Quantum Effects in the Sticking of Ne on a Flat Metal Surface

H. Schlichting,[a] D. Menzel,[a] T. Brunner,[b] and W. Brenig[b]

Physik Department, Technische Universität, München, D-8046 Garching, Federal Republic of Germany

and

J. C. Tully

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 13 October 1987)

The sticking coefficient of thermal neon atoms on a flat Ru(001) surface ($T_s = 7$ K) is found experimentally to be very low and strongly dependent on gas temperature (1×10^{-3} to 8×10^{-2} for T_g from 600 to 30 K) on the *clean* surface, and to increase strongly with coverage to about 0.7. The zero-coverage values are incompatible with classical mechanical theory, irrespective of assumed interaction parameters, requiring substantial zero-phonon scattering. Calculations treating the energy transfer to phonons quantum-mechanically can reproduce the data with reasonable parameters.

The importance of quantum mechanical effects in the sticking of gases on surfaces is not adequately understood. While complicated behavior can occur for molecular or dissociative adsorption because of the many participating degrees of freedom and adsorption states,[1] a simple situation should prevail for sticking of atoms, in particular of rare gases,[2] for which the potential-energy surfaces should be simple as well. Nevertheless, except for He for which the dominance of quantum behavior is unquestioned, there has been no direct measure of the magnitude of quantum effects in the sticking of rare gases to surfaces. Theoretical results[3,4] indicate that neon, in spite of its higher mass, should exhibit substantial zero-phonon (nonclassical) scattering. Measurements of the scattering of Ne from Cu(100) reveal a zero-phonon contribution of up to 20%–30% for the surface temperatures and gas energies reported.[5] A larger zero-phonon contribution would be expected by extrapolation of these results to zero surface temperature and gas energy. However, this extrapolation cannot be carried out with confidence. Thus the scattering experiments establish an upper limit of 0.7 to 0.8 for the low-energy sticking probability, significantly but certainly not grossly different from the classical mechanical value of unity. Existing measurements of accommodation coefficients[6] do not help to refine this upper limit. We report direct measurements of the sticking probability of Ne on Ru(001) which demonstrate that the low-energy sticking probability is of order 0.1. Thus, at least for this system, quantum effects are very large. The quantum behavior is not associated with the wavelength of the Ne atom, but with the response of the lattice; i.e., zero-phonon scattering.[3,4]

The UHV system used had a working base pressure of about 10^{-12} mbar (mainly H_2), which was very important for the success of the experiment. The crystal was mounted on a manipulator with integrated cryostat and heating devices which made surface temperatures T_s between 7 and 1600 K accessible. Because of the desired flatness and cleanliness of the crystal, Ru(001) was used for which ample experience in cleaning and obtaining high-quality surfaces exists in this laboratory.[7] A microchannel-plate (MCP) doser heatable and coolable from its circumference for gas temperatures T_g between 30 and 600 K was used for dosing. In order to ensure constant temperature across the MCP despite its low thermal conductivity, twenty layers of fine Cu mesh had to be packed on either side of the MCP leading to a thermally diffuse beam despite the directional effect of the MCP. The MCP assembly (25 mm diam) was placed in front of the crystal (10 mm diam), parallel to it about 15 mm away, thus leading to some depletion of the thermal flux at high angles from the surface normal (see below). Exposures were calculated from the pressure before the MCP, the time of opening (set by a fast-action pneumatically actuated valve), and a calibration factor, taken from the sticking coefficient of multilayer Xe.[8] The reproducibility of doses was $\pm 1\%$. Amounts adsorbed were determined by integration of thermal desorption traces obtained with an enclosed mass-spectrometer ion source,[9] whose detection efficiency is independent of pumping-speed variations. The crystal-aperture distance was set by a capacitance monitor to within 5 μm which made signals reproducible to $< \pm 3\%$. The background in desorption spectra corresponded to 10^{-10} monolayer (ML), so that coverages of 0.1%–0.2% ML could be determined to 3%. Great care was employed to obtain accurate temperature calibration, resolution, and reproducibility. Desorption spectra from multilayers showed clear separability of up to the fifth layer. These and other interesting aspects of thermal desorption will be discussed elsewhere.[8]

Sticking coefficients s were obtained by division of peak integrals by the dose. Over a considerable range

$(0 < \theta < 0.7$ ML) the coverage θ grows exponentially with exposure, i.e., s increases linearly with θ up to about 0.7 ML, according to $s = s_0 + \theta s_1$. Extrapolation to $\theta \to 0$ yields s_0, the sticking coefficient on the clean surface, which can also be obtained by integration over a very small (0.2% to 1% ML) coverage. As an example, $s_0 = 2.8 \times 10^{-3}$ and $s_1 = 0.52$ are obtained at $T_g \approx 300$ K. While s_1 is essentially independent of T_g, s_0 varies strongly with T_g, as shown in Fig. 1. The exponential increase with coverage and the s_1 value can be understood by collisions of incoming Ne atoms with adsorbed Ne; the effective cross section for sticking via this mechanism is estimated to be 1.2 times the gas kinetic cross section. While it is interesting that this effect is so clearly seen, it is not too surprising.[6,10] More surprising are the very low and strongly T_g-dependent s_0 values on which we now concentrate.

