Limitations of the Trajectory Approximation in Atom-Surface Scattering

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We have scattered low energy (100–400 eV) Na^+ from a Cu(001) surface, and studied the peak in the energy spectra that corresponds to collisions in which the Na^+ interacts primarily with a single Cu atom. This peak is broadened by the thermal fluctuations in the momentum of the Cu atom. Its width has been measured as a function of surface temperature, scattering geometry, and incident energy. Our data agree well with a rigorous statistical analysis (within 10%) but poorly with the trajectory approximation (TA), demonstrating that the TA can fail when recoil is substantial.

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To find the energy loss spectrum of a particle scattered from a many-body bath, one often assumes that the particle moves on a classical trajectory. The excitation spectrum of the bath is then calculated quantum mechanically, and the actual loss spectrum of the incident particle is deduced from energy conservation. This is the so-called trajectory approximation (TA), which is designed to include quantum corrections to classical scattering. The TA has been successfully applied to the scattering of electrons [1], neutral atoms [2–4], and ions [5,6] from surfaces and has recently been used to analyze multiphonon peaks in He scattering experiments [7]. In many of these applications the interaction with the bath does not significantly modify the trajectory, and it has long been speculated [8] that this restriction is a necessary condition for the validity of the TA [9–11].

In this Letter, we describe the first clear experimental demonstration of the failure of the TA due to substantial modification of the trajectory by the bath. We performed completely classical scattering experiments, using 100–400 eV Na^+ ions incident on Cu(001), in which the dominant energy loss was to phonons. The scattering conditions were similar to those proposed by Burke, Jensen, and Kohn [12] (hereafter BJK). The fractional energy loss of the ions, i.e., their recoil, was substantial, and is a measure of the modification of the trajectory by phonons in the surface. We analyze the results using both the classical limit of the TA and a rigorous classical statistical treatment. The excellent quantitative agreement of the data with the rigorous calculation, and the disagreement with the TA, provide compelling evidence that the TA does not account for strong recoil correctly in these experiments. Since the TA calculation itself gives no indication that its results may be incorrect, caution must therefore be used in interpreting scattering data with the TA when the interaction with the bath significantly modifies the trajectory. (In contrast, the TA has been used to analyze *charge transfer* for the Na^+/Cu system at these incident energies [13], where it is expected to work well because the recoil involving the electronic degrees of freedom in the surface is small [5].)

The idea behind our experiment is simple. Imagine an ion scattering from a single oscillator in one dimension. We may treat this problem classically when the wavelength of the ion is short, and $k_BT \gg \hbar\omega$, where T is the initial temperature of the oscillator and ω is its frequency. Classical statistical mechanics [14] says that the final energy spectrum of the ion is given by

$$I(E) = \frac{1}{Z}\int dX\, dP\, \delta(E - E_f(X,P)) \times \exp[-H_{\rm osc}(X,P)/k_BT], \quad (1)$$

where X and P are the oscillator's initial position and momentum, respectively, and are both integrated from $-\infty$ to ∞, $H_{\rm osc}(X,P) = P^2/2M + M\omega^2X^2/2$, where M is the oscillator mass, $Z = \int dX\, dP \exp[-H_{\rm osc}(X,P)/k_BT]$ is the classical partition function, and $E_f(X,P)$ is the final energy of the ion, as a function of the initial conditions of the oscillator. As $T \to 0$, this spectrum approaches a single delta function at $E = E_f(0,0)$. However, if T is small but finite, i.e., $k_BT \ll E_i$, where E_i is the incident energy of the ion, this peak will be slightly broadened. Expanding $E_f(X,P)$ around $E_f(0,0)$, the square of the peak width, defined as the second moment of the intensity about the mean, is found to be [15]

$$(\Delta E)^2 = \left[\frac{\partial E_f}{\partial P}\bigg|_{P=0}\right]^2 \langle P^2\rangle + \left[\frac{\partial E_f}{\partial X}\bigg|_{X=0}\right]^2 \langle X^2\rangle \quad (2)$$

to leading order in k_BT/E_i, where $\langle X^2\rangle$ and $\langle P^2\rangle$ are the mean square thermal position and momentum expectation values of the oscillator, respectively. In this classical limit, $\langle P^2\rangle$ is proportional to T for any lattice potential, and for a harmonic lattice potential, $\langle X^2\rangle$ is also proportional to T, while their coefficients in Eq. (2) are temperature independent.

