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Metallic adhesion and tunnelling at the atomic scale

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Abstract. We simultaneously measured the distance dependence of the force and the tunnelling current between a W(111) tip and a Au(111) sample in an ultrahigh vacuum at $T = 150$ K. The tip was characterized by field ion microscopy. Even at atomically close contact no evidence of structural instabilities was found. The scaling of the force curves show an unexpectedly long distance scaling parameter of $\lambda = 0.2$ nm. We conclude that not only the apex atoms contribute to the adhesion forces, but the first three layers play an almost equal role. Using a model that correlates the force and the tunnelling current, we are able to extract the tip density of states. Possible reasons for the long scaling length are discussed.

The study of metallic adhesion on the atomic scale lays the foundation for the understanding of the physics of nanometre-sized structures. In particular, issues surrounding nanoscale tribology find widespread interest in newly developing fields such as nanotechnology. Adhesion has also been found to play a crucial role in understanding imaging mechanisms in scanning tunnelling microscopy (STM) [1, 2] and atomic force microscopy (AFM) [3–5] with special attention given to the influence of the geometric and chemical nature of the probe itself [6–8]. Earlier adhesion studies [9–11] were handicapped by the inability to analyse the geometric structure and chemical nature of the tip. This limitation was finally addressed using \textit{in situ} field ion microscopy (FIM) [12]. It was found that the typical range over which metallic exchange correlation forces act is much larger than expected from theoretical models [14, 15] and simulations [16]. In this paper we take a further step and present for the first time simultaneously acquired force and tunnelling current of a defined tip–sample junction as a function of the tip–sample separation.

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Details of the experiment and the procedures are described elsewhere [13]. In summary, we simultaneously measure the force interactions and the tunnelling current of a W(111) tip approaching a Au(111) surface under ultrahigh vacuum (UHV) conditions ($p < 2 \times 10^{-11}$ mbar) at a temperature of 150 K. The W tip, oriented in the (111) direction, was electrochemically etched and annealed in a UHV, treated with field emission and finally imaged and engineered on the atomic level using FIM.

The sample, Au(111) evaporated on mica, was cleaned using repeated cycles of sputtering with 1 keV Ne ions and annealing at 500 K. The Au sample itself was mounted on a glass cantilever beam, which acted as a force sensor. The spring constant was calibrated ex situ to be $c_{cb} = 50$ N m$^{-1}$ at the point where the W tip approached the sample.

The tungsten tip was analysed using FIM. Typical images were taken at 3.8 kV and featured an apex radius of about 2.5 nm. The initial tip shape was engineered to terminate in a trimer configuration. It was previously shown [12] that this tip configuration is stable when approaching a gold surface.

We performed three sets of 32 approach–retraction cycles at a rate of 1 nm s$^{-1}$, each set with a successively smaller tip–sample separation. In figure 1 we show the retraction part of a single force– and current–distance curve taken from the third run. For better presentation a 5–15 Hz band block filter was used to filter out external vibrations picked up during the measurement in the force channel.

All force values are negative, i.e. the forces between the tip and the sample are attractive throughout the entire distance range. Starting from small tip–sample separations the forces rapidly increase, show a maximum adhesion peak of 5 nN and then fall off to zero again. As expected for a very sharp tip [4] the long-range van der Waals forces are negligible in this regime and the curve is dominated by the metallic adhesion forces due to electron wavefunction overlap.

Experimentally, the tip excursion $\Delta z$ is the control parameter. Hence the true tip–sample separation must be calculated from the tip excursion and the cantilever beam movement. The true tip–sample separation is $\Delta s = \Delta z - (\Delta F / c_{cb})$, with $c_{cb} = 50$ N m$^{-1}$ as the spring constant of the cantilever. One should note that a zero tip–sample separation is set arbitrarily at the point of the force cross over. This is a convenient choice because at $z = 0$ we have $\Delta s = \Delta z$ (no correction.
Figure 2. Force against tip–sample separation curve for a W(111) tip, which was examined by FIM before and after the interaction experiment, facing an atomically flat Au(111) surface. The smooth curve shows no indications of a sudden jump to contact with large hysteresis. A small hysteresis develops upon indenting the Au sample (lower part). These curves are an average of 32 approach–retraction cycles. The full curve is a fit to the Rydberg function with a decay length of 0.2 nm.

due to cantilever beam deflection) and it also marks the point of maximum adhesion energy. A second-order correction to $\Delta s$ is due to the compliance of the gold. This would shift the adhesion peak in figure 1 towards smaller tip–sample distances (some 0.01 nm) and slightly change the slope of the force curve before and after the peak.

