on the more interesting problem, of the spatial autocorrelations of energy eigenstates in a disordered medium, about which there has been so much speculation lately.

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Differential Cross Section for Atoms Inelastically Scattered from Surfaces

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The trajectory approximation is shown to explain the angular distribution of heavy rare-gas atoms scattered from close-packed metal surfaces, and the energy transfer for Ar on polycrystalline W. An empirical parameter, the mean energy transfer δ, is extracted.

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Energy exchange between atoms and surfaces plays a key role in phenomena such as adsorption, desorption, and accommodation. The atom-surface impact generally involves a large number of phonons. The exceptions are light atom, weak atom-surface potential V, and low surface temperature T_S, situations encountered in highly specialized He and Ne surface scattering experiments at very low temperatures. Detailed information on the scattering mechanisms in both few-phonon and multiphonon regimes is potentially contained in differential cross-section measurements in monoenergetic atomic beam scattering from single-crystal surfaces.[1-4]

It may be thought that, especially in the multiphonon regime, emphasized in this paper, these relatively complex scattering events are understandable only via detailed numerical simulations.[5] We claim below, however, success for a model more realistic than the conventional "cube" models,[6] based on the trajectory approximation (TA),[7] described shortly. From comparison with experiment, a useful energy exchange parameter for each atom/surface system can be extracted.

The trajectory approximation calculates energy and momentum transfer on the assumption that the scattering atom follows a unique classical trajectory $\vec{R}(t)$. The TA neglects surface corrugation, for which there is experimental support in the weakness of diffraction of light rare-gas atoms from close-packed metal surface,[8] making the effective atom-surface potential approximately a function $V_{\rm eff}(z)$ only of distance normal to the surface. $V_{\rm eff}$ is asymmetric, with a repulsive hard wall at small z near the surface and a long attractive tail going as z^{-3} at large z. The asymmetry of the well ensures that for high energies near the top of the well the level spacing of atoms in the well is small and can be replaced by a continuum except at very low temperatures, T, justifying a *classical* trajectory. Energy transfer to phonons occurs mostly at small z, and is normally small compared to the well depth. The insensitivity of energy or momentum trans-

fer to the fate of the particle at large z (e.g., energy gain, energy loss, or trapping) makes it a good approximation to employ a *unique* trajectory. In adding that thermal noise in the trajectory itself is also neglected, we have summarized the physical basis of the TA.

For the purposes of this Letter we shall make the additional approximation that the substrate degrees of freedom involved with energy and momentum exchange are dominantly the Rayleigh phonons. There is good experimental evidence for this in scattering of light rare-gas atoms in the one-phonon regime.[1,2] Then in the TA the phonons (if we neglect anharmonicity for high-cohesive-energy solids) obey the time-dependent Hamiltonian

$$H(t)=\sum_{\vec{k}} \omega_{\vec{k}} b_{\vec{k}}^{\dagger} b_{\vec{k}} + \sum_{\vec{k}} f_{\vec{k}}(t)(b_{\vec{k}}^{\dagger} + b_{\vec{k}}). \quad (1)$$

Here $b_{\vec{k}}^{\dagger}$ and $b_{\vec{k}}$ are creation and destruction operators for Rayleigh phonons of frequency $\omega_{\vec{k}}$ and wave vector $\vec{k}$ parallel to surface. If $f_{\vec{k}}(\vec{R})$ is the coefficient of the (assumed linear) displacement of the bosons induced when the atom is at $\vec{R}$, then $f_{\vec{k}}(t)=f_{\vec{k}}(\vec{R}(t))$ represents the time-dependent perturbation. $f_{\vec{k}}(t)$ tends to zero for $t \to +\infty$ or $-\infty$.

We wish to calculate the probability that the final phonon state differs from the initial one by energy ϵ and wave vector $\vec{Q}$:

$$N(\epsilon,\vec{Q})=\sum_n Z_0^{-1} \exp(-\beta E_n)\langle n|U^{\dagger}\delta(\epsilon - H_0 + E_n)\delta(\vec{Q}-\hat{K}+\vec{K}_n)U|n\rangle . \quad (2)$$

Here $|n\rangle$ is the excited state of phonon system of energy E_n, H_0 is the first term in (1), $\hat{K}=\sum_{\vec{K}} \vec{K} b_{\vec{K}}^{\dagger} \times b_{\vec{K}}$ is the momentum operator, $U=U(\infty,-\infty)$ is the evolution operator for (1), and $\beta=1/kT$. As is well known, U may be calculated exactly. The result for $N(t,\vec{\rho})$, the triple Fourier transform of (2), is then found to be

$$N(t,\vec{\rho})=\exp\left[\sum_{\vec{K}} |f_{\vec{K}}|^2 \{\coth(\tfrac{1}{2}\beta\omega_{\vec{K}})[\cos(\omega_{\vec{K}}t+\vec{K}\cdot\vec{\rho})-1]-i\sin(\omega_{\vec{K}}t+\vec{K}\cdot\vec{\rho})\}\right] \quad (3)$$

if $f_{\vec{K}}=\int_{-\infty}^{\infty} dt f_{\vec{K}}(t)\exp(i\omega_{\vec{K}}t)$.