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In a TA calculation, we first find the unique zero temperature classical trajectory of the ion, i.e., with $X = P = 0$ initially. This produces a time-dependent force on the oscillator. Using this force, we find the oscillator's final energy gain, $E_g(X,P)$, by solving the oscillator's equation of motion for all initial conditions. Since the energy gain of the oscillator must equal the energy loss of the ion, this results in an expression for the width identical to Eq. (2), but with E_f replaced by E_g in the derivatives. As we shall show, these two results can differ, even under purely classical conditions.

In a real three-dimensional scattering experiment at fixed incident and final angles, there are several peaks in the scattered ion energy spectrum corresponding to different trajectories. In our experiments 100 to 400 eV Na^+ were scattered from Cu(001) along the ⟨100⟩ azimuth at an incident angle of $\theta_i = 45°$ from the surface normal. Both the surface temperature, T_s, and the final angle measured from the normal, θ_f, were varied. Figure 1 shows four measured energy spectra with $E_i = 201.2$ eV and $\theta_f = 45°$. The spectra, which were taken at surface temperatures ranging from 141 to 970 K, are offset vertically. The three peaks are each broadened by the thermal fluctuations of the surface atoms, with the width of each peak increasing with the surface temperature. The trajectories which contribute to each peak have been determined by comparing the measured energy spectra to classical zero temperature simulations using the code SAFARI [16]. The two highest energy peaks ($E_f/E_i = 0.55, 0.65$) are due to multiple scattering trajectories. In this Letter, we analyze the lowest energy peak ($E_f/E_i = 0.46$, labeled QS), which is due to ions that scatter from primarily one surface atom. Since these single scattering trajectories also, in general, undergo small momentum transfer collisions with other nearby surface atoms, we refer to them as quasisingle (QS) trajectories.

The experiments were conducted under ultrahigh vacuum conditions. The scattering chamber and beam line have been described in detail elsewhere [17]. Typical beam currents, spot sizes, and angular divergences were less than ≈1 nA, 1 mm (FWHM), and less than ±0.5°, respectively. Sample dosing was minimized by using low beam currents and by periodically flashing the sample to 600 °C to desorb trapped Na, since it was found that the dosing broadened the peaks. The scattered ion flux was energy analyzed using a 180° hemispherical electrostatic analyzer with an energy resolution of $\Delta E/E = 0.016$ ($\Delta E = 2\sigma$, where σ is the standard deviation), and an effective angular acceptance of approximately ±0.5°.

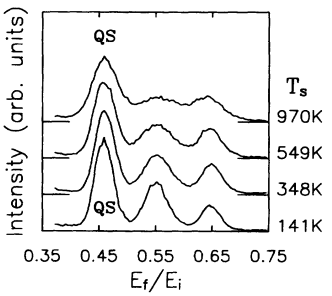

FIG. 1. Typical measured energy spectra for 201.2 eV Na^+ scattering from Cu(001) as a function of surface temperature. The beam was incident along the ⟨100⟩ azimuth, with $\theta_i = \theta_f = 45°$. The peak labeled QS is due to a quasisingle collision with a Cu atom (see text).

The sample was prepared by repeated sputter-anneal cycles using 500 eV Ar^+, and was clean within Auger detection limits. The sample temperature, which was monitored using a Chromel-Alumel thermocouple, could be varied from 130 to 1300 K. It was cooled by Cu braids attached to a liquid nitrogen reservoir and heated from behind by an e^- beam heater. Low energy electron diffraction patterns indicate that the sample was stepped along the ⟨100⟩ direction. We determined that, as expected, these steps do not influence our results by comparing the QS peak width to previous measurements on a nonstepped surface which yielded the same widths as the stepped sample.

The QS peak (see Fig. 1) can be treated as if it were due to an impulsive collision with a single surface atom, as is argued below. A reliable semiempirical potential has been deduced by comparing measured final energy and angular distributions to SAFARI simulations for Na^+ scattering from Cu(001) and Cu(110) [16]. These simulations indicate that, for $E_i \geq 100$ eV and $\theta_i = \theta_f = 45°$, the trajectory leading to the QS peak is dominated by the interaction of the ion with a single Cu surface atom. Furthermore, the potential is sufficiently short ranged that at these incident energies the Cu atom has no time to relax during the collision, i.e., $\tau \ll 2\pi/\omega_D$, where τ is the collision time and ω_D is the surface Debye frequency. Thus we model the impact as a collision between two free particles, in which energy and momentum conservation are sufficient to determine the final state of the system [12]. The classical final energy is then given by $E_f = f(\theta)E_i$, where f is a kinematic factor depending only on the total scattering angle θ and the ratio of the ion mass to the target atom mass μ,

$$f(\theta) = \left(\frac{\sqrt{1 - \mu^2 \sin^2\theta} + \mu \cos\theta}{1 + \mu} \right)^2 . \qquad (3)$$

