Application of the semiclassical perturbation approximation to scattering from surfaces. Generalization to include phonon inelasticity

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The semiclassical perturbation (SCP) approximation of Miller and Smith is applied to the inelastic scattering of atoms from solid surfaces. Earlier applications of this approach have been to diffraction [i.e., elastic scattering] of He from LiF and to diffraction and rotationally inelastic scattering of H\textsubscript{2} from LiF, and the present work is an extension which allows for motion of the surfaces atoms (and thus phonon inelasticity). Therefore, phenomena that involve energy transfer between the surface and gas molecules can be described. In the present work sticking probabilities are calculated for He–W[110] and Ne–W[110], and the results show that a simple model such as this one can be quite useful in predicting energy transfer in gas–solid scattering systems.

I. INTRODUCTION

Gas–solid surface scattering experiments have advanced to a point that observations of energy exchange between an incoming gas particle and the vibrational degrees of freedom of a solid surface are now being made. Recent experimental studies of rare gas scattering from metal surfaces provide excellent data on detailed inelastic gas–surface interactions, such as energy exchange between the gas particle and the surface phonons, and trapping and desorption mechanics.\textsuperscript{1–4} This new experimental data is thus stimulating the development of a variety of theoretical models for describing energy exchange between the gas and the surface.\textsuperscript{5–9}

Recently we reported\textsuperscript{10} the successful application of the semiclassical perturbation approximation\textsuperscript{11} (SCP) to the study of both diffraction and rotationally inelastic scattering of atoms and molecules from rigid solid surfaces, and in the present paper this model is generalized to include the dynamical effects of surface motion, i.e., phonons. Although more accurate theoretical treatments are possible, and of course desirable in some situations, it is still of great use to have simple semianalytic models that are qualitatively reliable over a wide range of conditions. The purpose of this paper is to demonstrate that the SCP model is capable of describing the effects of phonon inelasticity correctly (as well as diffraction and intramolecular inelasticity in the gas molecule).

Section II describes the form we use for the potential energy, which includes the motion of the surface atoms, and gives the derivation in the SCP approximation of the probability \( P(ΔE) \) of an exchange of energy \( ΔE \) between the gas and the solid. One of the advantages of this model is that the necessary averages which define \( P(ΔE) \) can be carried out analytically so that a simple compact expression is obtained for this quantity. Section III discusses the calculation of sticking probabilities as a function of incoming gas atom translational energy and temperature of the surface, with application to He and Ne scattering off of W[110]. The results are in qualitative agreement with previous calculations and observations.\textsuperscript{6,12}

II. ENERGY TRANSFER IN ATOM–SURFACE SCATTERING IN THE SCP APPROXIMATION

The potential for the interaction between a gas atom and a solid surface must account for the motion of the surface atoms in order to describe energy transfer between the gas and the solid properly. The coordinate system used here places the solid surface in the \( x–y \) plane with \( z \) normal to the surface. The \( y \) coordinate will be ignored in the formalism that follows; extension to include the \( y \) dimension is straightforward. Denoting the \( x \) and \( z \) displacements of the \( j \)th surface atom from its equilibrium position by \( Q^+_j \) and \( Q^-_j \), respectively, the specific potential energy function we have used is

\[
V_j(x,z,Q) = -2De^{-yz} + Da\frac{\alpha}{\pi} \sum_{\text{atoms}} e^{-a(x - Q^+_j - ja)^2} - 2yz - Q^-_j. \tag{2.1}
\]

If the displacement coordinates \( Q^+_j \) and \( Q^-_j \) are set to zero, one can show by application of the Poisson sum formula that Eq. (2.1) reduces to the familiar Lennard-Jones Devonshire potential\textsuperscript{16} used previously by us\textsuperscript{10} and many others\textsuperscript{13–15} for describing the gas atom–solid surface interaction:

\[
V_j(x,z,Q = 0) = D(e^{-2yz} - 2e^{-yz}) - 2\beta De^{-2yz} \cos\left(\frac{2\pi x}{a}\right)
= V'_{j}(x,z) + V_{j}(x,z). \tag{2.2}
\]

\( V'_{j}(x,z) \) is a Morse potential with \( D \) the dissociation energy and \( V_{j}(x,z) \) is the potential for a corrugated surface with the lattice spacing given by \( a \).

