CHAPTER 1
Introduction

1 Clusters and Nanoparticles

Particles with a size between 1 and 100 nm are normally regarded as *nanomaterials*. Figure 1 shows the size of nanoparticles in comparison with other small particles. In general, nanomaterials may have globular, plate-like, rod-like or more complex geometries. Near-spherical particles which are smaller than 10 nm are typically called *clusters*. The number of atoms in a cluster increases greatly with its diameter, demonstrated in Figure 2 for sodium clusters. At 1 nm diameter there are 13 atoms in a cluster and at 100 nm diameter the cluster can accommodate more than 10^7 atoms. Clusters may have a symmetrical structure which is, however, often different in symmetry from that of the bulk. They may also have an irregular or amorphous shape. As the number of atoms in a cluster increases, there is a critical size above which a particular bond geometry that is characteristic of the extended (bulk) solid is energetically preferred so that the structure switches to that of the bulk.

It is below a dimension of 100 nm where properties such as melting point, colour (*i.e.* band gap and wavelength of optical transitions), ionisation potential, hardness, catalytic activity and selectivity, or magnetic properties such as coercivity, permeability and saturation magnetisation, which we are used to

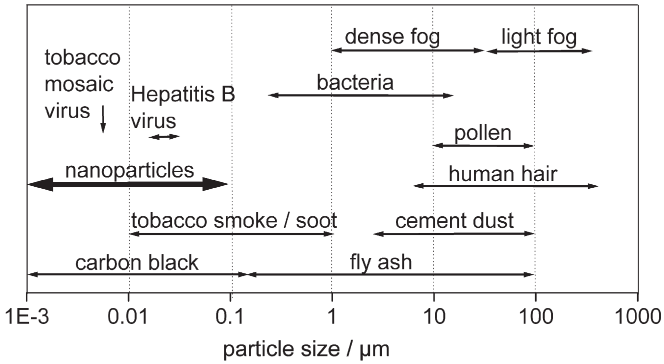

Figure 1 *Typical size of small particles. The regime below 0.1 µm corresponds to the dimension of nanoparticles*

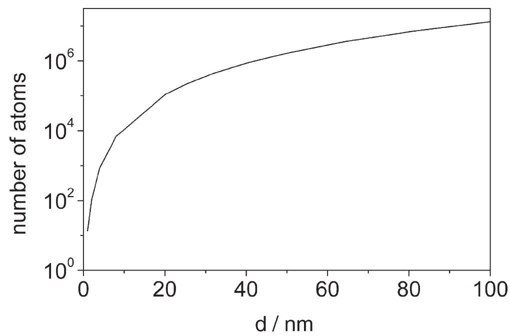

Figure 2 *Number of sodium atoms in a spherical cluster of diameter d*

thinking of as constant, vary with size. We basically distinguish two types of variations as a function of size:

- *Scalable effects*: Surface atoms are different from bulk atoms. As the particle size increases, the surface-to-volume ratio decreases proportionally to the inverse particle size. Thus, all properties which depend on the surface-to-volume ratio change continuously and extrapolate slowly to bulk values.
- *Quantum effects*: When the molecular electronic wave function is delocalised over the entire particle then a small, molecule-like cluster has discrete energy levels so that it may be regarded like an atom (sometimes called a *super atom*). The simplest model for it is that of a particle in a box. Adding more atoms to the cluster changes the size of the box continuously so that the energy levels close up to some extent. More importantly, adding more atoms means adding more valence electrons to the system. Thus, whenever a shell of sometimes multiple degenerate energy levels is filled the next electron has to be accommodated in the next shell of higher energy. The situation is analogous to the evolution of properties with increasing atomic number in the periodic table. Filled shells represent a particularly stable configuration. Properties such as ionisation potential and electron affinity are well known to display a discontinuous behaviour as one moves along the periodic table. For clusters consisting of atoms with strongly overlapping atomic orbitals, *i.e.* for metals and semiconductors, the situation is analogous.

Quantum effects are more pronounced for small clusters and often superimposed on a smoothly varying background of a scalable effect. Clusters are interesting intermediates between single atoms and bulk matter and represent a natural laboratory to 'see both ends from the middle'.

2 Feynman's Vision

On 29 December 1959, at the annual meeting of the American Physical Society, Richard Feynman addressed the audience with his visionary and by now historical and legendary lecture under the title – *There is Plenty of Room at the Bottom: Invitation to Enter a New Field of Physics*.[1] With this talk on the problem of *manipulating things on a small scale*, Feynman opened the field of nanotechnology. Today, more than four decades later, the field is finally seen to really take off. It is amazing how closely some of the key developments follow Feynman's vision. *Why cannot we write the entire 24 volumes of the Encyclopaedia Britannica on the head of a pin?* he asked. We know how successful information technology has been in its work towards this goal and we should be aware of how much this has influenced our lives. *Make the electron microscope hundred times better*, Feynman said. The development of the atomic force microscope was one of the milestones on the way not only to observe but also to manipulate in atomic dimensions. Amazingly, Rohrer and Binnig achieved this goal with their cantilever-based instrument in a single step, rather than by a hierarchy of smaller and smaller robots – *training an ant to train a mite* – as Feynman suggested. In 1986, the two scientists were honoured for their achievement with the Nobel Prize in Physics. It is quite obvious today that the invention of the scanning tunnelling microscope finally triggered the boom in nanotechnology to which the direct observation of very small scale structures down to individual atoms is essential. Obviously, seeing things directly is more convincing for vision-based beings than just having measurements which are in agreement with a model.

Some of the inspiration came from biology. Feynman understood that information is stored on a molecular level in biology, that cells manufacture substances and operate on a small scale, that the human brain is a wonderful and efficient miniaturised computer. *Consider the possibility that we too can make a thing very small which does what we want, an object that manoeuvres at that level*, he suggested. While his talk was primarily technology oriented, he knew that physics, chemistry, biology and engineering are all relevant and must all be involved. He realised that making things smaller was not just a technological problem of scaling down. He saw that certain things changed principally. Magnetism, for example, is a cooperative phenomenon and involves domains which cannot be reduced down to an atomic size. Atoms differ from the bulk in their quantum nature. Most significantly, Feynman predicted that *when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have*. It is exactly the arrangement of things on a small scale which is the foundation for all the excitement about nanomaterials and for the success of modern materials science.

References

1. R.P. Feynman, *Eng. Sci.*, 1960, 23, 22; *J. Micromech. Syst.*, 1992, 1, 60; www.zyvex.com/nanotech/feynman.html.