Nanostructures and Nanomaterials: Characterization and Properties

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Kindly send your comments and feedback for improvement at this email address.
References

1. *Nanomaterials, Nanotechnologies and Design: an Introduction to Engineers and Architects*
   D. Michael Ashby, Paulo Ferreira, Daniel L. Schodek

2. *Handbook of Nanophase and Nanostructured Materials (in four volumes)*
   *Eds: Z.L. Wang, Y. Liu, Z. Zhan*

3. *Encyclopedia of Nanoscience and Nanotechnology*
   *Ed.: Hari Singh Nalwa*
Introduction to Nanoscience, Nanomaterials & Nanotechnology

Overview of Fundamental Concepts
What determines the properties of materials?

- Cannot just be the composition!
  - Few 10s of ppm of Oxygen in Cu can degrade its conductivity

- Cannot just be the amount of phases present!
  - A small amount of cementite along grain boundaries can cause the material to have poor impact toughness

- Cannot just be the distribution of phases!
  - Dislocations can severely weaken a crystal

- Cannot just be the defect structure in the phases present!
  - The presence of surface compressive stress toughens glass

The following factors put together determine the properties of a material:

- Composition
- Phases present and their distribution
- Defect Structure (*in the phases and between the phases*)
- Residual stress (*can have multiple origins and one may have to travel across lengthscales*)

These factors do NOT act independent of one another (*there is an interdependency*)

Hence, one has to *traverse across lengthscales* and look at various aspects to understand the properties of materials.
Properties are classified into *Structure Sensitive* and *Structure Insensitive* properties.

The key word to note is *sensitive* and not *dependent*.

- E.g. density would be *dependent* on the concentration of vacancies. But, usually the concentration of vacancies is small and density would not be *sensitive* to the presence of vacancies.
- Another example would be: Elastic modulus would not be a sensitive function of the dislocation density.
- On the other hand a structure sensitive property like yield stress would be strongly dependent on the presence (or absence of dislocations). The yield stress in the absence of dislocations would be typically of the order of GPa and in the presence of dislocations it would become of the order of MPa (*reduction by a few orders of magnitude*)!

In the usual sense the word STRUCTURE means **MICROSTRUCTURE** *(and not crystal structure etc.)*

In case of structure sensitive properties the *Defect Structure* in the material plays an important role in determining the properties.
What kinds of phases exist?

To understand the material behaviour one must have a through understanding of the phases and their distribution. That raises the next question as to what kind of phases exists and how can they be classified. A phase can be defined based on the structure (of atomic entities) or based on a physical property. When one comes across terms like 'ferroelectric' or anti-'ferromagnetic', it is viewing matter from the perspective of a physical property.
A few methods of classifying atomic form of matter are as in the figures below. Plasma and other non-atomic form of matter (like the stuff neutron stars are made of) are left out from the figure.
A simplistic look at the definition of crystals, quasicrystals (QC) and amorphous phases.

<table>
<thead>
<tr>
<th>Long range →</th>
<th>ORDERED</th>
<th>PERIODIC</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRYSTALS</td>
<td>✓</td>
<td>✓</td>
<td>Have 1, 2, 3, 4, 6-fold rotational symmetry + translation</td>
</tr>
<tr>
<td>QC</td>
<td>✓</td>
<td>×</td>
<td><em>Can</em> have symmetries disallowed in crystals + inflationary symmetry</td>
</tr>
<tr>
<td>AMORPHOUS</td>
<td>×</td>
<td>×</td>
<td>No symmetries present</td>
</tr>
</tbody>
</table>
Classification of crystals based on the bonding characteristics

In Molecular Crystals there are covalently bonded molecules (e.g. Fullerene- C_{60} molecules, iodine, water molecule, carbon dioxide, sucrose), which are bonded together by weak van der Walls bonds (or other weak interactions: hydrogen bonding/dipole-dipole bonding). It is to be noted that molecules can bond together to form amorphous materials as well. It is to be noted that melting of the crystal does not mean the dissociation of the molecule. On the other hand the non-molecular crystals are made of metallic, covalent or ionic bonds. Hence, they can have high melting points.

- Actual bonding in non-molecular crystals could have characteristics which are a combination of covalent, ionic and metallic
- Other weak interactions may mediate the crystal formation in molecular crystals
- The bonding responsible for the formation of a molecule may not be fully covalent.

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**Molecular crystals**
- Covalently bonded molecules forming a crystal with van der Walls bonds
  - e.g. Fullerene

**Non-molecular crystals**
- Covalent
  - e.g. Diamond
- Ionic
  - e.g. NaCl
- Metallic
  - e.g. Au, Fe

---

Diagram illustrating hexagonal ice and diamond cubic structures.
Bonding in Molecular crystals

Inter-molecular

- Hydrogen bond
- Van der Waals
  - Dipole-dipole
  - Dipole-Induced dipole
  - Instantaneous dipole-induced dipole
  - Ion-dipole
  - Cation-Pi
  - Pi-Pi

Intra-molecular

- COVALENT
  - \( \sigma, \pi, \delta \ldots \)

Relative strengths:
- dispersion forces < dipole-dipole interactions < hydrogen bonds

The term ‘Van der Waals forces’ is sometimes used for a specific type (London Dispersion) rather than the class.

Further reading

What kinds of bulk materials exist?

Between the component scale and the scale of phases comes the scale of the material. Materials can be monolithic or can be Hybrids.

- Composites: have two (or more) solid components; usually one is a matrix and other is a reinforcement
- Sandwich structures: have a material (material-1) on the surface (one or more sides) of a core material (material-2)
- Lattice Structures: typically a combination of material and space (e.g. metallic or ceramic forms, aerogels etc.).
- Segmented Structures: are divided in 1D, 2D or 3D (may consist of one or more materials).

It is to be noted that one or more of the parts of the hybrids can become nanosized. Examples include nanolayers in sandwiches, nanorods as reinforcement in composites, nanosized pores in lattices etc.

Functionally graded materials (FGM).

In FGM the properties are not uniform across the material; but change from position to position (graded), to fulfill certain needs of the component, which is location specific. This can be achieved by a change in composition, material, treatment etc. across the material. A classic example of this would be case carburized steels.
Atoms come together to form Many Phases.

Many Phases come together to form Molecules.

Many Microstructures come together to form Many Materials.

Many Materials come together to form Component.

Many Hybrids come together to form 'Atoms/molecules' to Bulk.
Microstructure → a functional definition (*across lengthscales*)

- Atom
- Structure
- Crystal
- Electromagnetic

Thermo-mechanical Treatments
- Casting
- Metal Forming
- Welding
- Powder Processing
- Machining

Component
- Avoid Stress Concentrators
- Good Surface Finish

Microstructure
- Phases + Defects + Residual Stress & their distributions

- Structure based
  - Crystalline
  - Quasicrystalline
  - Amorphous

- Property based
  - Ferromagnetic
  - Ferroelectric
  - Superconducting

- Vacancies
- Dislocations
- Twins
- Stacking Faults
- Grain Boundaries
- Voids
- Cracks

Processing determines shape and microstructure of a component
Importance of the distribution of phases

The distribution of phases is an important factor which determines the properties of a material. For a fixed volume fraction (or weight fraction) of phases present; the shape, connectivity and distribution of the phases will play a decisive role in determining the properties of the material.

Four distributions of phase-B (a brittle but hard phase) in phase-A (the tough phase) is considered.

Phase B can be nanosized

Cementite in steel along prior austenite grain boundaries

Intergranular glassy film in Lu-Mg doped Si$_3$N$_4$ sample
What is meant by Defect Structure?

- The term *Defect Structure* hides in it a lot of details (similar to the word *Microstructure*) and a lot of parameters have to be specified to characterize this term *(and then try and understand its effect on the properties).*
- The following points go on to outline ‘Defect Structure’:
  - Kinds of defects present along with their *dimensionality* (vacancies, dislocations, grain boundaries etc.)
  - The nature of these defects in terms of their origin: *Statistical* or *Structural*
  - The nature of these defects in terms of their position: *Random* or *Ordered*
  - Density and spatial distribution of these defects
  - *Interaction and association* of these defects with each other

Needless to say the task of understanding properties based on the defect structure is very difficult. The starting point would be to look at each defect in isolation and then put together parts of the picture.
Path to understanding Defect Structure

1. Take an isolated defect
   Stress fields, charges, energy etc.

2. Consider pair-wise interaction of defects
   Short range interactions* (Stress fields, energy, charge)

3. Behaviour of the entire ‘defect structure’ with external constraints
   Long range interactions & collective behaviour & external constraints**

*Examples of pair-wise interactions would include:
- Vacancy-vacancy interaction leading to the formation of a di-vacancy
- Vacancy cluster’s interaction with an vacancy leading to a larger vacancy cluster
- Dislocation interstitial solute interaction leading to the formation of a “Cotrell atmosphere”

**This is a difficult problem of materials science
- Example would include the collective motion of dislocations (along with their interactions) leading to plastic deformation and work hardening
In an elementary text it may not be practical to consider all the possibilities in detail. But, the student should keep in mind the possibilities and some of their implications on the properties or phenomena.
CLASSIFICATION OF DEFECTS BASED ON DIMENSIONALITY

0D (Point defects)
- Vacancy
- Impurity
- Frenkel defect
- Schottky defect

1D (Line defects)
- Dislocation
- Disclination
- Dispiration

2D (Surface / Interface)
- Surface
- Interphase boundary
- Grain boundary
- Twin boundary
- Stacking faults
- Anti-phase boundaries

3D (Volume defects)
- Twins
- Precipitate
- Faulted region
- Voids / Cracks
- Thermal vibration
SYMMETRY ASSOCIATED DEFECTS

- Translation
  - Dislocation
- Rotation
  - Disclination
- Screw
  - Dispiration

Atomic Level

SYMMETRY ASSOCIATED DEFECTS

- Mirror
- Rotation
- Inversion

Multi-atom

- Twins
Based on symmetry breaking

Hence association with symmetry

A DEFECT "ASSOCIATED" WITH A SYMMETRY OPERATION OF THE CRYSTAL

➢ TOPOLOGICAL DEFECT
- **Structural defects** play a very different role in material behaviour as compared to “Random Statistical Defects” (*non-structural*)
- Structural defects make certain kind of configurations possible in the material (and hence are *localized*).
- E.g.: Angular misorientation in grain boundary produced by an array of dislocations.
In principle any defect can get ordered

