Surface Effects and Physical properties

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Lecture - 14
Nanostructures and Nanomaterials: Characterization and Properties

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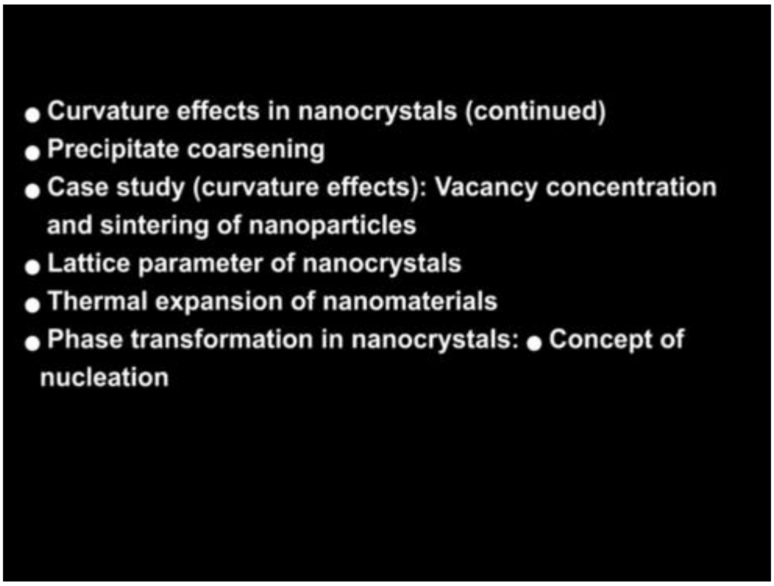

- Curvature effects in nanocrystals (continued)
- Precipitate coarsening
- Case study (curvature effects): Vacancy concentration and sintering of nanoparticles
- Lattice parameter of nanocrystals
- Thermal expansion of nanomaterials
- Phase transformation in nanocrystals: ● Concept of nucleation

Hence, the size of the precipitates increases with time, and here I am talking about the average size of the precipitate.

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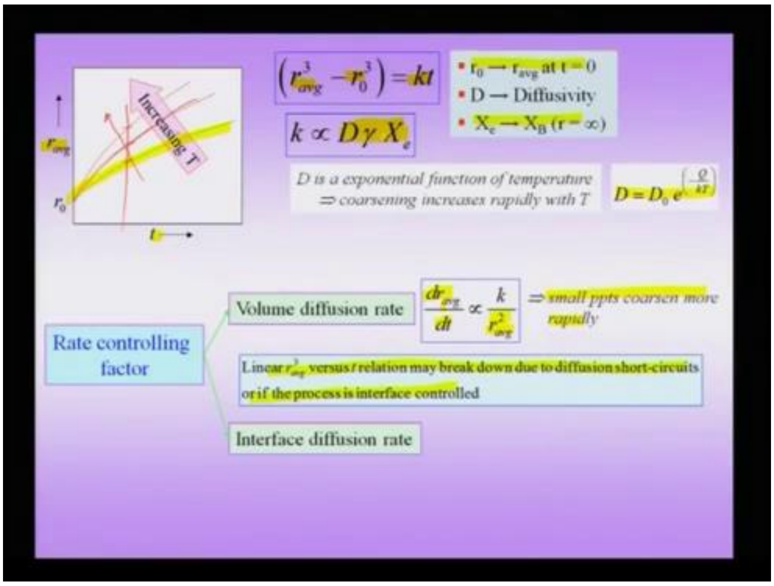

$$(r_{avg}^3 - r_0^3) = kt$$

- $r_0 \rightarrow r_{avg}$ at $t = 0$
- D → Diffusivity
- $X_e \rightarrow X_B (r \rightarrow \infty)$

$$k \propto D \gamma X_e$$

D is a exponential function of temperature
⇒ coarsening increases rapidly with T

$$D = D_0 e^{\left(-\frac{Q}{kT}\right)}$$

Rate controlling factor

Volume diffusion rate $\frac{dr_{avg}}{dt} \propto \frac{k}{r_{avg}^2}$ *⇒ small ppts coarsen more rapidly*

Linear r_{avg}^3 versus t relation may break down due to diffusion short-circuits or if the process is interface controlled

Interface diffusion rate

And the function by which it increases is that r cube average minus r 0 square r 0 cube is equal to k into t. That means, it is the cube of the average size, which is related to the time, and r 0 is the average radius at time into t equal to 0. And this constant k is given by is directly proportional to a product of the diffusivity, the interface energy, and the equilibrium concentration X c, which is in adjacent to the precipitate, which we have seen already, how to look up X c from the common tangent construction.

This implies that with increasing time, the average precipitate size increases. And if you look at the diffusivity, the diffusivity goes as exponential with temperature D equal to D 0 exponential Q by kT. That implies that at higher temperature the rate of coarsening is going to be much faster. So, if you plot the curve at a lower temperature, I would get a r versus, r average versus t curve, which looks like this, but with increasing temperature you will see that the r versus t curve shifts upward. That means, at for a given time I will have a higher r average, if I have a higher temperature.

Now, this diffusivity I am talking about is typically the volume diffusion rate, and if there are other mechanisms of diffusion in the material like interface diffusion, pipe diffusion which is at coarse of dislocations. Then, this kind of a linear r cube versus t relation may break down, and these sharp short circuit paths even though they have a smaller cross section may tend to dominate especially in nanocrystals. And if you look, if you differentiate this function r cube average minus r 0 cube is equal to kT.

Then, you can see that dr average by dt, which is the rate of increase of the precipitate size with time, is proportional to 1 by r square average. That implies that, smaller precipitates coarsen more rapidly as compared to larger precipitates, because if r 0 square increases, then you see that this rate increases. Therefore, if you have a smaller collection of smaller precipitate that will coarsen faster as compared to a collection of larger precipitates.

And with time you will find that, you initially wanted to retain a small distribution of fine precipitates to have a higher hardness, and we have already previously done a solved example, wherein we have seen, how the a frank read source operates around these fine particles, which is giving rise to hardening. And if these particles are coherent, then in some cases, if the stress is good enough these the dislocations can actually glide through the precipitates.

While if they are incoherent, then they go around the precipitates leaving dislocation loops around them, which is called a Franklin mechanism or an equivalent mechanism known as the ((Refer Time: 03:22)) mechanism. Therefore, with time, if the precipitates coarsen and they also tend to go from as I pointed out from the meta stable precipitates to the equilibrium precipitates, then I lose my hardness.

So, how can I retain the hardness? The crux lies in these 3 terms, which is related to the constant in this equation, which is D gamma and X e. If, I can maintain a small value of D gamma and X e, then I can actually reduce amount of coarsening in the material. And therefore, I can control the rate of coarsening by actually having a small value of this product D gamma and X e.

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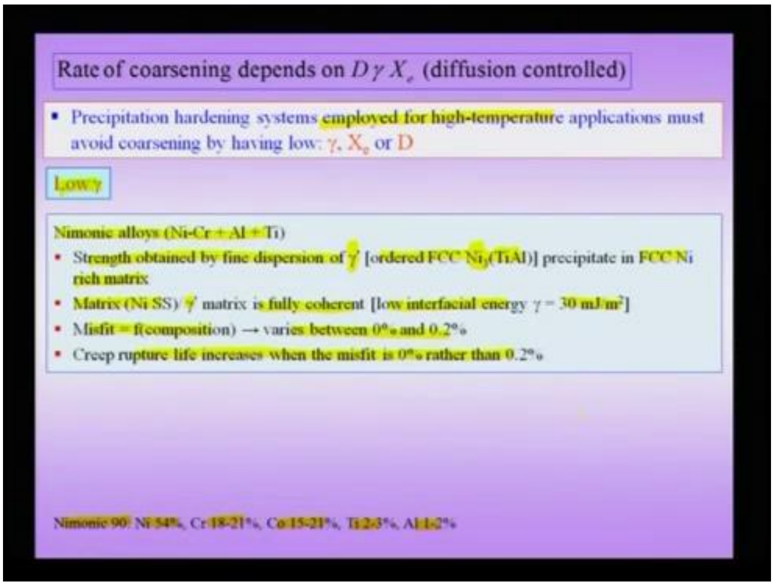

Rate of coarsening depends on $D \gamma X_e$ (diffusion controlled)

- Precipitation hardening systems employed for high-temperature applications must avoid coarsening by having low: γ, X_e or D

Low γ

Nimonic alloys (Ni-Cr + Al + Ti)

- Strength obtained by fine dispersion of γ' [ordered FCC $Ni_3(TiAl)$] precipitate in FCC Ni rich matrix
- Matrix (Ni SS) γ' matrix is fully coherent [low interfacial energy γ = 30 mJ/m^2]
- Misfit = f(composition) → varies between 0% and 0.2%
- Creep rupture life increases when the misfit is 0% rather than 0.2%

Nimonic 90: Ni 54%, Cr 18-21%, Co 15-21%, Ti 2-3%, Al 1-2%

So, the 3 strategies either I can start with a, I can have a low gamma or I can have a low X e value or I can have a low D value such that, overall my coarsening rate is small. And if you are looking at precipitation hardening systems, which have to be employed at high temperature, then we have to have these conditions satisfied, so that I can have hardness even at high temperatures.

Mnemonics alloys are special alloys, which are designed for high temperatures and a typical mnemonic alloy, for instance a mnemonic 90 alloy would have a composition in which there is about 44 percent nickel, about 18 to 20 percent chromium, about 15 to 20 percent cobalt, some small percentage of titanium and aluminum. And this composition retains its strength at high temperatures.

The basis of strength in these alloys, these mnemonic alloys is a presence of fine dispersion of gamma prime precipitates, and the prime here refers to the fact that you actually have an ordered structure here, which is an ordered FCC Ni 3 TiAl structure, which is, in which case there are 2 sub lattices, one occupied by nickel or one of the sub lattice occupied by 3 of the sub lattices occupied by nickel and 2 of them, one of them occupied by titanium or aluminum and this ordered precipitate sits in an FCC nickel rich matrix.

Of course, as you can see that it is not pure nickel matrix, but there are other alloying elements, which also sits in the matrix, and this fine dispersion of gamma prime ordered precipitate. And since, the precipitate is ordered, we expect that it is harder and because we know that ordered structure always has a larger ((Refer Time: 05:30)) and it is going to be harder. That means, it is going to have a higher pearl stress, and in the process it is going to give me hardness.

But the important thing is that, if you look at the matrix, which is a nickel rich solid solution and the interface between the matrix and the gamma prime precipitate is fully coherent with a low interfacial energy of about 30millijoule per meter square. And since, the interfacial energy is very low, there is low tendency for this precipitate to coarsen. That means, I am keeping a low gamma between the matrix and the precipitate, and this is at the heart of the strategy to keep these precipitates or to avoid the precipitates from coarsening. And in the process, this alloy can be used as a precipitation hardened alloy at high temperatures.

Now, this misfit obviously is a function of composition of the precipitate and of course, the composition of the matrix and typically it varies between 0 percent and 2 percent. And it is observed that, if my misfit is large, which implies that there is going to be coherency stresses, then the creep structure life actually increases when the misfit is actually small.

