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Force interactions and adhesion of gold contacts using a combined atomic force microscope and transmission electron microscope

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Abstract

We have investigated force interactions between two gold samples using a combination of atomic force microscope (AFM) and a transmission electron microscope (TEM) (TEM–AFM). The size and shape of the tip and sample as well as size of contact area and interactions type (elastic–plastic) is observed directly. The force was measured by direct measurement of the displacement of the AFM tip.

An anomalous high value of the jump-to-contact distance was found, which we interpret as due to an enhanced surface diffusion of gold atoms towards the tip–sample gap due to the van der Waals force, leading to an avalanche situation where the gap is quickly filled until the ordinary jump-to-contact distance.

The contact radius at zero applied load were measured and compared with adhesion theories. The results were in the Maugis transition region, between the limiting cases of the Derjaguin–Müller–Toporov (DMT) and the Johnson–Kendall–Roberts (JKR) models.

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Keywords: TEM–STM; TEM–AFM; Jump-in-contact; Adhesion

1. Introduction

Force interactions and adhesion between nanoparticles has been studied for a long time. One technique is transmission electron microscopy (TEM), where direct visualization of the interacting particles gives an understanding of the interaction (see for example [1]). However, direct measurements of nN forces are not easily employed, except for some special cases [2,3].

Another method is the atomic force microscope (AFM), where a small tip is placed on a cantilever spring, which is used to measure the interaction forces [4,5]. However, in the AFM the shape of the tip and sample is unknown.

Here, we use a combination of the two techniques called TEM–AFM [6,7]. This is a modification of the TEM–STM technique [3,8–11] which is a scanning

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tunneling microscope (STM), placed inside a TEM. We replace the STM tip with an AFM cantilever.

With this set-up the contact between the AFM cantilever tip and the sample can be imaged, the size and the shape of the tip can be measured and, which is important, at the same time as the experiment is performed. In addition, deformation (elastic–plastic) of the contact region can be studied and changes followed by TEM imaging.

Here, we used a gold sample and a gold coated AFM tip, and are reporting on results from the full cycle of approach and retraction. Firstly, the jump-in-contact was studied and compared with simple calculations of the corresponding van der Waals force. Secondly, at zero applied force we compared the contact radius with adhesion theories. Lastly, during the retraction, a thin nanowire was created and broken.

2. Experimental

The TEM–AFM consists, in short, of a modified TEM–STM [11] with a piezo tube (25 mm long and 3 mm diameter) which was used for fine motion and of a geared stepping motor for coarse z-motion. Detailed description of constructions can be found in [7] The TEM–AFM was inserted into a field emission gun TEM (Philips CM200 Super TWIN FEG microscope) with attached video camera. The vacuum inside the TEM was 10^{-3} Pa (10^{-5} mbar). The electron irradiation density during the observation was 2.8×10 A/m^2.

The samples were electrochemically etched gold tips, made from a 0.25 mm 99.99% pure gold wire. The gold tips were cleaned by argon milling before TEM operation. The AFM cantilever tips were of standard silicon nitride contact mode type. The AFM tip and cantilever were coated with 5 nm Cr adhesive layer and 15 nm of Au. The force constant of the cantilever was measured to 0.4 N/m, by using calibrated cantilevers [12]. For conductance measurements the current signal was monitored on a digital oscilloscope simultaneously with video TEM images. Inside the TEM, by several times pressing the AFM cantilever tip hard into the sample and retracting, clean surfaces created.

The standard technique of force detection in AFM is a thin cantilever spring with an integrated tip, and an optical system, which is used to detect the cantilever deflection. However, in an out case, the motion of the tip was simply imaged directly in the TEM images. With a known force constant of the cantilever, the force was calculated. One might note that the tips have some stiffness and the cantilever motion and tip motion might not be the same, but the small force constant of the cantilever used here minimizes this effect.

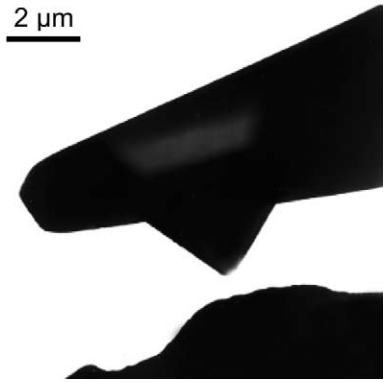

Fig. 1. TEM image overview of the sample gold tip and the gold coated AFM tip.

In Fig. 1, a low magnification TEM image is presented, which shows the AFM tip on the cantilever and an electrochemically etched Au tip. The force versus separation measurements were performed by moving the gold tip close to the AFM cantilever tip using manual control of the voltages applied to the piezo tube.