The ordering of defects is in principle no different from ordering of other species
- leads to a change in symmetry (and hence can lead to change in crystal structure)

Examples include:
- Vacancy ordering → Vacancy Ordered Phases (VOP)
- Stacking fault ordering

Once ordered a defect becomes part of the structure
- In the chapter on geometry of crystal we have seen that a crystal could be defined based on a geometrical entity (like atoms, molecules) or a physical property (like magnetic moment vector) or both.
- If the physical property is kept in focus, then the defect could be with respect to the physical property. E.g. in a ferromagnetic material magnetic moments are aligned inside the domain and they rotate into a new orientation in a domain wall (and hence domain wall is a defect associated with magnetic moment).
THE OPERATION DEFINING A DEFECT CANNOT
BE A SYMMETRY OPERATION OF THE CRYSTAL

E.g. a twin plane in a mirror twin cannot be a mirror plane of the crystal
Interstitial

Substitutional

Vacancy
Associated with stress fields

Missing Anion

Missing Cation

Schottky defect

Edge dislocation

Grain boundary in SrTiO₃

Surface

Terraces

Ledges

Kinks

Grain boundaries in SrTiO₃
No visible Grain Boundary

Dislocation structures at the Grain boundary

Fourier filtered image

2.761 Å

~8º TILT BOUNDARY IN SrTiO₃ POLYCRYSTAL
Mirror twins

Twinning of physical property

Geometrical entity

Twinning of magnetization vectors

Twin Plane

Twinning of atomic positions

Two ‘variants’ of the twin related by a mirror plane

Twin plane

Note: these are schematics
Rotation twins

Schematic of a rotation twin with a combined 5-fold symmetry

Note that these are mirror planes

Two ‘variants’ of the twin related by a 72° rotation
Schematic pictures with some defects

*Porous Alumina- a 2D crystal*

- Disclination
- Vacancy
- Low angle grain boundary
  *(with dislocations)*

Photo Courtesy- Dr. Sujatha Mahapatra (Unpublished)
Example

Effect of a fine distribution of second phase particles on the shear strength

Let us consider a distribution of 0.5\( \mu \)m sized incoherent precipitates in an Al-Cu alloy matrix. Assuming an average inter-particle spacing of 5\( \mu \)m, let us calculate the increase in shear strength. [Data: Lattice parameter of Al (\( a_{Al} \)) = 4.05 Å, The modulus of the Burgers vector (\( b_{Al} \)) = \( \frac{4.05}{\sqrt{2}} \) = 2.864 Å, Shear Modulus of Al (\( G_{Al} \)) = 25 MPa]. Note: \( \vec{b}_{Al} = \frac{a_{Al}}{2} [110] \).

For simplicity let us assume that the particles are spherical. Let us further consider a scenario, wherein for plastic deformation to take place, dislocations will have to bow around these precipitate particles (as the particles are incoherent dislocations cannot glide through the particles) by the famous Frank-Read (FR) mechanism. This gives rise to an additional strengthening effect, up and above that due to the solid solution strengthening. The stress required to operate the FR source (\( \tau_{FR} \)) is given by:

\[
\tau_{FR} = \tau_{\text{max}} = \frac{G b}{L} \quad \text{where, } L \text{ is the distance between the particles.}
\]
The distance between the particles (L) is seen to be 4.5 μm (figure below) and the increase is shear stress required for plastic deformation is:

\[
\tau_{FR} = \tau_{\text{max}} = \frac{(25 \times 10^9)(2.864 \times 10^{-10})}{4.5 \times 10^{-6}} = 1.59 \text{ MPa}
\]

For comparison the critical resolved shear stress (\(\tau_{\text{CRSS}}\)) for Al is 0.75 MPa. This implies that finer the distribution of particles, harder the material becomes.

![Diagram showing particle distribution](image)
A dislocation can be pinned between two incoherent precipitate particles (or in other ways), thus hindering the motion of the dislocation. For motion of the dislocation, leading to plasticity the dislocation has to bypass the pinned segment, under the action of the applied stress (shear stress on the slip plane drives the motion).

The dislocation takes a series of configurations (as shown in the figures) under the action of the applied stress → leading to the formation of a dislocation loop (leaving the original pinned segment).

This leads to an increase in dislocation density (one of the mechanisms by which dislocation density increases with plastic deformation).

As the original segment is retained the ‘source’ (Frank-Read source) can operate repeatedly forming a loop each time.

As the preexisting loops would oppose the formation of the next loop (repulsive stresses-dislocations of the same sign), higher stresses are required to operate the source each time.

Till the formation of the half-loop (semi-circle), increasingly higher stresses are required. After this the process occurs downhill in stresses.

The maximum stress ($\tau_{\text{max}}$) required to operate the source thus corresponds to the formation of the half-loop (with radius $r_{\text{min}}$).

$$\tau_{\text{max}} \sim \frac{Gb}{2r_{\text{min}}}$$
Initial configuration

Dislocation line segment pinned at A and B by precipitates*

* Pinning could (also) be caused by:
  - Dislocation in the plane of the paper intersects dislocations in other planes
  - Anchored by impurity atoms or precipitate particles
  - Dislocation leaves the slip plane at A and B
As the dislocation line gets curved the energy of the system increases ⇒ work has to be done by external stresses to cause this extension.

- Line tension (opposes the shear stress on the slip plane \( \tau \)). At a given stress there might be a balance of forces leading to a curved geometry of the dislocation line.
- Further extension of the dislocation line occurs by increasing the stress.

**Force on dislocation line** = \( \tau \, b \, ds \)

**Line tension force** = \( 2 \gamma \, \sin\left(\frac{d\theta}{2}\right) \sim \gamma \, d\theta \)

For equilibrium in curved configuration

\[ \gamma \, d\theta = \tau \, b \, ds \]
Increasing stress

Direction of dislocation motion is \( \perp \) to the dislocation line (except at A and B)

Increasing stress

semicircle → corresponds to maximum stress required to expand the loop

After this decreasing stress is required to expand the loop

+ and – segments come together and annul each other

Original segment

New loop created
Frank-Read dislocation source

- Can operate from a single source producing a loop each time
- This loop produces a slip of $1b$ each time on the slip plane
- The maximum value of shear stress required is when the bulge becomes a semi-circle ($r_{\text{min}} = L/2$) → $\tau_{\text{max}} \sim Gb/L$
  ⇒ $\tau \downarrow$ as $L \uparrow$ i.e. The longest segments operate first
  ▶ When the long segments get immobilized shorter segments operate with increasing stress
    ⇒ work hardening
- If the dislocation loops keep piling up on the slip plane the back stress will oppose the applied stress
- When the back-stress $> \tau_{\text{max}}$ the source will cease to operate
- Double ended F-R sources have been observed experimentally they are not frequent ⇒ other mechanisms must exist

Orowan bowing mechanism

$$\tau_{\text{max}} = \alpha Gb / L$$

$\alpha = 0.5$ for edge dislocations and $\alpha = 1.5$ for screw dislocations.
This is an interesting concept to explore.

We will consider some examples to explore this concept.

0D
- Vacancy is a point defect. Vacancies can get ordered to form Vacancy Ordered Phases.
- There could be a point defect in the Vacancy sublattice → an atom present where a vacancy should have been there (Atom is a defect in the vacancy sublattice!) → this is a defect in a defect!

1D
- Dislocation is a defect.
- A kink or a jog is a defect in the dislocation line → a defect in a defect.

2D
- Surface is a defect.
- Defect in a defect → Steps in a surface is a defect in the surface.
- Defect in a defect in a defect → Steps in these steps is a defect in the steps.
In a Vacancy Ordered Phase (VOP) there could be a vacancy in the ‘vacancy sublattice’ → this is an atom!

we can conceive such a hierarchy of ‘higher order’ defects!
We can even further visualize things like a kink in the jog!
Defect in the surface

Defect in the Ledges

Terraces

Ledges

Terraces

Ledges

Kinks
This is another interesting concept
We will try to understand this using the example of VOP
We have seen that an atom is a defect in the vacancy sublattice of the VOP.
These atoms could be randomly present in the vacancy sublattice or be ordered in the sublattice to give a sub-sublattice
A defect in this atom sub-sublattice of the vacancy sublattice is again a vacancy!
This process of formation of defects in ‘sub’, ‘sub-sub’ … can be carried forward and we can conceptualize this hierarchy of defects!
Defects can exist in isolation or can be associated with each other.

- Defects of one dimensionality (e.g. 0D defect: interstitial atom) can associate with a defect of another dimensionality (e.g. 1D defect: dislocation).
- The association takes place to reduce the energy (i.e. the ‘Defectiveness*’ of each of the defects is reduced) \( \Delta H \) is negative
  (the \( \Delta \rightarrow \) difference is between the unassociated state and the associated state).
- This association (whenever it occurs!) leads to a reduction (↓) in the entropy of the system → if the defects were independent then the number of configurations would be more than if they are associated (as they can configure independently)
  \( \Delta G = \Delta H - T\Delta S \)
  due to association:
    - \( \Delta H \) is negative → ‘helps’ the process
    - \( \Delta S \) is negative → opposes the process

As we started with the assumption that the association does occur this implies that at the given temperature \( \Delta G \) is negative (the enthalpy effects dominate).

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* Defectiveness has been used casually in this context. Heterogeneous nucleation (e.g. of precipitates at GB) can also be thought of in these terms (i.e. when a precipitate nucleates in the middle of the grain there are two defects in the perfect crystal- the GB and the precipitate. When the nucleation occurs at the grain boundary, then the defect association makes each of these defects less defective- thus lowering the energy of the system).
Long range interaction between the defects can* take place through their stress fields and if ‘kinetics permits’ then the one or both of the defects may move and get associated.