That means, if I have low interfacial energy, and also a low misfit, then actually I get better properties with this kind of an alloy, in which my main strategy is keeping my low gamma. But as I pointed out that not only can you keep a low gamma and get a good property, a good high temperature property of the material, which does not deteriorate with time at high temperatures, but also I can use a low X e.

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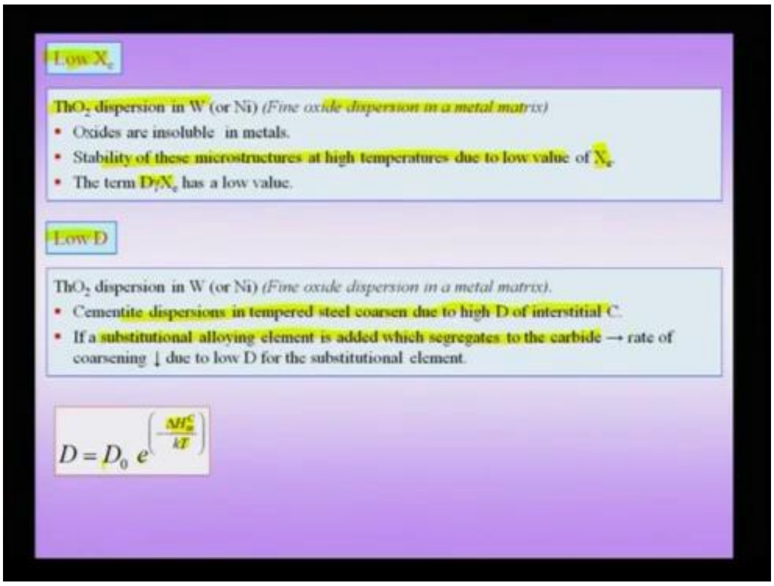

Low X_e

ThO_2 dispersion in W (or Ni) *(Fine oxide dispersion in a metal matrix)*

- Oxides are insoluble in metals.
- Stability of these microstructures at high temperatures due to low value of X_e
- The term $D_\gamma X_e$ has a low value.

Low D

ThO_2 dispersion in W (or Ni) *(Fine oxide dispersion in a metal matrix).*

- Cementite dispersions in tempered steel coarsen due to high D of interstitial C.
- If a substitutional alloying element is added which segregates to the carbide → rate of coarsening ↓ due to low D for the substitutional element.

$$D = D_0\, e^{\left(-\frac{\Delta H_m^C}{kT}\right)}$$

This example given here, is actually an extreme example wherein the solubility of when I am taking about the solubility, I am talking about the solubility of the solute in this beta phase is actually extremely small. Now, in this case, if I am talking about thoria dispersed in tungsten. Thoria and tungsten are, there is very little solubility of the metals in thoria or thoria in the metal, and this can be actually thought of as in dispersion hardening system rather in a precipitate hardening system.

Because if it is a precipitation hardening system, then actually have the precipitate coming out of the normal reaction of the slid solution, but in this case it is not true. The thoria is actually intentionally added as a fine dispersion in the metal matrix and oxides being insoluble in metals. The stability of these microstructures can be retained at high temperatures, and as I pointed out this is an extreme example, because there is practically no solubility of thoria in tungsten.

Therefore, you have low value of X e, which gives you a low value for the term D gamma X e. And the same example I, if you note that in the same example actually you can cite the fact that there is a very low diffusivity and in the process actually I can have low coarsening taking place because the matrix does not dissolve into the precipitate, the precipitate does not dissolve into the matrix.

And therefore, there is very little diffusivity or thoria into tungsten. But if you look at cementite dispersions in tempered steel, they coarsen due to high D of the interstitial carbon. If you look at, I think you know that there are 2 kinds of diffusion, interstitial diffusion and substitutional diffusion. If you look at interstitial diffusion, then there is only one term in the exponential, and D equal to D 0 exponential minus H m, delta H m, which is the migration enthalpy of the interstitial carbon from one interstitial site to the other and as expected this goes exponentially with temperature.

And if you see that when you temper steel, actually you get a fine dispersion of many of these cemantite or equivalent carbides, and these carbides in the fine scale actually give you a very high hardness, but they tend to coarsen because now the carbon can easily diffuse through the matrix. Now, if you add a substitutional alloying element, which specially segregates the carbide. In other words you just do not have iron carbide, but also an iron alloying element combination carbide. The rate of coarsening actually decreases due to low D for the substitutional element.

In other words, now I can design my alloy in such a way now, that there is an additional alloying element, which segregates the carbide. This implies that when the carbide has to grow not only has to carbon to diffuse, but also the alloying element has to diffuse. And since, that is going to be a substitutional alloying element, its diffusivity is going to be smaller than that of the carbon, which is an interstitial solid solution.

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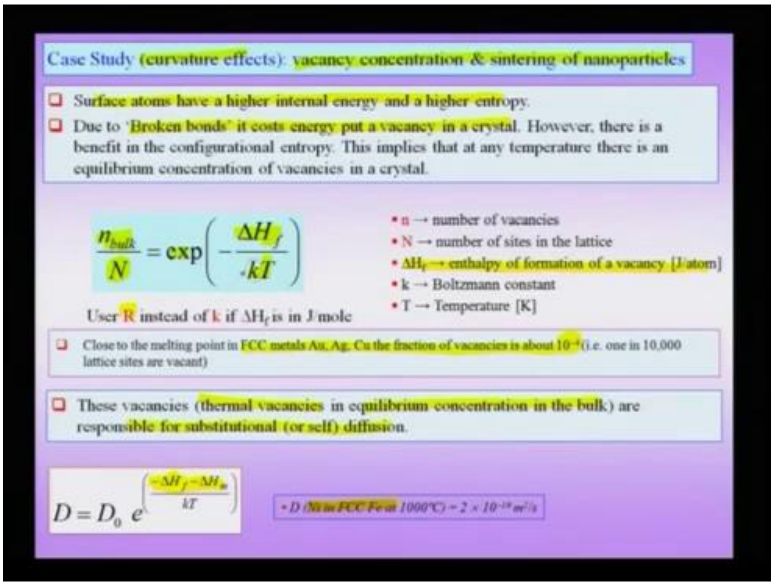

Case Study (curvature effects): vacancy concentration & sintering of nanoparticles

- ☐ Surface atoms have a higher internal energy and a higher entropy.
- ☐ Due to 'Broken bonds' it costs energy put a vacancy in a crystal. However, there is a benefit in the configurational entropy. This implies that at any temperature there is an equilibrium concentration of vacancies in a crystal.

$$\frac{n_{bulk}}{N} = \exp\left(-\frac{\Delta H_f}{kT}\right)$$

User R instead of k if ΔH_f is in J/mole

- n → number of vacancies
- N → number of sites in the lattice
- ΔH_f → enthalpy of formation of a vacancy [J/atom]
- k → Boltzmann constant
- T → Temperature [K]

- ☐ Close to the melting point in FCC metals Au, Ag, Cu the fraction of vacancies is about 10^{-4} (i.e. one in 10,000 lattice sites are vacant)

- ☐ These vacancies (thermal vacancies in equilibrium concentration in the bulk) are responsible for substitutional (or self) diffusion.

$$D = D_0\, e^{\left(\frac{-\Delta H_f - \Delta H_m}{kT}\right)}$$

- D (Ni in FCC Fe at 1000°C) = 2×10^{-16} m²/s

Because if you look at diffusivity of substitutional elements, you have an additional term delta H f, which means that substutional elements diffuse by vacancy mechanism, and that implies that the exponential term has 2 terms, one related to the enthalpy of formation of vacancy. That means the chance of finding a vacant neighboring site, so that the substitutional element can actually jump into that site. And second, which is the usual migration enthalpy for the substitutional element.

This implies that. the diffusion of the alloying element is going to be, which is a substitutional alloying element is going to be difficult as compared to carbon. And overall you find that the coarsening rate actually comes down. So, we have seen so far that you have. you can produce a fine dispersion of precipitates to increase the hardness typically say of an aluminum copper alloy. This precipitation hardened system tends to not only change the character the precipitate. The characteristic of the interface with time, but also the precipitate coarsens with time, which leads to a loss in hardness.

And therefore, I would like to keep the fine particle distribution. We had also seen the reason behind the actually the coarsening, one of the heart of the reason is the Gibbs Thomson effect wherein, there is a curvature dependent solute concentration around the precipitate followed by a diffusion down the concentration gradient. And we have seen the strategies so that, I can actually avoid the coarsening of precipitates.

So, that I can retain a fine dispersion of precipitates at high temperatures. And of course, when I am talking about high temperatures, I mean a temperature, which is above the recrystallization temperature, which is typically about 0.5 the melting point of the material. Now, let us take up some more studies wherein, we can see the importance of curvature effects. That means, we had already pointed that, small particles are curved more and therefore, there the curvature effects tend to dominate.

And here, we take up this specific example of vacancy concentration and sintering of nano particles. We have already seen and we have said that suppose I want to retain gold nanoparticle by nanoscale, then I have to isolate one particle from the other using some kind of a passivating molecule like thiol. Otherwise, this particle will tend to sinter with each other and would coarsen and become large grain.

Therefore, we will see that what is the underline mechanism that you actually have, which is giving rise to this kind of a sintering in nanoparticles at a temperature much lower than what you would expect for bulk particles. Now, we know that the surface atoms have an higher internal energy, and then higher entropy because there is a larger freedom for the surface atoms. Now, they are in a different state as of energy as an entropy as compared to the bulk of the material.

Now, we also know that the broken bonds cause energy to put in a crystal. That means, if you have a vacancy in a crystal, then it cause you excess additional energy we need to put, but there is a configurational benefit, which you get. And therefore, there is an increase in configurational entropy, and at any given temperature, any positive Kelvin temperature there is an equilibrium concentration of vacancies, which is given by the formula n bulk by n. Where n is the total number of atoms in the crystal, n bulk is a number of vacancies in the bulk crystal is given by exponential minus delta h f by kT, where delta h f is the enthalpy of formation of a vacancy that means, joules per atom.

And if I am talking about I can replace this k with r, if I am talking about joules per mole of vacancies. That means, that any given temperature t, positive Kelvin temperature there is an equilibrium concentration of vacancies in a bulk crystal. Now, if you heat a metal and take it close to the melting point, you would notice that the fraction of vacancies about 10 powers minus 4 that is 1 in about 10000 is vacant. That means, this is the concentration or the mole fraction of vacancies, when you actually heat the metal close to the melting point.

Though this is a small number, but there are actually theories, which are called the critical vacancy concentration theories, which are related that the, which tell you the importance of these kind of vacancies in the melting process. So, approximately 1 in about 10000 is a concentration of vacancies close to the melting point of metals like gold silver and copper.

These vacancies, otherwise called thermal vacancies, because they are coming from temperature alone have an equilibrium concentration of the bulk, and we are just now seeing that they are responsible for substitutional or self-diffusion. And for instance, the diffusivity of nickel in iron at 1000 degrees is 2 into 10 powers minus 16 meter square per second, which is purely coming from the vacancies present in the crystal.