If we assume that the displacements of the surface atoms are small and therefore linearize \( V \) in the atom displacement coordinates, Eq. (2.1) becomes

\[
V_j(x,z,Q) = D(e^{-2yz} - 2e^{-yz}) + 2De^{-\pi/(\alpha a)} e^{-2yz} \cos\left(\frac{2\pi x}{a}\right)
+ 2\alpha Da \sqrt{\frac{\alpha}{\pi}} e^{-2\pi a} \sum_j e^{-a(x - ja)^2} (x - ja)Q_j^x.
\]
\[ + 2\gamma Da \sqrt{\frac{\alpha}{\pi}} e^{-2\gamma z} \sum_{j} \text{atoms} e^{-a x - jz} Q_j, \]  
where the first two terms are the same as Eq. (2.2) (with the identification that \( \beta = e^{-v'/(\alpha a)} \)), and are the part of the potential which describes specular reflection and diffraction, and the last two terms account for the change in the static surface potential due to the displacements of the surface atoms in the \( x \) and \( z \) directions, respectively (i.e., due to surface atom vibrations). Equation (2.3) is expressed in a more convenient shorthand form as

\[ V(x, z, Q) = V_0(x) + f_s(x) \cos \left( \frac{2\pi x}{a} \right) + \sum_{j} \text{atoms} f_j(x, z) Q_j, \]  

where \( f_s(x) = 2D \exp \left( -\frac{\pi^2}{2a^2} \right) e^{-2\gamma z} \),

\[ f_j(x, z) = \frac{\partial V}{\partial Q_j} \bigg|_{Q=0}, \]

\[ f_j^2(x, z) = \frac{\partial^2 V}{\partial Q_j^2} \bigg|_{Q=0}, \]  

\[ f_j(x, z) = 2\pi Da \sqrt{\frac{\alpha}{\pi}} e^{-a x - jz} e^{-2\gamma z}. \]  

The potential described here is applicable when an Einstein solid description of the surface is assumed. The formalism which follows, however, is developed for a system with \( N \) normal modes, and we use the general form for the potential given by

\[ V(x, z, Q) = V_0(x) + f_s(x) \cos \left( \frac{2\pi x}{a} \right) + \sum_{k} f_k(x, z) Q_k, \]  

where

\[ f_k(x, z) = \frac{\partial V}{\partial Q_k} \bigg|_{Q=0}, \]

and \( Q_k \) is the displacement coordinate for the \( k \)th normal mode. Later in this section the formalism will be specialized to an Einstein solid description of the surface, and the potential form given by Eq. (2.4a) will be used.

In the present paper we focus explicitly on energy transfer between the gas and phonons and consider specifically the probability distribution for the gas atom having a change \( \Delta E_x \) in the \( z \) component of its translational energy. This involves a sum over all phonon and diffraction transitions and an average over initial phonon states, and is given by

\[ P(\Delta E_x) = \sum_{n} \frac{e^{-\beta n}}{Q} \sum_{a} \delta(\Delta E_x + \omega_x n_x + \omega \cdot \Delta n) |S_{n, n_x, a}|^2, \]  

where \( \omega_x n_x = \Delta E_x \) is the translational energy transferred into the \( x \) direction (parallel to the surface), with \( \omega_x = 2\pi\nu_x / a \) and \( n_x = m \Delta v_x / 2\pi (\bar{\varepsilon}_x \text{ and } \Delta v_x \text{ are the average } x \text{ velocity and change in } x \text{ velocity, respectively}) \). Also, \( n_x \) is the vector of initial quantum numbers for the phonon modes with frequencies \( \omega \) and initial energy \( \varepsilon_n \), \( \Delta n = n_x - n_s \), \( Q \) is the phonon mode partition function, \( \beta \) is the temperature factor for the surface at temperature \( T \) (i.e., \( 1/kT \)), and \( n_x \) is the diffraction order quantum number. The delta function in Eq. (2.5) insures energy conservation and the square modulus of the \( S \) matrix element gives the transition probability for each \( (0,n_s) \rightarrow (n_x,n_s) \) event. Units are such that \( \hbar = 1 \) everywhere. The \( S \) matrix in the SCP approximation has been described elsewhere and is given by

