot{\delta}_{\epsilon_F}(t)$ describes the rate at which new states are created below the Fermi level. As these new states cannot be occupied instantaneously, this is the cause of the inelastic effects.

If we restrict ourselves to the special assumption about the adsorbate level to the metal states, $P(\epsilon)$ can be calculated once $\delta_{\epsilon_F}(t)$ is given.[7] The case when the affinity level crosses the Fermi energy is of particular interest. As shown in I, a two-parameter expression for $\delta_{\epsilon_F}(t)$ can be given, which in one limit describes such a crossing and allows the analytical evaluation of $P(\epsilon)$ for $T_s=0$:

$$\dot{\delta}_{\epsilon_F}(t) = f(t) - f(t+T) , \tag{24}$$

where

$$f(t) = -\frac{\Delta t/2}{t^2+(\Delta t/2)^2} . \tag{25}$$

We have assumed that the affinity level crosses the Fermi energy at $t=0$ when the adsorbate approaches the surface, and at $t=T$ when the adsorbate leaves the surface. The time needed to cross the Fermi energy is described by Δt. This model for $\delta_{\epsilon_F}(t)$ describes the crossing of a sharp level for $\Delta t << T$. Inserting in (23) yields

$$|\lambda(\epsilon)|^2 = 2(1-\cos\epsilon T)e^{-\epsilon\Delta t} . \tag{26}$$

For zero temperature we can perform the integral (22) analytically and obtain

$$P_{T_s=0}(\epsilon) = \frac{(\Delta t)^2}{(\Delta t)^2+T^2}\delta(\epsilon) + \frac{(\Delta t)^2 T^2}{(\Delta t)^2+T^2}\epsilon e^{-\epsilon\Delta t} , \tag{27}$$

while for $T_s \neq 0$ the integral must be calculated numerically.

Inelastic effects are most drastic when the crossing time Δt is much smaller than the round-trip time T. In the following, we consider the case $\Delta t = 2T/3$. For $T_s=0$ this gives a substantial elastic scattering probability ($p_0 \approx 0.31$) and we can study the effects due to the reduction of p_0 as T_s is increased. The energy (and temperature) scale is given by $1/T$, which for low kinetic energies of the incoming particle is of the order of the vibrational frequency of the adparticle in the adsorption well and is typically a few tenths of an eV. In our calculations we arbitrarily choose $T=15$, which determines the temperature range in Figs. 1 and 2.

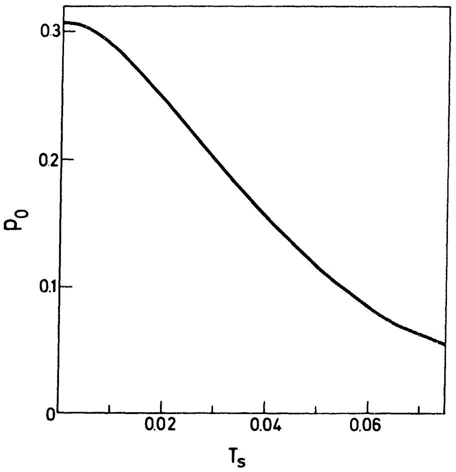

FIG. 1. Elastic scattering probability for a single round trip as a function of surface temperature T_s ($T=15$).

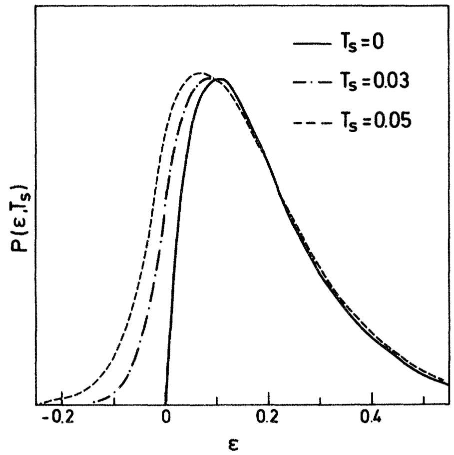

FIG. 2. Spectrum of excitations created (annihilated) per round trip for different surfaces temperatures T_s ($T=15$).

In Fig. 1 we show the decrease of the elastic scattering probability with temperature. The inelastic part of $P(\epsilon)$ is shown in Fig. 2. For $T_s=0$ the spectrum is restricted to loss processes and starts out linearly with energy. With increasing T_s this sharp onset is smoothed out due to the increasing probability for gain processes. In the following section we use the first round-trip distribution $P(\epsilon)$ as a "microscopic" input for the stochastic description of the sticking process at finite surface temperatures.