* Depends on ‘how long-range’ the stress fields of the two defects are
Di-vacancies

- Roughly speaking, formation of a divacancy leads to a lesser number of bonds broken (6 broken bonds instead of expected 8 for two separate vacancies) and hence a lower energy. However, this will lead to a decrease in the entropy of the system (as compared to two mono-vacancies). This implies that minimization of Gibbs free energy will dictate the number of divacancies which are present at a given temperature.

- Hence at any temperature there will be an equilibrium concentration of mono-vacancies, di-vacancies and higher association of vacancies.

- Higher the temperature more will be the preference for dissociation of associated vacancies.

Examples of defect association

\[ \text{Two mono-vacancies} \Rightarrow 8 \text{ broken bonds} \]

\[ \text{Di-vacancy} \Rightarrow 6 \text{ broken bonds} \]

These are schematics: in the actual situation local relaxations will occur and will be more complicated.
Dislocation point defect association

- We shall consider the example of an interstitial atom (Carbon) in BCC Fe → associated with compressive and shear stress fields.
- The carbon atom can be attracted towards the tensile stress field of an edge dislocation → segregation of C in the core region of the dislocation (formation of the Cottrell atmosphere).
- The energy of the associated defect (dislocation-interstitial) is lower than the independent defects ⇒ if the dislocation has to move, then the external stress has to do additional work to pull the dislocation out of the ‘energy valley’. (Once the dislocation has broken free then lower stress is required to move the dislocation- until of course this ‘locking’ again takes place)
- This leads to the well known effect of Yield Point Phenomenon.
- Vacancies (0D) can also be attracted to the compressive regions of the edge dislocation (1D) stress fields → leading to climb of edge dislocation (*plays role in phenomenon like creep*)

\[ \varepsilon \rightarrow \sigma \rightarrow \]
Substitutional atom Grain boundary association

- Substitutional atoms which are insoluble in the grain tend to segregate to the grain boundaries.
- Grain boundaries being regions of higher free volume can better accommodate the substitutional atoms.
- As in the case of the interstitial solute atom-dislocation association, this combination association of substitutional atom with the grain boundary leads to a lowering of energy.
- This solute segregation leads to a ‘pinning effect’ on the grain boundary → the grain boundary feels a ‘drag’ if it tries to migrate (move).
  (This is similar to the pinning effect of interstitial solute atoms on the dislocation which ‘wants’ to move.)
Dislocation-dislocation association

- There are many ways in which dislocations can associate with each other. Here we shall consider an interesting example which we have already dealt with before.
- Dislocations can arrange in an array one below another to form a wall → the low angle grain boundary. This can happen during recovery* of a cold worked* material.
- Compressive stress field of one dislocation partly annuls the tensile stress field of an adjacent dislocation in the wall → thus reducing the energy of the configuration (such a wall does not have very long range stress fields).

* We will be exposed to these terms in later chapters
Dislocation-interface association

- Hetero-epitaxial interfaces (schematic below) are associated with misfit stresses*. Misfit dislocations may partly alleviate these stresses. Misfit dislocations are structural dislocations.
- There will be an array of misfit dislocations decorating the semi-coherent interface (*dislocations per unit length along 1D*)
- If the strain is biaxial (as usually is) then there will be more arrays at an angle to the first array.

* entire film and part of the substrate will be under stress as shown in FEM calculation above (finite substrate)
Precipitate- grain boundary association

- In this case the association could take place due to nucleation at the grain boundary of the precipitate or a moving grain boundary being associated with the precipitate. (A growing precipitate may also touch a grain boundary).
- Once the association has occurred, grain boundary diffusion may help in the growth of the precipitate
Microstructure

- Phases
- Defects

Defects

- Vacancies
- Dislocations
- Twins
- Stacking Faults
- Grain Boundaries
- Voids
- Cracks

Residual Stress

Residual Stress can be beneficial (+) or detrimental (−)
E.g.

\[ \Rightarrow \text{Stress corrosion cracking} \]
\[ \Rightarrow + \text{Residual Surface Stress} \]

Physical properties

- Thermal
- Magnetic
- Ferroelectric

Geometrical entities

- Residual Stress
- Phase Transformation & reactions
- Defects

Thermal origin

- Mismatch in coefficient of thermal expansion

Macro-scale

Based on scale

Micro-scale
Residual stresses due to an edge dislocation in a cylindrical crystal

Due to phase transformation

Residual stresses due to an coherent precipitate

Due to a dislocation (a crystallographic defect)

Stress state (plot of $\sigma_y$) due to a coherent $\gamma$-Fe precipitate in a Cu–2 wt.%Fe alloy aged at 700 C for (a) 30 min.

Simulated $\sigma_y$ contours

All values are in GPa

Due to phase transformation
Importance of residual stress

- Residual stresses are those which arise in a body in the absence of external loads or constraints.
- Processing will influence all the three origins of residual stress.
- These origins also represent various lengthscales.

  Vacancies and dislocations give rise to stress fields at the atomic scale, while residual thermal stresses could pervade the entire component.

Some points in this regard are:

a) the stress fields associated with GP zones in Al-Cu alloys is of the same scale as dislocation stress fields
b) large cracks in the material can lead to macroscopic stress fields, while microcracks may have much small effective region of stress fields
c) in micron sized components, the scale of thermal residual stress may is expected to be smaller than that in their large scale counterparts.

- In the example of GP zones in Al-Cu alloys, the stress/strain fields are intricately associated with the distribution of GP zones (~ the phases); which further highlights the importance of adopting a definition of microstructure as done in here.

[Note. Cracks themselves are not sources of stresses; they merely amplify a far field stress. As they can amplify a small far field stress (which could be residual in nature), they have been included in this section].
The reason for elevating residual stress to be an integral part of the definition of microstructure will become further clear in the next two examples considered.

- It is well known that nucleation is preferred at any of the high-energy sites in a material (heterogeneous nucleation). Typical examples of heterogeneous nucleation sites are: surfaces, internal interfaces (grain boundaries, interphase boundaries, stacking faults etc.), crystallographic defects (dislocations), cracks, voids etc. Stressed (and hence strained) regions also can act like heterogeneous nucleation sites.

- In corrosion formation of a galvanic cell leads to corrosion of the anode. At the level of the individual phases, one phase may be more anodic as compared to another, thus forming a 'micro'-galvanic cell. Similarly, tensile regions in the sample may behave anodically with respect to compressive regions in the sample which can behave cathodically.
Often one gets a feeling that residual stress is *only* harmful for a material, as it can cause warpage of the component—this is far from true. Residual stress can both be beneficial and deleterious to a material, depending on the context. Stress corrosion cracking leading to an accelerated corrosion in the presence of internal stresses in the component, is an example of the negative effect of residual stresses. But, there are good numbers of examples as well to illustrate the beneficial effect of residual stress; such as in transformation toughened zirconia (TTZ). In this system the crack tip stresses (which are amplified over and above the far field mean applied stress) lead to the transformation of cubic zirconia to tetragonal zirconia. The increase in volume associated with this transformation imposes a compressive stress on the crack which retards its propagation. This dynamic effect leads to an increased toughness in the material. Another example would be the surface compressive stress introduced in glass to toughen it (Surface of molten glass solidified by cold air, followed by solidification of the bulk $\rightarrow$ the contraction of the bulk while solidification, introduces residual compressive stresses on the surface $\rightarrow$ fracture strength can be increased 2-3 times).
At the atomic level there is order only in the average sense (at $T > 0\text{K}$) as the atoms are constantly vibrating about the mean lattice position. Hence, in a strict sense the perfect order is missing (a). The unit cell level is the level where the atomic arrangement becomes evident (crystal structure develops) and concepts like Burgers vector emerge, b. It is at this level that averaging with respect to probabilistic occupation of lattice positions in disordered alloys is made (say Ni$_{50}$-Al$_{50}$ alloy is defined by a 50-50 probability of Ni or Al occupying a lattice position). At the grain level (c, which is a single crystal), there is nearly perfect order (as the scale of atomic vibrations are too small compared to grain scale); except for the presence of defects like vacancies, dislocations etc. At this scale the material is also anisotropic (e.g. with respect to the elastic stiffness, which is represented by three independent numbers: $E_{11}$, $E_{12}$ & $E_{44}$). It is to be noted that the Cu crystal may be isotropic with respect to other properties. At the material level (d), assuming that the grains are randomly oriented, there is an averaging of the elastic modulii and the material becomes isotropic. At this scale, the crystalline order which was developed at the grain level (c) is destroyed at the grain boundaries and there is no long range order across the sample. When the material is rolled or extruded, it will develop a texture (preferred directional properties), which arises due to partial reorientation of the grains. That is, we have recovered some of the inherent anisotropy at the grain scale. As we can see, concepts often get 'inverted' as we go from one lengthscale to another.
Atoms are constantly vibrating (at $T > 0K$)
Order only in the average sense
Hence, the ‘perfect’ order is missing
The unit cell level is the level where the atomic arrangement becomes evident (crystal structure develops) and concepts like Burgers vector emerge.
Microstructure

- Nearly perfect order (scale of atomic vibrations are too small)
- Presence of defects like vacancies, dislocations etc.
- Material is anisotropic (e.g. with respect to the elastic stiffness, which is represented by three independent modulus vectors: $E_{11}$, $E_{12}$ & $E_{44}$)
- Crystal may be isotropic with respect to other properties
Assuming that the grains are randomly oriented
Averaging of the elastic modulii and the material properties are isotropic
Consider a magnetic material (E.g. Fe, Ni) below the Curie temperature (but $T > 0K$), where it is ferromagnetic in nature. In this condition the atomic magnetic moments try to align, but thermal effects lead to partial disordering. This takes place within regions in the sample called domains which are typically of micrometer size. The configuration of the domains is in such manner so as to reduce the magnetostatic energy. This arrangement of domains, wherein they are not preferentially aligned, leads to no net magnetization of the sample. Hence the story as we traverse lengthscales is:

