Table 13.1: Main features of SEM and STEM

	SEM	STEM
Electron beam energy	5-15 keV	50-200 keV
Electrons detected	secondary	transmitted
Beam size at sample	to 5 nm	0.2-1 nm
Practical resolution	50 nm	0.2-1 nm

The practical resolution refers to the scale on which structural features can be distinguished. In SEM, a better resolution is sometimes quoted, but it usually means the smallest distance resolvable between two particles under optimal conditions. The numbers in the table make it clear that SEM is best suited for examining what we have called the microstructure of a material, whereas in STEM one may be able to observe features on the atomic scale. It goes without saying that this is only possible under strictly controlled experimental conditions (temperature, vibrations, etc.) and with optimally prepared samples.

13.1.3 Atomic Force Microscopy

The final example of a method to visualize material features at the atomic scale is the atomic force microscope (AFM). This is a type of instrument that does not rely on photon or electron radiation as a probe. Rather, it is scanning mechanical probe with an extremely fine stylus mapping out the atomic geometry of a surface. The physical principle is illustrated in Fig. 13.5:

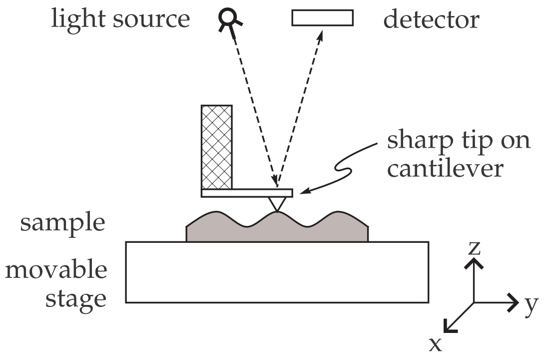

Figure 13.5: Schematic of an atomic force microscope. Parts not to scale.

The probe is a very fine, sharp tip on a small, flexible cantilever. The stage with the sample is brought very close to the tip so that there is observable interaction between the sample surface and the tip. The stage is then raster-scanned in the xy-plane, and the deflection of the tip in the z-direction is recorded as a function of its xy-position relative to the sample.

An AFM can be operated in different modes, depending on what the nature of the interaction is between the tip and the surface.

- In the so-called ***contact mode***, the tip touches the surface so that a measurable deflection of the tip results. A surface profile can be obtained in one of two ways:
  1) The tip deflection can be recorded as a function of the (x,y) position of the stage, with the stage being scanned horizontally at constant z, or
  2) The tip deflection is held constant by a feedback mechanism on the z-position of the stage, and the z-position of the stage is recorded vs (x,y).
- In the ***non-contact mode***, the tip does not touch the sample but is oscillating at its resonant frequency with a certain amplitude, at a distance close to the surface but subject to nearly zero force. As the stage is being scanned, a feedback loop between the z-position and the tip keeps the oscillation amplitude constant while the varying z-position is recorded.
- There is yet a third mode called ***tapping mode***, which is similar to the non-contact mode in that the tip is oscillating, but the tip is close enough to the surface so that the force on the tip reduces its oscillation amplitude by 50% or so. Again a feedback loop on the z-position of the moving stage keeps the tip amplitude constant as the z-position is recorded.

An AFM tip with cantilever and support is a monolithic structure, most often fabricated out of Si or Si_3N_4 using microelectronics techniques (see Fig. 13.6 below). Typical dimensions and physical parameters of cantilevers and tips are listed in Table 13.2 below:

Table 13.2: Typical specifications of AFM cantilevers and tips

	Contact mode	Tapping mode
Cantilever (l × w × t)	450 × 50 ×2 μm	125 × 30 ×4 μm
Tip height	17 μm	17 μm
Radius of curvature	<10 nm	<10 nm
Apex angle	45°	45°
Force constant	0.1 N/m	40 N/m
Resonant frequency	10 kHz	300 kHz

Parameters such as the force constant and the resonant frequency can be designed by the proper choice of the cantilever dimensions. It should be pointed out that in contact mode, the force exerted by the tip on the sample may be large enough to dislodge atoms and thus damage the sample. This is why the tapping mode is often the preferred method of examination.

