2. Nanoparticles

Nanoparticles are the simplest form of structures with sizes in the nm range. In principle any collection of atoms bonded together with a structural radius of $< 100$ nm can be considered a nanoparticle.

These can include, e.g., fullerens, metal clusters (agglomerates of metal atoms), large molecules, such as proteins, and even hydrogen-bonded assemblies of water molecules, which exist in water at ambient temperatures.

Nanoparticles are very commonplace in nature - for instance proteins exist in almost all biological systems, metal-oxide nanoparticles are easily produced, etc . . .
2.1. Physically manufactured nanoparticles

2.1.1. Nanoclusters

When studying nanoparticles a distinction must necessarily be made between condensed “hard” matter nanoparticles, generally termed nanoclusters, and “soft” bio-organic nanoparticles and large molecules.

A nanocluster is a nanometer sized particle made up of equal subunits. These subunits can be atoms of a single element, molecules or even combinations of atoms of several elements in subunits with equal stoichiometries (alloys, etc.)

E.g.: Na$_n$, (SF$_6$)$_n$, (H$_2$O)$_n$, (Cu$_3$Au)$_n$, (ClCH$_3$C$_6$H$_3$CO$_2$H)$_n$, (TiO$_2$)$_n$, . . .

The greatest difference arises from the fact that molecules have functionality which directly depends on the inter-positioning of their atoms, whereas the properties of nanoclusters are solely guided by the number of subunits they contain.
For this reason clusters can be seen as an intermediate stage between single atoms/molecules and bulk materials.

In general, the physical properties of materials are dependent on the dimensions of the material in question – its properties (e.g. conductivity, elasticity, etc.) are scaleable with respect to the amount of atoms in the material.

- scaleable size-regime – $N^{-\gamma}$

Once the particles are small enough - nanoclusters - these properties vary greatly with every addition or subtraction of an atom.

- non-scaleable size-regime – every atom counts!

2.1.2. Size does matter – small is very different!

2.1.2.1. Geometric structure

Usually the crystal structure of a large nanocluster is the same as the bulk structure of the material,
with somewhat different lattice parameters (in general clusters are slightly contracted as compared to bulk).

E.g. Cu clusters tend to have an FCC structure (Wulff polyhedra).

Some exceptions do, however, occur. Smaller clusters of Cu (e.g. Cu_{55}, Cu_{147}, ... ) have perfect icosahedral structures.

- structural magic numbers: occur when an exact amount of atoms is needed for a specific structure

Even smaller clusters can be amorphous-like (spherical, etc.), although a general tendency of the clusters is to form structures where the total surface energy (and internal energy) is minimized -
the exact structure then depends on the surface energies related to the specific crystal facets of the material.

2.1.2.2. Electronic structure

Structural magic numbers affect the formation and abundancies of larger clusters, whereas for the case of smaller clusters the combined electronic structure of all the atoms is of greater importance.

For instance in a Pb\(_n\) cluster spectrum, clusters with \(n=7\) or 10 are more abundant than others. When the ionization potentials of sodium clusters are plotted as a function of the number of atoms in the clusters, peaks are observed at clusters having two and eight atoms. This can be compared to the high ionization potentials observed for example in rare-gas atoms, where electrons are removed from filled orbitals.

- electronic magic numbers are observed for clusters (although most apparent for small clusters these magic numbers can be noticed even for very large clusters - up to several thousands of atoms.)
2.1.2.3. Jellium

The jellium model has successfully been used in the theoretical modelling of nanoclusters. The jellium model envisions a cluster of atoms as a single large atom, where the distribution of ionic
cores is replaced by a constant positive background, the so called “jellium density”, and only valence electrons are treated explicitly.

In effect a large spherically symmetric potential well is used to represent the potential describing the interaction of valence electrons with the positive spherical charge distribution. Energy levels can be calculated by solving the Schrödinger equations in a fashion analogous to that for the hydrogen atom.

As can be seen from the jellium model, the electronic structure of a cluster varies from that of a single atom, but it also varies greatly from that of a bulk material. When a bulk lattice is formed,
the discrete energy levels of the atoms are smuged out into energy bands. E.g. valence bands and conduction bands exist in semiconductors and metals. As particles shrink in size there is a dramatic change in these bands, as the continuous density of states in bulk is replaced with a set of discrete energy levels.

2.1.2.4. Optical properties

This leads to interesting optical properties. In semiconductors the band gap will be increased as cluster size is decreased – a blue shift in the absorption spectrum of the semiconductor (good for tailoring lasers).

Individual energy levels and energy level separations are also dependent on the size of the clusters,
which therefore affect the energies needed for the transitions of electrons to excited states. Clusters of different sizes will therefore have different absorption spectra – and hence different colours!