We now demonstrate that the measured thermally averaged sticking probabilities, $s_0(T_g)$, require a mono-

FIG. 1. Experimental results for the sticking coefficient s_0 of Ne at $T_s = 7$ K for very small coverages (points), vs (a) gas temperature and (b) reciprocal gas temperature. Inset: A blowup of the region around the origin. The dash-dotted line represents the best Gaussian fit [Eq. (2)] to the data, the dashed line the best Gaussian fit with $p_0 = 1$ (classical), and the full line the results of the quantum calculations, described in the text.

energetic sticking probability function that is inconsistent with classical mechanics at low energies. For this purpose we represent $s_0(T_g)$ by a convolution of the monoenergetic sticking probability, $p_s(E_\perp, E_\parallel)$, with the flux distribution of energies in the thermal source, $n(E_\perp, E_\parallel)$

$$s_0(T_g) = \int dE_\perp \, dE_\parallel \, p_s(E_\perp, E_\parallel) n(E_\perp, E_\parallel), \qquad (1)$$

where $E_\perp$ and $E_\parallel$ are the incident kinetic energies associated with normal and tangential motion, respectively. It is likely that the sticking probability of Ne on the flat Ru(001) surface is approximately independent of $E_\parallel$. However, this has not been established, and so we have carried out the analysis described below for the two limiting cases, normal-energy scaling and total-energy scaling. In either case, we have obtained the flux distribution $n(E_\perp, E_\parallel)$ exactly for our experimental geometry by numerical integration. Equation (1) was then integrated numerically for any assumed function $p_s(E_\perp, E_\parallel)$. We note that for our experimental geometry, atoms with parallel velocity much larger than perpendicular will not strike the surface, leading to a depletion of low-$E_\perp$ particles relative to a full Maxwellian distribution.[11]

As a parametrization of the data, we approximate $p_s(E)$ by a Gaussian centered at $E = 0$,

$$p_s(E) = p_0 \exp[-(E/E_c)^2]. \qquad (2)$$

Here E refers either to total energy, $E_\perp + E_\parallel$, or to normal energy, $E_\perp$. Our justification for employing such a simple form is that the thermally averaged sticking coefficients s_0 are found to be insensitive to the detailed shape of $p_s(E)$ throughout the temperature range of these experiments. Indeed, use of a simple exponential or a step function in place of Eq. (2) produces virtually as good fits to the data, and leads to the same qualitative conclusions. We prefer Gaussians as the zero slope at $E \to 0$ and the functional form of the decay at high E are in qualitative accord with classical and quantum-mechanical calculations of $p_s(E)$.

