Comparison to atom-resolution experiments

- Now we know how to simulate atom systems with a million atoms or so. However, if we can not compare what we do to experiments, all this is nothing more than playing 3D billiards with supercomputers.

- We have already indicated before during this course how atomistic simulation data can be compared to macroscopic quantities such as temperature, pressure, elastic constants, phonon spectra etc. All of these quantities are essentially averages over the properties of a large number of atoms.

  But nowadays several methods exist by which one can 'see' individual atoms. We have not described how comparison to these methods are possible. It would seem like doing a comparison is trivial, but in fact it turns out it in many cases is not! Knowing where the caveats lie, is very important to avoid doing really embarrassing mistakes.

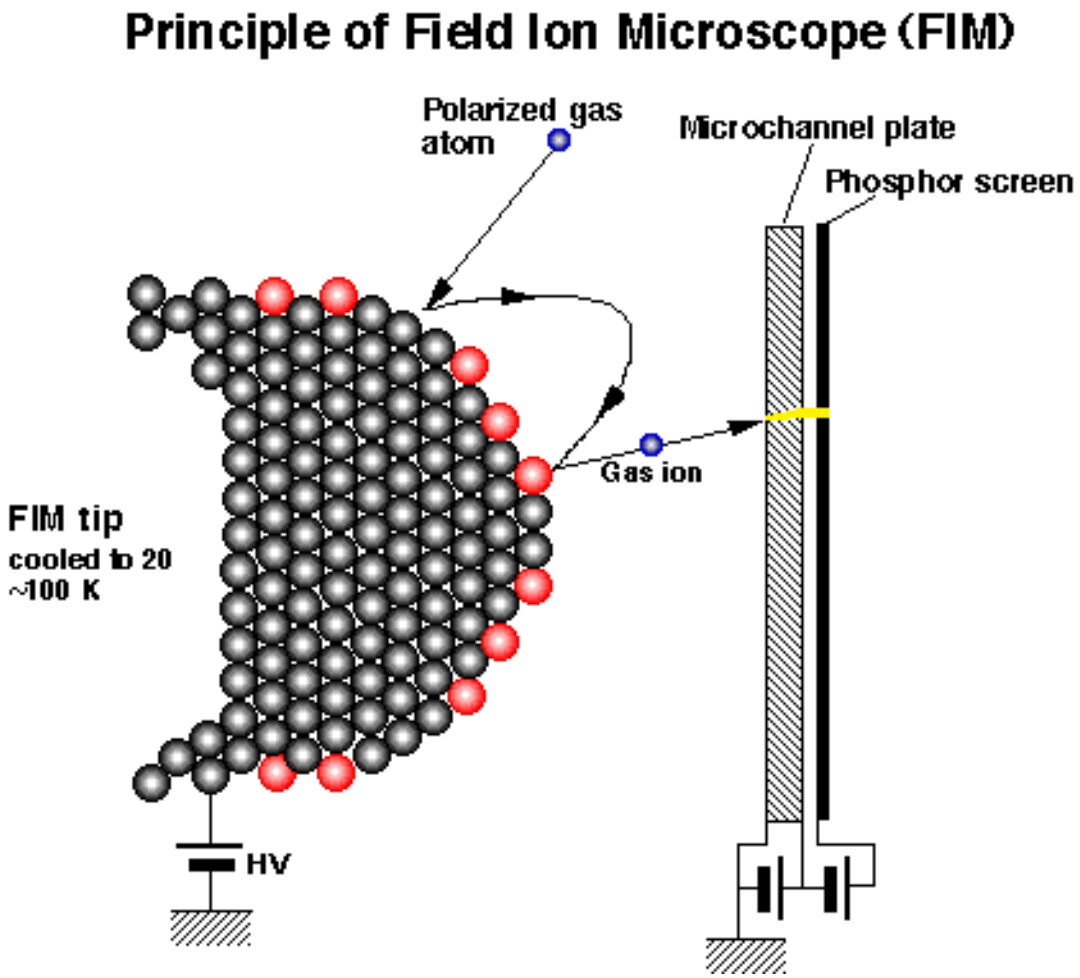
- Hence we will here describe the most import methods for seeing single atoms, and explain where the caveats lie.

FIM - Field Ion Microscope

- The oldest method by which the positions of individual atoms can be determined is the Field Ion Microscope, which was developed by Erin Müller in 1951 [http://inaba.nrim.go.jp/apfim/tutorial.html].

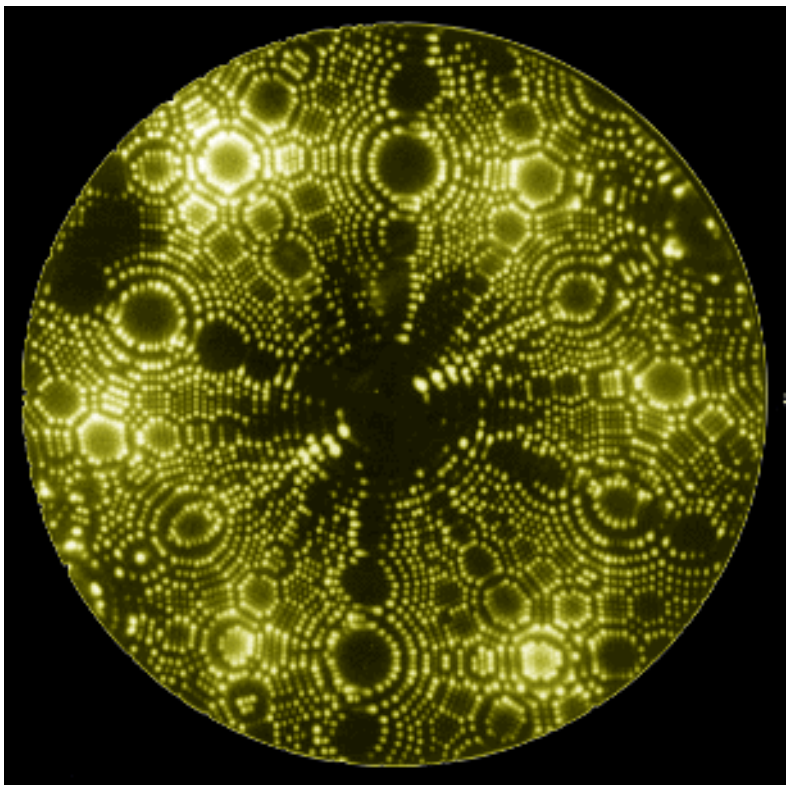
- The application areas of FIM are roughly speaking limited to metals, so it has in popularity now been superseded by AFM/STM-techniques. But still the FIM is unbeatable in some respects - it is the only method in existence which can actually give a 3D map of individual atom positions *inside* a material.