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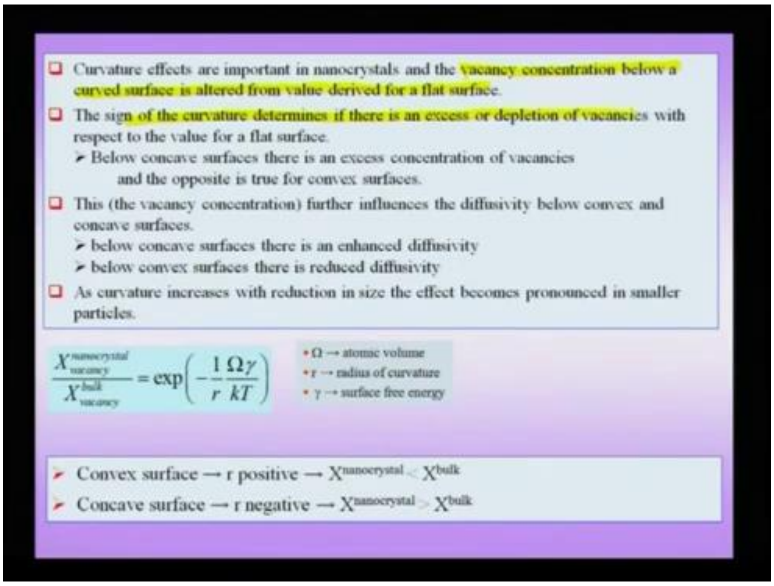

- ☐ Curvature effects are important in nanocrystals and the vacancy concentration below a curved surface is altered from value derived for a flat surface.
- ☐ The sign of the curvature determines if there is an excess or depletion of vacancies with respect to the value for a flat surface.
  - ➢ Below concave surfaces there is an excess concentration of vacancies and the opposite is true for convex surfaces.
- ☐ This (the vacancy concentration) further influences the diffusivity below convex and concave surfaces.
  - ➢ below concave surfaces there is an enhanced diffusivity
  - ➢ below convex surfaces there is reduced diffusivity
- ☐ As curvature increases with reduction in size the effect becomes pronounced in smaller particles.

$$\frac{X_{vacancy}^{nanocrystal}}{X_{vacancy}^{bulk}} = \exp\left(-\frac{1}{r}\frac{\Omega\gamma}{kT}\right)$$

- Ω → atomic volume
- r → radius of curvature
- γ → surface free energy

- ➢ Convex surface → r positive → $X^{nanocrystal} < X^{bulk}$
- ➢ Concave surface → r negative → $X^{nanocrystal} > X^{bulk}$

Now, curvature effects as we are known, is important in nanocrystals, and the vacancy concentration below a curved surface is altered from the value, which we assume for a bulk crystal. That means, if you have a flat crystal, the vacancy concentration below it can be given by a formula like this, which is n bulk by n, but suppose now I take into account the curvature effects. Then, the vacancy concentration can be altered with respect to the bulk.

An extreme example of this is the case, where when you make the crystal very small, then the crystal can spontaneously become free of vacancies. But before we go to that we will now deal with the aspect of curvature dependence on vacancies. The sign of curvature determines if there is an excess or depletion of vacancies with respect to the value for a flat surface.

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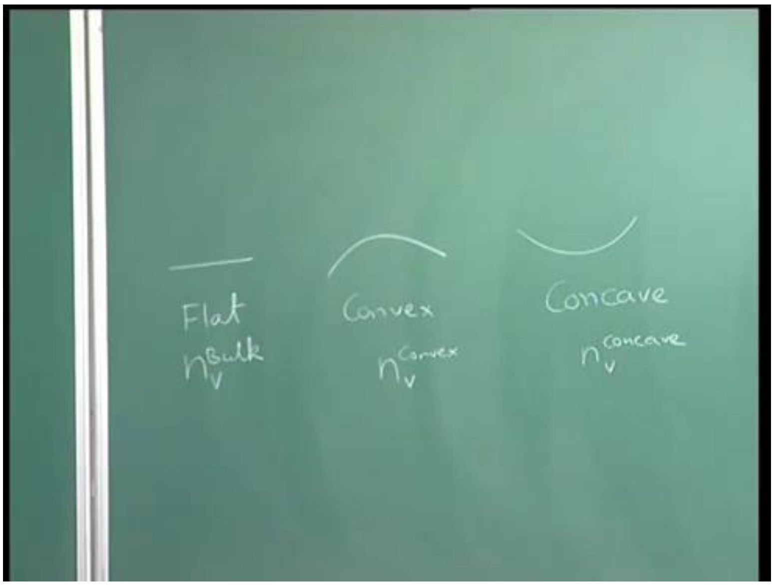

So, now I have 3 kinds of surfaces, which I can talk about a flat surface, a positively curved surface, and a negatively cured surface. So, this I can call a convex surface, and this is a concave surface. And for now, I will assume that this is the concentration of vacancies. Now, I want to compare this with the concentration of vacancies for convex and concave. So, 3 kinds of configurations, which I need to talk about and I need to see, how the concentration of vacancies changes.

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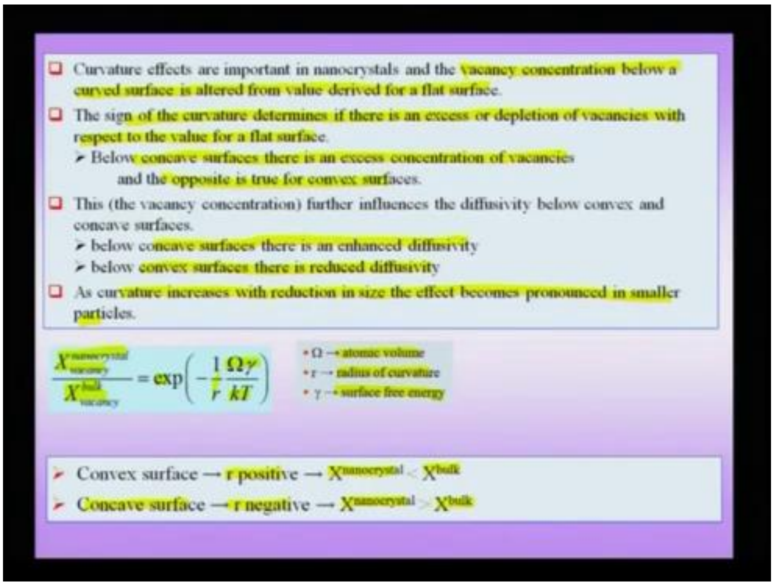

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Below a concave surface there is an excess concentration of vacancies, and the opposites true for convex surfaces. That means, if I am in concave surface there is an excess vacancy concentration, and this automatically implies that below concave surfaces. There is an enhanced diffusivity or there is an enhanced diffusion.

So, if I that means that if I am talking about diffusion below a flat surface or diffusion below a convex surface or diffusion below a concave surface, the value I would obtain is not going to be the same. For a concave surface, there is enhanced diffusion because now there is an excess vacancy concentration in a concave surface. And with respect to the flat surface, the convex surface would show a reduced diffusivity. This effect obviously depend on the curvature and as the curvature increases the reduction that means, by reduction of size. This effect becomes more pronounced, and which is going to be all the more slow in smaller particles.

Now, the concentration of vacancies in a nanocrystal can be written as n nanocrystals vacancy we saw, we saw, the fraction in a bulk crystal can be given as exponential minus 1 by r omega gamma by kT. Gamma is of course, the surface energy, omega is atomic volume, and r is the radius of curvature. For a convex surface r is positive this means that, X nanocrystals is going to be smaller than X bulk. For a concave surface, r is negative on the other hand. This implies that X nanocrystal is going to be greater than the X bulk and X of course, is the fraction of vacancies either below a convex surface or a concave surface? Therefore, now my vacancy concentration is altered in a convex surface or a concave surface, and this has importance consequences when we are talking about sintering of nanoparticles.

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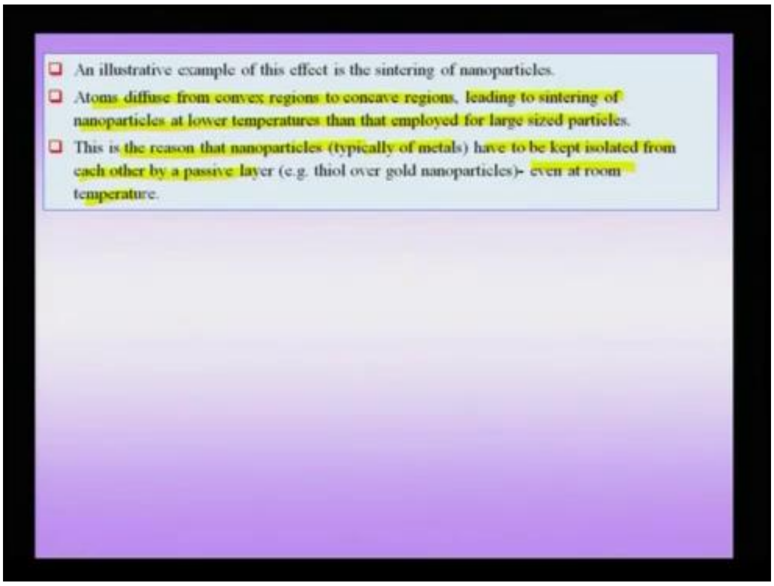

- ❑ An illustrative example of this effect is the sintering of nanoparticles.
- ❑ Atoms diffuse from convex regions to concave regions, leading to sintering of nanoparticles at lower temperatures than that employed for large sized particles.
- ❑ This is the reason that nanoparticles (typically of metals) have to be kept isolated from each other by a passive layer (e.g. thiol over gold nanoparticles)- even at room temperature.

Now, atoms will tend to diffuse from convex region to concave regions leading to a sintering of particles. And this sintering will occur at lower temperatures than that employed for large size particles because now it is enhanced by the presence of additional vacancies. And this is the reason we have seen that typically in metals have to be kept isolated from each other by a passivating layer that to be nanoparticles and nanocrystals have to be kept even at room temperature. So, now what is happening here in the case of nanocrystals is that suppose, I have two.

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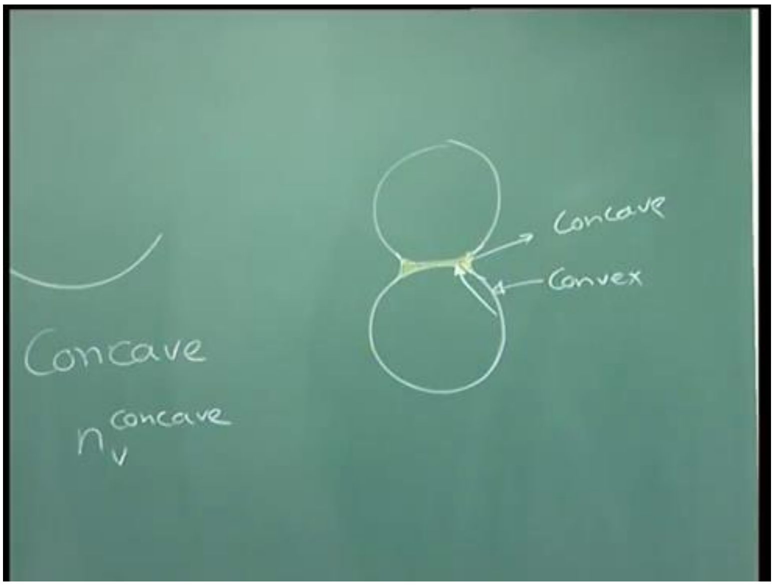

Now, so when the sintering process starts, you have a neck formation and here I have and this region is convex and I would have diffusion of mass from here to here leading to the sintering of the particle. Of course, this diffusion can be aided bulk diffusion and other kind of interface diffusions, which can finally lead to the sintering of the particle, which means that the neck is going to grow and the particles are going to, the material is going to center and join with each other.