III. STOCHASTIC DESCRIPTION OF THE STICKING PROCESS

Following Iche and Nozières[3] we want to describe the sticking process as a stochastic process in the energy variable. As mentioned in the Introduction we assume that there are no statistical correlations between two successive oscillations in the adsorption well: The sticking process is treated as Markovian from one round trip to the next.

We consider the sticking probability $s(\epsilon)$ of an incident particle with energy $\epsilon>0$. After one round trip it has the energy ϵ' with probability $P_\epsilon(\epsilon-\epsilon')$, where the method to calculate $P_\epsilon(\epsilon-\epsilon')$ has been described in the preceding section. The index ϵ indicates that the spectrum of excitations created (or annihilated) in the first round trip depends on the initial kinetic energy, because different trajectories lead to different $\delta_{\epsilon_F}(t)$. If the energy ϵ' after the first round trip is positive, the adparticle escapes, i.e., it does not stick. If $\epsilon'<0$ it starts the next round trip in the well with a sticking probability now equal to $s(\epsilon')$. If one restricts the discussion to temperatures $kT_s/(\text{well depth}) \ll 1$ one can treat the adsorption well as infinitely deep. Then the function $s(\epsilon)$ obeys the simple integral equation (3)

$$s(\epsilon)=\int_{-\infty}^{0} P_\epsilon(\epsilon-\epsilon')s(\epsilon')d\epsilon' , \tag{28}$$

which must be solved with the boundary condition $s(\epsilon)\rightarrow 1$ when $\epsilon\rightarrow-\infty$. The sticking probability is thus entirely determined by the energy-loss (gain) probability for a single round trip $P_\epsilon(\epsilon-\epsilon')$.

If like Iche and Nozières[3] we introduce the notation

$$s^{\pm}(\epsilon)=s(\epsilon)\Theta(\pm\epsilon) , \tag{29}$$

where Θ is the step function, we can rewrite (28) as

$$s^{-}(\epsilon)=\int_{-\infty}^{0} P_\epsilon(\epsilon-\epsilon')s^{-}(\epsilon')d\epsilon', \quad \epsilon<0 \tag{30}$$

and

$$s^{+}(\epsilon)=\int_{-\infty}^{0} P_\epsilon(\epsilon-\epsilon')s^{-}(\epsilon')d\epsilon', \quad \epsilon>0 . \tag{31}$$

One has to solve the integral equation (30) first and then obtain the "measurable" quantity $s^{+}(\epsilon)$ by integration. For $T_s=0$ the negative-energy sticking probability $s^{-}(\epsilon)=1$ and we obtain the result of I:

$$s^{+}(\epsilon)=\int_{-\infty}^{0} P_\epsilon(\epsilon-\epsilon')d\epsilon' . \tag{32}$$

For finite temperatures one has to solve Eq. (30). As we generally only have numerical results for $P_\epsilon(\epsilon-\epsilon')$ we have solved this integral equation numerically. To obtain an inhomogeneous equation we introduce the quantity

$$r^{-}(\epsilon)=1-s^{-}(\epsilon) , \tag{33}$$

which tends to zero for $\epsilon\rightarrow-\infty$ and obeys the inhomogeneous integral equation

$$r^{-}(\epsilon)=\int_{0}^{\infty} P_\epsilon(\epsilon-\epsilon')d\epsilon' + \int_{-\infty}^{0} P_\epsilon(\epsilon-\epsilon')r^{-}(\epsilon')d\epsilon' . \tag{34}$$

We now separate the elastic and the inelastic part of $P_\epsilon(\epsilon-\epsilon')$,

$$P_\epsilon(\epsilon-\epsilon')=p_{0,\epsilon}\delta(\epsilon-\epsilon') + (1-p_{0,\epsilon})w_\epsilon(\epsilon-\epsilon') , \tag{35}$$

where the inelastic contribution $w_\epsilon(\epsilon-\epsilon')$ is normalized to 1, i.e.,

$$\int w_\epsilon(\epsilon-\epsilon')d\epsilon'=1\ . \tag{36}$$

Inserting (35) into (34) we see that for negative energies $p_{0,\epsilon}$ drops out:

$$r^-(\epsilon)=\int_0^\infty w_\epsilon(\epsilon-\epsilon')d\epsilon' + \int_{-\infty}^0 w_\epsilon(\epsilon-\epsilon')r^-(\epsilon')d\epsilon'\ . \tag{37}$$