- In FIM the sample is a sharp needle, cooled to 20 - 100 K and placed in an ultra-high vacuum (UHV) chamber. The sample is charged to a high positive voltage, typically of the order of 5 kV, and a little bit of noble gas ions are let into the chamber. These atoms are polarized close to the needle, and collide with it. Sooner or later they may ionize, i.e. loose an electron to the positive specimen. Since the atom is now positive, it will be strongly repelled from the positive needle, and be accelerated radially outwards from the tip.



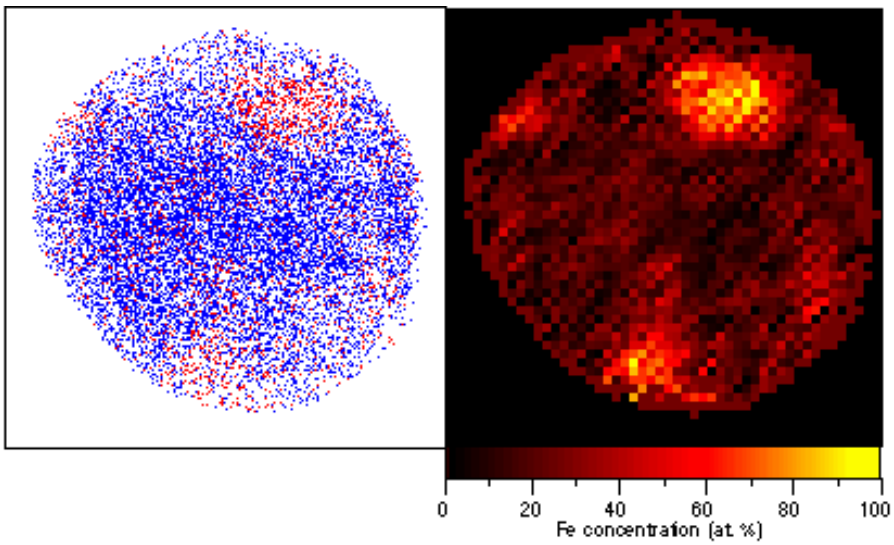
It will eventually hit a microchannel plate, from which about 100 electrons will be emitted and hit a phosphorizing screen where an image forms. Since the ion is always accelerated in the same direction, the position where it hits the screen will depend on where it lost the electron. Since losing an electron is more probably at an atom site, this process will eventually give an atom-level image of the specimen!

- A typical FIM image looks like the following. Every point corresponds to an atom position; this here is a W tip.



- If the voltage on the tip is in addition also pulsed (pulsed field evaporation), atoms from the tip itself can be emitted. And by still adding a time-of-flight equipment, it is even possible to measure the type of each atom. This gives a so called 3D atom probe.

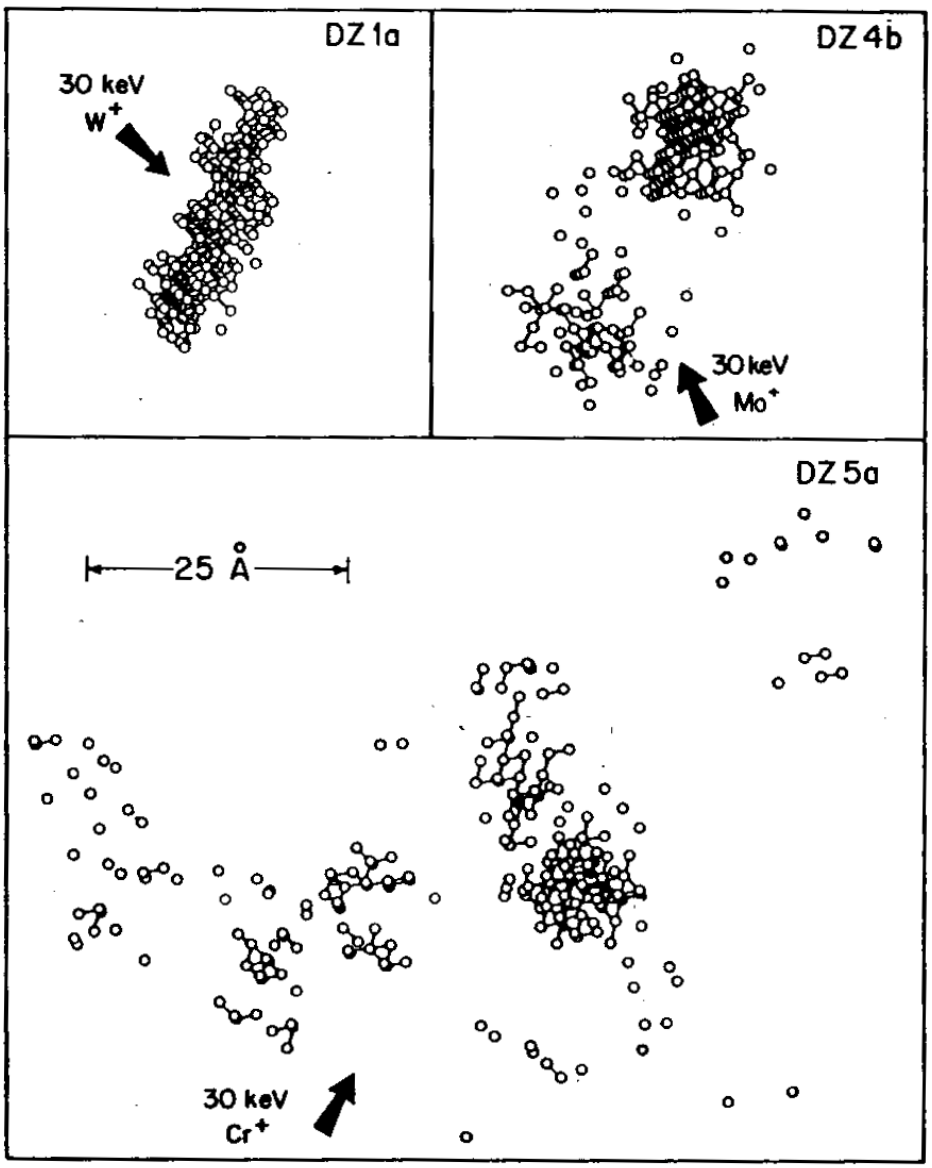
- Example: a Cr-Fe metal alloy. The red dots are Fe atoms and the blue ones Cr atoms:



- In this case, if the measurement was carried out correctly, comparison of simulated data to experiments is of course trivial. In fact, one could ask why are simulations needed any more? But they may still be very useful e.g. in explaining how the experimental atom configuration is reached.