- Atomic magnetic moments ($m_{\text{atomic}}$)
- Less magnetization in a domain than the number of atomic moments (domain) (say if $n$ atoms are there, then the net magnetic moment within a domain $\neq n \times m_{\text{atomic}}$; turns out to be less than $n \times m_{\text{atomic}}$)
- No net magnetization at the sample level.
In this example there will be a synthesis of concepts which have been presented before. It will also become amply clear as to how different length scales 'talk' to each other to determine a property. Let the component be a gear wheel, which requires good surface hardness and abrasion resistance; along with good toughness (for shock resistance). For simplicity assume that it is made of plain carbon steel (alloy of Fe and 0.1-2.0 %C). The Fe atom has a propensity for metallic bonding which ensures good ductility, thermal conductivity etc.; but, is soft compared to (say) a covalently bonded material (e.g. diamond). This 'softness' is also directly related to the metallic bond, which leads to a low Peierls stress. This ductility further helps in improving the microstructural level properties like tolerance to cracks (high fracture toughness). Sharp crack tips (e.g. in window pane glass), lead to high stress amplification (high stress intensity factor), which results in much lower stresses for causing fracture. But, when a crack tip gets blunted due to plastic deformation, it reduces the stress amplification and enhances the toughness of the material. The ease of deformation and good tolerance to cracks implies good ductility in a material. This available ductility is useful in the deep drawing/forming of the component (such as making long-form containers).
Pure Fe at room temperature has a BCC lattice; which implies that it has a higher Peierls stress (harder/stronger) as compared if it were FCC Fe (which will happen if you heat Fe beyond ~910°C). This is because Peierls stress is a strong function of the Burgers vector, which is determined by the crystal structure. Hence, there are two sides to the Peierls stress: one coming due to bonding characteristics and the other from the crystal structure. In the Fe-C alloy, C sits in the interstitial position (the octahedral void in BCC Fe) and gives rise to solid solution hardening. The slowly cooled alloy has a mixture of $\alpha$ (BCC solid solution) and Fe$_3$C (a hard phase) phases; which makes the microstructure harder than that of a single phase alloy. The surface of the gear wheel is carburized (Figure, i.e. increased carbon concentration at surface) and the wheel is quenched to produce a different phase of the Fe-C alloy: the Martensitic phase. Martensite is hard (but brittle) and provides the requisite surface hardness to the wheel; while the interior continues to be tough. This would constitute an early example of a functionally graded material.

At the component level, the similar concepts of toughening (via design features) should be incorporated, like there should be no sharp corners in the component (similar to cracks). Sharp corners will act like stress concentrators, which will become zones where cracks will initiate (at micron-scale) and might rapidly propagate to result fracture of bulk component.
Before we proceed to the exciting realm of the nano-worlds, it is necessary to learn the definition of a few important terms in this context. (The hyphens in the terms may not be used in many places).

**Introduction to Terminology**

- **Nano-**
  - In day-today terminology, the term ‘nano’ is quite often loosely used. Nano is just a prefix to define a factor of $10^{-9}$.
  - The term nano, by itself, is not a measure of length, mass, or time and hence should be used as a prefix to standard units. E.g. nanograms would mean $10^{-9} \text{g}$, nanohertz will mean $10^{-9} \text{Hz}$, and so on.
  - In the context of nanomaterials it denotes the size range between 1-100 nano-meters.
    - Literally → a factor of $10^{-9}$ (usually $10^{-9} \text{m}$).
    - Practically → the range of sizes from 1-100 nanometers (nm).

- The most important aspect of “nano-” is the appearance of interesting properties (often unexpected), which are absent in their bulk counterparts.
The term ‘nano-material’ usually implies that one or more of the components (entities) which make up the material are nanosized. These components could be grains, nanotubes, nanospheres etc.

Examples
- Nanocrystalline copper: the material itself is ‘bulk’, but is made up of grains which are nano-sized.
- A crystal made up of SiO₂ nanospheres (the nanospheres may themselves be amorphous)

This is to be contrasted with free-standing nano-structures.

Anything 'nano'. Used as general term, where specificity is being avoided.
Nanoscience is the ‘study’ of the fundamental principles of nanomaterials (molecules and structures with at least one dimension between 1 and 100 nm). This includes the physical, chemical and biological aspects of nanoentities. The study of nanomaterials has extended the frontiers of science and has warranted the existence of a new domain of research called nanoscience. Research in nanoscience (coupled with nanotechnology) has fueled the growth of conventional scientific disciplines as well.

- Example → Understanding the physics of superparamagnetism appearing on the reduction of the size of Iron nanocrystals because of easy alignment of nano-domains along the external applied magnetic field, which otherwise would be ferromagnetic in nature.
Nano-technology

In the broadest sense, nanotechnology is the application of the principles of nanoscience into useful deliverables. This includes the application of nanostructures/nanomaterials into useful nanoscale devices and components. Further, by tailoring (or manipulating) the concepts of nanoscience, nanotechnology aims at improving the lifestyle of the human race. It must be pointed out that the applications include those, which otherwise would not be possible with the use of conventional technology.

- Examples
  - a microchip that can be inserted into body for controlled drug-delivery
  - engineering exceptionally tough ropes for construction of space-elevators
Recently, a new term 'nano-manufacturing' is gaining wide attention, where nano-entities are to be manipulated (retaining their nano-structure) to evolve/manufacture nano/macro components. If the benefits of nano-science have to reach masses, "nano-manufacturing" has to play the key role. Physicists and Chemists have been doing science at the nanoscale for a long time now; but it is only with the advent of modern microscopes (FE-SEM, HR-TEM, AFM, SPM) and machining tools (E-beam Lithography and FIB) that it has become possible to manipulate and engineer atoms/nano particles to make a component or device. Nanomanufacturing falls under the general scope of 'nanotechnology'.

Example → Field emission gun can fuse the end of carbon nanotubes (CNTs) to a specific DNA and extract signals by applying a small current/voltage. This can act as a sensor for any genetic diseases that might be in its incipient stage. This is possible only because of manipulation ability at nano-scale.
A particle with size in the range of 1-100 nm is a nano-particle. It is typically an independent entity which exists in isolation. However, it may be present as a part of a composite. The importance of nanoparticles is not diminished even when they are embedded in a bulk matrix (such as their role in accelerated catalytic conversion) or dispersed in a solution (e.g. in determining the colour of colloidal dispersion of gold nanoparticles in a liquid medium).

- **Literally** → Single nano-entity which behaves as a complete unit.
- **Practically** → A nanoparticle can be a single crystal, quasicrystal, polycrystal or even amorphous.
- **Examples** → particles of amorphous alumina, crystalline gold, AlCuFe icosahedral quasicrystals.

**SiO₂ nanoparticles on glass substrate**

The nanoparticle may have sub-components

Nano-particle ~300 nm in diameter
Nano-crystal

- Typically free-standing monocrystalline nanomaterial with at least one dimension in the size range of 1-100 nm. It must be noted that a micro-meter sized particle can have multiple regions of crystallinity, and should not be termed as nanocrystal.
  - Examples → Gold nanocrystals, Diamond nanocrystals, etc.
  - In addition, these crystals could also be embedded in a matrix (such as Pb nanocrystals particles in Al matrix).

Al6061 was severely deformed and then heat treated at some low temperature (close to 200°C) to allow for nano-precipitates to form. This HRTEM image is shows one such precipitate.

Photo Courtesy- Prof. Shashank Shekhar
Nano-structure

- Nanostructure is a structural/geometrical entity with a distinct shape having at least one of the dimensions in the nanoscale.
- Nanostructures have a specific geometry.
- Carbon nanotubes (CNTs), fullerenes, carbon onions, nano-fibers ZnO, and nano-spheres are few of the most common nanostructures. Biology is abound with examples of nanostructures; this includes DNA double helix-structure (size of DNA single strand 2.2-2.6 nm), bacterial cell wall, protein nanolayers in nacre.
- Examples: Nanosphere, nanopillar, nanocage, fullerene, nanofiber, nanoflake, nanoring, nanobelt, nanohelix, nanobows, nanosphere, nanotube, quantum dot, micelle, nanocone, nanoflower, nanobrushes, etc. (*Bloch walls in ferromagnetic materials have a thickness in nanometers*).

![Pillars obtained by focused ion beam lithography of a thermally evaporated Gold film 200nm in thickness (on glass substrate). Size ~200nm.](image1.png)

**Carbon Nanotubes**

- 94% pure CNTs
- 40-70 nm Outer Dia
- Length 0.5-2 μm

Micrograph courtesy: Prof. S.A. Ramakrishna & Dr. Jeyadheepan, Department of Physics, I.I.T. Kanpur
The phase being referred to here can be crystalline, quasicrystalline or amorphous. While defining a phase, it was pointed out that it could be based on a property rather than a structural entity. Hence, the nanophase could be a magnetic phase or a ferroelectric phase.

- **Examples**
  - Amorphous nano-grain boundary film in Silicon Nitride ceramics, $\theta$" precipitates in Al-4%Cu alloys,
  - Superparamagnetic clusters in 90%Zn-10% Ni ferrite.

High-resolution micrograph from a Lu-Mg doped Si$_3$N$_4$ sample showing the presence of an Intergranular Glassy Film (IGF).
Nano-composite (Often used synonymously with hybrids)

- Is a composite of two materials, where at least one of them is a nano-sized. Often a synergistic enhancement in terms of properties is achieved on the formation of a composite.
- Examples → Carbon nanotubes (CNTs) reinforcing alumina (matrix), nano-particles of alumina in a bulk Ni matrix, and nano-protein layer sandwiched between calcite layers in an abalone shell.

- Fibre diameter in the nanoscale
- Pore size in the nanoscale
- Layer thickness in nanoscale

Hot Isostatically Pressing at 1773 K for ~3.1 h in argon pressure of 172.4 MPa) of Plasma sprayed Al₂O₃-4 wt.% CNT composite
Nano-porous materials

- Porous materials are a subset of hybrids called lattice structures, which are a composite of matter and voids. The pores may be isolated or interconnected. If the porosity size is in the order of few nanometers, the material is termed as a nano-porous material. Often, thermo-mechanical treatments may result in isolated pores a few nanometers in size. Such materials typically are not included in nano-porous materials.