2.1.2.5. Reactivity

Since the electronic structure of nanoclusters depends on their size, their ability to react with other species should also depend on size. This has important applications for the design of catalytic agents.
Reactivity is highly dependent on the electronic structure, leading to large variations in the reactivity of clusters even with sizes differing by only single atoms. In general, however, the reactivity of all nanoclusters is high as compared to that of bulk, due to their higher surface to volume ratio. E.g. gold nanoclusters are highly reactive if compared to the fairly inert bulk material.

2.1.2.6. Melting temperatures

Another effect caused by a high surface to volume ratio in clusters, is a substantially lower melting temperature as compared to bulk materials. Unusual phenomena such as negative heat capacities have also been observed in clusters (at the melting temperature, an increase of the internal energy of Na$_{147}^+$ by 1 eV leads to a decrease in temperature by about 10 K).

In large enough systems added energy is converted completely into potential energy, reducing continuously the fraction of its solid phase. The kinetic energy and thus the temperature remain constant. A small system, on the other hand, tries to avoid partly molten states and prefers to convert some of its kinetic energy into potential energy instead. Therefore the cluster can become colder, while its total energy increases.
2.1.2.7. Magnetic properties

Interesting **magnetic properties** have also been observed in small clusters. In a cluster the magnetic moment of each atom will interact with the moments of the other atoms, and can force all the moments to align in one direction with respect to some symmetry axis of the cluster – the cluster will have a net magnetic moment, it will be magnetized.

As cluster size decreases it therefore becomes easier for them to exhibit ferromagnetic behaviour. In some cases, even clusters made up of nonmagnetic atoms can have a net magnetic moment. For instance rhenium clusters show a pronounced increase in their magnetic moment when they contain less than 20 atoms. For clusters with less than 15 atoms these moments are fairly large.
2.1.3. Cluster production

In principle there are three different physical methods for producing clusters. Common for all methods is the initial vaporization of atoms from a bulk target.

2.1.3.1. Energetic vaporization

Energetic vaporization is the simplest of all cluster production methods. Clusters are the resulting product of the ejection of large numbers of atoms, at high energies, from the bulk material.

Various different vaporization techniques are used in different sources. Including:

- Laser vaporization sources, where atoms are irradiated with intense laser beams.
- Pulsed-arc sources, where intense electrical discharges cause vaporization.
- Ion sputtering sources, where atoms are ejected from the target through ion bombardment.
- Liquid-metal ion sources, where a needle is wetted with the material, after which a high potential is applied, causing intense electrical fields, due to which small droplets of the wetting material are emitted.

Clusters produced with these sources are generally rather small and extremely hot (with temperatures near the evaporation limit).
2.1.3.2. Seeded supersonic nozzle sources

In seeded supersonic nozzle sources the material is vaporized in a hot oven, after which the vapor is mixed with (or “seeded” in) an inert carrier gas, by pressurizing the oven with the inert gas.

Typically the inert-gas pressure is several atmospheres, whereas the metal-vapor pressure is in the range of 10 - 100 mbar. The vapor/gas mixture is ejected into a vacuum via a small hole (a nozzle), producing a supersonic molecular beam.
The expansion into the vacuum proceeds adiabatically and causes cooling of the mixture. The cooled metal vapor becomes supersaturated, condensing in the form of clusters. Cluster production continues until the expanding vapor density becomes too low to promote further growth, typically within a few nozzle diameters from the nozzle exit. Likewise, the cooling of the clusters continues until the inert-gas density becomes so low that its flow is molecular rather than hydrodynamic.

The cooling provided by the expanding gas may be adequate to stabilize a cluster against evaporation, but if it is not, the clusters may further cool by evaporating one or more atoms. There is evidence that both processes take place. Clusters produced with this method can have very low temperatures, although, as the final cooling step for large metal clusters involves evaporation of one or more atoms, these clusters typically have temperatures close to the evaporation limit.

Experimentally it is found that the more massive the carrier-gas atoms, the better the cluster production. This is related to the larger collision cross sections, so that the transition to molecular flow occurs later than for lighter gases.

Although the inert gas is very important, it is worth mentioning that neat expansions (without carrier gas) also produce clusters. In this case the cluster production is limited to small sizes, with usually fewer than ten atoms per cluster.
(NOTE: Clustering of atoms through binary collisions of single atoms can, according to the laws of classical mechanics, never occur. Initial cluster formation must take place through collisions between three or more atoms!)

Positive features related to seeded supersonic nozzle sources are:

- Intense cluster beams. Material consumption is about 0.1 mole per hour, of which a sizeable fraction (estimated in excess of 10 % under suitable conditions) condenses into clusters in the beam.