The tunnelling current was measured simultaneously (figure 1) up to values of 100 nA, corresponding to the limit of the current–voltage converter. Figure 1 thus allows, for the first time, an experimental determination of the forces present during imaging, manipulation and spectroscopy by STM. Both the force and the tunnelling current curves are essentially independent of the applied tip–sample voltage, the data in figure 1 was acquired at 100 mV. The observed exponential tunnelling decay constant of 0.05 nm translates into a reasonable workfunction of $4 \pm 1$ eV for the tungsten–gold contact. At larger tip–sample separations ($\Delta z > 0.75$ nm) the current decays more slowly with the tip–sample separation.

One of the most prominent features of this force– and current–distance curve is the absence of a sudden jump-to-contact behaviour. Previous theories and simulations [27] predicted that metallic contacts will undergo a sudden transformation, where, at a critical distance of tip and sample, the junction becomes unstable and undergoes plastic deformation. The instability is due to a large negative force gradient between the tip and the sample, as a result of sharp increases in force interaction at small changes of the tip–sample distance.

For the atomically defined W–Au contact this is clearly not the case. In a previous experiment the atomic stability of the tip was evidenced by a sequence of FIM images before and after the approach curves [12] (see figure 2). However, the signal-to-noise ratio only allowed one to
analyse the force–distance properties as an average of 32 approach cycles. This left room for speculations on the nature of the single-trace curve.

Force–distance curves for a sharp, yet not atomically characterized, W tip facing a Au surface have achieved single-trace resolution before [26]. Here, two different behaviours were present: smooth force–distance curves with no sudden force changes nor any measurable hysteresis were observed in the majority of cases, as well as sudden changes in the force with large hysteresis, indicating permanent changes of the tip–sample junction (figures 3(a) and 3(b) respectively).

The force–distance curve in figure 1 thus represents the mechanical behaviour of an atomically defined tip–sample junction with single-line-scan resolution. Again, we see no evidence of a mechanical instability, although the point of zero force, which can be identified as the point of contact of a tip and a sample, is reached during the approach. This conclusion is independently supported by observing retraction and approach cycles (not shown in figure 1) of the simultaneously measured tunnelling current. The observed absence of hysteresis and/or instabilities are an indication of an atomically stable metallic junction. We can therefore conclude that no jump-to-contact behaviour was present in our experiments.

The standard theory of metallic adhesion [14] predicts a universal behaviour for the binding energy against distance curves of metallic and bimetallic interfaces. Even for the particular geometry of a sharp tip against a flat sample it was theoretically found [17] that while the magnitude of the interaction energy is sensitive to the tip geometry and the material, there is a universal curve independent of those parameters. Using the scaling $E/E_{\text{max}} = f((d - d_m)/\lambda)$,
Figure 4. Scaled adhesion energy against the scaled distance (stars) and the Rydberg function (full curve). The adhesion energy curve was generated by integrating the force curve from figure 1 over the tip–sample separation. The scaling parameters were $E_{\text{adhesion}} = 21$ eV and $\lambda = 0.2$ nm.

with $E_{\text{max}}$ being the maximum adhesive energy, $d_m$ the distance of separation at $E_{\text{max}}$ and $\lambda$ a distance scaling parameter, all binding energy curves are predicted to follow the Rydberg function $f(x) = -(1+x) \exp(-x)$. The distance scaling length $\lambda$ is a fit parameter, related to the curvature of the adhesion curve at the point of maximum adhesion [15]. For metal–metal contacts it has been associated with the Thomas–Fermi screening length [14,15] although deviations have been observed [4] in simulations.