- **Example:** Simulation of ion bombardment of W. Seidman, Current & co used FIM for most of the 1970's to study the damage which ion bombardment causes in W [e.g. Current, Wei, Seidman, Phil. Mag. A **47** (1983) 407]. The result was 3-dimensional maps of the positions of **every** interstitial and vacancy atom inside the sample. The figure below shows vacancy positions in individual events:

Fig. 6



- One of the conclusions was that there are at least 10 times more vacancies than interstitials in the samples. This was a big mystery, since by the basic theory of ion irradiation there should be equal numbers of vacancies and interstitials formed. Moreover, most other experiments gave 3-5 times smaller numbers of defects per deposited energy than the FIM experiments, and these nunbers were generally accepted.

- Still, the other experiments did not see individual defects. Thus for some 20 years there existed the paradoxical situation that the best experiments ever carried out in the field were in contradiction to the general consensus!

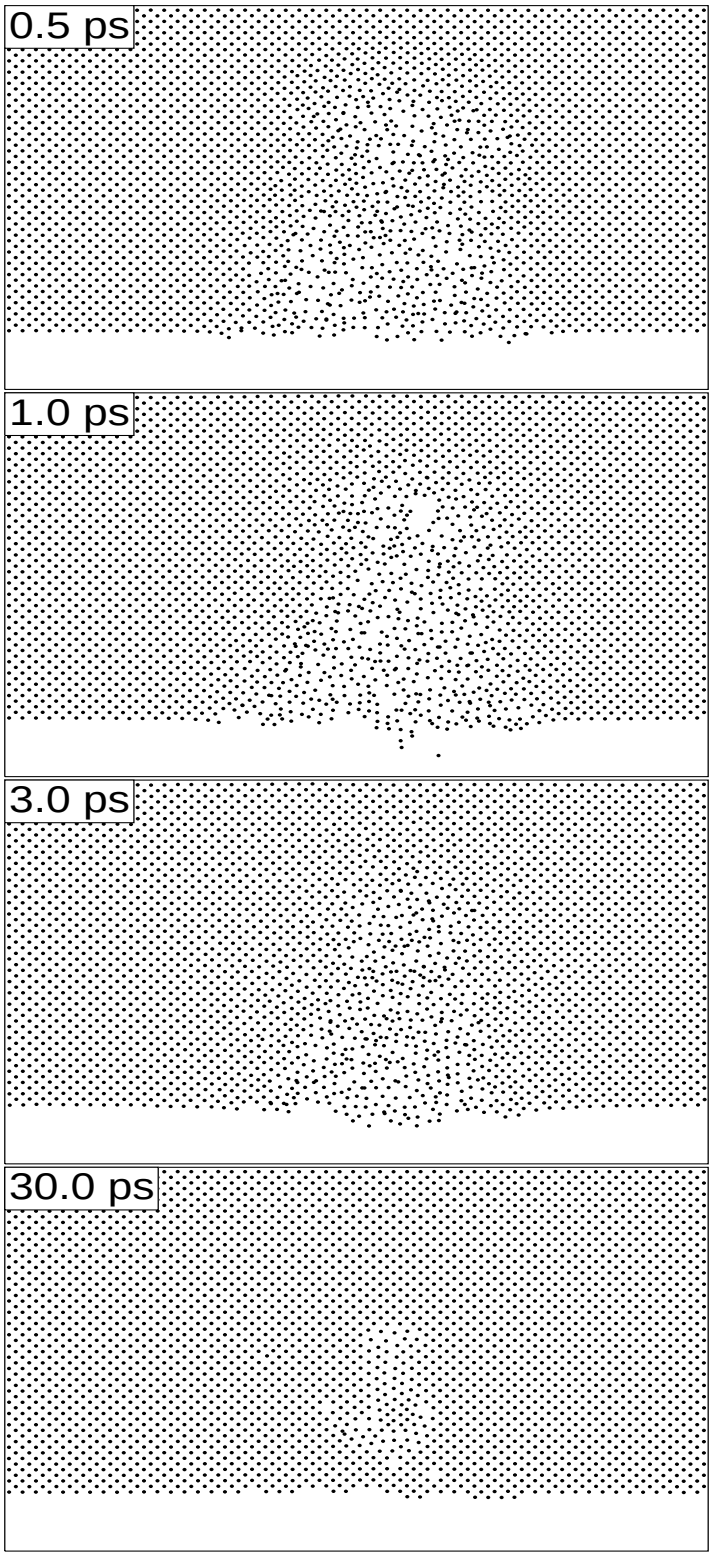
Event	N_{VAC}	N_{INT}
Expt.*	125	< 10
Bulk sim.	23	23
Surf. sim.	136	7

*** (Current et al., Phil. Mag. A 47, 407)**

- The matter was finally resolved by our MD simulations [Zhong *et al.,* Phys. Rev. B **58** (1998) 2361]. The results showed that the whole thing was essentially a surface effect. Because the irradiation during the FIM experiments was always close to the surface, atoms can actually flow to the surface during the experiment. This vastly increases the number of vacancies. Also, the interstitials can escape to the nearby surface because of their high mobility.

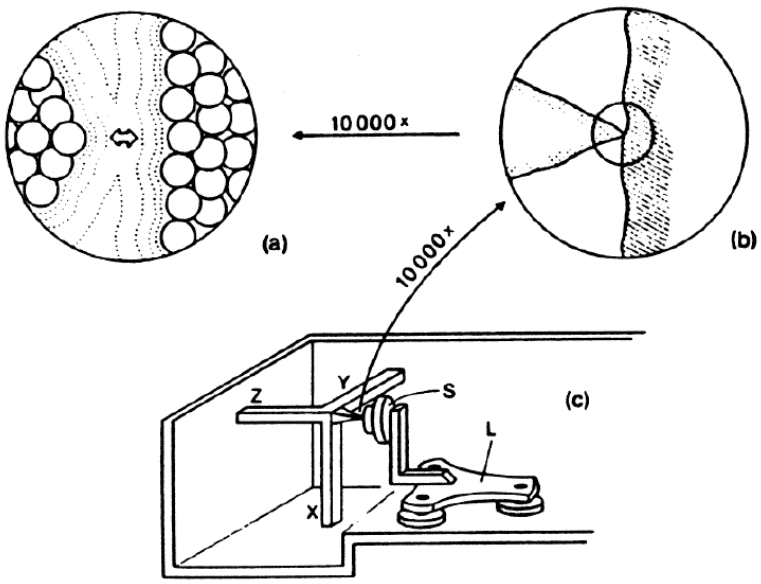
- This explained both the imbalance between vacancies and interstitials, as well as the discrepancy between FIM and the other, bulk experiments.

