Introductory guide to measuring the mechanical properties of nano-objects/particles with AFM on flat surfaces

Jeremias Seppä
MIKES Metrology, VTT Technical Research Centre of Finland Ltd
P.O. Box 1000, FI-02044 VTT, Finland

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AFM Cantilever calibration

At the core of mechanical, force-related, measurements with AFM is measuring the stiffness of the AFM probe cantilever, or measuring directly the forces corresponding to e.g. measured cantilever bending. This information can then be used to measure the probing force during mechanical testing of nanoparticles with AFM probes, in a similar way as with an indentation tester.

Typically, an AFM measures the deflection of the probe cantilever by measuring the light of a laser diode reflected from the cantilever upper surface by a position sensitive photodetector (PSPD).
ISO 11775 [1] gives a good overview about the available methods to calibrate cantilever normal stiffness. Most often the cantilever stiffness is measured using

- the thermal vibration of the cantilever [2]
- the Sader method based on the dimensions of the cantilever [3]
- with balances/force sensors of known stiffness (see German DIN 32567 [4]), or
- measuring against calibrated reference cantilevers [5].

These methods have been tested in the MechProNO project, and analysed in related reports. The thermal vibration method is suitable for cantilever stiffnesses approximately in the 0.2..4 N/m range. The Sader method is sensitive to the unknown roughness of e.g. the cantilever underside making its use problematic. Measurement against scales is not very easy to do accurately. The cantilever-on-cantilever seems relatively easy/widely applicable. And the thermal method is possibly a quite easy option for suitable cantilevers if implemented in the AFM software. Building own thermal method requires some carefulness on e.g. the calibration of the PSPD and the analysis of the measured noise spectra.

In the cantilever stiffness, and PSPD calibration in e.g. the thermal method, the angle of the cantilever in the AFM head is one complication that needs to be accounted for, since usually

the cantilever is tilted 10-15 degrees. A further consideration is the possible sliding or non-sliding of the probe tip if the tip approaches the sample vertically but the bending cantilever is at an angle. However usually treating the cantilever just as a spring without considering the effects due to the tilted angle results in differences of only a few per cent [6].

Pushing the cantilever on a force sensor provides the possibility of relating directly the PSPD output signal to force values without knowing cantilever stiffness or angle.

Mechanical properties like stiffness of the flat substrate affect the measurement, but this tends to be a minor factor in the measured mechanical response of particles with a sharp tip, unless the substrate is soft compared to the nanoparticle.

To obtain accurate results, it is naturally important to have high-quality, calibrated position or displacement sensors for the measurement of the vertical movement of the AFM probe/head relative to the sample. Laser interferometry of sample position with vertically moving sample has direct traceability, but suffers from periodic nonlinearity, higher cost and noise, and slower movement - compared to strain gauge or piezo voltage based measurement of AFM tip movement in systems with vertically moving AFM probe holder. If strain gauge or piezo voltage are used with predefined parameter/setting ranges with which a traceable calibration of the vertical position sensing has been done, they can provide better resolution and even accuracy for small vertical displacements in the (sub)nanometre range.

F-d curves and cantilever bending

Main tool in mechanical testing is the force-distance or force-displacement (f-d) curve. Figure 1 shows the vertical movement of a sample relative to the AFM head, and the corresponding forces for loading (red) and unloading (blue) on an appr. 20 nm - 30 nm diameter palladium nanoparticle.
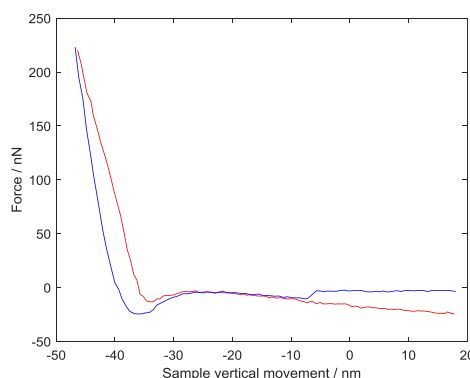

Figure 1. Loading (red) and unloading (blue) curve indenting a Pd particle by an AFM tip. Sample movement relative to AFM frame/head. The difference in the right side between the horizontal parts of loading and unloading curve is an anomaly in this measurement.