Independent of surface temperature, the mean energy transfer is found to be

$$\delta=\int_{-\infty}^{\infty} d\epsilon\, \epsilon \int d^2K N(\epsilon,\vec{K})=\sum_{\vec{K}} \omega_{\vec{K}} |f_{\vec{K}}|^2. \quad (4)$$

We shall not dwell here on the standard Born-approximation results (elastic line plus one-phonon loss/gain spectrum) obtained by expanding (4) to first order in the exponent.

The multiphonon limit of interest here corresponds to expansion of the trigonometric functions in the exponent of (4) for small arguments. The results are presented here for high temperature, isotropic scattering, and linear phonon dispersion. The first assumption neglects zero-point energy relative to kT. Isotropic scattering $f_{\vec{K}}=f_K$ will occur when the well depth is much larger than incident particle energy, so that the trajectory $\vec{R}(t)$ is nearly normal to the surface at small z. Experiments[1] with Ne show that, because of the "raft effect," the inelastic cross section and hence f_K fall off rapidly towards the zone edge, enabling us to put $\omega_{\vec{K}}=vK$, where v = Rayleigh mode velocity. With these approximations, expanding the exponent in (4) to leading order in t and ρ, and performing the inverse Fourier transform, we obtain the very simple result $N(\epsilon,\vec{Q})=N(\epsilon)N(\vec{Q})$, where

$$N(\epsilon)=(\pi^{1/2}\Delta\epsilon)^{-1}\exp[-(\epsilon-\delta)^2/\Delta\epsilon^2], \quad (5a)$$

$$N(\vec{Q})=2(\pi\Delta K^2)^{-1}\exp[-Q^2/\Delta K^2], \quad (5b)$$

with $\Delta\epsilon=2(k_B T\delta)^{1/2}$, $\Delta K=2^{-1/2}\Delta\epsilon/v$.

The result (5), whose derivation, we shall see, depends on physically satisfiable conditions, implies that the energy-momentum distribution is just a product of two Gaussians in energy and momentum separately. Their widths are both proportional to $\delta^{1/2}$ and can be related through the Rayleigh mode velocity, if it is known. A result similar to (5a) has earlier been obtained by the authors for scattering via electron-hole pairs.[9]

Suppose a beam of atoms of mass m_A, energy E_0, and parallel wave vector $\vec{K}_0$ is directed at the surface with angle of incidence θ_0 with respect to surface normal OZ. After scattering the energy and momentum will by conservation be $E=E_0-\epsilon$, $\vec{K}=\vec{K}_0-\vec{Q}$. The fraction whose "perpendicular" energy $E_\perp=E-K^2/2m_A$ is positive escapes from the surface and forms the "direct" or "lobular" fraction. The fraction with negative $E_\perp$ is trapped and subsequently forms the "trapping desorption" or "diffuse" fraction. The two fractions are separable in narrow-angle detectors. We consider the direct fraction probability $J(\theta,$

TABLE I. Energy-transfer efficiency.

	V(K)	δ(K)	δ/δ_B
Ar/Ag	1000	215	0.27
Kr/Ag	2000	415	0.21
Xe/Ag	3200	794	0.25
Xe/Pt	3200	794	0.26

φ) for scattering into angle of incidence θ and azimuthal angle φ from scattering plane.

We shall see that the spread (5b) in $\vec{K}$ leads to a relatively narrow distribution over angle. The distribution over θ essentially derives from the energy spread (5a) through the relation $E/E_0 = \sin^2\theta_0/\sin^2\theta \equiv a$, using conservation of $\vec{K}$. Hence from (5a) one obtains for the distribution in θ integrated transverse to the scattering plane

$$J(\theta) = 2\Delta\epsilon^{-1}\pi^{-1/2}E_0 a \cot\theta \exp\{-[(a-1)+\delta]^2/\Delta\epsilon^2\}.$$

The distribution over azimuth φ at a given θ may be obtained similarly as the projection onto K_y of (5b).