\[ S_{n,n_s-a,0,n_s} = \int_{0}^{2\pi} \int_{0}^{2\pi} e^{-in_s \cdot \varepsilon \cdot q} e^{-idn_s \cdot q} e^{iA(q_s,q)}, \]

where \( (n_s, q_s), (n,q) \) are the action-angle variables for the respective degrees of freedom, and where the phase is given by the time average of the potential,

\[ A(q_s,q) = -\int_{-\infty}^{\infty} dt V[q_s(t),q(t)]. \]

Expanding the \( \delta \) function in terms of a Fourier integral in the usual way,

\[ \delta(\Delta E_x + \omega_x n_x + \omega \cdot \Delta n) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\Delta E_x t} e^{-i\omega_x n_x t}, \]

Eq. (2.5) can be written as

\[ P(\Delta E_x) = e^{-\beta \Delta E_x / 2} \sum_{n} \frac{e^{-\beta n}}{Q} \sum_{a} \delta(\Delta E_x + \omega_x n_x + \omega \cdot \Delta n) |S_{n, n_x, a}|^2. \]

The factor \( \exp(-\beta \Delta E_x / 2) \) appears in Eq. (2.8) because the quantum numbers \( n_x, n_s \) and \( n \) in Eq. (2.9) now refers to the average quantum numbers \( \langle n_x + 0 \rangle \) and \( \langle n_s + n_x \rangle \); i.e., the delta function requires that \( \varepsilon_n = \langle \varepsilon_n + \varepsilon_{n_x} + \Delta \varepsilon \rangle. \) Switching to average quantum numbers facilitates the remainder of the calculation because, in order to insure symmetry of the \( S \) matrix and thus microscopic reversibility, average quantum numbers are used in calculating the function \( A \) below. By invoking the closure relationships
\[
\int_0^{2\pi} \frac{dq}{2\pi} \sum_{n_k} e^{-in_k(q_x + \omega_k t)} = 1, \quad q'_x = q_x + \omega_k t
\]
and
\[
\int_0^{2\pi} \frac{dq}{(2\pi)^N} \sum_{n_k} e^{-i\Delta \theta \cdot (q_x + q_y)} = 1, \quad q' = q + \omega t
\]
the expression for the correlation function \(C(t)\) simplifies to
\[
C(t) = \sum_n \frac{e^{-\beta_n}}{Q} \int_0^{2\pi} \frac{dq_x}{2\pi} \int_0^{2\pi} \frac{dq}{(2\pi)^N} x^{i4(\{q_x,q_y\}) e^{-i\Delta (q_x + \omega_k t + q_y + \omega k t)}}.
\]

(2.10)

Progress can be made on obtaining an analytic expression for \(C(t)\) by using the general form for the potential in Eq. (2.4e). The calculation can only be carried through analytically for the case of normal incidence, to which we now specialize the treatment. In this case \(\omega_k = 0\), so that \(x(t) = x = q_x(a/2\pi)\). Expressing \(Q_k\) in terms of its action-angle variables for a harmonic oscillator,
\[
Q_k = \left(\frac{2n_k + 1}{m\omega_k}\right)^{1/2} \cos(q_k + \omega_k t),
\]
the correlation function of Eq. (2.10) becomes
\[
C(t) = \sum_n \frac{e^{-\beta_n}}{Q} \int_0^{2\pi} \frac{dq_x}{2\pi} \int_0^{2\pi} \frac{dq}{(2\pi)^N} \left[ \sin(q_k + \omega_k t) \int_{-\infty}^{\infty} dt f_k[x, z(t)] \cos(\omega_k t) \right.
\]
\[
+ \left. \cos(q_k + \omega_k t) \int_{-\infty}^{\infty} dt f_k[x, z(t)] \sin(\omega_k t) \right].
\]