- Clusters can be produced from almost any material. E.g. gaseous clusters and metal-oxide clusters can readily be produced.

Negative features:

- Cluster sizes are rather limited, as the largest produceable cluster contain around 100 atoms.

- As large amounts of carrier gas flow through the nozzle high vacuum is difficult to sustain in the deposition chamber.
2.1.3.3. Gas-aggregation cluster sources

In gas-aggregation cluster sources, or condensation-cell type sources, the cluster material is vaporized (e.g. by magnetron sputtering) and introduced into a flow of cold inert gas. This causes the vapor to become highly supersaturated. Pressures in the aggregation chamber are necessarily high in order to cause initial cluster growth.

After this, due to the low temperature of the inert gas, cluster production proceeds primarily by successive single-atom addition.
Since the reverse process (i.e. reevaporation) is negligible, the cluster abundances are not sensitive to the thermodynamic stabilities of the clusters and, consequently, the cluster abundances are relatively smooth functions of the cluster size determined mainly by collision statistics.

The cluster size distribution is determined by the parameters of the source, such as:

- sputtering rate
- metal-vapor density (pressure in the chamber)
- gas flow rate (and type and temperature of the gas)
- length of the drift region
- dimensions of various components, such as apertures
Suitable cluster materials for a source with a magnetron sputter are e.g. metals, semiconductors, all magnetic materials and metal oxides.

Ar and He are typically used as aggregation gases.

Positive features related to this source type are:
- large clusters can easily be produced, even > 20000 atoms
- relatively intense beams
- lower contamination of deposition chambers, UHV is possible
- a large fraction of the produced clusters are ionized (typically $\frac{1}{3}$ each positive and negative single charged, $\frac{1}{3}$ neutral), which allows for easy beam manipulation with ion optics

Negative features:

- not all materials can be used (gaseous clusters not possible)

2.1.3.4. Multiple ionization

Multiple ionization of clusters is almost impossible, as this causes a rapid redistribution of the charges on the atoms of the cluster, making each atom more positive. Due to this, the clusters become highly unstable and rapidly fragment in a very high-energy dissociation or explosion. The velocities of single fragments from this process, often called a Coulombic explosion, are very high.

One dramatic manifestation of this is the observation of nuclear fusion in deuterium clusters subjected to femtosecond laser pulses. The fragments after dissociation have energies up to 1 Mev, and can fuse upon collision!
2.1.4. Nanocluster applications

Applications of physically manufactured nanoclusters generally rely on the use of nanocluster beams and the deposition of clusters on surfaces with the help of these. The inherent properties of “free” clusters can therefore seldom by used, as this forced interaction with a substrate of some sort, which slightly alters the cluster properties, is almost always necessary.

The use of beams and deposition of clusters, however, opens new possibilities as the range of energy and mass deposition in cluster beams greatly differs from that of conventional ion beams and atomic or molecular beams.
The resulting features produced with cluster beams generally rely on the energy at which the clusters are deposited.

2.1.4.1. Low-energy deposition

When nanoclusters are deposited at low energies, they generally retain some memory of their initial shape. This is useful in the manufacturing of complex nanometer sized structures (e.g. quantum dots, magnetic domain structures, etc.)

In the development of potential applications for low-energy deposition one almost always strives towards the formation of structures which utilize the properties of clusters as they occur in a “free” state.
Another alternative, however, is direct utilization of the interaction between the clusters and surfaces, and structures resulting from these. It is for instance know that metal clusters of small enough sizes will align epitaxially (with the same lattice directions and structure) with a single-crystal substrate upon impact. This allows for the possibility of growing “perfect” thin films at low energies.

With larger clusters one can alternatively grow nanocrystalline films!

2.1.4.2. High-energy deposition

At higher deposition energies the usefulness of cluster beams is at its fullest. Irradiation with high
energy cluster ions can be used for instance in the manufacturing of high standard thin films, for shallow implantation of cluster material and surface cleaning.

Cluster ion beams are superior to conventional ion beam methods due to the high energy densities during bombardment and the low charge to mass ratio of clusters which leads to a more dense deposition of material at every impact. As a result of the simultaneous impacting of several atoms, multiple collisions occur at the impact point. This causes a very high increase in the local temperatures, which is suitable for the rearrangement of local atoms, at the same time as it limits the depths to which cluster atoms can penetrate into the substrate. Implantation depths for cluster ions are several times more shallow than implantation depths for single atom ions.
2.1.4.3. Surface smoothing

The high energy density associated with cluster ion impacts, coupled with a high degree of lateral sputtering and multiple near-surface collisions are ideal for smoothing surfaces. Cluster impacts cause local melting of existing surface structures, and flow of atoms into valleys on the surface.

Commercial cluster-smoothing equipment already exists!