- Examples →
  - Anodized aluminum oxide templates with hexagonal arrayed nano-pores
  - Atomic layer deposition of ZnO layer leaving nanopores on membranes
  - Nano-pores in nano-filtration membrane to filter bacteria from water
Additional ‘nano’ terms

- Additional terms with "nano" in them are:
  - nano-size
  - nano-chemistry
  - nano-mechanics
  - nano-tribology
  - nano-ethics
  - nano-fluidics
What else can be nano?

Nano-cracks

Nano-indentation

Nano-surface steps

Zigzag spiral structure made of MgF₂ on glass slide substrate by electron beam deposition.

Photo Courtesy- Ms. Jhuma Dutta & Prof. Anantharamakrishna

Hot Isostatically Pressed Al₂O₃ at 1773 K for ~3.1 h in argon pressure of 172.4 Mpa.

Photo Courtesy- Prof. Shashank Shekhar
What is ‘nano’ in ‘nano’?

- Given the diverse variety of terms associated with ‘nano’ and their usage in specific contexts, it is important to know what is ‘nano’ in ‘nano’. Some examples are considered to clarify the point.

- A collection of free-standing Fullerene molecules (C60, C80 etc.): this represents a collection of nanostructures.

- A collection of free-standing diamond crystals: these are just nanocrystals. We can visualize a collection, wherein only some of the crystals are nanosized and the remaining are larger. There could be two different types of crystals in the collection (say diamond crystals and NaCl crystals- only one of which could nanosized (say the diamond crystals).

- Micron sized particles which are an assemblage of nanocrystals: here the particles are not nanosized; but the crystals which join together to form the particle are nanosized. The bonding between the nanocrystals could be weak or strong.

- A polycrystal with nanosized grains, which can be terms as a 'nano-polycrystal': this is in some sense an extension of the above. Here there is a macro-sized material which is made up of nanometer sized grains. Herein again we can visualize a range of grain sizes, at least some of which are nano (to qualify an entry here).
Nanostructures or nanocrystals embedded in a matrix: the matrix may be amorphous or polycrystalline or even a single crystal (of course with interruptions to its crystallinity in the form of the second nanostructure or nanophase). The point to note is that only the second entity is nanosized and not all the components. Taking this further we can construct a material which has nanostructures embedded in a nano-polycrystal.

Some of the domains in ferromagnetic materials could be in the nanometer size range; while, the grain size could be in microns. Additionally domain walls (Bloch walls) in ferromagnetic materials typically are few 100 atomic diameters wide.

Pore size in a lattice structure (lattice as in a hybrid and not with relation to crystal lattices), such as pores in anodic aluminium oxide template.

Micelles, a collection of hydrophobic heads and hydrophilic tails (of molecular chain) aligned as a sphere of hydrophobic heads merging as the central-cluster with their tails dangling out.

Nanoentities of biological origin: DNA, while the nucleus of the cell could be in few nanometers ~ 2-3 nm), Virus (5-300 nm) , cell walls (while the cell itself could be a few micrometers in size)
Core-shell nanostructures, nanoflower, nanospring, nanorods and quantum dots also fall under the class of nanostructures.

Sometimes, the structure itself may not be nano-meter sized, but the resulting response might resemble that occurs at nano-length scale. For example, when current is driven through micron sized rods, it may behave like a nanosized conductor as far as the conduction property along the axis of the rod is concerned. This may happen in particular systems under certain voltages. To reiterate the structural entity is not nanoscale but the manifestation of a physical property could be as-if the material is nanoscale. Another familiar example of this would be the conduction of alternating current leading to the 'skin effect'. When the frequency is in the range of 100s of GHz, the skin depth is of the order of 100s of nm.

Nano-roughness: in this case the surface roughness is in the nanoscale (i.e. it may so happen that nothing within the bulk is in the nano-scale).
The region with residual stress could be in the nano-scale. E.g. the solidification of liquid glass could be carried out in such a fashion that the compressive region on the surface of glass could be a few 100s of nanometers. Epitaxial films (which can be grown to a thickness of a few hundred nanometers can be in compressive or tensile stress (e.g. in the case of GeSi film on Si substrate, the film is under compressive stress). The stress in the GeSi film can be used to engineer the bandgap of the material.
What is 'Bulk'?  

1) What are 'bulk nanostructured materials'? 

The phrase seems an apparent contradiction in terms. What is implied is that the material under consideration is bulk (i.e. it is of 'tangible size'; typically size > 1mm in any dimension), but it is made of 'some unit' which are in the nanoscale. Typically, this phrase is applied to bulk materials with grain size in the nanometer regime. E.g. a Cu wire 2mm in diameter with grain size of 100nm.

These materials with a nanometer sized microstructure are referred to by many equivalent terms: (i) nano-structured materials, (ii) nanophase materials, (iii) nanocrystalline materials (usually a more restrictive term as compared to (i) & (ii)).
2) What are 'bulk properties'?

As we have noted, some properties can change drastically when a relevant dimension in the material is reduced to the nanoscale. On the contrary, in bulk materials of different sizes (e.g. a 1cm cubical copper block or a 1m diameter copper sphere) properties are not size dependent (assuming that all other aspects except size are the same in the samples).

However, many of the properties may show 'bulk-like' behaviour even when the relevant dimension is reduced to the nanoscale. E.g. dielectric permittivity (or refractive index) of glass does not change much even when the size of a sample is reduced to 100nm. Additionally, much of the physics describing the 'bulk system' (including the equations which arise from the 'physics') may be applicable to the small scale system as well. E.g. the equations describing stress field of dislocations (derived from linear theory of elasticity and valid outside the core of the dislocation) for bulk crystals, can also be used for 100nm crystals. We have already described an effect exactly opposite to this one: i.e. the structure is 'bulk' but the property is in the 'nanoscale' (e.g. 'skin effect' when high frequency alternating current is passed through a 'bulk' wire).

\[
\sigma_{x, \text{edge dislocation}} = \frac{Gb}{2\pi(1-\nu)} \frac{y(3x^2 + y^2)}{(x^2 + y^2)^2}
\]
Nanomaterials can be classified based on the dimension of the entity which is nanosized. To impart special properties to component/material all the parts of the material need not be nanosized. Additionally, the parts need not be nanosized in all the three dimensions. Of course at least one of the parts has to be nanosized at least in one dimension, in order to impart the special property (ies) which arises due to the size factor (and to warrant its inclusion here!). Next slide shows a classification based on the dimension of the nanoentity. Two ways of looking at dimensionality is to look at the number of dimensions which are bulk or the number of dimensions which are nanosized. Examples are:

- Composite of carbon nanotubes (2D nanostructure) reinforcement in a ceramic matrix (Al₂O₃).
- Epitaxial layer of Nb of nanometer dimensions (1D nanostructural metal) on a sapphire substrate (Al₂O₃, ceramic)- which is like a one dimensional sandwich structure.
- Carbon nanofoam (a lattice structure of carbon clusters and lot of void spaces).
<table>
<thead>
<tr>
<th>Number of nanosized dimensions ( \text{nano-D} = nD )</th>
<th>Number of bulk dimensions ( D )</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 ((\text{Nanoparticles, nanocrystals}))</td>
<td>0</td>
<td>Nanocrystals of gold</td>
</tr>
<tr>
<td>2 ((\text{Nanowires, nanorods, nanotubes}))</td>
<td>1</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>1 ((\text{Nanolayers, nanofilms}))</td>
<td>2</td>
<td>SiGe epitaxial layer on Si substrate</td>
</tr>
<tr>
<td>0</td>
<td>3</td>
<td>Bulk single crystal of silicon</td>
</tr>
</tbody>
</table>
**Dimensionality of a system** (How many dimensions does an object have?)

We have already addressed the question: "what is a bulk material". We had noted that 'bulk' can be usefully defined by considering a given property. Similarly the question can be asked: 'what is the dimensionality of a system?'. We live in a 3D world and hence all tangible objects are 3-dimensional. Graphene (a single layer of graphite) is nearly an ideal 2D crystal (i.e. the thickness being just one atomic layer).

But, with respect to properties or their variations we can effectively call a material or structure as 2D or even 1D. A cantilever beam with \( L/D > 20 \) is called a thin beam and the variation of shear stresses in the radial direction during bending can be neglected for this case. This implies that the beam is effectively treated as a 1D beam. A 3D plate with one dimension much longer than the other two can be treated as 2D one with respect to strain (i.e. it is in *plane strain* condition).

In nanomaterials there are similar concepts which are applicable. In the case of Ni films on Cu(100) substrates, when the thickness of the Ni film is greater than 7 monolayers (ML) the systems behaves as a 3D Heisenberg ferromagnet and below 7ML it behaves like a 2D system. In the 2D system all the spins are in the plane, while in the 3D system out of plane spin (cants out of plane) orientation is also observed.
### What is new about Nano?

- Purists and pundits alike will point out that 'nano' always existed. Some examples confirming their assertions are:
  - Stained glass (F-centres and nano-crystals to provide colour/stain to transparent colourless glass).
  - GP zones (strengthening coherent/semi-coherent precipitates in Al-Cu alloy to provide enhanced strengthening/hardness).
  - DNA (basic genetic molecule present in all the living organisms).
New effects and phenomenon not observed in bulk counterparts are observed in nanomaterials. A few of the “new” aspects about nano are:

- **Inverse Hall-Petch effect**
  It is well established that decreasing the grain size results in an increased hardness and strength as grain boundaries pose an impediment to dislocation motion (dislocation 'pile-up mechanism- the usually accepted mechanism!). But, when grain size reduces to tens of nanometers (< 15 nm) the grain is not able to support a dislocation pile-up. Hence the trend of increasing hardness/strength with a decrease in grain size is broken in the nanocrystalline materials. The are even reports in literature of decreasing strength with decreasing grain size at very small grain sizes (< 5 nm).