Heavy rare-gas atoms scattered from close-packed metal surfaces seem to fulfill the requirement of our theory. Their adsorption potentials are quite deep (see Table I), and the mass ratios are favorable for large energy transfer (multiphonon process). Lighter rare gases, He and Ne, scatter in the few-phonon regime.[1,2] Our approach is to use the present theory as a means of *data analysis* with one free parameter

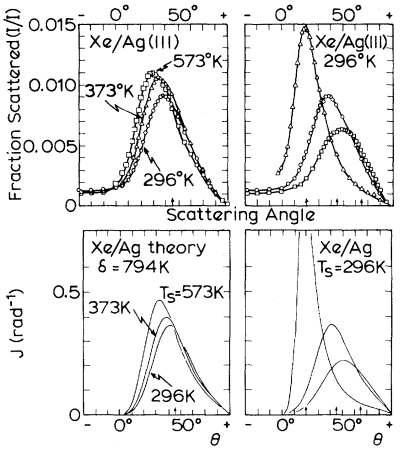

FIG. 2. Experimental (Ref. 3) (top) and theoretical (bottom) polar angle distributions for Xe on Ag (111), showing temperature of surface and angle of incidence (arrow on θ axis).

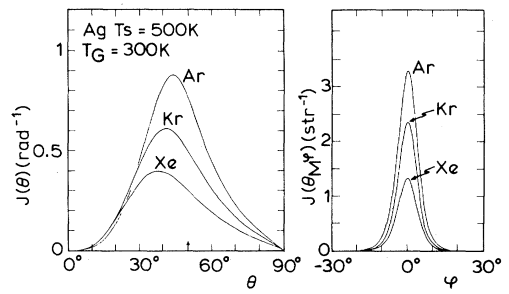

FIG. 1. Calculated distribution in polar angle (left) and azimuthal angle (right) for noble gases on Ag (111), to be compared with Fig. 2 of Ref. 4.

δ [Eq. (4)]. This circumvents the requirement of an *ab initio* approach to have knowledge of the trajectory, i.e., of V_{eff}, itself a kind of nonlinear optical potential because of yielding of the surface under impact. The values of δ employed in this paper (see Table I) are essentially best fits to the differential cross-section data. However, they are in broad agreement with available (probably less accurate) trapping fraction data.

In Fig. 1 we show the calculated distributions

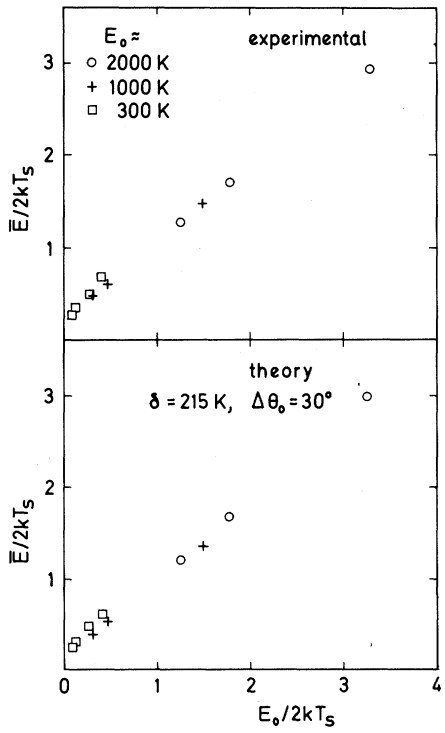

FIG. 3. Experimental (Ref. 10) and theoretical mean final energy $\bar{E}$ vs initial energy E_0, both divided by $2k_BT_S$, for Ar on polycrystalline W.

in θ and φ for the same beam parameters as in Fig. 2 of Ref. 4. The agreement of the shape of the curve with the data cited is excellent, although there are some slight disagreements in scaling of absolute intensities. The φ distributions are based on the Rayleigh mode velocity $v = 1500$ m/s for Ag.[2] The calculated widths $\Delta\varphi$ are somewhat smaller than experiment,[4] especially for Xe where the error approaches a factor of 2. We attribute this to the importance of corrugation effects in the almost chemisorbed Xe(111)/Ag system.

Figure 2 shows θ distributions for Ar, Kr, and Xe scattered from Ag(111). These are compared with experiments[3] with the effusive beam for whose distribution a suitable convolution has been made in the theoretical curves. We see that the agreement is very satisfactory.

In Fig. 3 we show a comparison of theory with experimental energy transfer in scattering of Ar from polycrystalline W.[10] Here we have introduced a temperature-independent Gaussian distribution in θ of half-width 30° to model the effect of the polycrystallinity. It is estimated to be still adequate to neglect the diffuse fraction. The good agreement with experiment is further evidence in favor of the correctness of our analysis, though it has also been obtained with the "cube" model.[6] Excellent agreement has also been obtained with a similar experiment done with N_2, using $\delta = 800$ K, though rotational energy transfer is neglected.[11]

Finally our derived values of δ (Table I) may be compared with the Baule energy transfer $\delta_B = 4V\nu/(1+\nu)^2$, where ν is the mass ratio m_A/m_s. With values of the well depth V in Table I, the ratio δ/δ_B lies in the range 0.2–0.27 for all three rare gases, though somewhat larger, 0.37, for Ar/W (Fig. 3). If proved to hold more generally, this would provide a helpful rule of thumb in discussing energy transfer at surfaces.

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