(2.11)

and the integration over the \(q\) variables yields zero order Bessel functions:
\[
C(t) = \sum_n \frac{e^{-\beta_n}}{Q} \int_0^{2\pi} \frac{dq_x}{2\pi} \prod_k \int_{-\infty}^{\infty} dt f_k[x, z(t)] e^{i\omega_k t}.
\]

(2.12)

where
\[
A_k(q_x) = \left(\frac{2n_k + 1}{m\omega_k}\right)^{1/2} \int_{-\infty}^{\infty} dt f_k[x, z(t)] e^{i\omega_k t}.
\]

(2.13)

For the collision integrals \(A_k(q_x)\) small, as they must be for our perturbative treatment to be valid, we can use the following expansion for \(f_k(x)\):
\[
J_0[2 \sin(\omega_k t/2) A_k(q_x)] \sim 1 - \sin^2(\omega_k t/2) A_k^2(q_x) + \ldots,
\]

(2.14)

so that Eq. (2.12) further simplifies to
\[
C(t) = \sum_n \frac{e^{-\beta_n}}{Q} \exp \left[- \sum_n \frac{\sin^2(\omega_k t/2)}{2} \int_0^{2\pi} \frac{dq_x}{2\pi} A_k^2(q_x) \right].
\]

(2.15)

Equation (2.15), with Eq. (2.13), is the final result of the SCP model for \(P(\Delta E, z)\) via Eq. (2.8). It would be possible, for example, to utilize a distribution of phonon frequencies \(\{\omega_k\}\) in evaluating the correlation function via Eq. (2.13).

Now, however, we specialize the treatment to an Einstein solid and to the specific potential function described above [Eq. (2.3)]. The trajectory \(x(t), z(t)\) needed for evaluating collision integrals of Eq. (2.13) is the one determined by the zeroth-order potential \(V_0(z)\); i.e., \(z(t)\) is the inverse function of
\[
t(z) = \pm \int_{z_0}^{z} dz \left[ \frac{E - V_0(z')}{m} \right]^{-1/2},
\]

(2.16)

and since we are considering normal incidence,
\[
x(t) = x(q_x(a/2\pi)).
\]

Using the Morse potential form for \(V_0(z)\), the integral which defines \(z(t)\), Eq. (2.16), is evaluated in the same way as in our previous atom surface treatment\(^16\) to give
\[
\exp[-\alpha z(t)] = \lambda \left[ \cos(\alpha \gamma z(t)) - \lambda \right],
\]

(2.17)

where \(\lambda = (1 + E/D)^{-1/2}\) and \(\gamma\) is the average of the initial and final velocities in the \(z\) direction.

The sum over modes in Eq. (2.15) becomes a sum over atom motion for both the \(x\) and \(z\) directions:
\[
C(t) = \sum_n \frac{e^{-\beta_n}}{Q} \prod_k \int_{-\infty}^{\infty} dt f_k[x, z(t)] \exp \left[- \sum_n \frac{\sin^2(\omega_k t/2)}{2} \int_0^{2\pi} \frac{dq_x}{2\pi} A_k^2(q_x) \right].
\]

Using the potential given in Eqs. (2.4), the time integrals in the \(A_k(q_x)\) expressions [Eq. (2.13)] can be evaluated to give
\[
C(t) = \sum_n \frac{e^{-\beta_n}}{Q} \prod_k \int_{-\infty}^{\infty} dt f_k[x, z(t)] \exp \left[- \frac{\sum_n \sin^2(\omega_k t/2)}{2m \omega_x} \sum_k (2n_k + 1) J^z_k \right].
\]