The elastic scattering probability enters only in the determination of $s^+(\epsilon)$ via the integration in (31):

$$s^+(\epsilon)=(1-p_{0,\epsilon})\int_{-\infty}^0 w_\epsilon(\epsilon-\epsilon') \times[1-r^-(\epsilon')]d\epsilon'\ . \tag{38}$$

In principle, there is no problem in evaluating $w_\epsilon(\epsilon-\epsilon')$ for the proper intial energy for each round trip. As we restrict ourselves in the following to initial kinetic energies and temperatures small compared to the well depth, we neglect this energy dependence and replace $P_\epsilon(\epsilon-\epsilon')$ by $P_{\epsilon_{\text{in}}}(\epsilon-\epsilon')$, where ϵ_{in} is the initial kinetic energy of the adparticle. For the case we want to describe ($\epsilon_{\text{in}},kT_s <<$ well depth), this is a reasonable approximation: The particle is accelerated in the adsorption well and all classical trajectories with energies near the top of the well lead to almost the same energy-loss (gain) spectrum.

With this simplification the integral equation (37) is of the Wiener-Hopf type and the exact analytical solution[7] can be given for a special (exponential) analytical form of $w(\epsilon-\epsilon')$. This exact solution can be used as a test of our numerical procedure to solve (37) by discretizing the energy variable and matrix inversion. In Figs. 3 and 4 we show the numerical solution for the sticking coefficient for the model behavior of the phase shift at the Fermi level as described in Eqs. (24)–(26).

For a given kinetic energy of the incoming particle the sticking coefficient shows a small variation with surface temperature T_s. This is shown in Fig. 3 for two different kinetic energies. This small variation with T_s shows that the two effects mentioned in the Introduction, i.e., the decrease of the probability to leave the surface after the first round trip due to stimulated emission of particle-hole pairs and the possibility of leaving the surface after a few round trips before falling to the bottom of the well, largely cancel each other. This can be understood in a discrete model for $w(\epsilon-\epsilon')$ discussed in the Appendix. The sticking coefficient in our model first rises slowly, as shown in Fig. 3, and then decreases. To show the relevance of the two effects separately, Fig. 3 also shows the sticking probability after the first round trip.

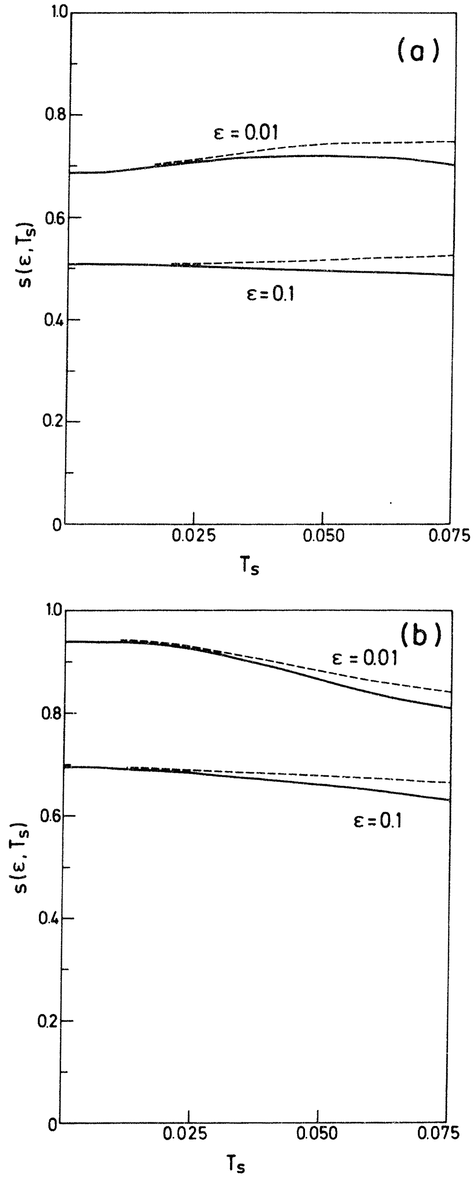

FIG. 3. Sticking coefficient as a function of surface temperature T_s for different kinetic energies of the adparticle. (a) $T=15$, (b) $T=40$, and $\Delta t=10$. The dashed curve shows the sticking coefficient after the first round trip.