3. Jump-in-contact

Fig. 2 shows a typical sequence of TEM images where the sample is moved towards and away from the AFM tip. The corresponding force curve is found in Fig. 3. In Fig. 2 the AFM tip has a radius of 30 nm and the sample surface has a protrusion with a radius of 7.6 nm. Fig. 4a shows another tip with a conical shape approaching the AFM tip. When the gradient of the attractive tip–sample force exceeds the spring constant k of the cantilever, the sudden jump-to-contact occurs. A simple expression of this event, using a model with van der Waals forces between two spheres is [13]

$$k < \frac{\mathrm{d}F}{\mathrm{d}s} = \frac{AR}{3s^2}, \tag{1}$$

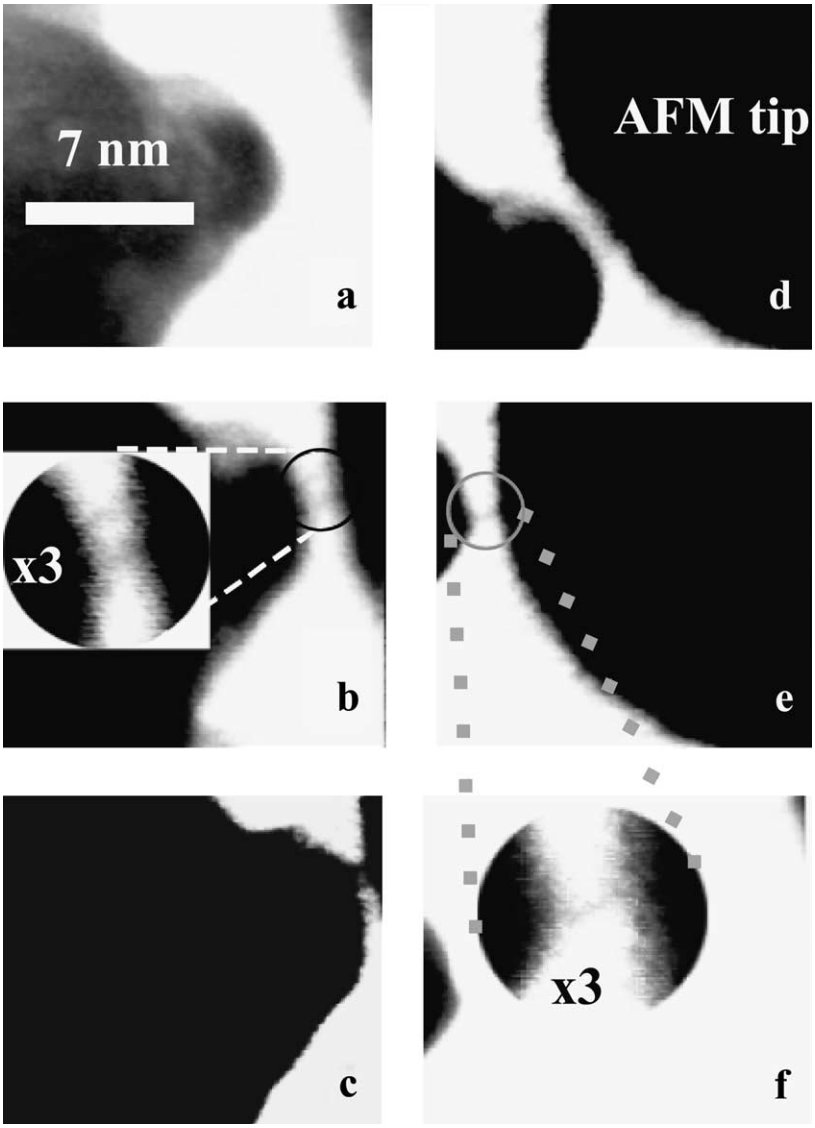

Fig. 2. A set of TEM images of a gold tip and a gold coated AFM tip. (a) No contact. (b) Jump-to-contact. (Inset: neck ormed in the gap in connection with the jump-in-contact event). (c) Moving further in. (d) Withdrawal of the sample. (e) By lateral motion of the sample a small nanowire is formed between the sample and tip. Just before breaking, the diameter of the wire is about 1 nm, which corresponds to about 10 atoms. (f) Jump-off-contact. (Inset: nanowire area magnified three times).

where A is the Hamaker constant, s is the distance between the spheres, and R is the reduced radius of the spheres R_1 and R_2: $R = ((R_1 + R_2)/R_1R_2)^{-1}$.