- An illustration of how the atoms flow to the surface, in a 30 keV W -> W event.



Scanning probe methods

- In the so called scanning -probe - methods (SPM) the surface of the sample is examined by placing a thin needle against it and moving it in the xy directions so that a 2D contour map image is obtained of the sample surface.

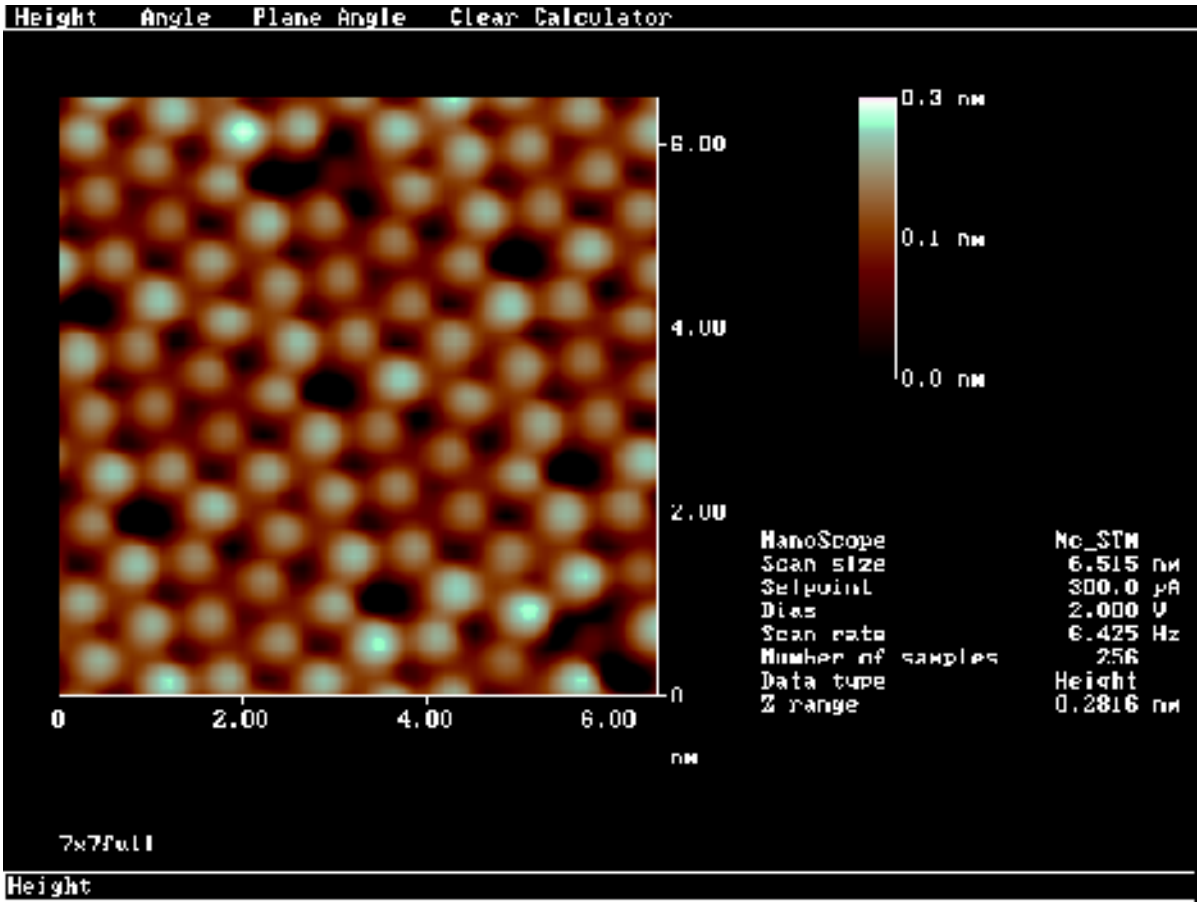


Kuva 11.1. *Pyyhkäisytunnelointimikroskoopin toimintaperiaate. X, Y ja Z ovat piikkiä liikuttelevia pietsosähköisiä kiteitä ja S on tutkittava näyte.*

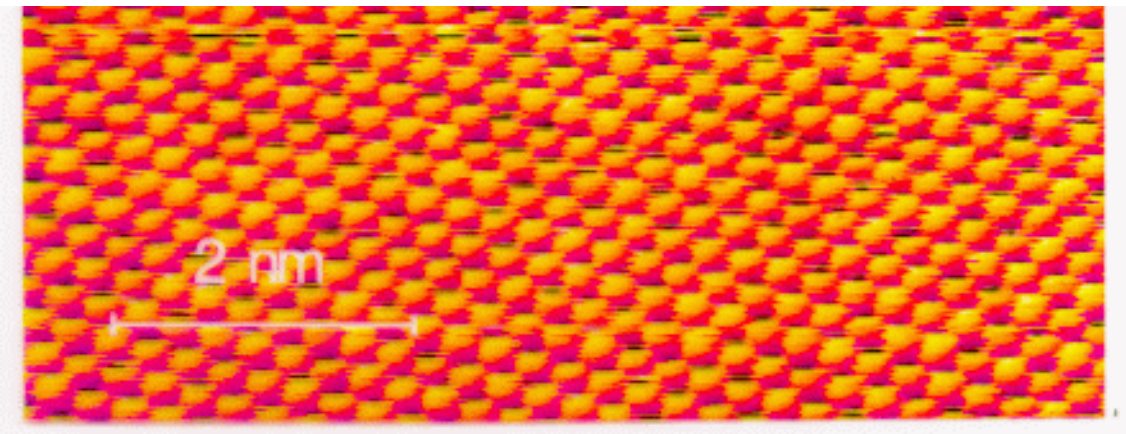
- The best known SPM methods are Scanning Tunneling Microscopy, STM and Atomic Force Microscopy, AFM. STM measures the tunneling current of electrons to the tip of the needle, whereas atomic force microscopy measures the force acting on the tip while it moves over the surface.