Note that we measure $\theta = 180° - \theta_i - \theta_f$ relative to a straight-through trajectory [18]. The final energy predicted by Eq. (3) is in excellent agreement with the measured mean energy of the QS peak under most of the scattering conditions described in this Letter. The only significant deviation occurs at angles approaching the rainbow angle at $\theta_f \approx 72°$. SAFARI simulations indicate that this is due to the strong interaction of the ion with additional nearby surface atoms (see [16], and references therein), which is not accounted for by Eq. (3).

Next we calculate the width of the QS peak using Eq. (2) generalized to three dimensions [12]. For an impulsive collision, only momentum fluctuations contribute [12], and we find

$$(\Delta E)^2 = 2g(\theta)E_i k_B T_s, \tag{4}$$

where $g(\theta)$ is another kinematic factor [18],

$$g(\theta) = \frac{2\mu f(\theta)}{(1+\mu)^2}\left(\frac{1+\mu\sin^2\theta}{1-\mu^2\sin^2\theta} - \frac{\cos\theta}{\sqrt{1-\mu^2\sin^2\theta}}\right). \tag{5}$$

Note that because we used a classical analysis, Eqs. (4) and (5) work well only for $T_s \gtrsim \Theta_{SD}/2$ (see Fig. 12 of Ref. [12]), where Θ_{SD} is the surface Debye temperature, a condition well satisfied in our experiments [19]. Furthermore, although substantial charge exchange can occur under these scattering conditions [13], a simple calculation [5] shows that the energy transfer to electron-hole pairs is small, and its temperature-dependent contribution to the width, which behaves as T_s^4, is negligible [20].

Why do we concentrate our analysis on the QS peak width alone? Firstly, for a single impulsive collision, the interaction potential between the incident ion and the surface is irrelevant, because we can model the impact as a collision between two free particles. Moreover, because we probe only momentum fluctuations at high temperatures, the dynamics of the lattice plays no role [21]. Thus there are no parameters to adjust in the theory, and simple kinematics determines this width.

In the experiment, the widths are determined from the measured spectra, four of which are shown in Fig. 1, by fitting the three peaks in a spectrum with a sum of three Gaussians with an additional linear term to correct for the small background. The mean energies, widths, and amplitudes of the Gaussians, as well as the linear background, are treated as free parameters in the fit. In Fig. 2 we show a plot of $(\Delta E)^2$ versus T_s for the QS peak with $E_i = 201.2$ eV and $\theta_f = 45°$. The data fall on a straight line which does not pass through the origin. This offset is at least partly due to the finite energy and angular resolution of the detector, the energy spread and angular divergence of the incident beam, and the isotopic mix of Cu on the surface.

The slope of the best-fit straight line through the data in Fig. 2 is 0.0101 ± 0.0007 eV^2/K, where the data were fitted from 300 K $\leq T_s \leq$ 700 K. This slope yields a value of g of 0.291 ± 0.020, which agrees well with the theoretical value, 0.287, calculated from Eq. (5). Similar plots for $E_i = 99.7$ and 401.3 eV produce slopes also agreeing with Eq. (5), yielding $g/0.287 = 1.03 \pm 0.06$ and 1.09 ± 0.05, respectively.

To analyze the data within the classical limit of the TA, we note that when an oscillator experiences an impulse of $\Delta\mathbf{p}$, its energy changes by

$$E_g(\mathbf{P}) = [(\mathbf{P}+\Delta\mathbf{p})^2 - \mathbf{P}^2]/2M. \tag{6}$$

Inserting this result into Eq. (2) (generalized to three dimensions) with E_f replaced by E_g, and with $\Delta\mathbf{p}$ set to the value of the momentum loss of the ion in the zero temperature trajectory, we find a result of the same form as Eq. (4), but with a different kinematic factor,

$$g_{\mathrm{TA}}(\theta) = \mu[f(\theta) + 1 - 2\cos\theta\sqrt{f(\theta)}]. \tag{7}$$

In contrast to Eq. (5), this results in a slope that is 1.8 times larger than that of the straight line fit of Fig. 2.