- **Giant Magnetoresistance**
  Giant magnetoresistance is the dramatic decrease in the electrical resistance on the application of magnetic field, in an otherwise antiferromagnetic hybrid. Giant magnetoresistance is seen in a hybrid consisting of a non-magnetic- nano-film placed between ferromagnetic layers. In the absence of external magnetic fields the magnetic layers are anti-ferromagnetically coupled. The resistance of this state is very high. On application of a magnetic field, the spin vectors in the ferromagnetic layer tends to align in parallel leading to a drastic reduction in resistivity.
Superparamagnetism

Ferromagnetic materials consist of magnetic domains within which the spins are parallel. When the particle size is reduced to very small sizes (typically less than 20 nm) the entire particle becomes a single domain. On further reduction in size (about less than 5 nm) the spins get thermally disordered in the absence of magnetic fields. When an external magnetic field is applied the spins are able to align in the direction of applied magnetic field, making them behave as super paramagnets (i.e., in the absence of external field the particle is paramagnetic and in the presence of a field all the spins are aligned in parallel, leading to a large increase in magnetization). This is an interesting example in which a ferromagnetic material in bulk behaves like a paramagnet when particle size is made very small.

Super-hydrophobicity

As the surface roughness is increased from micron-scale to nano-scale, the actual contact area of the surface decreases (assuming the apparent contact to be constant). The tip of each asperity supports part of the water droplet. This shifts hydrophobicity to higher level of superhydrophobicity; wherein, contact angles of greater than 165° can be obtained. The normal (maximum) contact angle obtained in the case of hydrophobicity is about 120° (with the best available substrate of least surface energy). The phenomenon of superhydrophobicity can lead to the development of non-wetting clothes, self-cleaning windows, non bio-fouling surfaces etc.
Super surface activity

With decreasing dimension of the particles, the number of surface atoms increases drastically (calculation shown later in an example). This leads to a significant energy contribution to the system from the unsatisfied bonds of the surface atoms. Hence, the surface becomes extremely 'active' due to the high available surface energy. This effect finds applications in: adsorption of toxic gases, catalysis, etc.
New functions can be performed using nanomaterials which were otherwise not possible. Some of these functions rely on the effects described before.

- **Targeted drug delivery**
  Nanoparticles can be loaded with specific sensor and drug molecule(s). The drug can be transported to the required site through blood stream. On detection of the affected tissue/cells/area by the functionalized surface group the drug is released locally on desired target (targeted drug delivery).

- **Achieving superhydrophobic/antibiofouling surfaces**
  Nanoscale surface roughness enhances material properties like hydrophilicity or hydrophobicity, which is otherwise unattainable (by exploring different materials). The phenomenon of superhydrophobicity relies on achieving Cassie Baxter state (allowing support of water droplet on nano-roughness, without actually wetting the entire surface). Correspondingly, these water-repelling surfaces do not allow fungal/algae growth on their surfaces by rejecting water deposition on their surface.

- **Transparent ceramics**
  Ceramics are usually opaque due to light scattering at grain boundaries and porosities, of size comparable size to that of the incident light. Limiting the grains and porosities to much finer scale (few nanometers) can make ceramics transparent. (Al₂O₃ has been made transparent by sintering nanosized particles).
Rapid catalysis
Surface activity of nanoparticles enhances multifold (few orders of magnitude) because of two reasons: (i) the surface area available to react increases as we go down in size, and (ii) the unsatisfied bonds lead to instability of nanoparticle itself. Hence the synergistic combination of enhanced surface with high energetic associated with nanoparticles enhances their catalytic activity dramatically.

Functionalization
Functionalization is the addition of one (or more) functional groups on the surface of a material (or particles). Usually this surface modification is achieved by chemical synthesis methods to impart certain properties to the surface (e.g. enhance affinity of surface for a particular species or make the surface water repellent). It is easier to functionalize nanoparticles as they possess higher surface activity. Functionalized nanoparticles find applications in rapid catalysis, targeted drug delivery, sensors etc.
These effects have been used to make devices/products which would not function without the effect observed at the nanoscale

- **Nanoporous membrane filters**
  Membrane filters sieve out harmful bacteria and are permeable only to the molecules which can pass through the nano-porous membrane. These are utilized in the filtering of water to get bacteria-free water.

- **Sanitizing washing machines**
  Billions of silver ions are released during the wash. Owing to the anti-bacterial property of silver ions fabrics are sanitized (disinfected).

- **Non-wetting clothing**
  Non-wetting clothes have been developed by coating nanoparticles on the fabric. If you spill coffee on your trousers made of such a material, it will just flow away without leaving a stain. This layer of nanoparticles is transparent and is invisible to eye!

- **Biological Sensors**
  Surface functionalized nanoparticles can trap a single carbon monoxide molecule which elicits a sharp change in the surface potential. This potential can be detected and can trigger an alarm for this harmful gas before the carbon monoxide leak becomes fatal. Another example of such an application of surface functionalized nanoparticles is in the diagnosis of diabetes by detecting acetone in the breath of a patient.
Scratch resistant lenses
Nanometer sized alumina particles can be used as a feedstock for thermal spraying or spark plasma sintering to form fully dense pellets of transparent ceramic. These optical components being made of a ceramic provides for superior strength, hardness and thermal shock resistance as compared to their glass/plastic counterparts. Wear resistant optical components can be utilized in aerospace applications.

Spin Valves
Spin valves essentially utilizes the giant magnetoresistance (GMR) effect. An applied magnetic field can be used to switch the material showing GMR effect from a high resistance state to a low resistance state. This makes these devices behave as ‘spin valves’ or micro-switches. Spin valves have been used in the fabrication of spin valve transistors (using silicon emitter and collector), which can be used in the detection of magnetic fields.

Spintronics (spin transport electronics or magneto-electronics)
In spintronics the spin (and associated magnetic moment) of an electron is utilized along with the usual electronic charge in the fabrication of solid state devices. Spin dependent electron transport is at the heart of such devices. Spin polarized electrical injection has been used in the construction of semiconducting lasers. Spin based transistors have also been envisaged.
These “new” phenomena have led to awareness about ‘nanomaterials and nanotechnology’. This consequently has developed:

- An increased quest towards understanding the size dependence of various physical phenomena (i.e. nanoscience along with their applications)
  - Thrust in academic and industrial research
- Fascinating possibilities that can be achieved using nanomaterials and nanotechnology
  - Enhancing the living standards of community
- Favourable governmental policies
  - Thrust in funding
In hierarchical construction a basic building block is used as a sub-unit of a larger block. This method could be iterated a few times to obtain larger and larger units.

The fundamental building block does not lose its identity during the hierarchical construction.

Schematic explaining the meaning of hierarchical development: the rectangular block forms a part of the larger rectangular block, which in turn form a part of an even larger rectangular block.
Gecko: Gecko is known for its super sticky feet, as it can stick even to a glass surface (works on almost any surface!). In spite of the strong adhesion provided by the gecko's feet the animal can move around with ease (i.e. de-adhesion is carried out with considerable ease). Gecko's foot contains rows of setae (~106 setae on each foot, ~ 5 μm diameter), each of which is tipped with few hundred fine hair-like structures called spatulae. These fine spatulae increase the surface area of contact and the adhesion is through van der Waal's forces. The setae can be detached by increasing the angle it makes to the surface and low forces are required for this process. It spite of having this 'sticky' property gecko feet are self cleaning (clean within a few steps) and don't stick to each other!

Nacre: The sea-shell (or nacre) has tablets or plies of calcium carbonate sandwiched by a very fine protein layer. This protein layer acts as glue to hold the layers (similar to cement) in a brick-cement structure. Correspondingly, the fracture toughness of the nacre exceeds 1000 times the toughness of calcium carbonate (a very brittle material). Hence rearrangement and gluing by protein nano-layer can drastically enhance the fracture toughness while retaining its hardness.
Lotus Leaf: Water does not stick to the surface of lotus leaf (small droplets 'bead up') and cleans the surface-dirt as it rolls off. Microscopically, the lotus leaf surface has fine distribution of micro-protrusions (~ 10 µm long, ~ 10 µm high and spread ~ 15 µm apart), which enhance the surface roughness and increase contact area by a few orders of magnitude. Further, these micro-protrusion and the base surface have nano-hairs (~ 80-150 nm diameter) spread over the entire surface of Lotus leaf, making the surface superhydrophobic. It is to be noted that the wetting angle (purely arising from the chemical nature of the surface and as characterized by the surface energy) can reach a maximum of 120°. Contact angles >165° are observed on a lotus leaf and this increase of 45° arises from the hierarchical structure of the lotus leaf (i.e. from micro-protrusions and nanohairs on the surface of a lotus leaf).
Lotus leaf - a hierarchical structure

- Protrusions
- Hairs on protrusion
- Hairs on the base
Why Nano?

- **Certain structures exist only in the nanoscale** (i.e. there are no bulk counterparts to these structures).
  - Examples: carbon nanotubes (CNTs), Fullerenes, carbon onions etc.

- **Certain properties arise only in the nanoscale** (i.e. if the size of the relevant unit is made larger the property under consideration would not be observed).
  - Examples: super-hydrophobicity, super-catalytic activity, superparamagnetism, giant magneto resistance etc.

- **Certain combination of properties can only be obtained** with nanomaterials and nanostructures
  - Example: Abalone shell has a fracture toughness reaching more than 1000 times that of calcium carbonate the chief ingredient in the shell; while still retaining the hardness of nacre.

- **Drastic change in properties** may be observed on approaching the nanoscale
  - Example: Fracture strength of Ni has shown to increase from 100 MPa to 900 MPa once the nanometer-sized grains are obtained.

- **The performance of some systems depend on a functional entity in the nanoscale**
  - Example: A devise sensing a signal from a single DNA strand has to be in the nanoscale so as to extract the local signal from one strand. Nanoscale entity (such as CNTs) can be utilized for measuring the electrical signal in response to a stimulus.

- **In multi-lengthscale structures** (with special properties) the fundamental unit has to be nanoscale for the other lengthscales to be effective
  - Example: non-buckling nano-hairs are at the heart of the hierarchical structure on a lotus leaf, which gives it superhydrophobicity.
How do the Properties come about at the nanoscale?

- It must be clear at the outset that certain benefits can be derived by working with materials/structures at the Nanoscale. If there are no such special effects derived, then needless to point out such an exercise is futile. Assuming that there is a radical change in property/properties, which can be utilized for making devices, components etc.; the important question to be asked is how does this come about?
Four methods by which a given property can arise in nanomaterials → for those materials/structures which have a bulk counterpart.