A typical tapping mode Si cantilever with tip is shown below:

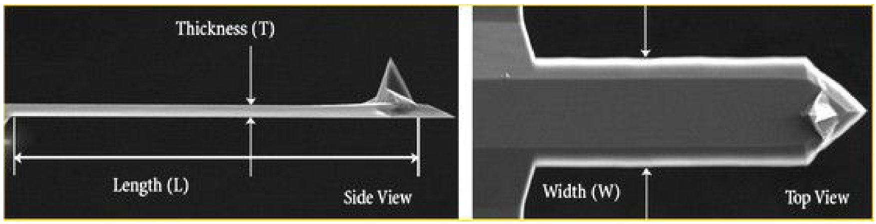

Figure 13.6: Typical tapping mode Si cantilever with tip.

As with all microscopies, the resolution is of interest for AFM, too. This can be illustrated with a simple geometrical argument:

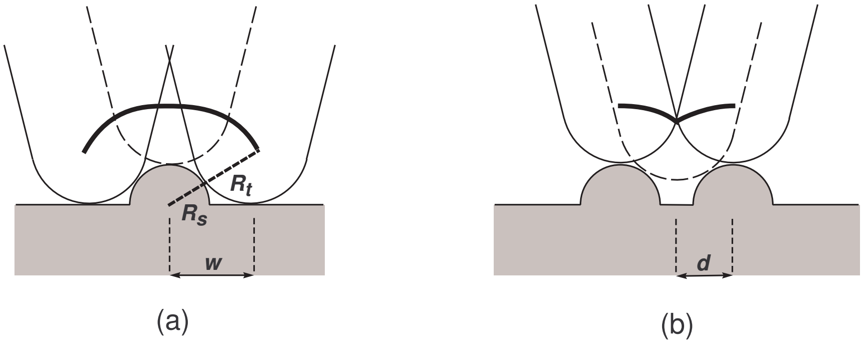

Figure 13.7: Geometries for AFM resolution. a) an individual feature; b) two closely-spaced features.

We assume that the AFM tip has a radius of curvature of R_t. In the panel on the left of Fig. 13.7, we are trying to detect an individual feature, a hemispherical particle with radius R_s. The heavy solid line indicates the trajectory of the center of the tip as it traces the particle. The excursion in the vertical direction is equal to R_s as the tip moves across. Thus the resolution of the AFM in the z-direction must be better than R_s in order that the *presence* of the particle is detected. The *apparent width* of the particle w is

$$w = \sqrt{(R_s + R_t)^2 - R_t^2} = \sqrt{R_s^2 + 2R_sR_t} \tag{13.1}$$

This can be evaluated easily. When the goal is atomic-level resolution, usually $R_t \gg R_s$, in which case Eq. 13.1 can be approximated by

$$w \approx \sqrt{2R_sR_t} \tag{13.2}$$

The point to note here is that detection of an atomic-level feature can be achieved with a tip with dimensions much larger than atomic, as long as the sensitivity of the AFM in the z-direction is atomic. However, for a proper description of the shape of the feature, including its width, the measured tip trajectory has to be further analyzed taking into account the shape of the tip.

Now consider Fig. 13.7b, for the purpose of determining when two hemispherical particles separated by a distance 2d can be resolved. Again the heavy solid line indicates the trajectory of the center of the tip, as it moves from exactly above one atom to exactly above the other atom. Hence one must be able to detect the small dip in the heavy solid line.

Let us say that when the tip is exactly on top of a particle, its center is at a distance $z_1 = R_s + R_t$ above the reference plane. When the tip is exactly in the middle between the two particles, it is at a distance z_2 above the plane, where

$$z_2 = \sqrt{(R_s + R_t)^2 - d^2} \tag{13.3}$$

and the change in position of the tip, $\Delta z = z_1 - z_2$ is equal to

$$\Delta z = z_1 - z_2 = R_s + R_t - \sqrt{(R_s + R_t)^2 - d^2} \tag{13.4}$$

As above, we can assume that $R_t \gg R_s$, in which case Eq. 13.4 can be approximated by

$$\Delta z \approx \frac{1}{2}\frac{d^2}{R_s + R_t} \tag{13.5}$$

As a numerical example, let us consider two hemispherical particles with R_s = 2 nm and a space of 2 nm between them, i.e. d = 3 nm. Let us also assume that R_t = 10 nm. Then Eq. 13.5 yields Δz = 0.15 nm. Note that in this case the separation of the two particles is given accurately by the trace of tip, but Δz is much less than the particle radius. Of course, the sharper the tip, i.e. the smaller R_t, the better the resolution.