In order to compare our results with this model we integrated the force curve of figure 1 over the distance axis. In figure 4 we show the resulting energy against distance relationship, which is well approximated by the Rydberg function (full curve) with scaling parameters $E_{\text{max}} = 21$ eV and $\lambda = 0.2$ nm. The Thomas–Fermi screening length for the bimetallic contact W on Au predicts $\lambda_{TF} = 0.05$ nm [18], which neglects a specific surface orientation. Ness and Gautier [16] calculated a value of $\lambda \approx 0.04$ nm for a W(100) single-atom tip approaching a W(100) surface. We thus measure a scaling length four to five times larger than predicted by theory.

The tip stability and reproducibility of the experiment is a further indication for a large scaling length. With an estimate of $E_{\text{max}} = 2$ eV/atom and a typical Thomas–Fermi screening length of $\lambda_{TF} = 0.05$ nm, a trimer tip would experience a maximum positive force gradient close to $\partial f/\partial z \approx 50$ N m$^{-1}$. This would lead to a spontaneous jump to contact of our cantilever beam with a spring constant of 50 N m$^{-1}$. Experimentally, we find no indication of such an instability in our force or tunnelling curves.

As a consequence of the long distance scaling parameter of 0.2 nm not only do the three apex atoms of the W tip contribute to the total force, but also the atoms from the second, third and fourth layers. The layer separation of W in the (111) direction (which is parallel to the tip axis) is 0.0912 nm and the tip radius as analysed by FIM is $R = 2.5$ nm. The arrangement and number of the atoms per layer can be modelled from FIM images [19], where we find 3 (the trimer), 12, 31 and 48 atoms in the first, second, third and fourth layers, respectively. The relative force contribution of consecutive layers is then 20%, 30%, 30% and 15% (contributions from higher layers fall off rapidly) at the distance of maximum adhesive force. These values of course depend on the number of atoms in each layer and thus on the mesoscopic tip shape as characterized by its radius. This drastically changes the conventional picture for metallic
tip–sample interactions, where it is assumed that only the atoms of the first layer dominate. With a scaling parameter of 0.2 nm, the first three layers account for 80% of the total force, each of them contributing roughly an equal amount. As a consequence for imaging, one would expect inferior lateral resolution in AFM, as opposed to STM operation. Specifically, atomic resolution imaging in AFM should be much more difficult to achieve in the metallic adhesion regime.

The true tip–sample separation is conventionally thought of as the distance between the first atomic layer of the tip and the surface atoms of the sample. However, since the first, second and third layers contribute about an equal amount to the total force, the centre of force interaction is located at the second layer. Therefore we expect a shift of about one lattice constant between the force interaction of the whole tip as opposed to the force contribution of the first layer only. This means, for example, that the first-layer atoms (in our case the trimer) can already experience repulsive forces, whereas the measured total force interaction is still attractive. In particular, the first-layer atoms will touch the surface before the point of zero force is reached. This needs to be taken into account in realistic models of nanometre-scale mechanical contacts in the field of tribology.

Since the three apex atoms account for about 20% of the total force, we can calculate a maximum adhesion energy of 1.4 eV/atom for W on Au, which compares well to Ness and Gautier’s [16] values of 1.1–6.2 eV for a W(100) single-atom tip facing a top or a hollow W(100) sample site.

The first experiments drawing attention to the connection between adhesion forces and tunnelling were performed by Dürig et al [9]. Following a suggestion by Herring [20], Chen [21] proposed a model that links force and conductance. The model relies on the idea that the splitting of eigenstates due to the overlap of the electron wavefunctions is well described by the Bardeen integral $M$, which gives rise to the force $f = -\partial|M|/\partial z$ as well as the tunnelling conductance $G = ((2\pi)^2/R_K)\rho_{\text{tip}}\rho_{\text{sample}}|M|^2$ (with $\rho = \text{local density of states (LDOS)}$). Using the experimental fact that $G \sim \exp(-2\kappa z)$ where $\kappa = (2m_e\phi)^{1/2}/\hbar$, Chen found that for a metallic contact

$$f = -\frac{\alpha \kappa}{2\pi} \left( \frac{GR_K}{\rho_{\text{tip}}\rho_{\text{sample}}} \right)^{1/2}.$$  

Here $\alpha$ is a geometric shape factor, with $\alpha = 2/\pi$ for a paraboloidal tip, and $R_K = h/e^2$ is the von Klitzing constant.