- Thus STM will only work for conducting and semiconducting samples, whereas AFM can be used for almost any sample.

- The methods can give, as you probably well know, an (almost) atom-resolution image of the surface. A classical example is the reconstruction of the 111 Si surface:

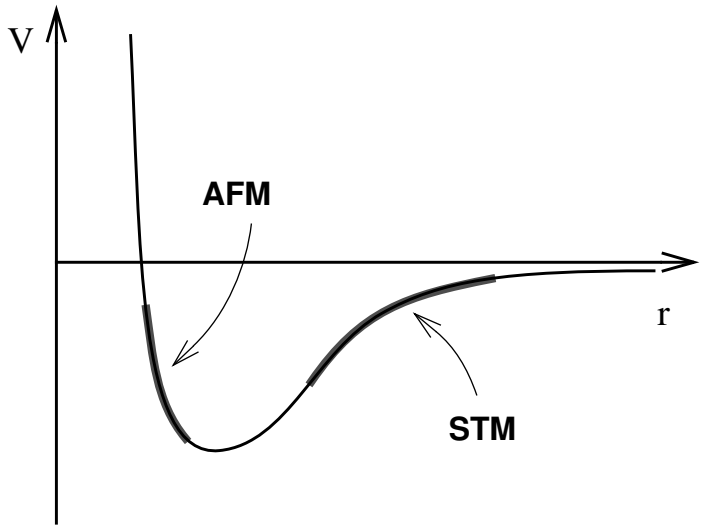


and another standard case the 0001 surface of graphite:



- So it would seem that here as well the comparison with simulations is trivial. **But in fact this is far from the truth!**

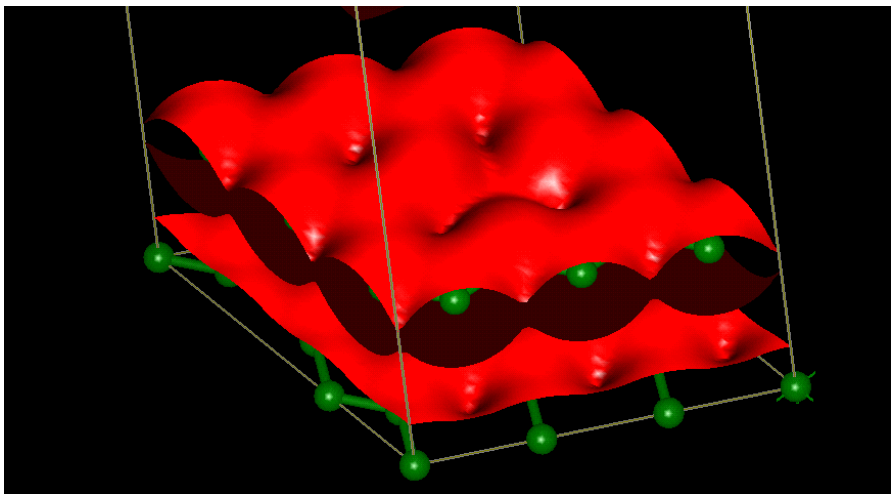
- The basic problem is that neither AFM nor STM really measure the atom positions. Instead they measure different parts of the electron cloud. In terms of a pair potential, one could roughly describe the situation as:



  But this is a bit of an oversimplification, as AFM has different modes, some of which measure the weaker part of the forces in about the same region as STM.

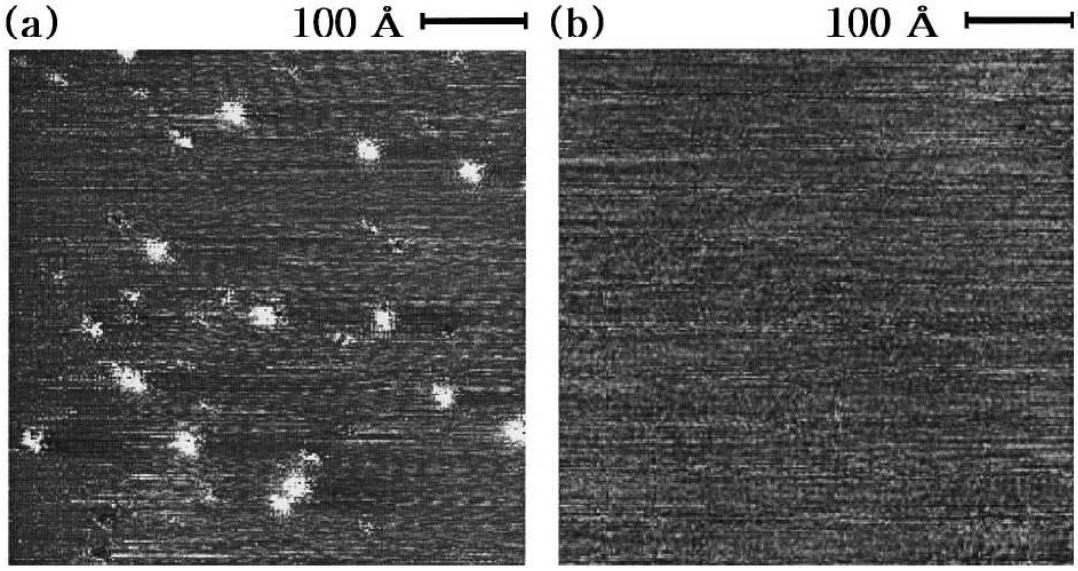
- Another, somewhat more accurate way to describe this is that AFM measures the total valence electron density, whereas STM measures the outermost electron levels near the Fermi level.