We observed jump-to-contact distances of 3.2 nm (Fig. 2b) and 3.3 nm (Fig. 4). Theoretically, using Eq. (1) and $A = 4 \times 10^{-19}$ J [13], the corresponding distances will be 1.2 and 0.9 nm (with a radius of 2 nm for the tip in Fig. 4). This corresponds to a force constant of the AFM cantilever that is 20–50 times lower than 0.4 N/m. It is difficult to explain this discrepancy. It could not be contributions of van der Waals forces from the larger tips in the background. For example, if the smallest tip is removed and we use Eq. (1) again, now with the AFM tip as the

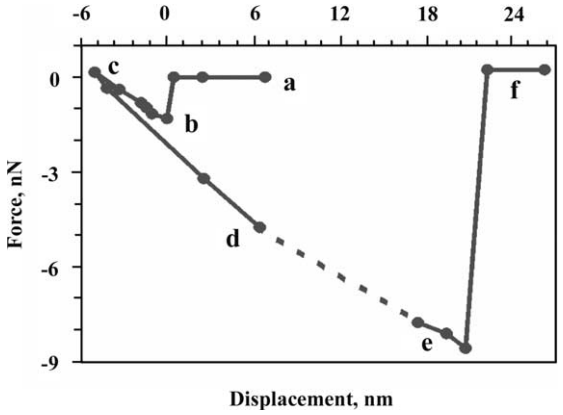

Fig. 3. Experimental force–distance curve where the labels a–f corresponds to the TEM images in Fig. 2 (a–f).

smallest tip, we will get an additional force gradient contribution of only 60%. The electrostatic force, due to the small voltage of 10 mV that we applied to the tip in order to check for contacts outside of the imaging frame, will give a very small contribution.

However, due to the very high mobility of the gold atoms at room temperature, the above static view might not be relevant. A single extra atom on top of one of the tips will reduce the gap by about 10%. The attractive interaction force tends to concentrate the diffusing atoms towards the area near the tip apex and shortening the gap further. This highly unstable situation would lead to an avalanche situation, where a protrusion rapidly builds up in the gap, until the usual jump-to-contact event occurs. This avalanche should be too fast to be directly observed on the 25 images per second as was available. We might just note that the hopping frequency is about 40 GHz for a diffusing gold atom on a gold surface at room temperature [14]. However, some proof of the avalanche can be seen in the inset in image 2b, where an extra protrusion is visible in the gap. This extra neck must have been created between two consecutive TEM images. Our experiment is similar to earlier STM studies on the electric field induced changes of gold surfaces [15–17], but instead of an electric field gradient, as in these cases, we have a force gradient due to the attractive van der Waals force. In fact, we can use similar arguments as for the model developed by Mayer et al. [16,18], just replacing the electric field with the van der Waals force. However, no such model is developed today.

4. Adhesion

By continuing the forward motion, the sample pressed the AFM tip back to its original rest position (Fig. 2c). The contact radius at zero applied force was 2.2 nm for the contact in Fig. 2c and around 1 nm for the contact in Fig. 4b. At zero load, the cantilever spring constant is not necessary to know, and uncertainties in the force constant is not important.

There are two well-known adhesion theories that describe two limiting cases. The Johnson–Kendall–Roberts (JKR) [19] theory is suitable for soft materials with strong adhesion forces and large tip radii.

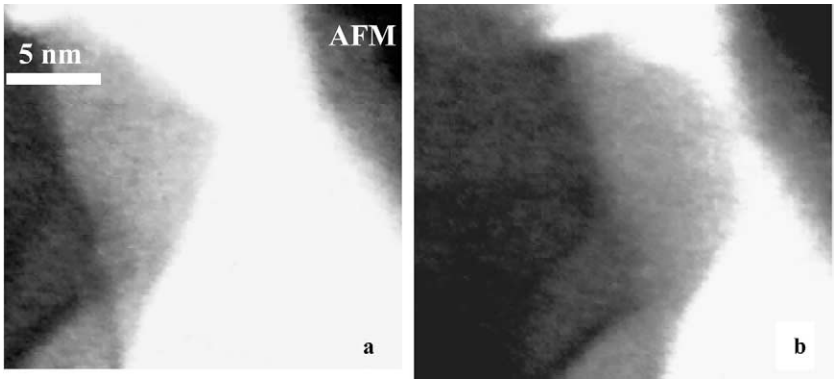

Fig. 4. TEM images of a different sample–AFM tip. (a) before contact, and (b) at zero applied load.

The Derjaguin–Müller–Toporov (DMT) theory [20] is covering the opposite limit, with stiff material, weak forces, and small tip radii. These theories are for elastic contacts, but we can still use them for cases with limited plastic deformation, as in the present case.

These limiting cases, and the transition between them, can be described by a dimensionless transition parameters called Tabor parameter μ [21] and Maugis parameter λ [22]. Both the parameters are related and for contact between identical materials can be expressed as

$$\lambda = 1.157\mu = \left(\frac{64R\gamma^2}{9K^2z_0^3}\right)^{1/3} \quad (2)$$

where z_0 is a typical atomic dimension, γ is surface energy and the reduced Young modulus K is given by $K = 4/3((1-\nu_1^2)/E_1 + (1-\nu_2^2)/E_2)^{-1}$, where ν_1 and ν_2 are Poissons ratio and E_1 and E_2 are Young modulus for two contacting spheres.