Therefore, we are seeing that purely from curvature effects, we have important phenomena coming like coarsening, and enhanced or reduced diffusivity in selected regions or the nanoparticle, which is going to give you actually an enhanced sintering. So, just to go through the sintering part again we have a bulk concentration of vacancies, which we call the equilibrium concentration of vacancies, which is coming from a thermodynamic stabilization, a configurational stabilization in a bulk.

But when we go to nanoscale material that means, where there is a curvature effect, there the vacancy concentration is either elevated or depressed with respect to the normal bulk material, a flat material where there is no geometrical contribution. And below concave surfaces there is an excess of vacancies, and therefore an enhanced diffusion and below convex surface, on the other hand there is depression of number of vacancies or fraction of vacancies and therefore, there is reduced diffusion.

And this implies that when you have a connection of particles between two particles, these particles can be centered because of mass transport from regions of convexity to regions where the neck is formed. And this implies to me that one of the thermodynamically nanoparticles are very much unstable as compared to bulk particles. And they have to be kept in an isolated environment otherwise they will, they will be sintered and further of course, these grain size of these crystallites might grow, and finally, I will end up with the system, which is not, there are no nanoparticles anymore. Now, let us move on to the next topic, which is again closely related to surface effect, which is the lattice parameter of nanocrystals.

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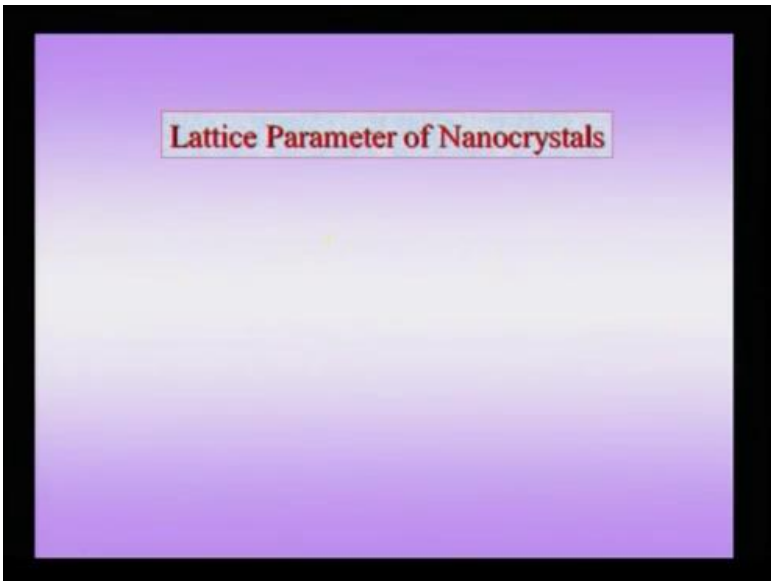

Lattice Parameter of Nanocrystals

Now, when we are talking about lattice parameter of bulk crystals, we know that if you talk about cubic crystals, then you have 3 lattice parameters, the a, b, and c. Of course, the alpha equal to beta is equal to gamma is 90 degrees is a typical lattice parameter, which we used to describe a cubic crystal. And so forth there are many, if you are talking about a lower symmetry system, then you have need more number of lattice parameters to describe the crystal. And one important quantity, which we can come from all these lattice parameters is the volume of the unit cell.

So, in of course, we can track each, track each one of these lattice parameters as you reduce the crystallite size or we can track the atomic or the unit cell volume. And in this current discussions, we will stick to the unit cell volume, because that makes consideration easy, we have to deal with a single number rather than independent lattice parameters, which may actually show increase or decrease with when the size is reduced.

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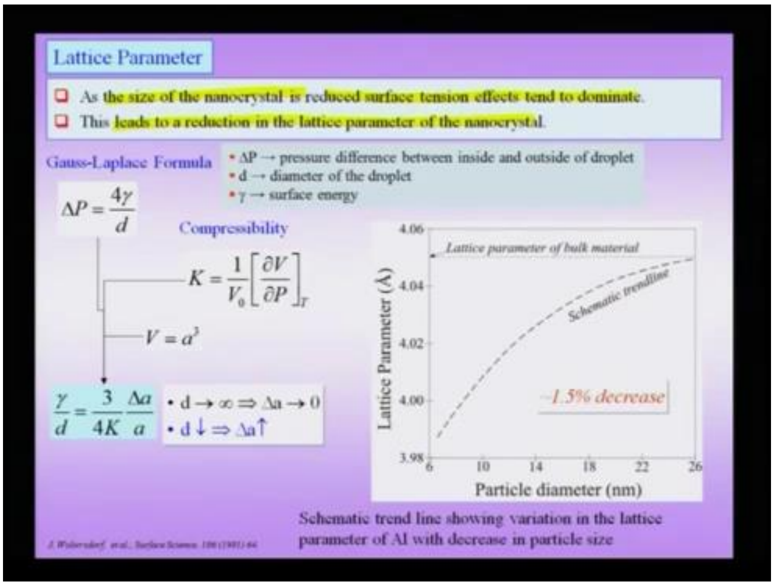

Lattice Parameter

- ☐ As the size of the nanocrystal is reduced surface tension effects tend to dominate.
- ☐ This leads to a reduction in the lattice parameter of the nanocrystal.

Gauss-Laplace Formula

- ΔP → pressure difference between inside and outside of droplet
- d → diameter of the droplet
- γ → surface energy

$$\Delta P = \frac{4\gamma}{d}$$

Compressibility

$$K = \frac{1}{V_0}\left[\frac{\partial V}{\partial P}\right]_T$$

$$V = a^3$$

$$\frac{\gamma}{d} = \frac{3}{4K}\frac{\Delta a}{a}$$

- $d \to \infty \Rightarrow \Delta a \to 0$
- $d \downarrow \Rightarrow \Delta a \uparrow$

Schematic trend line showing variation in the lattice parameter of Al with decrease in particle size

It is obvious that as the size of the nanocrystals is reduced, surface tension effects tend to dominate because now we have more number of atoms on the surface for a given volume of material. Additionally you have more unsaturated material that means, the now because of the increase curvature we already pointed out in the some of the previous lectures that your surface atoms are less bonded as you go down to smaller and smaller size. This implies that surface tension effects tend to dominate in nanocrystals. This surface tension effect can lead to a reduction in lattice parameter of the crystal. Now, how is this happening, is that now I have atoms sitting on the surface.

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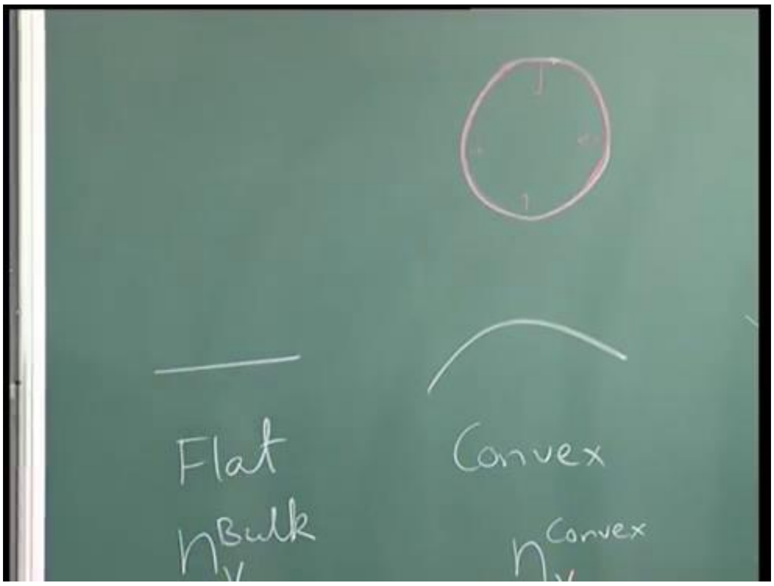

So, I will assume a spherical particle and there is a layer, which we I can call the surface and we have already pointed out that when I am talking about the surface actually it need not be a mono layer, it could be one more than one layer, which we together call the surface.

Now, these atoms on the surface are in a state of higher energy and therefore, the surface would want to shrink itself. It wants to pull itself on itself and in the process it will tend to exert a pressure into the crystal. Because now the surface does not want, the atoms on the surface want to get bonded more, they want to get closer to each other, and in the process they actually employ a some sort of a compression on the particle. Now, this effect actually leads, let leads to a decrease in the lattice parameter of the crystal, and the typical link decrease when you decrease the size.

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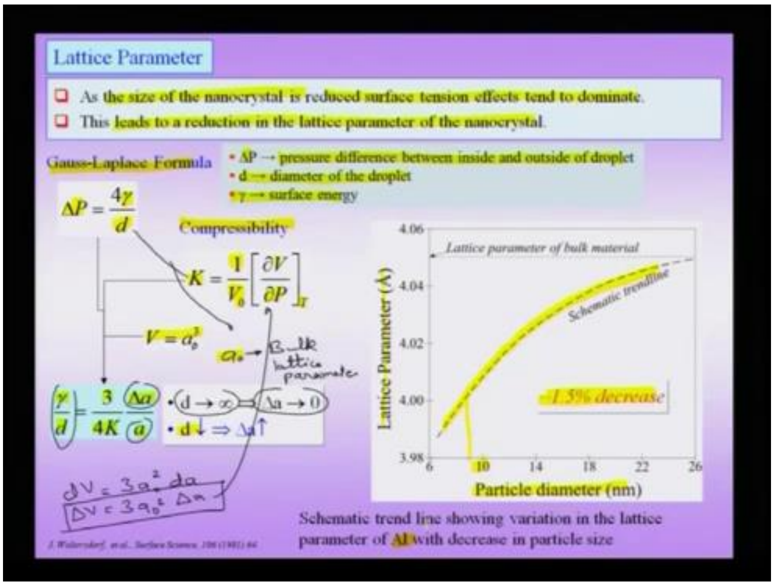

Lattice Parameter

- ☐ As the size of the nanocrystal is reduced surface tension effects tend to dominate.
- ☐ This leads to a reduction in the lattice parameter of the nanocrystal.