In Fig. 4 we show the sticking probability for two given surface temperatures as a function of the initial kinetic energy of the adparticle. As the probability for the adparticle to be "trapped" after the first round trip decreases, the sticking coefficient decreases with kinetic energy.[9] For a thermalized beam the average sticking coefficient

$$s_{T_g}=\int_0^\infty s^+(\epsilon)(e^{-\epsilon/kT_g}/kT_g)d\epsilon$$

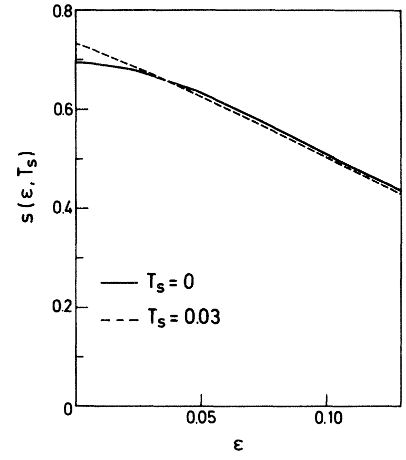

FIG. 4. Sticking coefficient as a function of the kinetic energy of the incoming particle for different surface temperatures ($T = 15$).

decreases with the gas temperature T_g. Comparing Figs. 3 and 4 we conclude that the variation of the sticking factor with the gas temperature is more pronounced than the variation with surface temperature.

At low gas and surface temperatures the sticking coefficient tends to a value $s < 1$ for the case considered here where the elastic scattering probability is nonzero. For this reason absolute rate theory,[8] which is equivalent to the assumption $s = 1$,[3,9] is not correct in contrast to the conclusion reached by Iche and Nozières,[3] who do not include the possibility of elastic scattering.

IV. CONCLUDING REMARKS

We have calculated the sticking probability for finite surface temperatures T_s in a model that includes the electron-hole pair energy-loss (gain) mechanism. In contrast to the $T_s = 0$ case considered in I, the calculation of the sticking probability proceeded in two steps.

The first step required the $T_s \neq 0$ result for the energy-loss (gain) probability in one round trip. The method presented here for calculating this spectrum is an expansion around the adiabatic limit where the "bosonization" introduced in I is not used. That the basic result equation (22) obtained by this approach provides the *exact* solution for a slow perturbation follows from the fact that in this case the fermion problem can be exactly reformulated in terms of bosons, as shown in the Appendix of I.

In the second step the motion of the adparticle near the top of the well is described as a Markov process in the energy variable, following Iche and Nozières.[3] With our "microscopic" input for the single round-trip energy-loss (-gain) distribution we have solved the master equation for a given kinetic energy of the incoming particle. We have found a very *weak* dependence of the sticking coefficient with surface temperature. For a thermal beam of adparticles, the sticking coefficient decreases with surface temperature. In the calculation of the single round-trip energy-loss (-gain) probability we have not included the energy loss (gain) to phonons, which usually will be the dominant energy exchange mechanism when the (adparticle-to-solid atom) mass ratio is not small. Therefore, our calculation is restricted to light chemically active adsorbates, like hydrogen atoms or molecules. *Ab initio* calculations by Lundqvist *et al.*[10] show that, e.g., for the chemisorption of hydrogen molecules on metal surfaces the level crossing effect included in our calculation [Eq. (26)] plays an important role.

APPENDIX

In this appendix we discuss a discrete version of the integral equation (37). Such a discrete master equation has been studied in the classic paper by Montroll and Shuler.[11] In the notation of Sec. III we consider the most simple case

$$w(\epsilon) = w_{\downarrow}\delta(\epsilon - \epsilon_0) + w_{\uparrow}\delta(\epsilon + \epsilon_0) \tag{A1}$$

with $w_{\downarrow} + w\uparrow = 1$, i.e., in one round trip the adparticle can only lose or gain the discrete energy $\epsilon_0 > 0$. If the kinetic energy of the incoming particle is less than ϵ_0, there is nonzero sticking coefficient and the adparticle can drop down on a discrete ladder of negative energies, which we label $n = 1, 2, \ldots$ (see Fig. 5). With the definition

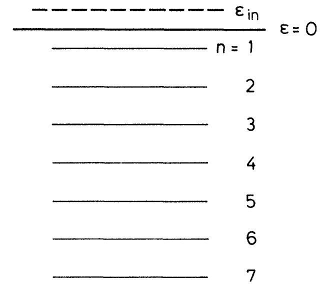

FIG. 5. Level scheme for the discrete model discussed in the Appendix.