The DMT theory is valid when $\mu < 0.1$ and the JKR theory is valid when $\mu > 5$. Maugis [22] provides a more general theory suitable for the full range, with λ as a transition parameter. A dimensionless contact radius at zero applied load, $\breve{\alpha}_0$ is described by

$$\breve{\alpha}_0(\lambda) = \alpha_0\left(\frac{K}{2\pi\gamma R^2}\right)^{1/3}, \quad (3)$$

where α_0 is the real one. Maugis solution is analytical, but here we used a simplified fitting version given by Carpick et al. [23]

$$\breve{\alpha}_0(\lambda) = 1.54 + 0.279\left(\frac{2.28\lambda^{1.3}-1}{2.28\lambda^{1.3}+1}\right). \quad (4)$$

To calculate λ (and μ), the following values for gold were used: $\gamma = 1.37$ J/m^2 [24], $E = 117$ GPa, $\nu = 0.42$ [25], $z_0 = 0.28$ nm. These values are depending on the lattice orientation and the reported values in the literature do have a spread of up to 50%, which could change the picture quite a bit. The theoretical and experimental values of the contact radius at zero applied load are shown in Fig. 5. Our experimental results were in the transition region between the DMT and JKR models.

So far, very few experimental verification on the Maugis theory is reported, we found the one by Lantz et al. [26]. This TEM–AFM method, if extended to include also the critical load, could mean that this question could be addressed experimentally in an adequate way. In this way, one could measure γ independently, and arrive with a safer λ.

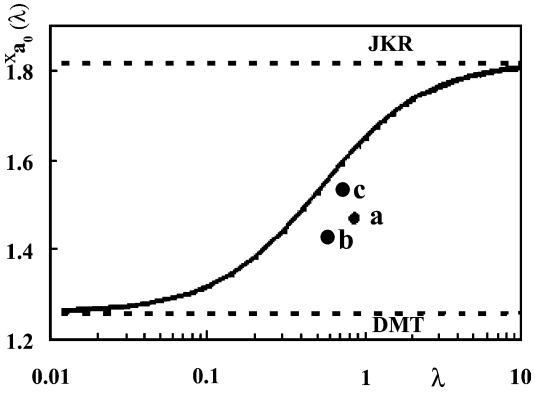

Fig. 5. Dimensionless contact radius at zero applied load for three contacts (a) corresponds to the contact in Fig. 2, (b) to the one in Fig. 4, and (c) is not shown. The solid line is the Maugis theory (Eq. (4)) and the JKR and DMT limits are shown with dotted lines.

5. Jump-off-contact

To break the contact in Fig. 2c, a force of 100 nN is required. With a weak cantilever of 0.4 N/m, as in our case, a retraction of 250 nm was required, which was more than five times larger than the frame size used. To reduce the contact radius we applied instead a shear force by a lateral motion of the sample during the withdrawal, because the lateral force constant of the AFM cantilever is much higher (Fig. 2d, e). During this process, a nanowire with a diameter of less than 1 nm was created (Fig. 2e and inset). The nanowire broke at a retraction of 22 nm (Fig. 2e, f) which corresponds to an attractive force of about 9 nN. The length of the created nanowire was approximately 2 nm (Fig. 2e and inset). The area of the neck just before rupture was 0.6 nm^2, which is about 8–10 atoms (area per atom 0.08 nm^2). This gives a yield strength of 14 GPa. If we subtract surface forces of 9 GPa in the same way as Stalder and Dürig [27], we obtain an intrinsic yield strength of 5 GPa, which is consistent with values calculated by Landman et al. [28] (3 GPa), and with experiments by Stalder and Dürig [27] (5–8 GPa) and Agrait et al.

[25] (2–6 GPa). This gives a cohesion force of about 1 nN per atom, in agreement with gold nanowire force experiments (1.6 nN for the last atom) [29] as well as by theoretical calculations (from 1 to 2.2 nN) [30].

6. Conclusions

We have investigated force interactions between two gold samples TEM–AFM, which is a combination of an atomic force microscope and a transmission electron microscope. The size and shape of the tip and sample as well as size of contact area and interactions type (elastic–plastic) were observed directly. The force was measured by direct measurement of displacement of AFM tip.

An anomalous high value of the jump-to-contact distance was found, which we interpreted as due to a van der Waals force enhanced diffusion of gold atoms into the tip–sample gap.

In contact, the adhesion results were between the limiting of JKR and DMT, and fitted reasonably well to the Maugis theory.

This study also indicates that the TEM–AFM technique would be a promising tool for investigation of adhesion, friction, or to understand tip–sample interactions in the STM and AFM.

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