Fig. 2 shows for comparison a similar curve for pushing against the hard silicon substrate. Measuring the slope of the photodetector signal when pushing the tip against a hard material (or the asymptotic slope when pushing a softer material with increasing contact area), gives the conversion of photodetector signal units to bending distance of the cantilever, and thus with known cantilever stiffness, also the force scale.
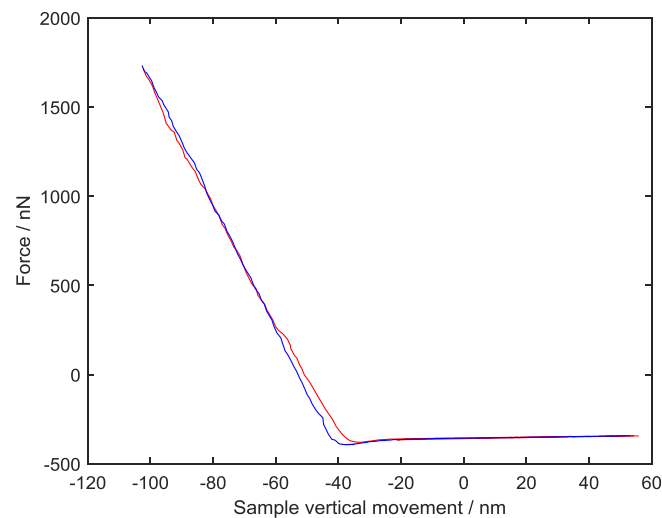

Figure 2. Force-deflection curve for pushing the AFM tip to the silicon substrate (quite hard pushing, possibly some tip fracture). Vertical scale is in force units, i.e. cantilever stiffness multiplied by measured bending distance. Bending distance can be obtained by relating the PSPD voltage readings to the sample movement during contact to a hard sample.

However, when assessing the mechanical properties of materials, like nanoparticles, a more interesting curve is the plot of the movement of the *tip of the AFM probe relative to the sample* against applied contact force. This can be done by subtracting the cantilever bending corresponding the PSPD values from the displacement values. When measuring very stiff or hard samples, one can also estimate and subtract the compression of the (usually silicon) AFM probe tip.

The movement of the AFM probe tip can be calculated e.g. for Fig. 1 using the slope of Fig. 2 and subtracting for each position value the cantilever bending. The result is shown in figure 3.

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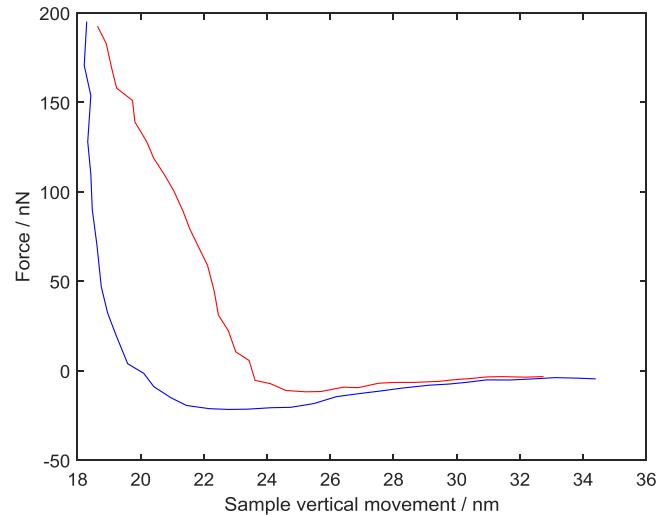
Figure 3. AFM palladium nanoparticle indentation curve showing force versus indentation depth with arbitrary zero offset (red: loading, blue: unloading)

The calibration of photodetector values corresponding to bending in length units has to be done for each AFM probe separately because of e.g. different cantilever length and reflectance. Cantilevers with metal coated top side provide more stable and higher reflected intensity because of higher surface reflectance.

In figure 3, it can be observed that the particle is mostly plastically deformed during loading and the unloading curve is, in this scale, almost vertical. This might also be expected since the metal particle was compressed over 10 %. In case of purely elastic deformation the loading and unloading curves overlap, excluding e.g. probe snap-in and snap-out due to adhesion forces when contacting and detaching from the particle.

Commercial AFMs can have very high resolution position sensors facilitating the calculation of curves, but due to the focus on accuracy and traceability in metrology AFMs, metrology AFMs often have heavy sample stages and laser interferometric position measurement that may have more noise and small periodic nonlinearities that complicate the analysis of the f-d curves of nanoscale indentation experiments.

Hitting the particles and keeping them in place

On flat substrates, nanoparticles that are only weakly bound to the substrate, may sometimes "escape" the AFM probe so that the probe partially slips on the surface of the particle, or the particle slips away from under the probe to another location.
The palladium particles in the examples were somewhat attached/bonded to the flat (within 1-3 nm) silicon surface due to the manufacturing process. Often it was possible to see with

AFM imaging before and after f-d measurement that the particle, or part of it, was still there after testing. Also, total sudden particle escape, or tip fracture, would be seen in the f-d curve as a backward kink/jump during the loading phase.