Gauss-Laplace Formula

- $\Delta P \rightarrow$ pressure difference between inside and outside of droplet
- d → diameter of the droplet
- $\gamma \rightarrow$ surface energy

$$\Delta P = \frac{4\gamma}{d}$$

Compressibility

$$K = \frac{1}{V_0}\left[\frac{\partial V}{\partial P}\right]_T$$

$$V = a_0^3$$

$a_0 \rightarrow$ Bulk lattice parameter

$$\frac{\gamma}{d} = \frac{3}{4K}\frac{\Delta a}{a}$$

- $(d \rightarrow \infty) \Rightarrow (\Delta a \rightarrow 0)$
- $d\downarrow \Rightarrow \Delta a\uparrow$

$dV = 3a_0^2\, da$

$\boxed{\Delta V = 3a_0^2\, \Delta a}$

Schematic trend line showing variation in the lattice parameter of Al with decrease in particle size

To say about 10 nanometer is about 1.5 percent decrease in the lattice parameter, when you go from a bulk crystal, bulk single crystal particle to a particle, which of the size of 10 nanometer. So, this is the decrease, we are talking about in the value of the lattice parameter.

Now, we can understand this by actually looking at what is known as the gauss Laplace formula, which is related to the change in pressure delta p with the surface energy, and the diameter of the droplet. So, this is originally developed for liquids, but we will use it for solids. So, the delta p is the pressure difference between the inside and outside of the droplet, d is the diameter of the droplet and gamma is the surface energy. That means, if I decrease my droplet size, the delta p is actually going to increase.

Now, for the bulk I can write down the definition of compressibility k as 1 by v naught dough V by dough P at constant temperature. Now, this V 0 is the volume of the unit cell, when the particle size is large. That means, it is in a crystal where surface tension effects are negligible, and this V can be written as a cube, and in fact when I am saying a cube, I actually mean an a 0 cube, which is the a 0 is the bulk lattice parameter.

Now, I can actually substitute, I can take, now I can differentiate this dV is equal to 3a 0 square da, and I can actually write instead of dV, I can write it in terms of delta V and I can make this a delta a. And I can now substitute this relation into this relation here, and additionally I can substitute this gauss Laplace formula into this relation here.

And therefore, I can get a relation between my gamma by d and delta a by a, where delta a is the change in lattice parameter as I reduce my crystal size from infinity. That means I have if d goes to infinity, then delta a goes to 0 that means, delta a is the change in or reduction in lattice parameter from a bulk crystal to small nanocrystals.

Now, therefore, if you look at this function, which is gives that gamma by d is equal to 3 by 4 k, where k as we notice is the bulk compressibility, and 2 delta a by a, where a as I pointed out is the lattice parameter of the bulk crystal, which can otherwise be written as a 0. Now, this formula implies that, as I decrease my d that means, as I decrease my particle diameter, then my delta a increases, that means asymptotically goes with my ((Refer Time: 26:05)) in my lattice parameter the size.

Therefore, you can see here in this reduction of lattice parameter with particle size. This is schematic trend line arrived at looking at many systems, and you can see that if you reduce the particle size, and the effects seems to dominate, only when the particle diameter is below about 50 nanometers.

So, if you can safely say that you take a nanoparticle or nanocrystals, which is above 50 nanometers in size, then that behaves like a bulk. Even though that is a nanoscale with respect to lattice parameter, it is as good as a bulk crystal. And this is an important point to mention when we try to understand, what is bulk and what is nano with respect to this specific parameter lattice parameter or the atomic volume, then you see that it is as good as the bulk.

Now, but on the other hand if you take very small particles like 5 angstrom, 5 nanometer particles or 10 nanometer particles, there is depression about lattice parameter of 1.5 percent. And this is, this schematic trend line is basically for aluminum, but other metals also show similar kind of trend schematic trend lines.

Therefore, we have now come across an important effect that purely because of surface tension effects, the lattice parameter of nanocrystals is actually reducing and this decrease could be as large as around 1.5 to 2 percent. Next, we take up the another aspect wherein certain interesting phenomena, interesting effect are seen and that is related to thermal expansion of nonmaterials.

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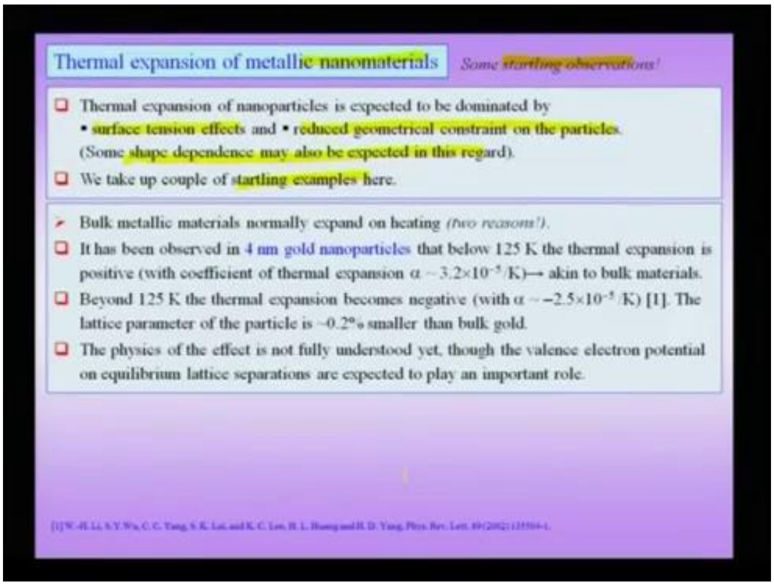

Thermal expansion of metallic nanomaterials

Some startling observations!

- ☐ Thermal expansion of nanoparticles is expected to be dominated by
  - surface tension effects and • reduced geometrical constraint on the particles.
  - (Some shape dependence may also be expected in this regard).
- ☐ We take up couple of startling examples here.

- ➢ Bulk metallic materials normally expand on heating *(two reasons?)*.
- ☐ It has been observed in 4 nm gold nanoparticles that below 125 K the thermal expansion is positive (with coefficient of thermal expansion $\alpha \sim 3.2\times10^{-5}$/K)→ akin to bulk materials.
- ☐ Beyond 125 K the thermal expansion becomes negative (with $\alpha \sim -2.5\times10^{-5}$/K) [1]. The lattice parameter of the particle is ~0.2% smaller than bulk gold.
- ☐ The physics of the effect is not fully understood yet, though the valence electron potential on equilibrium lattice separations are expected to play an important role.

[1] W.-H. Li, S.Y. Wu, C.C. Yang, S.K. Lai and K.C. Lee, H.L. Huang and H.D. Yang, Phys. Rev. Lett. 89 (2002) 135504-1.

Thermal expansion on nonmaterial as a first expectation, we may think is going to be dominated by surface tension effects and reduce geometrical constraint on particles. So, when I mean reduced geometrical constraint, I would expect that because it is a nanoparticle and there is very little of material around each atom to constraint it from actually expanding on heating that this I would expect to play an important role in thermal expansion of material apart from the fact, which I mentioned just now, which is the surface tension effects.

And obviously, we do expect some shape dependence in this regard, but we are in store for some surprise regarding this that, there are other effects which also come in, which is going to actually alter this scenario and we are going to obtain some very interesting and startling observations, which we will actually consider here. If, you talk about normal materials, then when you heat the normal material, bulk material, it actually expands of because of two reasons, and the two reasons we already know.

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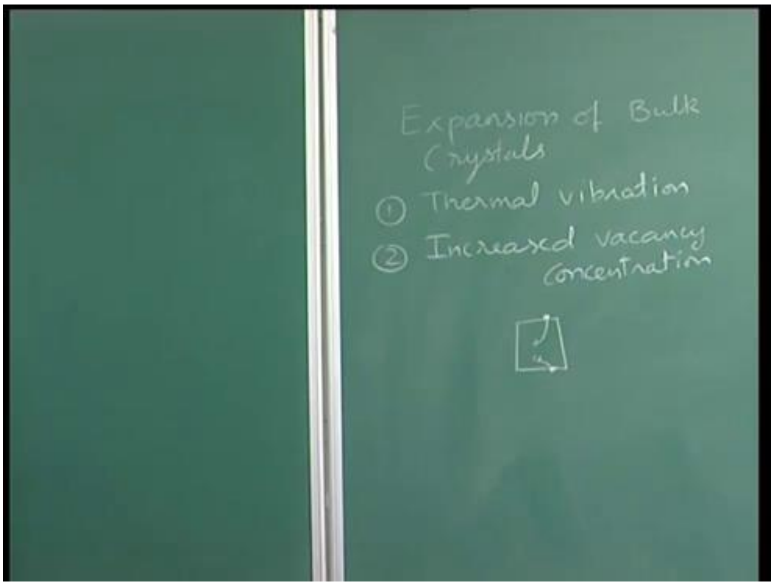

Expansion of Bulk Crystals

① Thermal vibration

② Increased vacancy concentration

So, you have two contributions here, the dominant contributions, the thermal vibration contribution, and we know that the potential energy versus the distance plot actually is asymmetric. And average distance actually moves out to larger distances, when there is a the potential, well that means therefore, when there is a thermal vibration the material would expand.

The increased vacancy concentration is a much smaller effect, one in about 1 in 10000 effect. Nevertheless when vacancies are created within the crystal these atoms go and sit on the surface and this as we know that is because with higher temperature there is an higher equilibrium concentration of vacancies. And now this is the thermodynamic equilibrium concentration we are talking about. And this movement of creation of vacancies and the movement of atoms would lead to an increase in the size of the material, in other word there would be an expansion with temperature.

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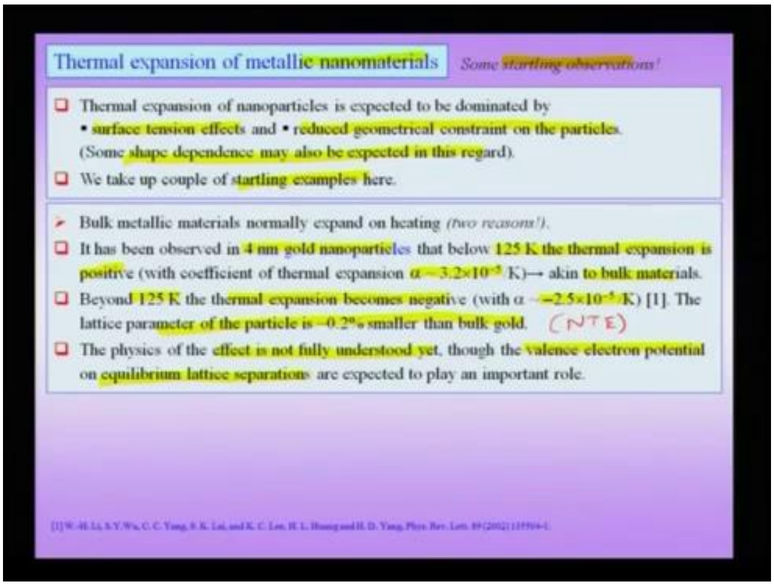

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- ☐ The physics of the effect is not fully understood yet, though the valence electron potential on equilibrium lattice separations are expected to play an important role.

[1] W. H. Li, S. Y. Wu, C. C. Yang, S. K. Lai, and K. C. Lee, H. L. Huang and H. D. Yang, Phys. Rev. Lett. 89 (2002) 135504-1.

Now, even though that we noted again that, the second effect is actually a smaller effect. Now, it has been observed and this is a very startling example, that in 4 nanometer gold nanoparticles that below 125 degrees, 125 Kelvin, the thermal expansion is positive.