To make our analysis more thorough, we repeated the measurements of Fig. 2 for a range of values of θ_f, keeping θ_i fixed at 45°, and using initial energies in the range 200.9–201.5 eV. Figure 3 shows the resulting measured values of g, $g(\theta)$ from Eq. (5), and $g_{\mathrm{TA}}(\theta)$ as a function of $\theta_f = 180° - \theta - \theta_i$. Clearly the TA disagrees with the data, and even yields the wrong functional dependence of g on angle. The rigorous classical statistical treatment of the impulsive model, i.e., Eq. (5), however, is in excellent agreement with the data except for $\theta_f \geq 60°$, where the impulsive model breaks down, even for the mean energy of the QS peak, as discussed earlier.

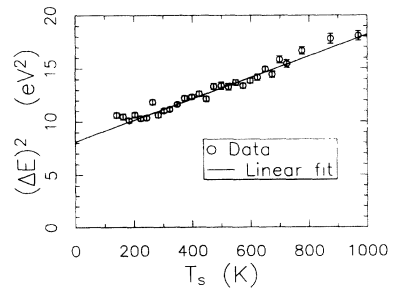

FIG. 2. The width squared of the QS peak versus surface temperature under the same experimental conditions as in Fig. 1, where four of the spectra are shown. The points are the data, while the solid line is the best fit to the data for 300 K $\leq T_s \leq$ 700 K. The nonzero intercept on the y axis is partly due to the limited resolution of the detector (see text).

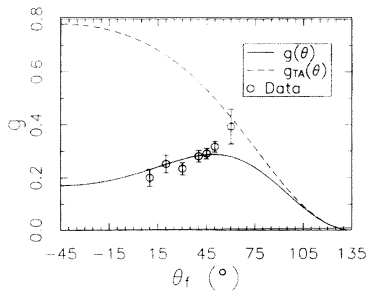

FIG. 3. The geometric factor g as a function of θ_f. The experimental values of g (open circles) are determined from the slopes of plots of $(\Delta E)^2$ vs T_s (see Fig. 2) for 200.9 eV $\leq E_i \leq$ 201.5 eV, and $\theta_i = 45°$. The solid line is the prediction of the rigorous theory, Eq. (5), while the dotted line is the TA result, Eq. (7).

The error made by the TA may be understood as follows. The ion trajectory depends on the initial conditions of the target. Therefore, the time-dependent force on the target also depends on the target's initial conditions. Thermal-averaging the outcome due to these differing forces produces the exact result of Eq. (2). The TA, however, approximates all these forces by a single force: that due to the ion trajectory when the target is at zero temperature. Indeed, in the limit of small recoil, the force on the target *is* independent of the initial conditions, and so the TA does become correct in this limit [22]. For our impulsive collision, as μ or $\theta \to 0$, $g_{\mathrm{TA}}(\theta) \to g(\theta)$.

Although our experiments probed only the classical limit ($\hbar = 0$) of this ion-surface scattering system, our results have implications for the quantum scattering problem. To see this, we rewrite Eq. (2) in the general form

$$(\Delta E)^2 = \sum_i C_i \langle O_i \rangle , \tag{8}$$

where the C_i are coefficients depending only on the scattering dynamics (e.g., $\partial E_f / \partial P|_{P=0}$), and the $\langle O_i \rangle$ are thermal expectation values of surface coordinates (e.g., $\langle P^2 \rangle$). Jensen, Chang, and Kohn [23] have shown rigorously that the leading quantum corrections to $(\Delta E)^2$ come entirely from fluctuations in the target, so that the above is valid quantum mechanically (to order $\hbar$), once the $\langle O_i \rangle$ are evaluated quantum mechanically. These quantum corrections become important when $T_s < \Theta_{SD}/2$, and zero point fluctuations contribute significantly to the peak width. By construction, the TA results also apply to the quantum problem, again once the $\langle O_i \rangle$ are evaluated quantum mechanically. In both treatments, the coefficients C_i are determined *completely* classically. In the present experiments, in which recoil is substantial, the TA makes significant errors in the prediction of these coefficients. Therefore, the TA can also be expected to fail in the quantum case, i.e., the same ion scattering conditions, but at lower surface temperatures. Experiments which can test this directly are in progress.

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