An example of particle "escaping" partly the indentation test is shown in figure 4.
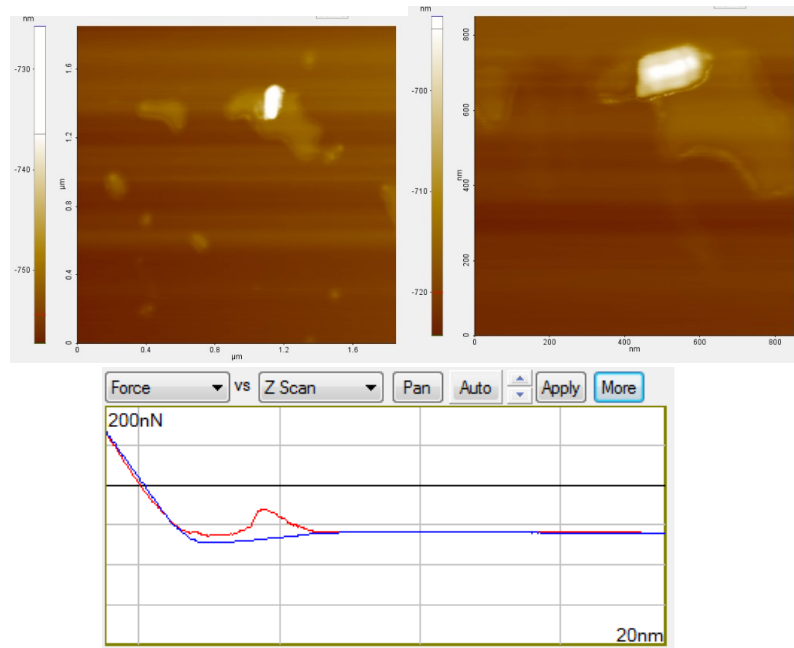

Figure 4. A gold nanorod before and after f-d measurement (upper images) and the measured f-d curve (lower image). The upper images have different magnification and the sides/shape of the AFM tip make the rod appear artificially wider in the Y direction especially in the image after indentation (right). The AFM tip has probably displaced and rotated the gold nanorod by hitting it to its side. The gold nanorod was deposited on the mica surface from applied liquid nanorod suspension. In the f-d graph the cantilever bending is not subtracted. The force rises until the nanorod starts to slip away and finally the tip meets the substrate and force starts to rise accordingly.

Attaching particles to substrates by coating the sample and then removing most of the coating has been tested by the National Physical Laboratory (NPL) in the MechProNO project.
Another method to better hold particles in place during indentation is to use not-entirely-flat substrates with grooves or pits.

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EMRP Project NEW05 MechProNO Traceable measurement of mechanical properties of nano-objects

Another challenge in measuring nanoparticles is their small size. A 10 nm diameter particle may easily, because of e.g. thermal drifts in the system, drift away from the apparent place where it was imaged, before the indentation with the AFM tip is done.

The indentation on the palladium particles was done with a slow laser-interferometrically traceable metrology AFM so that the XY scanning of the custom-built AFM with commercial AFM controller running the Z piezo was stopped, i.e. XY scanning was paused right over the particle, and then the f-d curve measurement mode of the Z controlling system was used to make the f-d measurement. This was useful for minimizing drift, scanning hysteresis and similar effects that can result if the whole AFM image is taken first and then locations selected from the image are used after imaging for f-d measurement.

One indentation can last from a few seconds to a e.g. minute depending on instrument parameters and settings and measuring one AFM image from less than a minute to several hours. If the instrument with sample has been in a thermally stable environment, powered on already for e.g. a few hours, the drift can be in the order of just 1 nm/minute, but with changing temperatures it can be several orders of magnitude higher.

Light-weight stages with small scan range can have very small stage noise, but often e.g. metrology AFMs can have several nanometres of stage noise. These factors can result in movement of the tip on the particle during indentation, or missing the particle altogether.

Contact area, f-d curve and mechanical stiffness

Estimating the apex radius/form of the AFM probe in addition to the f-d curve measurement enables one to estimate stiffness properties of the nano-object, and to compare to e.g. atomistic simulations or bulk material values in larger scale. Apex estimation can be based on e.g. electron microscopy or indentation experiments on reference materials, or ensuring the tip has a flat bottom in the scale of the objects measured.

The f-d curve in itself, possibly with information of tip size and shape, can tell about the stiffness of the object in a rather direct way. However, to get to the classical continuum mechanical properties of the particles and their material, e.g. the Oliver and Pharr model [7] for relating contact area and probe stiffness to elastic moduli and Poisson ratios of tip and sample, or the classical models for contact like Hertz model [8] can be tried. This has several obstacles, since the continuum models naturally do not work perfectly near the scale of single atoms - and with the tiny apex of the AFM tip, with reasonable indentation depths the slope of the upper part of the unloading curve, that can be used to analyse elastic modulus and behaviour, happens during so small a displacement that position measurement noise can prevent estimating the slope with any accuracy at all.

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Nevertheless, with suitable bulk reference material, vertical position sensor, indentation depth and tip radius, and cantilever stiffness, the Oliver and Pharr model might be usable for estimating the contact area of AFM tips for use with nano-object indentation.
Measuring e.g. bending stiffness of nanowires/beams with AFM probe is a measurement that suffers less from these known complications, since contact area does not play such an important role there.

It is to be noted, that in the nanoscale, the adhesion forces between tip and sample, due to e.g. Van der Waals and ambient humidity can be in the same order of magnitude as the indentation forces, possibly complicating the analysis.

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