That means, it is a normal kind of a thermal expansion, and the thermal expansion coefficient is about 3.2 into 10 power minus 5 per Kelvin. And this is not very different from what you expect for bulk materials, but if you look at the expansion in the regime beyond about 125 Kelvin on heating the thermal expansion actually becomes negative. That means, the material tends to contract after you heat above 125 Kelvin and the negative coefficient of expansion turns out to be about minus 2.5 into 10 power minus 5 per Kelvin.

That means, that the lattice parameter of the particle is about 0.2 percent smaller than bulk gold. And this is a very startling effect and the physics of this effect is not fully understood yet. And the important contributions, which go into giving rise to what you might call the negative thermal expansion, which is often written in acronym as NTE. So, this effect can be called negative thermal expansion effect is thought to arise from valence electron potential and equilibrium lattice separation.

So, these are thought of as 2 important mechanisms, which is supposed to play an important role towards contributing through this negative thermal expansion in gold nanoparticles. And we are talking about extremely small gold nanoparticles of the size of about 4 nanometers, and we are talking about temperatures, which are also pretty cold, which is below the room temperature.

And this happens as we know, in only a certain temperature regime, and not in all temperature regimes. And perhaps with time you will come to know, what is really the mechanism behind such an effect. Nevertheless, it is very interesting to note that in nanoparticles and nanocrystals, you can actually have negative coefficient of thermal explanation and such that two of the same order of magnitude as you notice here as the positive coefficient of thermal expansions, both of the order of 10 power minus 5, and even the magnitude is pretty much simpler. So, it is a definitely a very significant effect.

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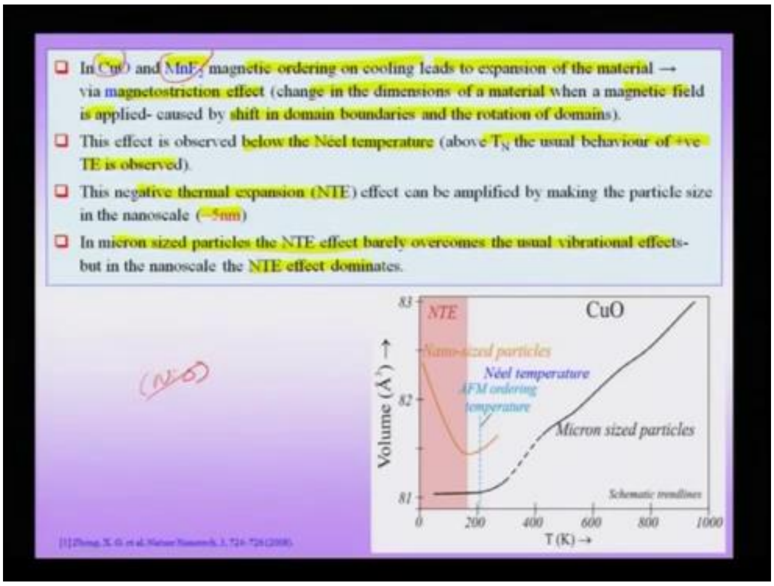

- In CuO and MnF_2 magnetic ordering on cooling leads to expansion of the material → via magnetostriction effect (change in the dimensions of a material when a magnetic field is applied- caused by shift in domain boundaries and the rotation of domains).
- This effect is observed below the Néel temperature (above T_N the usual behaviour of +ve TE is observed).
- This negative thermal expansion (NTE) effect can be amplified by making the particle size in the nanoscale (~5nm)
- In micron sized particles the NTE effect barely overcomes the usual vibrational effects- but in the nanoscale the NTE effect dominates.

(NiO)

Now, there is another reason why you could actually have negative thermal expansion. And this is seen beautifully in the system like cobalt or copper oxide or manganese fluoride MnF 2. Both these are anti ferromagnetic materials, though we have not yet dealt with magnetic properties of nanocrystals in detail, and we will take up some of it in lot of detail in some of the coming lectures, but it is an, this one is related to thermal expansion we are considering the system here.

And copper oxide, and manganese MnF 2 unlike a very similarly, related system like Ni o. Ni o is also a system, wherein you actually have antiferromagnetic ordering, but Ni o does not show this effect. So, we do not construct here and we take up the example of Cu o or MnF 2. We notice that, these systems show magnetic ordering on cooling and this leads to an expansion in the material via the magnetostriction effect.

And all of you must be familiar with magnetostriction because that is the hum created, when you send an AC signal through a transformer core. The transformer core actually hums and that is, that humming sound is actually coming from acoustic emissions, which is coming from this magnetostriction effect. Wherein the magnetic field is leading to change in the dimension of the materials, which is coming from in the presence of a magnetic field, which is applied and this is caused by shift in domain boundaries and rotation of domains within the material.

So, there is a shift in domain boundaries, there is a rotation of domains and this leads to a change in dimensions of the crystal, when you are applying a magnetic field. And this effect is called magnetostriction, and this magnetostriction as I pointed out give rise to the familiar effect of hum in a transformer, when you actually apply an AC signal.

And the important thing to note is that, in these materials like Cu o and MnF 2, there are two important criteria under, which you actually see this negative thermal expansion effect. One is that the temperature has to be below the kneel temperature, and the neel temperature as you know is the antiferro magnetic ordering temperature. That means, below the neel temperature, the material is antiferro magnetic, and above the neel temperature the material is actually paramagnetic. And above TN only the, above TN of course, the neel temperature, the material you can actually see a positive thermal expansion, which means it behaves like a normal material. Therefore, it is essential that I retain this the antiferro magnetic state to observe the special negative thermal coefficient, negative expansion state.

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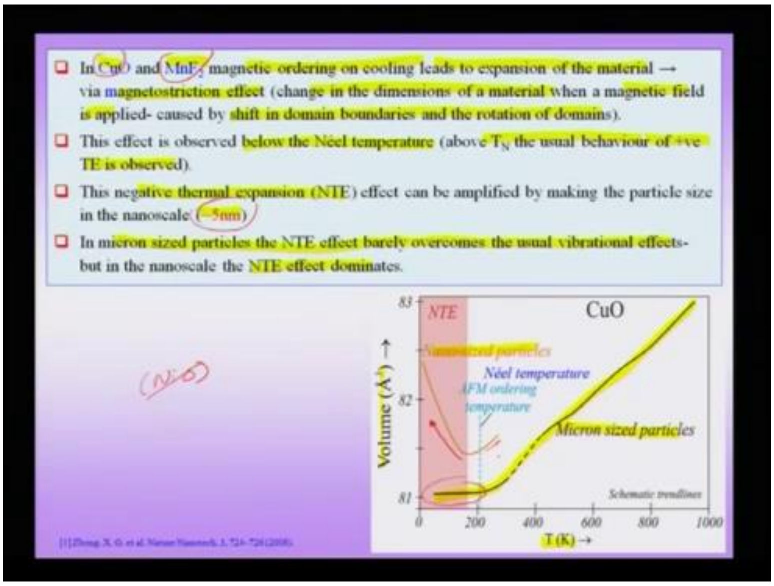

- In CuO and MnF$_2$ magnetic ordering on cooling leads to expansion of the material → via magnetostriction effect (change in the dimensions of a material when a magnetic field is applied- caused by shift in domain boundaries and the rotation of domains).
- This effect is observed below the Néel temperature (above T_N the usual behaviour of +ve TE is observed).
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- In micron sized particles the NTE effect barely overcomes the usual vibrational effects- but in the nanoscale the NTE effect dominates.

Additionally, the particle size has to be small, it has to be in the nanoscale, it has to be very-very small and you have to be about 5 nanometers, and if you look at micron size particles, the negative thermal expansion barely is able to come out, go around, get around the thermal vibration effects and actually you will see that only you observe a positive coefficient of expansion.

So, let me write down the two criteria for negative thermal expansion. In antiferro magnetic materials let me take an example like copper oxide and MnF 2. So, if I observe my volume of the crystal with respect to the temperature, I would notice that, for if I now take my nano size particles and compare it with my micron size particles. You see that, in micron size particles, you see the normal coefficient of expansion, though there is a pronounced alteration in the coefficient below the antiferro magnetic order in temperature, which is shown by the vertical dotted line.

So, in nano size particles though, there is this hidden effect, which is giving rise to an altered, what you might call coefficient of expansion. But the coefficient of expansion still remains positive, because it is not able to overcome the normal vibrational expansion, which is what is going to dominate in micron sized to larger sized particle.

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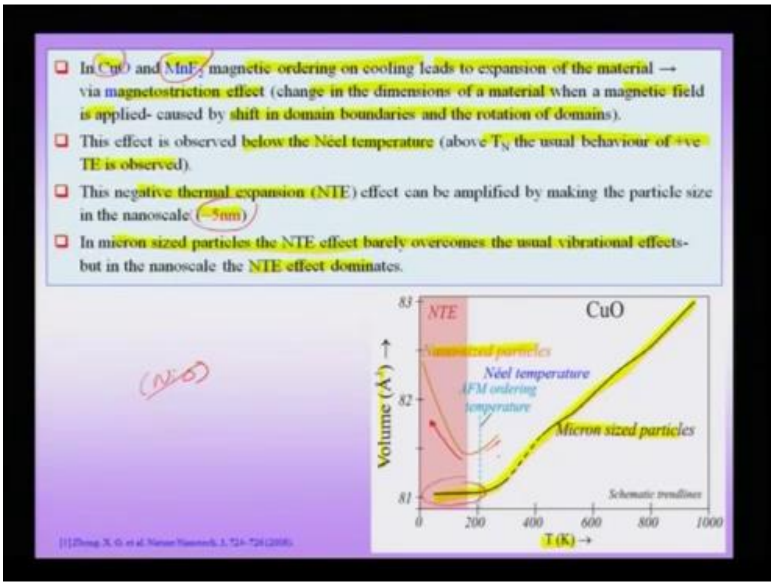

- In CuO and MnF_2 magnetic ordering on cooling leads to expansion of the material → via magnetostriction effect (change in the dimensions of a material when a magnetic field is applied- caused by shift in domain boundaries and the rotation of domains).
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(NiO)

But if you take nano size particles, and I am talking about Very small sizes like 5 nanometers, then it is clear that if you look at the plot here, which is shown in the orange line, you can see that below the, above the neel temperature, the coefficient is positive. And if you go slightly below the neel temperature, you will see that the region marked in red box is the region where you actually see an expansion in the volume of the volume as you are reducing the size.

This is the expansion of the volume in the unit cell, when you reduce the size and you can see that there is, this is a significant effect, and this cannot be what you call accounted by other methods. And we have to invoke the fact that, there is an antiferro magnetic ordering in these particles, and this antiferro magnetic ordering is giving rise to a magnetostriction effect. And this magnetostriction effect is able to actually overcome the usual thermal vibrational effect, which is normally seen for all normal materials.

So, we have seen at least couple of examples straight away wherein, we are noticing that there can be negative thermal expansion coefficient, one of which is not fully understood yet, which is in the case of gold about 125 Kelvin. But in this case, there seems to be a better understanding in the underlying mechanism, which is giving rise to this negative thermal expansion, in these nano particles of copper oxide or magnesium manganese difluoride. Now, this is not true of course, that it is only nanoparticles where you see negative thermal expansion.