We have varied p_0 and E_c to achieve the best fit to the experimental $s_0(T_g)$. The assumption of normal-energy scaling yields the dash-dotted curves of Figs. 1 and 2, with the best-fit values $p_0 = 0.11$ and $E_c = 65$ K. Total-energy scaling produces a fit of almost identical quality, but with parameters $p_0 = 0.10$ and $E_c = 85$ K. Acceptable fits are obtained in the range $0.07 < p_0 < 0.20$ with correlated E_c values between 100 and 40 K. Our constraining p_0 to be unity as required by classical mechanics, with normal-energy scaling, produces the dashed curves of Figs. 1 and 2, with $E_c = 13$ K. Total-energy scaling gives a marginally improved fit with $E_c = 17$ K, but neither is compatible with the data. Also the concave upward behavior of the dashed curve in Fig. 1(b) contradicts experiment. The same qualitative behavior is found for exponential or step-function forms for $p_s(E)$. The accuracy of the experimental points is sufficiently
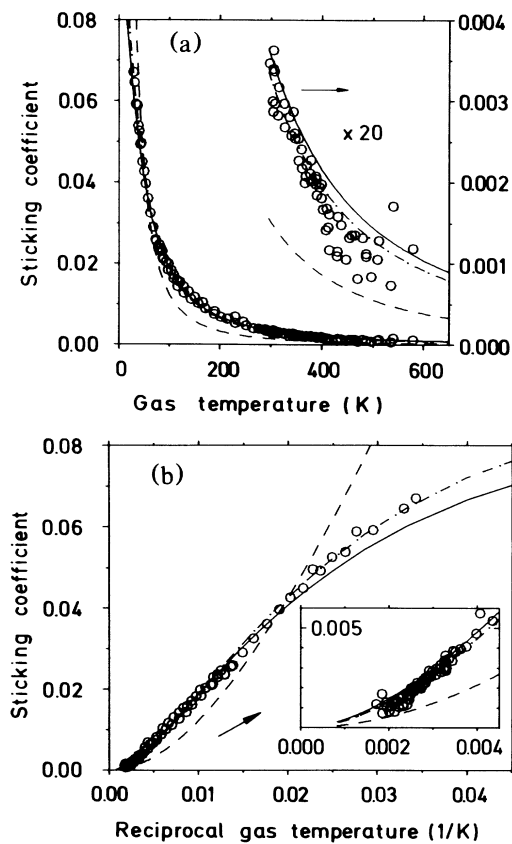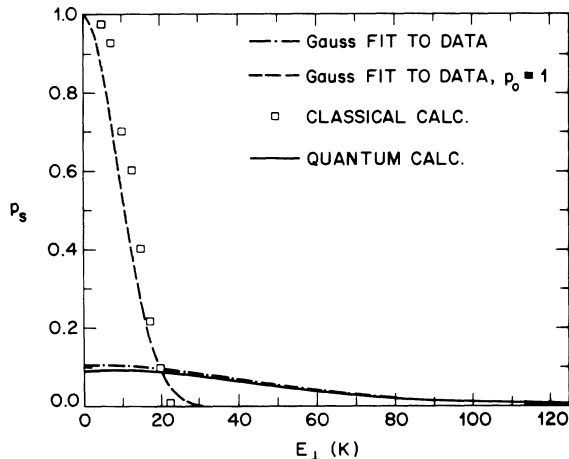
FIG. 2. The monochromatic sticking probability $p_s(E_\perp)$ as a function of normal energy of the Ne atoms; meaning of symbols as indicated.

good to conclude that *no* reasonably behaved function $p_s(E)$ that is constrained to unity as $E \to 0$ can reproduce the experimental temperature dependence of the sticking probability. This is a central result of this study. It means that classical mechanics does not adequately describe the sticking of Ne on Ru(001), despite the relatively large atomic masses and the averaging over energy and angle. We support this conclusion with extensive classical, quasiclassical, and quantal calculations.

Classical stochastic trajectory calculations[12] were carried out employing a two-layer, 64-atom/layer slab of Ru atoms, with periodic boundary conditions parallel to the surface. White-noise friction and random forces normal to the surface were introduced to second-layer atoms to maintain the slab at the desired temperature. First- and second-neighbor harmonic force constants were used. Parameters were chosen to reproduce the bulk phonon spectrum ($\theta_D \approx 415$ K). The surface was taken as truncation of the bulk, resulting in a surface Debye temperature of 246 K.[13] Ne-Ru interactions were assumed to be pairwise additive Lennard-Jones 6–12 potentials ($\epsilon = 27.7$ K, $\sigma = 4.187$ Å) which were adjusted to reproduce the experimental binding energy of Ne on Ru(001), 350 K,[14] and the overall magnitude of the measured sticking probability. Runs at $T_s = 0$ and 7 K produced almost identical sticking probabilities, so most calculations were performed for $T_s = 0$ where the definition of sticking is unambiguous. $p_s(E_\perp, E_\parallel)$ was computed for a range of $E_\perp$ and $E_\parallel$ and shown to be approximately independent of $E_\parallel$ for $E_\parallel < E_\perp$. The squares in Fig. 2 give the resulting $p_s(E_\perp)$. The fit to experiment is similar to the dashed curves of Figs. 1(a) and 1(b). This is the best that classical mechanics can do. The calculated $p_s(E_\perp)$ are sensitive to phonon frequencies and to the potential form and parameters. But regardless of assumptions and parameter choice, $p_s(E)$ calculated by

classical mechanics approaches unity as $E \to 0$, and has the qualitative shape shown by the squares of Fig. 2. Also the value of σ required for these results is somewhat larger than might have been anticipated. Choice of $\sigma = 3.62$ Å, e.g., would result in calculated thermally averaged sticking probabilities a factor of 8 larger than experimental. Thus not only is the temperature dependence of s_0 incompatible with classical mechanics, but also its magnitude is somewhat difficult to reconcile.

Two important features are omitted by classical mechanics.[3,15] First, it does not contain the zero-phonon line responsible for reduction of $p_s(E)$ below unity as $E \to 0$. Second, nonzero values of $p_s(E)$ extend to higher values of E in quantum mechanics because of excitation of high-frequency phonons that are classically unattainable. Both of these effects are very important to transform the dashed curve of Fig. 2 into the dash-dotted curve, as required to match experiment.