Property*: refers to the value of a specific property (like surface energy/grain boundary energy) and not that of the whole material.

It should be noted that when fundamental studies are carried out (say on single nanoparticles), the primary focus is usually to look for fundamental change in mechanisms or properties and attention is not usually paid to performance (in an application) in these studies.
Change in crystal structure on reduction of size

The crystal structure of bulk materials could be different from that of nanocrystals. Two important effects may be observed on reduction of crystallite size:

(i) change in crystal structure,
(ii) anisotropic lattice distortion (i.e. direction dependent change in lattice parameters), leading to a change in symmetry of the crystal.

The second effect, though a subtle one in comparison to point (i), can have profound effect on the properties of a nanocrystal. In metallic nanoparticles, the dominance of surface tension effects is expected to lead to a contraction of the lattice parameters. However, in non-metallic particles with a polar surface, there maybe an expansion of lattice parameters when the particle size is reduced in the nanometer regime (e.g. in $\gamma$-Fe$_2$O$_3$ which is stable between 5-30 nm crystallite size, there is an expansion in cell volume with a decrease in size).

Bulk silver crystal have cubic close packed (CCP) structure also referred to as the 3C structure (based on the packing of close packed planes along the [111] direction). On reduction of the size of the silver particles below about 30 nm the 4H hexagonal phase is stabilized. The tetragonal phase of ZrO$_2$ is stabilized at room temperature when the particle size is $< 10$ nm (the stable bulk structure being monoclinic). When the crystallite size is above $\sim 30$ nm $\alpha$-Fe$_2$O$_3$ with rhombohedral (corundum) structure is stable, between 5-30 nm the cubic $\gamma$-Fe$_2$O$_3$ with inverse spinal structure is stable and below 5nm the formation of an amorphous phase is observed. Tetragonal ferroelectric phase of BaTiO$_3$ converts to paraelectric cubic phase when particle size is below a certain particle size. In materials like Al$_2$O$_3$, Fe$_2$O$_3$, PbTiO$_3$, YBa$_2$Cu$_3$O$_{7-\delta}$ etc. it is seen that with a decrease in crystal size the crystal structure changes to one of higher symmetry.
Why do the properties change at the nanoscale?

A few of the important reasons are as listed

⭐ Lack of sufficient material (including quantum size effects)

There is just not 'enough material' to qualify the system as 'bulk'. E.g. electronic energy levels of isolated atoms become nearly continuous bands, when the atoms come together to form a bulk solid (due to a huge number of atoms involved in the process). This implies that electromagnetic radiation with a range of frequencies can be absorbed by the solid unlike the discrete frequencies at which an isolated atom would absorb. However, in nanocrystals, wherein there are insufficient number of atoms involved in the formation of the solid, the energy levels (albeit being closely spaced) will remain discrete. Bulk metals are opaque, but thin films of metals are semi-transparent as there is not sufficient material to absorb the light. In x-ray diffraction peak broadening occurs when crystallite size is small and Scherrer's formula can be used for calculation of the crystallite size. This happens because sufficient atomic planes are absent to destructively interfere with rays scattered just off Bragg angle.
Dominance of surface/interface effects

Surface layer is a 'disturbed' high energy region which can undergo relaxation and reconstruction. Impurities insoluble in the bulk will segregate to the surface and gases may adsorb on the surface.

In bulk materials surface is but a minor fraction of the material and can be 'ignored' under most circumstances. However, in nanomaterials (including nanostructured materials) surface and interface effects can play a dominant role. The 'so called' surface layer may become a large fraction of the material. Oxidation at the surface of nanoparticles may become a serious issue. In metallic particles surface tension may lead to a contraction of the lattice parameters (e.g. Ni clusters 1 nm in size showed a lattice parameter contraction of about 10%).

Polar surfaces (e.g. dipoles on the surface pointing radially outward from a small spherical particle) may lead to surface compression. Surface plasmon resonance may dominate the absorption spectrum of nanostructures.

It is imperative to point out at this stage that even in bulk materials 'surface effects' can be very important. In corrosion, erosion, fatigue crack nucleation etc. the surface is the key player. The area of surface engineering deals with understanding and modifying surfaces for better properties and longer service life (of a component).
Proximity of surface to most of the 'bulk'

This implies that any stimulus applied to the surface is automatically felt by the entire material and not restricted to only the surface. In cases where time is involved this can take place within a very short time scale. If a nanocrystal is exposed to a chemical species soluble in the material, the species will permeate the entire material in a short time. This is unlike bulk materials wherein, it is easy to maintain a surface composition different from the bulk (e.g. in case carburizing; wherein the surface carbon concentration can be 0.8%, while the bulk composition can be 0.1% carbon). Photochemical reactions in translucent materials will not be restricted only to a small volume fraction of the material.

- Altered defect structure

(i) Lack of sufficient material and/or (ii) proximity of surfaces may lead to an altered defect structure in the material, thus leading to a change in properties. E.g. the largest crack a particle can have will have to be less than the diameter of the particle. Hence, nanosized particles can have nanosized cracks only. Nanocrystals may become totally dislocation free due to the proximity of free surfaces (dislocations will be attracted to free surfaces by image forces and when the image force exceeds the Peierls stress dislocations will spontaneously leave the crystal). Very small sized crystallites will not support vacancies (vacancies will cease to be a 'thermodynamically stable' defect!).
One or more physical lengthscale becomes comparable to the geometrical dimension

This is a very important consideration. The physical lengthscales include: (i) mean free path of electrons, (ii) mean free path of phonons, (iii) a coherence length, (iv) screening length. A list of some of the important ones are as in the table.

Table: Some characteristic lengthscales in materials.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Length</th>
<th>Typical magnitude (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{MFP}}$</td>
<td>Electron mean free path</td>
<td>1-100</td>
</tr>
<tr>
<td>$\lambda_{F}$ (metal)</td>
<td>Fermi wavelength</td>
<td>0.1</td>
</tr>
<tr>
<td>$\lambda_{F}$ (semiconductor)</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>$d_{\text{ex}}$</td>
<td>Range of exchange interaction (magnetism)</td>
<td>0.1-1</td>
</tr>
<tr>
<td>$l_{\text{ex}}$</td>
<td>Exchange length (magnetism)</td>
<td>1-100</td>
</tr>
<tr>
<td>$l_{\text{SD}}$</td>
<td>Spin diffusion length</td>
<td>10-100</td>
</tr>
</tbody>
</table>
One totally distinct reason (actually an extraneous reason) for the emergence of new properties in the nanoscale is that nanoparticles are often embedded/supported in/by another media. Some of the reasons for this are: (i) to avoid coalescence of the particles, (ii) the particles may be synthesized in embedded form (e.g. nanocrystals in an amorphous matrix produced by crystallization).

- One good example of the role of the support structure is the use of Au nanocrystals supported on a TiO₂ substrate for catalysis. Particles with a high interface perimeter show a higher catalytic efficiency. It is to be noted that bulk Au is not a catalyst at all!
- Another nice example is ferromagnetic behaviour of thiol coated Au nanoparticles (~1.4 nm). The Au-S bond at the interface between the Au nanocrystal and thiol is postulated to be responsible for this effect. It is noteworthy that bulk metallic gold is diamagnetic.
- The Curie temperature of 1 nm Co film deposited on Cu (001) substrate can be lower than for bulk crystals. At a certain thickness the films start to behave like a 2D system.
Solved example: surface area of nanocrystals

a) Calculation of the surface area as the size of the particle is reduced

One important effect, which has bearings on the properties of nanomaterials, is the drastic increase in the surface area. Let us assume that the particles are spherical and find out the effect of increasing the number of particles keeping the total volume constant. Let us start with one particle of volume \( V_1 = \frac{4\pi}{3} \) (volume units). Radius of the particle \( r_1 = 1 \) (length unit). Area of the particle \( A_1 = 4\pi \) (area units). Note that the subscripts denote the number of particles.

Area per unit volume for one particle:

\[
\frac{A_1}{V_1} = \frac{4\pi r^2}{\frac{4\pi}{3} r^3} = \frac{3}{r}
\]
Area per unit volume for one particle: \( \frac{A}{V_1} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r} \)

If this particle is split into two spherical particles of equal volume, from volume constancy we get:

\[ \frac{4}{3}\pi (2r_2^3) = \frac{4\pi}{3} \Rightarrow r_2 = \left( \frac{1}{2} \right)^{\frac{2}{3}} = 0.79. \]

\[ A_2 = 2(4\pi) \left( \frac{1}{2} \right)^{\frac{2}{3}} = 2(7.92) = 15.84. \]

For any general 'n' (number of particles) the relevant quantities are given as:

\[ r_n = \left( \frac{1}{n} \right)^{\frac{1}{3}}, \quad V_n = \left( \frac{4}{3}\pi \right) \left( \frac{1}{n} \right), \quad A_n = n(4\pi) \left( \frac{1}{n^{\frac{1}{3}}} \right)^2 = 4\pi (n)^{\frac{2}{3}} \quad \text{and} \quad \frac{A_n}{V_n} = 3(n)^{\frac{1}{3}}. \]
Note the strong increase in area as the number of particle is increased. There is already a 100% increase in surface area when we have just 8 particles.

Note that the size does not decrease much in each step.
Let us consider a further example; wherein a spherical particle of \((r_1 =) \) 1 mm radius is reduced in size to \((r_n =) \) 10 nm (radius) particles. The number of particles can be calculated using volume constancy:

\[
\frac{4}{3} \pi (10^{-3})^3 = n \cdot \frac{4}{3} \pi (10^{-8})^3 \Rightarrow n = 10^{15}
\]

\[
\frac{A_n}{A_1} = 10^{15} \frac{4\pi (10^{-8})^2}{4\pi (10^{-3})^2} = 10^5 \Rightarrow \text{an increase in ratio of surface areas by a factor of } 10^5!
\]

Thus, such a large increase in the surface area implies that the physical properties will become surface dominant.
a) Calculation of the number of surface atoms as the crystal size is reduced.