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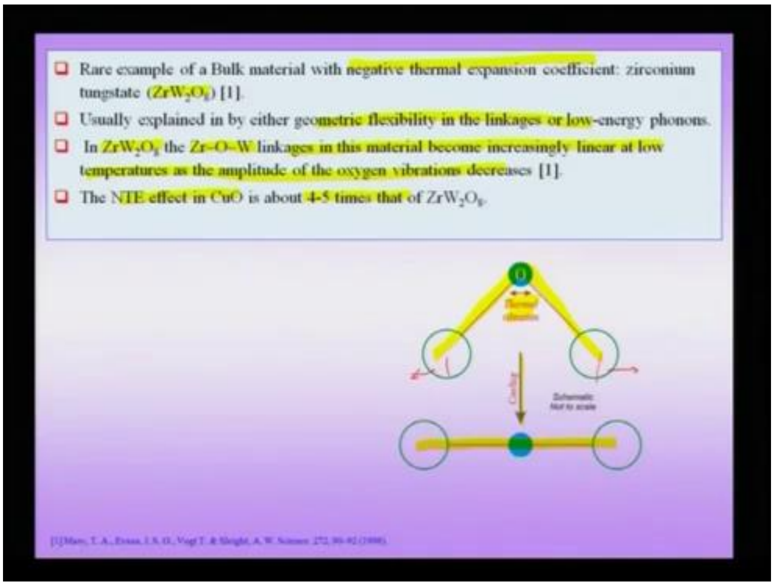

- Rare example of a Bulk material with negative thermal expansion coefficient: zirconium tungstate (ZrW_2O_8) [1].
- Usually explained in by either geometric flexibility in the linkages or low-energy phonons.
- In ZrW_2O_8 the Zr–O–W linkages in this material become increasingly linear at low temperatures as the amplitude of the oxygen vibrations decreases [1].
- The NTE effect in CuO is about 4-5 times that of ZrW_2O_8.

[1]Mary, T. A., Evans, J. S. O., Vogt T. & Sleight, A. W. Science 272, 90-92 (1996).

There are some rare examples of bulk materials also, which actually show a negative thermal expansion coefficient. And one such example is zirconium ZrW 2 O 8, which is called, a zirconium tang state. And here the geometric flexibility in the linkages is suppose to be the underlying mechanism, which is giving rise to this kind of an negative expansion coefficient.

In the ZrW 2 O 8 structure, the Zr O W linkages become increasingly linear at lower temperatures and therefore, the amplitude of, this is happening as a amplitude of the oxygen vibration decreases. Now, this is schematic explaining this effect. Now, there is a molecule, which is in angular form in which the oxygen is shown by this blue sphere, and what happens when you heat this, actually cool this material, is that the molecule tends to become progressively linear. As the thermal vibration of the oxygen molecules reduce, when you reduce the temperature, then the molecule goes from an angular kind of a shape to linear kind of a shape.

This implies that, actually the spacing between these molecules actually increases and therefore, actually by reducing temperature you are seeing a thermal expansion rather than a thermal contraction and this can be thought of as a negative thermal expansion effect. But the important point to note is that in this bulk kind of a material, which itself is a very rare example of NTE effect. The thermal expansion effect is negative expansion effect, it is only one-fifth of that, which is found for a material like copper oxide or MnF 2 wherein, we know that in nano particles the effect is much more pronounced.

Therefore, there are very interesting effects in nano particles, which includes this startling observation that you can actually have negative thermal expansion coefficient. And this the underlying mechanism can be more than one and you have to take a system by system and understand how this negative thermal expansion is actually occurring in nanocrystals of copper oxide or gold or other equivalent systems.

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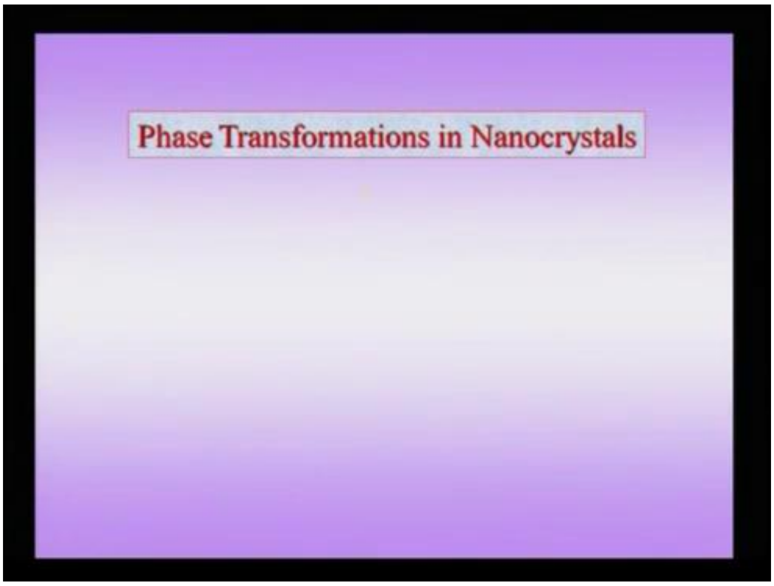

Phase Transformations in Nanocrystals

The next topic we take up is phase transformation in nano crystals. Now, phase transformation of course, is a broad area and it may not be possible to cover all aspects of phase transformations here. But we will take up selective examples of phase transformations in nano crystals, and important effects, which are coming because now you are talking about a scale of a system, which is 1 nanometer or 5 nanometer of a very small system.

Now, if you want to classify phase transformations, and we will understand that phase transformation means we are going from one phase to another phase ahis phase could be defined based on for instance a structure like you could be going from cubic phase to tetragonal phase. Or it could also be based on a property like you could be going from a paramagnetic phase to a Ferro magnetic phase or a antiferro magnetic phase to a paramagnetic phase. So, we could actually base it on a property, W could also be talking about a transition from a super conducting state to a normal state and etcetera.

Here, we restrict ourselves to what we call normal structural transformations, and we will take up couple of examples of melting and also crystal structure change. We will illustrate the point that, how actually nano crystals or nano materials can actually be very different from bulk materials. And what are the important effects, which we need to take into account when you are talking about very small size crystals?

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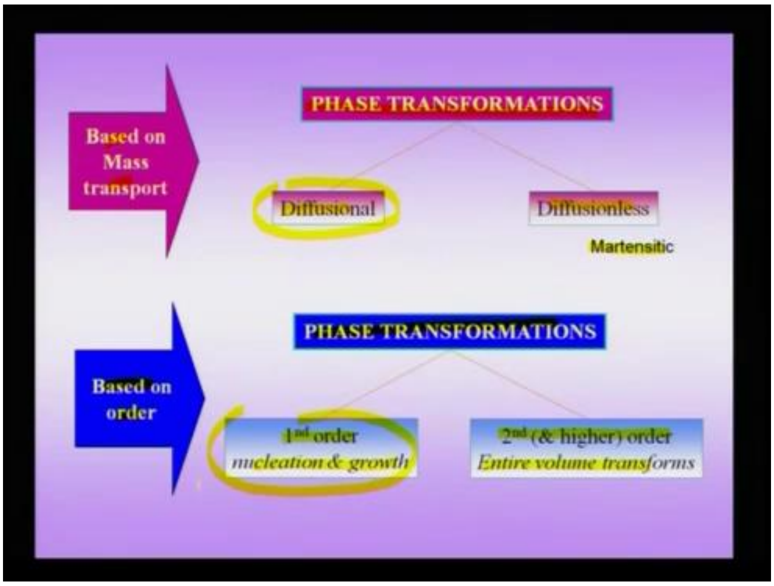

Based on Mass transport

PHASE TRANSFORMATIONS

Diffusional

Diffusionless

Martensitic

Based on order

PHASE TRANSFORMATIONS

1st order
nucleation & growth

2nd (& higher) order
Entire volume transforms

Now, phase transformations can be classified based on mass transport as diffusional or diffusion less, and in diffusional transport we imply that there is actually long range diffusion. And in an example of diffusion less transport like martensitic transformation, there is actually a sheer of the crystal, and there is no long range mass transport in ((Refer time: 41:45)). And therefore, diffusionless transformations can occur at a very fast speed. In fact martensitic transformation, the transformation front can move almost at the sheer revival velocity of the sound in the material.

Based on order of the transformation, typically they are, phase transformations are classified as first order, which involve nucleation and growth. And we also have second order transformations wherein, the entire volume transforms. In second order transformation, there I also included for instance, lambda transformation, other transformations. But here in this brief lecture series, we will worry about diffusional transformations, which are of the first order, and which implies that we are going to be talking about nucleation and growth, which is what is going to give rise to a phase transformation.

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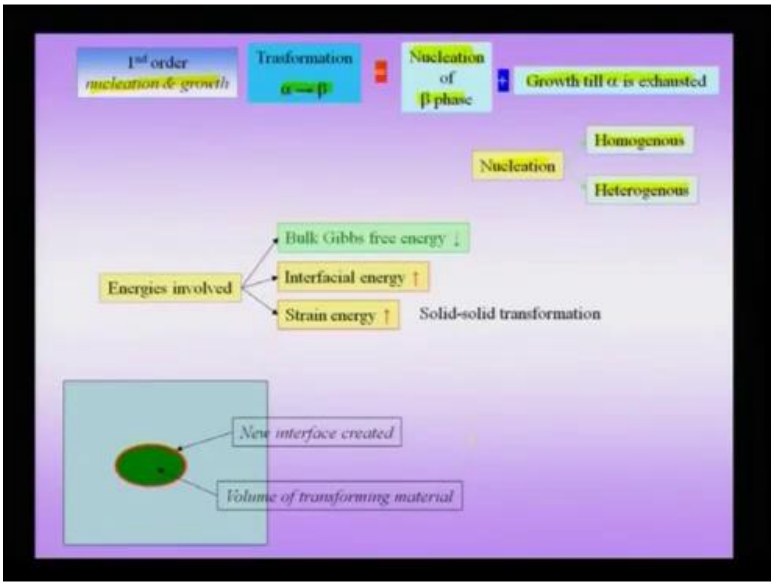

1st order *nucleation & growth*

Trasformation $\alpha \rightarrow \beta$ = Nucleation of β phase + Growth till α is exhausted

Nucleation
- Homogenous
- Heterogenous

Energies involved
- Bulk Gibbs free energy ↓
- Interfacial energy ↑
- Strain energy ↑ Solid-solid transformation

New interface created

Volume of transforming material

Now, since we are talking about the first order nucleation and growth kind of transformation, and I am talking about a phase transformation from the alpha phase to the beta phase. First of course, in the alpha matrix, I need to nucleate a beta phase and finally, and as a second step the alpha phase has to be exhausted.

That means, the beta phase has to grow to its final state such that, all the alpha is consumed. If of course, it is going to be a transformation wherein, both alpha and beta can coexists, then you will, at the end of the transformation, you will have certain volume fraction of the beta phase, and you will have a certain volume fraction of the alpha phase. Now, the important thing in this whole transformation is about nucleation is actually a technical term, and we will soon see why, what is meant by nucleation and why nucleation is actually a barrier to phase transformation.

And we will also consider the importance of nucleation especially in nano scale systems where we note that heterogeneous nucleation can dominate over homogeneous nucleation. In hetero homogeneous nucleation every point in the medium, suppose I am talking about a volume of alpha.