To demonstrate this we have carried out quantum-mechanical calculations by the procedure described before.[3] Briefly, the substrate model is essentially the soft-cube model (no momentum transfer parallel to the surface). Collisions are assumed to occur with one surface atom at a time only (no finite-size effects included). The embedding of this atom into the substrate is accomplished by our giving it a local density of vibrational states which reflects the coupling to the other substrate atoms. In its simplest form this can be the Debye density of states with an adjustable Debye temperature θ_D. We also tested a sharply peaked density of states similar to that resulting from the above molecular-dynamics calculation. The scattered particle is treated classically (see Ref. 3). The calculations yield the energy distribution of scattered particles after a single collision, for an incoming monoenergetic beam. The sticking coefficient is obtained from it by integration over all negative energies, i.e., the "prompt" sticking is calculated. This is a good approximation to the actual process for T_s much smaller than the average energy transfer, as here. Results for a Morse potential [well depth 350 K, slope parameter 0.65 Å^{-1} (Ref. 14)] and $\theta_{DS} = 245$ K are indicated by the solid lines of Figs. 1 and 2. The value of 0.09 at $T_g \to 0$ agrees with the experimentally derived solid curve within its uncertainly, and the entire curve is in quite reasonable accord with experiment.

In conclusion, the sticking coefficient of Ne atoms obtained experimentally on a flat, clean metal surface as a function of gas temperature is not consistent with classical mechanical theory, requiring a high probability of elastic scattering, 80%–90%, at low incident energies. Quantum calculations can reproduce the data and lead to the correct low-energy limit of the sticking probability. For heavier rare gases quantum effects are less important, as expected, but still significant, at least for Ar.[8]

---

[a]Institut für Festkörperphysik.

[b]Institut für Theoretische Physik.

[1]See, e.g., J. A. Barker and D. J. Auerbach, Surf. Sci. Rep. **4** 1 (1984).

[2]H. J. Kreuzer and Z. W. Gortel, *Physisorption Kinetics* (Springer-Verlag, Berlin, 1986).

[3]W. Brenig, Z. Phys. B **36**, 81 (1979); J. Böheim and W. Brenig, Z. Phys. B **41**, 243 (1981).

[4]M. Persson and J. Harris, Surf. Sci. **187**, 67 (1987), and work cited therein.

[5]J. Lapujoulade, Y. Lejay, and G. Armand, Surf. Sci. **95**, 107 (1980); S. Andersson, L. Wilzen, and J. Harris, Phys. Rev. Lett. **57**, 1603 (1986).

[6]J. Kouptsidis and D. Menzel, Ber. Bunsenges. Phys. Chem. **74**, 512 (1970).

[7]See, e.g., H. Pfnür and D. Menzel, Surf. Sci. **148**, 411 (1984), and references therein.

[8]H. Schlichting and D. Menzel, to be published.

[9]P. Feulner and D. Menzel, J. Vac. Sci. Technol. **17**, 662 (1980).

[10]E. G. D. Zhao and J. E. Adams, Langmuir **1**, 557 (1985).

[11]In principle, collisions *in* the source could further deplete low-$E_\perp$ atoms. This effect is negligible in this experiment because of the very low pressures employed in the source, and consequently high Knudsen numbers, as directly verified by the observation of no change in s_0 for systematic variations of source pressure. Even if such an effect did exist, the outer layer of copper mesh in our source would remove it.

[12]J. C. Tully, Surf. Sci. **111**, 461 (1981); C. Lim, J. C. Tully, A. Amirav, P. J. Trevor, and M. J. Cardillo, J. Chem. Phys. **87**, 1808 (1987).

[13]The experimental surface Debye temperature of Ru(001) is 216 K; G. Michalk and D. Menzel, unpublished.

[14]The binding energy of 350 ± 20 K for Ne on Ru(001) was obtained by temperature-programmed desorption (Ref. 8). Both the binding energy and range of the potential employed in the present calculations differ by a factor of 2 or more from parameters used to analyze scattering of Ne from Cu(100). See, e.g., B. Salanon, J. Phys. (Paris) **45**, 1373 (1984). Employment of Salanon's parameters in our calculations reduces the quality of fit to experiment, but does not affect the final conclusions.

[15]A possible third quantum effect is the decrease of sticking at very low energies due to reflection from the attractive potential. This occurs only at extremely low energies as shown by J. Böheim, W. Brenig, and J. Stutzki, Z. Phys. B **48**, (1982), and is unimportant here.