$r_n \equiv r(\epsilon_n)$ the integral equation (37) is replaced by the matrix equation

$$r_n = w_\uparrow \delta_{n,1} + w_\downarrow r_{n+1} + w_\uparrow r_{n-1} \tag{A2}$$

or in explicit form

$$\begin{bmatrix} 1 & -w_\downarrow & 0 & 0 & \cdots \\ -w_\uparrow & 1 & -w_\downarrow & 0 & \\ 0 & -w_\uparrow & 1 & -w_\downarrow & \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix} \cdot \vec{r} = w_\uparrow \begin{bmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{bmatrix} ,$$

i.e.,

$$\underline{A} \cdot \vec{r} = w_\uparrow \vec{e}_1 . \tag{A3}$$

To calculate the sticking coefficient we only need r_1, which is proportional to the 1-1 matrix element of the inverse of $\underline{A}$:

$$r_1 = w_\uparrow (\underline{A}^{-1})_{11} . \tag{A4}$$

Using the partitioning technique we can easily derive an equation for $(\underline{A}^{-1})_{11}$:

$$(\underline{A}^{-1})_{11} = \frac{1}{1 - w_\uparrow w_\downarrow (\underline{A}^{-1})_{11}} . \tag{A5}$$

The physical solution of this quadratic equation is

$$(\underline{A}^{-1})_{11} = \frac{1}{w_\downarrow} , \tag{A6}$$

i.e.,

$$r_1 = \frac{w_\uparrow}{w_\downarrow} .$$

The sticking probability can then be obtained from Eq. (38)

$$\begin{aligned} s &= (1 - p_0)(w_\uparrow - w_\uparrow) \\ &= p_\downarrow - p_\uparrow \end{aligned} \tag{A7}$$

where we have also introduced the loss and gain probabilities $p_\downarrow$ and $p_\uparrow$ defined by

$$P(\epsilon) = p_0 \delta(\epsilon) + p_\downarrow \delta(\epsilon - \epsilon_0) + p_\uparrow \delta(\epsilon + \epsilon_0) . \tag{A8}$$

The average energy transfer $\Delta\epsilon$ per round trip is given by

$$\Delta\epsilon = \int_{-\infty}^{\infty} \epsilon P(\epsilon) d\epsilon = \epsilon_0 (p_\downarrow - p_\uparrow) \tag{A9}$$

or

$$s = \Delta\epsilon / \epsilon_0 . \tag{A10}$$

If we calculate the average energy transfer $\Delta\epsilon$ per round trip for $P(\epsilon)$ given by (22) we find that $\Delta\epsilon$ is *temperature independent* for arbitrary $\lambda(\epsilon)$. If we now choose a $\lambda(\epsilon) = \lambda_0 \delta(\epsilon - \epsilon_0)$ and λ_0 small enough, we obtain a $P(\epsilon)$ of the form given in (A8), and because $\Delta\epsilon$ is independent of T_s so is the sticking coefficient according to (A10).

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[1] For a review see F. O. Goodman and H. Y. Wachman, *Dynamics of Gas-Surface Scattering* (Academic, New York, 1976).

[2] K. Schönhammer and O. Gunnarsson, Phys. Rev. B 22, 1629 (1980). This paper also contains a list of more recent publications on the subject.

[3] G. Iche and P. Nozières, J. Phys. (Paris) 37, 1313 (1976).

[4] S. Tomonaga, Prog. Theor. Phys. 5, 544 (1950).

[5] K. Schönhammer and O. Gunnarsson, Z. Phys. B 38, 127 (1980).

[6] E. Müller-Hartmann, T. V. Ramakrishnan, and G. Toulouse, Phys. Rev. B 3, 1102 (1971).

[7] U. Leuthäuser, Ph.D. thesis, TU Munich, 1981 (unpublished). See also H. Müller and W. Brenig, Z. Phys. B 34, 165 (1980).

[8] K. Gladsstone, S. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1965).

[9] W. Brenig and K. Schönhammer, Z. Phys. B 24, 9 (1976).

[10] B. I. Lundqvist, O. Gunnarsson, H. Hjeimberg, and J. K. Norskov, Surf. Sci. 89, 196 (1979).

[11] E. W. Montroll and K. E. Shuler, Adv. Chem. Phys. 1, 361 (1958).