- For instance, in the graphite picture above, the maxima are in fact not atoms, but there is one maximum for every two atoms. A DFT calculation [T. Mattila] illustrates this:



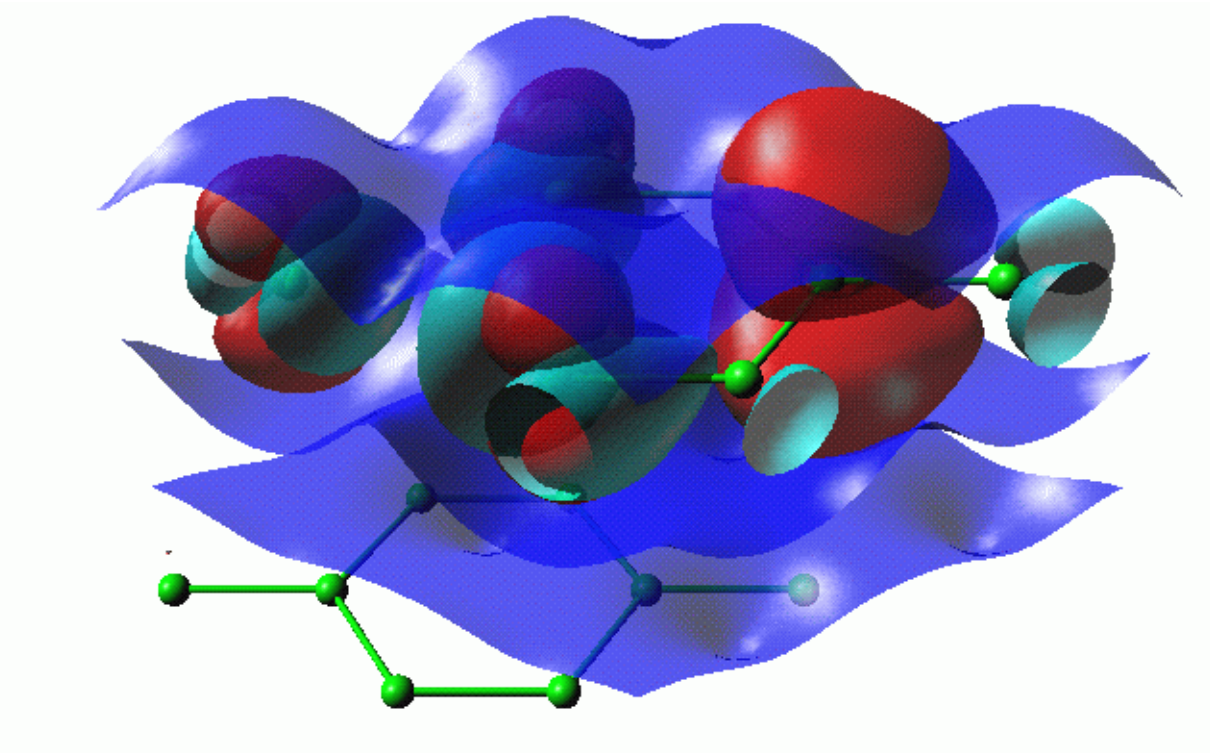
- The reason is subtle: the second atom layer breaks the symmetry of the first.

- Things get even more interesting if one considers a defective graphite surface. For many years STM groups bombarded graphite with various ions, and almost always tended to observe 'hillocks' on the surface. The height estimates of these hillocks ranged from 2 to 20 Å or so. But there was no satisfactory explanation to what these are; the numbers of the hillocks were somewhat larger than basic ion irradiation physics would predict. Then Hahn *et al.* [Phys. Rev. B **53** (1996) R1725] measured the same bombarded surface both with AFM and STM, and suddenly found that almost all the high hillocks seen by STM were invisible in AFM!



- So what the heck was going on? By combining DFT calculations and some reasoning, Hahn came to the conclusion they are in fact vacancies, that is, missing atoms in the surface layer.

- This can be understood with DFT calculations of a surface vacancy [Hahn *et al,* Phys. Rev. B **53** (1996) R1725; Nordlund, Keinonen, Mattila, Phys. Rev. Lett. **77** (1996) 699]. The picture below shows the valence electron density in blue and the outermost electron density in red. In the same 6-fold atom ring as the vacancy, but on the opposite side there is a bump in the electron density near the Fermi level. This bump is what STM actually measures. Since a higher electron density leads to an increased tunneling current, this appears as a large hillock. The valence electron density on the other hand is essentially unmodified, which explains why AFM sees nothing.



- So we can conclude that *in interpretation of STM- and AFM-experiments one should be very careful: everything may not be what it looks like!*

- We also see that electronic structure calculations may be very useful or even necessary to interpret AFM and STM experiments.

- In STM measurements determining the height scale may be a big problem. The current depends on the height, but there is no definite way to form the correspondence between the two.

- Within a perturbation approach the tunneling current can be estimated as [McKinnon and Choy, Phys. Rev. B 54 (1996) 11777]

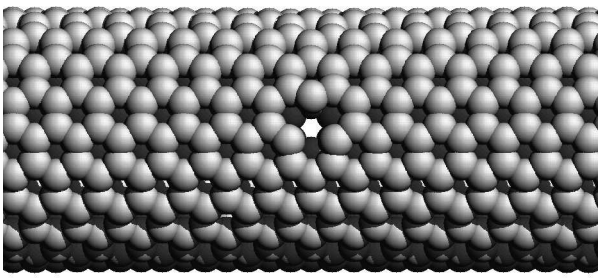
$$I(x, y, h) \sim V^2(x, y, h)\rho_{\text{surface}}(\varepsilon_F, x, y)\rho_{\text{tip}}$$

  where V is the voltage in the tip, ρ_{surface} is the local density of states close to the Fermi surface at the position of the tip, ρ_{tip} is the local density of states of the STM tip, and h is the tip height above the surface. ρ_{surface} can be calculated as

$$\rho_{\text{surface}}(\varepsilon, x, y) = \sum_{\nu} \left|\psi_\nu(x, y)\right|^2 \delta(E_\nu - \varepsilon)$$

  where ψ_ν the wave function of the surface electrons in state ν and E_ν the energy of this state. DFT or TB calculations can give ρ_{surface}, ψ_ν and E_ν from which the tunneling current and image shape can be predicted. ρ_{tip} is generally not well known because the exact tip shape is unknown.