(2.18)

with
\[
J^z_k = \frac{4\alpha \gamma \sqrt{\alpha \gamma}}{\gamma \gamma} \left[ \frac{\omega_k^0 E}{\gamma \gamma} \cosh \left[ \frac{\omega_k^0}{\gamma \gamma} (\pi - \cos^{-1} \lambda) \right] \right]^2
\]

(2.13)

\[
+ \sqrt{ED} \sinh \left[ \frac{\omega_k^0}{\gamma \gamma} (\pi - \cos^{-1} \lambda) \right]^2 \int_0^{2\pi} \frac{dq_x}{2\pi} \left[ q_x^0 - ja \right]^2.
\]

(2.19a)
and

\[
I_j^* = \left( \frac{4a\sqrt{\alpha\pi}}{\gamma^2} \right)^2 \left[ \frac{a_j^* E}{\gamma^2} \cosh \left( \frac{a_j^*}{\gamma^2} (\pi - \cos^{-1} \lambda) \right) \right] \times \sqrt{\frac{d}{2\pi}} \exp \left[ -2\alpha \left( \frac{a_j^*}{2\pi} - ja \right)^2 \right]. \tag{2.19b}
\]

Recognizing Eq. (2.18) as a geometric series in the phonon mode quantum numbers, the correlation function can be reduced to the simple form

\[
C(t) = \prod_j \left[ \frac{\sinh \left( \frac{\beta \omega_j}{2} \right)}{\sinh \left( \frac{\beta \omega_j}{2} + \frac{\sin^2 \frac{\omega_j t}{2}}{m\omega_j} I_j^* \right)} \times \frac{\sinh \left( \frac{\beta \omega_j}{2} \right)}{\sinh \left( \frac{\beta \omega_j}{2} + \frac{\sin^2 \frac{\omega_j t}{2}}{m\omega_j} I_j^* \right)} \right]. \tag{2.20}
\]

Although in principle the product over atoms extends over all surface atoms, the integrals in Eq. (2.19) become vanishingly small for \( j > 0 \) so that the product for large \( j \) reduces to simply factors of 1.

### III. STICKING PROBABILITY

The incoming beam of gas particles is composed of atoms with an initial translational energy \( E_{\text{in}} \) in the \( z \) direction (normal incidence). We define the sticking probability by assuming that if the incoming atom loses an amount of energy from the \( z \) direction equal to or greater than \( E_{\text{in}} \), then the atom will fall into the attractive well given by \( V_\gamma(x) \) and that atom is then stuck to the surface. The sticking probability is thus given by

\[
P_{ST}(E_{\text{in}}) = \frac{1}{N} \int_{-\infty}^{E_{\text{in}}} dE_z P(E_z), \tag{3.1}
\]

where \( N \) is the normalization factor

\[
N = \int_{-\infty}^{0} dE_z P(E_z). \tag{3.2}
\]

We can evaluate \( N \) by using in Eq. (3.2) the expression for \( P(E_z) \) given in Eq. (2.8), and changing the order of integration:

\[
N = \frac{1}{2\pi} \int_{-\infty}^{0} dt C(t) \int_{-\infty}^{0} dE_z \exp \left[ -iE_z (t - i\beta/2) \right]
= \frac{1}{2\pi} \int_{-\infty}^{0} dt \delta \left( t - i\beta/2 \right) C(t)
= C(i\beta/2). \tag{3.3}
\]

The correlation function is a function of \( t^2 \) so that Eq. (3.3) will be real.

Equation (3.1) can also be evaluated by changing the order of integration:

\[
P_{ST}(E_{\text{in}}) \times \text{Re} \left[ \int_{0}^{\infty} \frac{dt}{\pi} C(t) e^{-i\Delta E_z t} \right]
= \frac{1}{\pi N} \int_{0}^{\infty} dt C(t) \int_{-\infty}^{0} dE_z e^{-i\Delta E_z (\beta t / 2 - i\gamma t)}
- \int_{-E_{\text{in}}}^{0} dE_z e^{-i\Delta E_z (\beta t / 2 + i\gamma t)}
- \int_{E_{\text{in}}}^{0} dE_z e^{-i\Delta E_z (\beta t / 2 + i\gamma t)}
= 1 - \frac{1}{\pi N} \int_{0}^{\infty} dt \left( \frac{\beta}{2} \right)^2 e^{-imE_{\text{in}} t} \times \left[ \cos(E_{\text{in}} t) + t \sin(E_{\text{in}} t) \right]. \tag{3.4}
\]

Equation (3.4) provides a simple form for the sticking probability as a function of incoming gas atom translational energy and surface temperature.