The proportionality of $f$ and $G^{1/2}$ could not be observed in our experiments. As already mentioned, the tunnelling follows an exponential curve with a decay constant of $1/(2K) = 0.05$ nm, whereas the force shows a decay constant of $\lambda = 0.2$ nm. Therefore we observe $f \sim G^{1/4}$. Nevertheless, due to the lack of more sophisticated theories, we will proceed with an analysis of our results in the spirit of Chen’s model. As we will see later, this yields very reasonable values for $\rho_{\text{tip}}$. We hope that this will stimulate further interest in the development of theoretical models that correlate force and conductance, and hence allow a deeper understanding of the underlying mechanisms.

Figure 5 shows a graph of the square of the force $f^2$ against the tunnelling current $I_t$ from the data in figure 1. In the current regime between 20 nA and 90 nA, the graph shows a roughly linear relationship between the squared force and the tunnelling current, even though from the Rydberg fit we found that $f^4$ is proportional to $I_t$. However in figure 5 we are only looking at a small part (<1 Å) of the force–tunnelling curve, where it is not possible to discriminate between the two power laws within the noise. Below 20 nA we typically observe a much steeper
Correlation between force and tunnelling current using Chen’s model. The graph shows the square of the force against the current, where an approximately linear relationship can be observed for currents above 20 nA. The slope of the curve of $\Delta f^2 / \Delta I_t = 0.04 \text{nN}^2 \text{nA}^{-1}$ translates to a convoluted LDOS of the tip and the sample of $\rho_{\text{con}} = 0.1 \text{states/eV/atom}$.

slope, which seems to be due to a less than exponential behaviour of the tunnelling current. It is intriguing to notice that for atomic resolution imaging with STM on metals, currents of typically $I > 20 \text{nA}$ are used.

Using Chen’s model we can extract the convoluted LDOS of the tip and sample, $\rho_{\text{con}} = (\rho_{\text{tip}} \rho_{\text{sample}})^{1/2}$ from the slope in figure 5, which gives us a value of $\rho_{\text{con}} = 0.1 \text{states/eV/atom}$.

The influence of the tip shape on the force due to the observed large distance scaling parameter leads to a modification of $\rho_{\text{con}}$. Whereas 80% of the force originates from the first three layers of the tip, the tunnelling current is dominated by contributions only of the first-layer atoms (the trimer) owing to an exponential decay constant one-quarter the size of that of the force.

Let us recall that the Rydberg function implicitly describes the adhesion energy of a slab and a sample surface [6]. A slab is defined as a cylindrical volume terminated by an area. If fringing effects are neglected, a real tip can be modelled by a number of slabs at different tip–slab separations. One then only needs to explicitly consider the partial surface areas of each slab in order to define a particular tip geometry [6]. We will use the unit ‘atom’ to define the slab area in the following. For the force we have a slab with an area corresponding to three atoms in the first layer; but there are only three atoms contributing to the tunnelling current. A detailed analysis of Chen’s model shows that the measured DOS of the tip and sample has in fact to be multiplied by the ratio of the number of atoms contributing to the force against the number of atoms involved in the tunnelling process. We thus calculate an effective DOS of the tip and sample of

$$\rho = \rho_{\text{con,measured}} \frac{\text{No. force atoms}}{\text{No. tunnelling atoms}} = 0.5 \text{states/eV/atom}.$$ 

How does this measured DOS compare to theoretical expectations? For a first comparison we use a simple model following an idea of Friedel [22]. The total d-band of W has a width of...
We neglect the contribution of the s-electrons which play a minor role for the DOS of transition metals in general. On the other hand, Au has one s-like electron in a 4 eV wide band, therefore \( \rho_{\text{sample}} = 0.25 \text{ states/eV/atom} \). This gives us a value of \( \rho_{\text{con}} = 0.5 \text{ states/eV/atom} \), which is in surprisingly good agreement with the above experimental value.