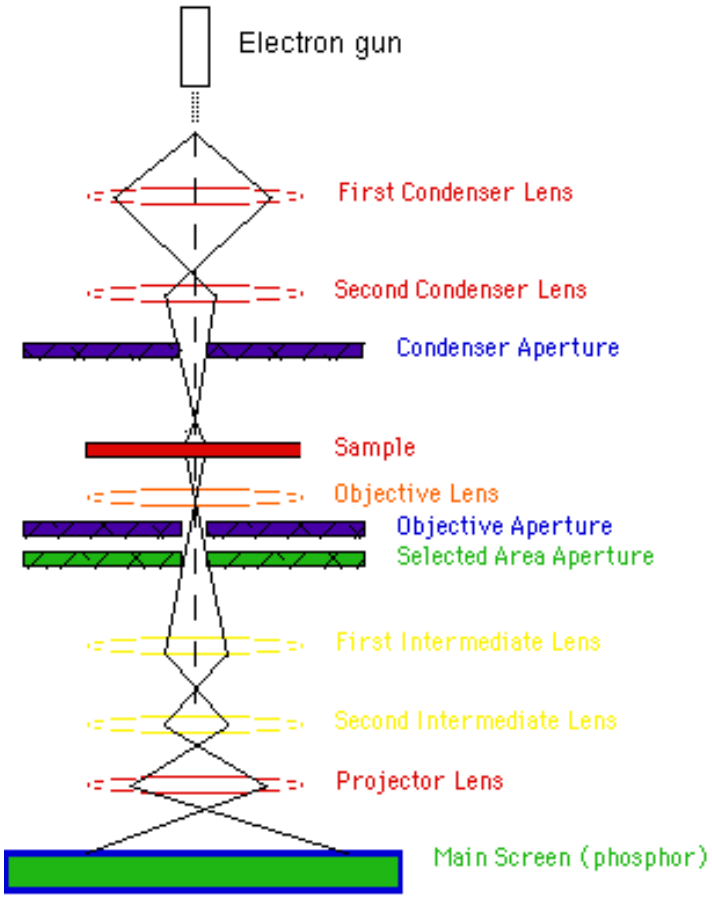
- Example: STM image of a vacancy in a nanotube. Classical MD simulations give the vacancy shape about correctly, then a TB approach can be used to predict the STM image [A. Krasheninnikov *et al.*, Phys. Rev. B (2001) accepted].



Transmission electron microscopy (TEM) image simulation

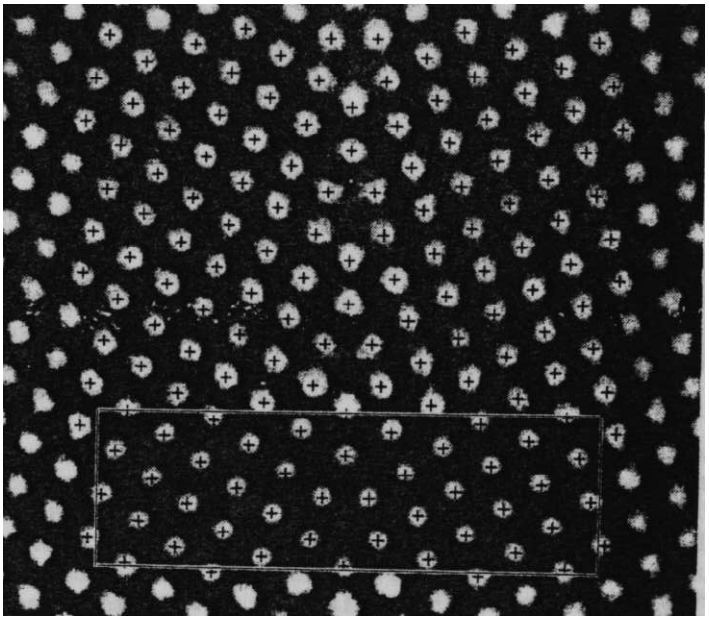
- The transmission electron microscope (TEM) gives images of materials by studying the diffraction and transmission of an electron beam through a thin specimen. The microscope has a large amount of lenses, and by changing the settings of these one can obtain both a real and reciprocal-space (diffraction) image of a sample.

  At best it is possible to obtain atomic resolution with TEM (High resolution TEM, HRTEM), and routinely about 1 nm resolution can be attained.



- The chief limitation here is that the sample which is imaged has to be so thin that the electron beam can pass through it without significant attenuation. This means that the maximal sample thickness is for dense materials of the order of 60 - 100 nm. What the TEM image actually does is to give a 2D projection of all the atoms in this region. Since TEM can give an atom-resolution image of an almost bulk sample (with much less limitations in sample shape than FIM) it is a very popular method nowadays.

- For HRTEM comparison with experiments can be very straightforward. An example of this is a grain boundary in aluminum: the +- signs are atom positions modelled by EAM, the white circles an HRTEM image [Mills, Ultramicroscopy **40** (1992) 247]



- But especially when the TEM resolution is not at an atomic level, it may be necessary to perform a **TEM image simulation** to understand what the underlying atom structure is.

- In fact, even in the picture above TEM image simulation has been used: the region inside the square is simulated rather than experimental!

- For a very thin (<~ 1 nm) sample (typical in HRTEM) the image simulation is relatively easy: first one calculates a Fourier transform (fast Fourier transform, FFT, in practice) from the atom positions which gives the so called projected potential $V_{p.}$ Then the transmission q_n through the layer of thickness Δz can be calculated as follows:

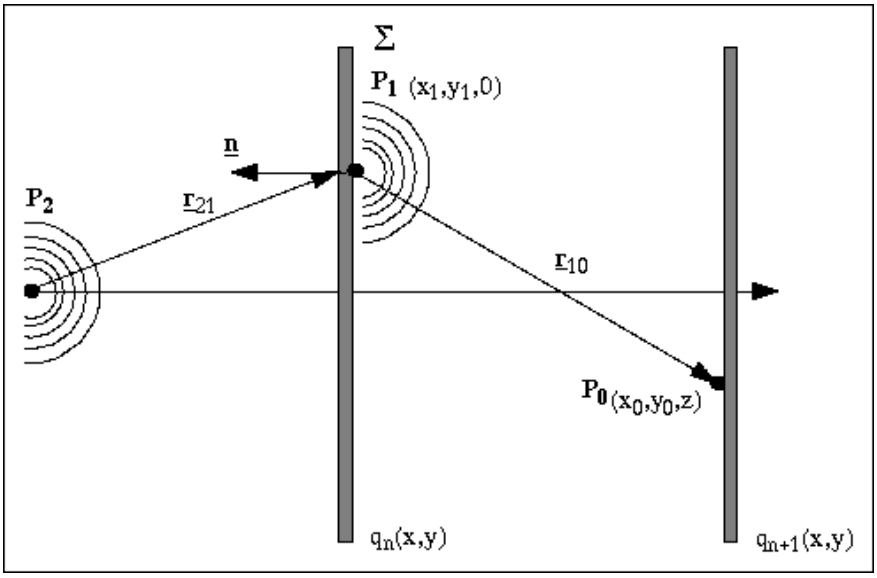
$$q_n(\underline{x}) = \exp[-2\pi i \Delta\alpha] = \exp\left[-2\pi i \frac{\chi}{2E} V_p(\underline{x},z)\,\Delta z\right]$$

$$q_n(\underline{x}) = \exp[-i\sigma V_p(\underline{x},z)\,\Delta z]$$

$$\text{with} \qquad \sigma = \frac{\pi\chi}{E} = \frac{\pi}{\lambda E}$$

i.e. an inverse Fourier transform.