The above definition of sticking probability is the probability that on a single encounter between the incoming gas atom and the solid surface enough energy is transferred from the gas to the surface that the gas atom is trapped. The dynamics of the gas atom-solid surface interaction after the gas atom is trapped are not taken into account. Thus one would expect this model to work best at low surface temperature where the probability for energy transfer from the surface back to the gas atom and subsequent desorption is small.

We have tested the model on He scattering off of a W(110) surface. The parameters for the Morse potential are the same as those given by Shugard et al.,$^6$ for the same system: \( \beta = 0.75 \text{ kcal/mol} \) and \( \gamma = 1.2 \text{ a.u.}^{-1} \). The corrugation parameter \( \beta \) is chosen at 0.01, a fairly low value appropriate for a metal surface. The lattice spacing for the (110)

![Graph](image)

**FIG. 1.** The sticking probability as a function of atom translational energy for He/W(110) at normal incidence and the three surface temperatures: $\bullet = 30 \text{ K}, \bigcirc = 100 \text{ K}, \triangle = 300 \text{ K}.$

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face of W is \( a = 5.97 \) a.u. The frequency for the Einstein solid is taken as the maximum of the density of states curve in Fig. 5 of Ref. 6, \( \omega = 0.2 \times 10^{-14} \) s\(^{-1}\), and as a first approximation we set \( \omega_s = \omega \).

Figure 1 shows the sticking probability as a function of gas atom initial translational energy for three surface temperatures: 30, 100, and 300 K. Several correct qualitative trends are apparent. First, as the temperature of the surface is increased, the sticking probability decreases, as it should. For the \( T_s = 30 \) K calculation, the drop off to \( P_{st} = 0 \) is quite abrupt at \( E_n = 1.0 \) kcal/mol. Increasing the surface temperature tends to broaden the energy range over which sticking occurs. In their use of a classical model generalized Langevin formalism, Shugard, et al., calculated sticking probabilities for noble gases scattering off of a W surface, at normal incidence of the gas (as here) and \( T_s = 0 \) K. They found there was a critical energy above which nothing trapped and below which everything traps. For He/W and \( T_s = 0 \) K they found the critical trapping energy at \( \sim 0.1 \) kcal/mol. Figure 1 shows the sticking probability for \( T_s = 30 \) K reaching a maximum value at \( \sim 0.5 \) kcal/mol, in reasonable agreement with the \( T_s = 0 \) K calculations mentioned above.

Figure 2 shows the dependence of the sticking probability on the temperature of the surface for both He and Ne off of W[110] at two different initial translational energies. With increasing temperature of the surface and increasing initial energy of the gas atom the sticking probability decreases, for both He and the heavier Ne gas. The model also predicts more sticking for Ne than He over the temperature range studied, in agreement with previous experimental and theoretical studies, i.e., it is well known that He undergoes elastic scattering off of metal surfaces to a greater extent than Ne or the heavier noble gases, as predicted here.

In summary, our results show how a relatively simple model of the gas–surface interaction, which is based on a perturbative approach with elastic scattering taken as zeroth order, can be quite useful in describing gas–surface scattering processes which involve energy transfer. For higher temperatures of the surface and larger incoming gas atom mass, the sticking probability as defined above becomes less appropriate since it does not account for any of the processes which occur after the initial adsorption of the gas atom. Thus, a more appropriate quantity to calculate with this model under the above conditions would be average energy transfer. Alternatively, the model could be extended to include more of the dynamics which occur after the initial trapping of the gas atom by the solid surface, i.e., by using the semiclassical branching model developed by Waite and Miller.

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