Instead of starting with a bulk crystal and reducing its size we shall do a 'atom-up' construction of a FCC crystal (the cubic close packed crystal: FCC lattice mono-atomically decorated). The first coordination shell in a FCC crystal is in the shape of a cuboctahedron (figure below) with 13 atoms. On adding further shells (shell number = n), the number of atoms \( N_t \) and the number of surface atoms \( N_s \) are given by:

\[
N_t = \frac{1}{3}(10n^3 - 15n^2 + 11n - 3), \quad N_s = 10n^2 - 20 + 12 \quad (n > 1)
\]
## Percentage of surface atoms with number of shells

<table>
<thead>
<tr>
<th>Number of shells</th>
<th>Total Number of atoms ($N_t$)</th>
<th>Number of surface atoms ($N_s$)</th>
<th>% atoms on surface (approximate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2,869</td>
<td>812</td>
<td>28.3</td>
</tr>
<tr>
<td>100</td>
<td>3,283,699</td>
<td>98,012</td>
<td>3</td>
</tr>
<tr>
<td>1,000</td>
<td>$3.33 \times 10^9$</td>
<td>9,980,012</td>
<td>0.3</td>
</tr>
<tr>
<td>10,000</td>
<td>$3.33 \times 10^{12}$</td>
<td>$1 \times 10^9$</td>
<td>0.03</td>
</tr>
<tr>
<td>100,000</td>
<td>$3.33 \times 10^{15}$</td>
<td>$1 \times 10^{11}$</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Essentially, the increased numbers in the % surface atoms directly relate to the enhanced surface activity, thus leading to improved catalysis, chemical reactions, diffusivity, biological response, sensitivity, etc. (per unit of volume of material).

\[
N_t = \frac{1}{3} \left(10n^3 - 15n^2 + 11n - 3\right) \\
N_s = 10n^2 - 20 + 12
\]
As we have seen, nanoparticles may have very specific shapes. We now see the effect of three general shapes on the surface to volume ratio. (sphere, cylinder, cube).

### Sphere

\[
\frac{A}{V} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}
\]

### Cylinder

\[
\frac{A}{V} = \frac{\pi r^2 h}{2\pi rh} = \frac{2}{r}
\]

### Cube

\[
\frac{A}{V} = \frac{6l^2}{l^3} = \frac{6}{l}
\]

For different ‘types of critical dimensions’ the functional behaviour is same (except for the factor involved)
Disadvantages and Challenges in the Nanoworld

Everything is not rosy about nanomaterials. There are many shortcomings and challenges which need to be addressed for successful and widespread use of nanomaterials.

**Issues related to Nanomaterials**

- Difficulty in synthesis and isolation

To start with synthesis of nanostructures, nanoparticles and nanomaterials is considerably more difficult as compared to their conventional bulk counterparts. Additionally, if the synthesis of nanoparticles has been carried out in a solution, it is extremely difficult to retain the size of nanoparticles. In applications where the particles need to be of the same size, obtaining a narrow size distribution poses additional challenges. In polycrystalline nanomaterials (i.e. with grain size in nanometers), grain growth can take place during their processing (leading to larger grain size, which is not in the nanoscale). For example when bulk nanostructured materials are produced by sintering of nanocrystals; grain growth becomes a serious issue.
• Instability of particles

Nanoparticles, especially metal nanoparticles are very reactive (i.e. they are thermodynamically metastable). The kinetics associated with nanomaterials is also rapid (with respect to diffusion, surface diffusion plays an important part). Fine metal particles can even be explosive owing to the high surface area coming in direct contact with oxygen (exothermic reaction). Nanomaterials have poor corrosion resistance and are prone to phase change. Hence, it is challenging to retain the particle size in the nanoscale and to maintain the properties of nanomaterials during service in an intended application (which may involve long timescales). Encapsulation of nanoparticles, embedding nanoparticles in a matrix, using protective layer over a nanomaterials etc. are possible solution strategies.

• Presence of Impurities

As stated before, nanoparticles have a very active surface; leading to adsorption and absorption. Additionally, once a species has been adsorbed on the surface of a nanoparticle, the path length for diffusion required to take the species to the centre of the particle is very small. Hence, the whole nanoparticle may easily be 'contaminated'. Often nanoparticles are very reactive as well; thus making it very difficult to maintain a pristine surface (formation of oxides, nitrides etc.). Thus it is challenging to not only synthesize pure nanoparticles, but also to keep it pure during its service in an intended application.
• Biologically harmful

Nanoparticles can be potentially harmful as cell-dermis can be permeable to them. Toxicity of nanoparticles is enhanced owing to their high surface area and activity. The possibility that of particles which are benign in the macroscale becoming toxic in the nanoscale has also to be considered. Nanoparticles have been shown to cause irritation to tissue and they can also be carcinogenic. If inhaled, they may be entrapped in the lungs and they cannot be expelled out of body. Their interaction with liver/blood could also prove to be harmful (though this aspect is still being debated on).

• Recycling and safe disposal

Given that the age of nanomaterials has practically only dawned, there is a lack of availability of set procedures or policies for safe disposal of nanomaterials. Issues regarding their toxicity are still being hotly debated and detailed studies of 'exposure experiments' are not yet available. As most of the current research and studies are devoted towards developing newer materials and allied technologies; very little thought has been put into aspects like recycling and safe disposal. Hence, these aspects need serious and immediate attention.
**Challenges ahead**

- **Consistency in quality**

  We need consistency in quality with control over the chemistry, size, structure, microstructure and morphology of the nanomaterials.

- **Fast and inexpensive characterization techniques**

  To ascertain if the parameters mentioned above (i.e. chemistry, size, structure, microstructure and morphology) have been achieved; fast and inexpensive characterization tools need to be developed. This is keeping in view the effort and cost (including time) associated with some techniques like transmission electron microscopy, atomic force microscopy, Auger electron spectroscopy etc.
Scaling of the production

Often the synthesis of nanomaterials requires special processing techniques, which can restrict the thickness of bulk nanostructured components to a few millimeters. As the size increases, prolonged heat treatment results in the grain-coarsening and loss of nanostructure. Eventually, either (i) secondary processing is required to break down the bulk structure into nano-structure, or (ii) requires multiple processing to retain the initial nanostructure. Hence scaling of the production remains a challenge. E.g.: in the use of MoSi$_2$ nanoparticles as nano-ball bearings, the production can be easily scaled up to few kilogrammes; but for successful commercial application, it needs to be further scaled up a few orders of magnitude.

Use of traditional processing routes for nanomaterials

If existing processing techniques can be put to use for case of nanomaterials, this would lead to considerable savings in effort and cost. Conventional processing techniques typically involve long timescales and/or high temperatures. But, as nanomaterials are not in their thermodynamic equilibrium state and there is always the tendency for grain coarsening or phase transformation. Hence, it is imperative to develop variants of current techniques (retain the nanostructure at bulk scale), which involve high pressure and low temperatures (along with rapid processing).
• Synthesis of Hierarchical structures

As we have seen structures at various length scales combine in hierarchical fashion, to provide exceptional performance at bulk scale. At the same time, the features present at various lengthscales (nano-, micro- & bulk-) are essential to allow for their synergistic contribution. For example, the nacre structure is composed of calcite layers glued by nanolayers of protein in the cement-brick platelet structure, which provides for exceptional toughening. But engineering of such a structure has appeared almost next to impossible, because the arrangement of nanoplatelets with an interlayer of soft glue-like material is highly complicated. The arrangement has to be followed in manner so as to give rise to different orientations, so that the resulting composite structure has exceptional toughness (even though its constituents are brittle). Hence, hierarchical synthesis across different length scale poses engineering & manufacturing challenges.

• Manipulation/Handling of Nanoparticles/Nanostructures

Often nanoparticles/nanostructures need to be handled individually (and further these need to be arranged in a precise way). The manipulation of individual nanoparticles requires a probe to pick, hold and translate/rotate the nanoparticle/nanostructure and hence the control unit must be equipped with a nanometer-sized 'forceps' (or manipulator tip) for arranging nanoparticles. Needless to say this has to be done without damaging/altering the nanostructure/nanoparticle. This is a challenging task requiring sophisticated instrumentation. Hence handling of nanomaterials into certain organization becomes highly challenging.
Recycling

Nanomaterials tend to agglomerate, and their recycling does not face a problem in this regard. But, when used without proper control (especially if released into the atmosphere or into the water system), their effects could be highly deleterious. Hence, certain policies in not only using, but also disposal of nanomaterials need to be evolved. Selectively isolating nanomaterials and evolving procedures for their recycling is going to be one of the important challenges ahead.
Traversing across lengthscales

To understand the properties of a material we need to transverse across lengthscales.

Let us consider the example of polycrystalline copper (FCC lattice decorated with Cu atoms/ions) and traverse three lengthscales:

Atomic level (Å) → Unit Cell level (few Å-nm) → Grain level (nm-μm) → Material level (cm)

At the atomic level there is order only in the average sense (at T > 0K) as the atoms are constantly vibrating about the mean lattice position. Hence, in a strict sense the perfect order is missing. The unit cell level is the level where the atomic arrangement becomes evident (crystal structure develops) and concepts like Burgers vector emerge. It is at this level that averaging with respect to probabilistic occupation of lattice positions in disordered alloys is made (say Ni50-Al50 alloy is defined by a 50-50 probability of Ni or Al occupying a lattice position). At the grain level (which is a single crystal), there is nearly perfect order (as the scale of atomic vibrations are too small compared to grain scale); except for the presence of defects like vacancies, dislocations etc. At this scale the material is also anisotropic (e.g. with respect to the elastic stiffness, which is represented by three independent numbers: $E_{11}$, $E_{12}$ & $E_{44}$). It is to be noted that the Cu crystal may be isotropic with respect to other properties. At the material level, assuming that the grains are randomly oriented, there is an averaging of the elastic modulii and the material becomes isotropic. At this scale, the crystalline order which was developed at the grain level is destroyed at the grain boundaries and there is no long range order across the sample. When the material is rolled or extruded, it will develop a texture (preferred directional properties), which arises due to partial reorientation of the grains. That is, we have recovered some of the inherent anisotropy at the grain scale. As we can see, concepts often get 'inverted' as we go from one lengthscale to another.