- For thicker samples, the best way to simulate TEM images is the so called multislice (dynamical) method [http://cimewww.epfl.ch/CIOL/ems.html]. In there the idea is to first simulate the transmission through a thin layer as above to find the electron wave function after this layer. Then the *new* wave function is allowed to pass through the next layer with the same method as for the first layer:



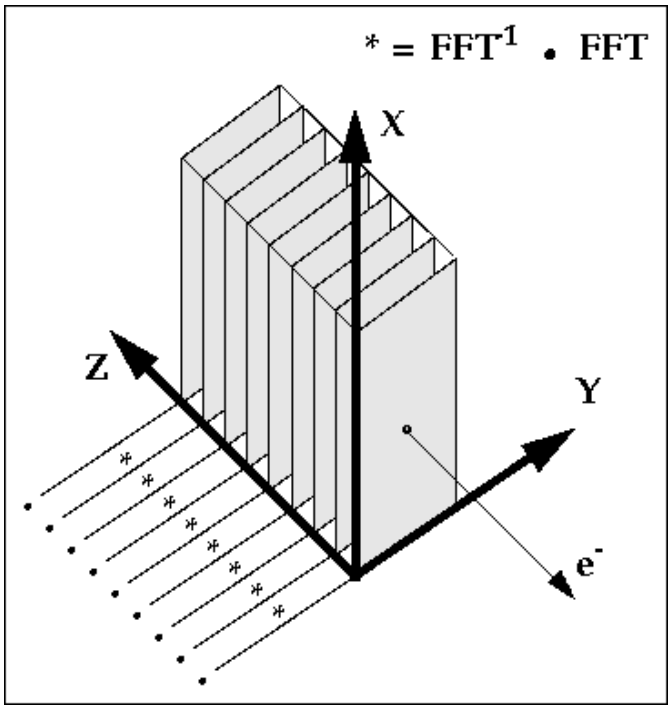
This operation can be formally written as

$$\Psi_{n+1} = [\Psi_n \cdot q_n] \otimes P_{n \rightarrow n+1}$$

I.e. the new wave function Ψ_{n+1} is the product of the old wave function Ψ_n and the transmission q_n of the previous layer propagated forward to the new layer by the propagator P.

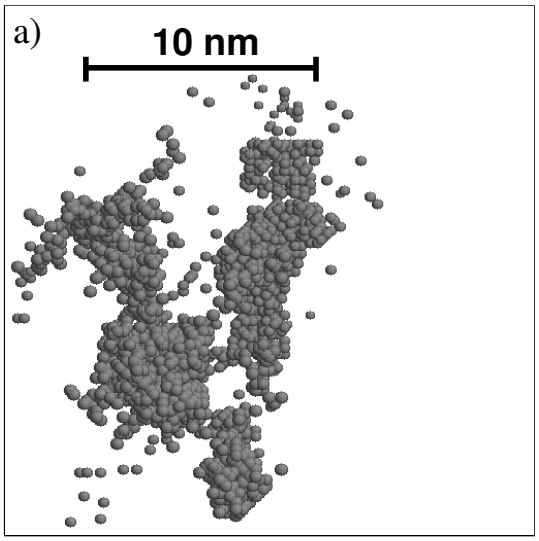
This process is then repeated for the whole sample.

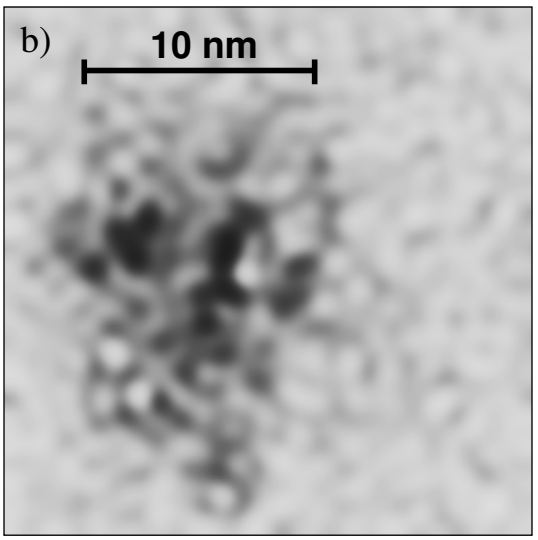
It is also possible to account for essentially all the properties of TEM lenses and imperfections in the simulations.

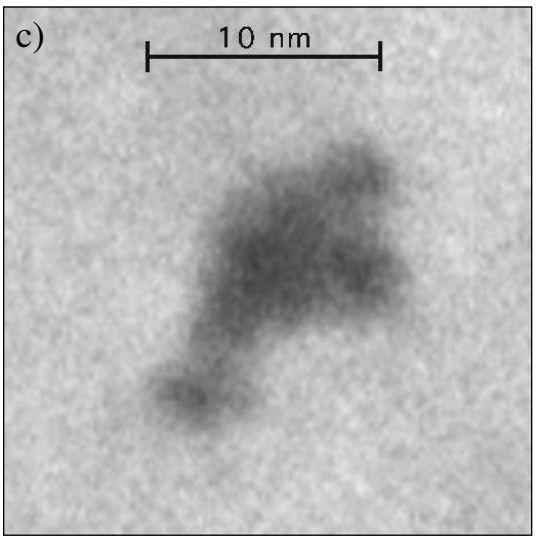


- All of the above is well established. In practice it is still, however, a computationally quite heavy procedure for a larger number of atoms; simulating the TEM image for a few hundred thousands of atoms may take several days. Hence it is only now become more popular.

- An example: a TEM image of defects in Ge. a) is a simulation result showing defect positions. b) is a simulated TEM image of the defects, and c) an experimental image of defects produced by a similar irradiation. The correspondence is not the best possible one (our own TEM image simulation code has some shortcomings) but clearly one sees that the simulated and experimental defect structure are of similar size.







- The best code available for TEM image simulation is EMS, or the newer java version jems. See http://cimewww.epfl.ch/CIOL/ems.html