A large variety of AFM tips are available commercially. These include not only tips with varying physical dimensions, but also e.g. extra sharp tips, tips coated with a thin diamond layer for extra wear resistance, and films coated with metal for magnetic interaction measurements.

The great advantage of AFM over the electron microscopies is that AFM can deal easily with all kinds of samples: insulating materials, biological samples, particles in an aqueous environment, etc. The electron microscopies generally require an evacuated instrument, and some types of samples may be damaged by the electron beam. On the other hand, with AFM one has to make sure that no mechanical damage is inflicted on the sample.

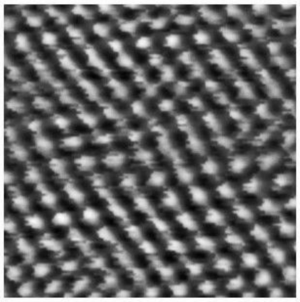

Figure 13.8:
AFM image of the basal plane of graphite.

We have encountered an example of AFM earlier, in Fig. 7.15, which showed the very detailed structure of a growing polymer spherulite. Another example, in Fig. 13.8, displays the surface of graphite.

13.2 Nanoscale Materials - Size Effects

Given that materials consist of assemblies of atoms, one could argue that all material properties are determined at the ***nanoscale***, i.e. at nm dimensions. What we have emphasized up to this point is what we have called the microstructure of a material. This means, roughly, structure that appears on the μm scale, for example grains and grain boundaries in normal polycrystalline engineering materials.

Here we will examine briefly the question whether materials have different properties when their internal structures are much smaller, for example materials containing nm-size particles or nm-size grains. We will refer to such materials as **nanocrystalline**. The general answer is that many material properties change at that scale, sometimes in beneficial ways. Again, we will look at a few interesting examples.

13.2.1 Surface vs. Bulk Atoms in Small Particles

You will recall that in most of our prior discussions, we made the assumption that the outer surface of a material, strictly speaking a 2D defect, did not have a significant effect on the material properties. On the other hand, one instance where we did deal with surfaces was in connection with the effects of grain boundaries as internal surfaces.

The basis for this assumption was that the number of atoms in the bulk was much larger than the number of atoms on the surface. For small particles this assumption is not valid anymore, and this is important because surface atoms generally differ in their properties and reactivities from bulk atoms. In other words: For small particles, the material properties become size-dependent. This fact has long been recognized by chemists and chemical engineers working with catalyst particles.

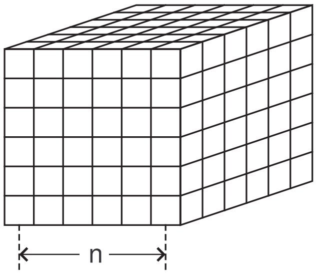

Figure 13.9:
Sample cube with side length n = 6, containing 216 atoms.

As a simple illustration of this size effect, let us determine the fraction of atoms residing on the surface of a small particle. Let us assume the particles have simple cubic crystal structure, with a cube length given by the parameter n. In the example of Fig. 13.9, there are six atoms along the side of the little cube, and thus $n = 6$. For an arbitrary n, the total number of atoms in the particle is obviously n^3. The number of bulk atoms, i.e. atoms not on the surface, is $(n-2)^3$. Hence, the fraction f_s of particles on the surface is

$$f_s = \frac{n^3 - (n-2)^3}{n^3} \tag{13.6}$$

Equation 13.6 can be evaluated as follows:

$$f_s = \frac{6n^2 - 12n + 8}{n^3} = \frac{6}{n} - \frac{12}{n^2} + \frac{8}{n^3} \tag{13.7}$$

As long as n is not too small (more exactly, if $n \gg 2$), Eq. 13.7 can be approximated by just the first term on the right-hand side:

$$f_s \approx \frac{6}{n} \tag{13.8}$$

This says that the fraction of atoms on the surface of a particle increases roughly as the inverse of the linear dimension of the particle.

The fractions of surface and bulk atoms as per Eq. 13.7 are plotted in Fig. 13.10 below. For example, for a particle with 1000 atoms, about half of the atoms are on the surface, and the approximation of Eq. 13.8 is still quite good.

13.2.2 The Melting Temperature of Small Particles

One of the earliest observations of a size-dependent materials property has been the melting temperature T_m of small particles. Data for T_m of small Au