Clearly, we used a very simplified model for the band structures in the above discussion. Ness and Gautier [16] calculated the DOS of W(100) and W(111) tips. Transition metals with a bcc structure exhibit a dip in the DOS at a d-band filling of five electrons, which is the case for Cr, Mo and W. The LDOS of surface atoms usually exhibits a peak at the Fermi energy, which, however, is less pronounced for densely packed surface orientations such as W(111) (as opposed to W(100), which has a strong surface peak). Furthermore, Ness and Gautier showed that the interaction of a W(100) tip with a W(100) sample splits the surface peak into bonding and antibonding states, the resulting minimum between these peaks leading to a significantly reduced LDOS at the Fermi energy.

Chen’s model correlates the force to the DOS only at the Fermi energy, which seems too crude a simplification considering that the total energy is the integral over all the states of the DOS. One might argue though that the force is proportional to the changes in the energy (with respect to tip–sample distance) and these changes are most prominent when peaks in the DOS move across the Fermi energy. This can be caused by wavefunction overlap, resulting in the formation of bonding and antibonding states, which split farther apart with decreasing tip–sample separation. Therefore the changes of the DOS at the Fermi energy can dominate the forces, and explain why we see such reasonable agreement of the density of states calculation with our experiment. It does, however, not explain the surprisingly large force decay constant \( \lambda \).

The major theoretical challenge is therefore to find out why we observe such a long distance scaling length \( \lambda \). The total electron density in a very confined volume, like a nanotip, might be much reduced in comparison to the bulk electron density. Since the Thomas–Fermi screening length is related to the electron density, via \( \lambda_{TF} = \frac{1}{\sqrt{3}} \left[ \frac{243\pi}{64} \right]^{1/6} n^{-1/6} \) [14], this could serve as an explanation for the altered distance scaling length \( \lambda \). In order to account for a fourfold increase in \( \lambda \), however, the electron density would have to be reduced by a factor of 4000. This would mean that the tip–sample separation under our tunnelling conditions is smaller than anticipated. We should then observe the point of contact (i.e. onset of strong repulsive forces) at a distance of 0.4 nm closer to the tunnelling point than expected.

A very promising concept in this respect was introduced by Burnham et al [24]. Since the workfunction of the tip varies with the different crystallographic poles an effective surface charge builds up. This so-called patch charge model (from the patches of charge building up on a polycrystalline surface) originates from the redistribution of surface charge, the total charge remaining zero.

In the spirit of this model we calculate, for very sharp tips, that in order to produce electrostatic forces in the nanonewton regime a surface charge of several electron charges must be present. The workfunction difference on W between the (111) and the (211) facets, for example, is around 0.3 eV [25]. Using the simple model from [24] we calculate that for our tips the patch charge amounts to a total of around \( 10^{18} \) C, which is too small to explain the observed forces. However, a more detailed study of the influence of the tip radius and crystalline structure on the force–distance curves in correlation with theoretical patch-charge calculation would answer whether this model could still pose a suitable explanation for the observed long distance scaling length \( \lambda \).
In conclusion, we have measured for the first time simultaneously the force interaction and tunnelling conductivity for a defined W(111) tip on a Au(111) surface. The tunnelling current shows the expected exponential behaviour with a decay constant of 0.05 nm. We can fit the adhesion energy against distance curve to the Rydberg function using an unpredicted large distance scaling parameter of 0.2 nm. We show that neck formation resulting from a jump to contact cannot explain this observation. This has several consequences which will impact the conventional ideas on AFM contrast mechanisms, contact mechanics and tribology. Most strikingly we find that 80% of the force originates from the first three layers, each contributing an equal amount. Therefore the simple model that the force is dominated by the first-layer properties only is not generally valid. Second, we point out that there is a shift between the position of the first layer of the tip and the centre of force interaction of the whole tip. Third, using Chen’s model to establish a quantitative relation between force and tunnelling current, we extract reasonable values for the DOS of the tip and the sample despite the complexity of the electronic structure and geometric shape of our W–Au system. A satisfying explanation for the observed long distance scaling length $\lambda$ cannot be given, however; the connection to a promising model, which takes into account the patch charge forces, is pointed out.

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