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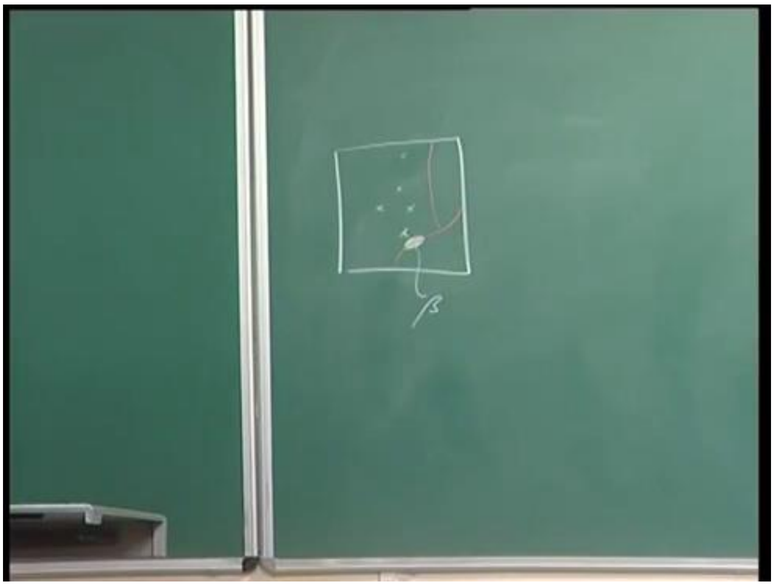

Now, this is my volume alpha, and I am talking about some region of it transforming to beta, then I would note that, any point in this material I can randomly take any point is as favorable to be a site for nucleation of the beta phase as any other. That means, there is no preferred site for nucleation. On the other hand, when I am talking about heterogeneous nucleation suppose, these were a poly crystalline material, then I would observe that this poly crystalline material would actually have grain boundaries inside. And it could so be that, this grain boundary would be a preferred site for the nucleation of the second phase, which is now my beta phase.

And if there are preferred sites, which includes the surface, the grain boundaries, stacking faults, dislocations etcetera, these would then be called heterogeneous nucleation. And the reason that heterogeneous nucleation takes place is that because it gives you a benefit in terms of the activation energy for the phase nucleation to take place. Now, what are the energies involved when I am talking about a phase transformation?

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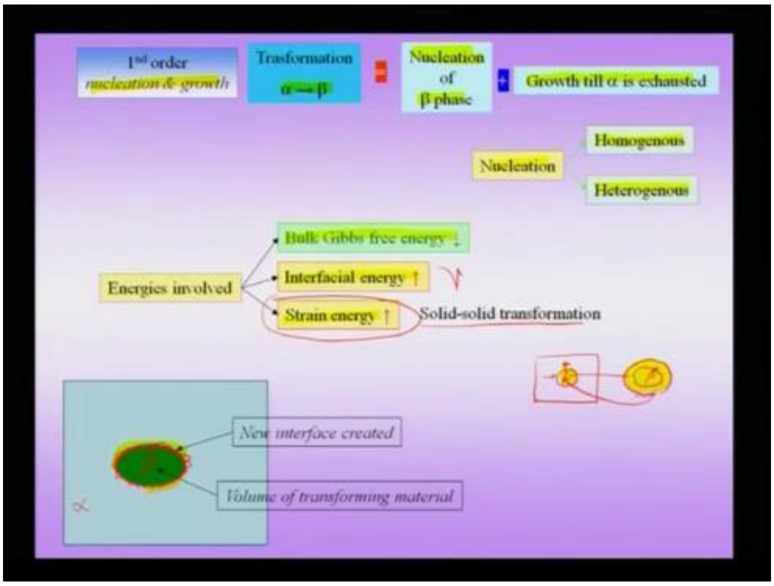

1st order *nucleation & growth*

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Energies involved
- Bulk Gibbs free energy ↓
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Volume of transforming material

The driving force comes from the fact that, below the transformation temperature, the beta phase is stable as compared to the alpha phase. And suppose, I am talking about a solid to solid phase transformation, then I have to consider 3 kinds of energies, and if I am talking about liquid to solid phase transformation for instance solidification, then I will note that one of these energies can be neglected.

Now, the reason that the phase transformation is taking place is because the Gibb's free energy of the system reduces if and that means, that the beta phase is stable as compared to the alpha phase. But when a nucleus for instance, now the green region of the beta phase forms in a matrix of alpha. So, I have a matrix of alpha in which there is a small region, which is the beta phase, which forms, then clearly the red region is the interface, which is forming between the two materials.

So, I can see that there is an interface region, which has to be created, if I have two nucleate beta within the alpha phase. And this implies that, my interfacial energy is actually going to increase. And in other words, this interfacial energy, which I call gamma, is going to oppose my phase transformation that is why it is marked in red. Also the beta phase is obviously not going to occupy the same volume as the alpha phase.

Now, suppose I make a construction, which is known as the SLB construction in which case I take a small region of material cut it out, and now I allow the phase transformation to take place and for a simplification I assume that only there is an volume change involved in the transformation. Then, the transformed volume for now I will take it to be larger therefore, this is my transformed volume as compared to the volume, which is the preexisting volume here.

That means, now my precipitate beta is going to occupy a larger volume as compared to the region from which it was cut out. Now, I obviously this cut, this beta phase is not going to exist in free space, but has to be accommodated in this hole from which I had cut it out. That means, that the beta phase is going to push out on a matrix, the matrix is going to push in on the precipitate and there will be an equilibrium configuration.

That means, there will be strain energy associated with the phase transformation and this strain energy is obviously going to oppose my transformation. Needless to say, this kind of strain energy is only involved in solid to solid phase transformation. Of course, this could play a role wherein, we have a bulk of material in a small liquid forms inside, but typically this is an important consideration in a solid to solid phase transformation and I am talking about for instance solidification, then I can actually ignore this strain energy contribution.

So, to summarize this slide, we are talking about first order phase transitions in which a second phase beta is forming from the first phase alpha. And as a further simplification, we assume that the entire alpha is turning into beta. This can happen only if I have a thing known as a nucleus forming of beta in various regions of the alpha phase, and then all these nuclei grow till or all the alpha is exhausted. So, this is the nucleation and growth process and we said that nucleation is a technical term, which we will try to understand very soon.

But before that, we also noted the nucleation can be homogeneous, which means that there are no preferred site for the nucleation of the beta phase or that can be heterogeneous in which case there are preferred size within the medium alpha wherein nucleation can take place. We also notice that, the reason of course, the beta transformation is taking place because now we are below the transition temperature from alpha to beta. That means, now the beta phase is thermo dynamically stable as compared to the alpha phase.

But as the nucleus of beta phase forms there are two energies, which will tend to oppose my phase transformation. One is of course, the interface energy between alpha and beta and the other is the strain energy. And now, whatever argument I make is what is called the continuum normal argument, and if you look at very small nuclei certain other atomistic arguments will have to come in.

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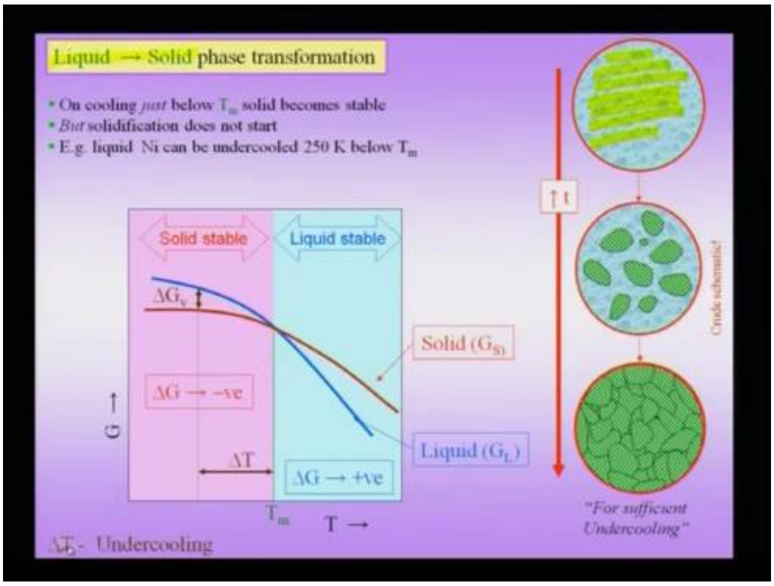

Liquid → Solid phase transformation

- On cooling *just* below T_m solid becomes stable
- *But* solidification does not start
- E.g. liquid Ni can be undercooled 250 K below T_m

But we will take up the standard classically accepted argument to understand this phase transformation. Now, suppose as I pointed out suppose, I am talking about a solid to liquid phase transformation, then I can ignore the strain energy contribution, and this would lead to my simplification in understanding the process of nucleation.

So, suppose I consider liquid to solid phase transformation that means, I have an uniform liquid as shown in the liquid on the right hand side, and then at some point of time when I under cool the system, under cool implies I am below the melting point of the material. And when I am talking about melting point, I usually define melting point in heating.

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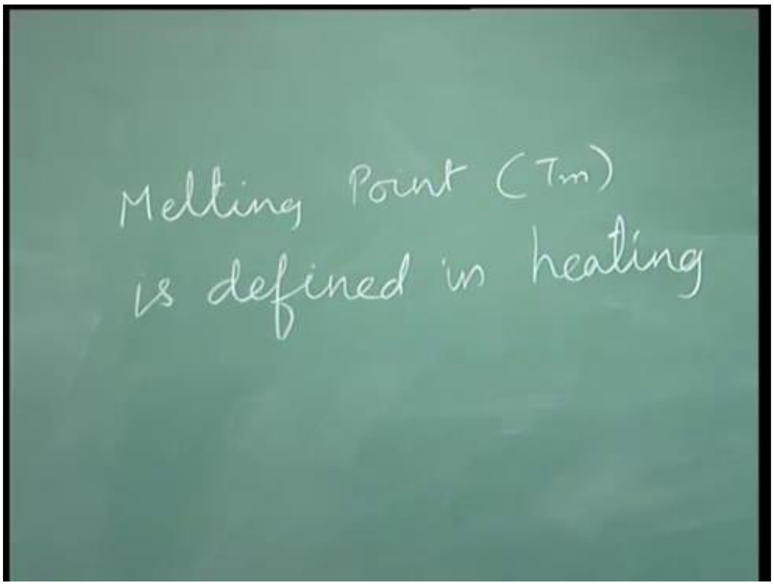

Melting Point (Tm)
is defined in heating

So, this is an important point to be noted, there never I referred to melting point, It is always melting point in heating. And this is a very surprising phenomena that you actually heat a say for example, a copper metal, then at suddenly at some temperature Tm, the entire lattice of copper collapses and therefore, you have the liquid state, which is very surprising, but nevertheless that is what happens.

Now, suppose you are doing the reverse process actually of cooling the metal, then solidification does not start at the melting point. That means, solidification freezing point is not the same as the melting point and we observe a phenomena, which is known as under cooling. And the reason we observe under cooling is the effect I told you is related to nucleation barrier, so we will understand that.

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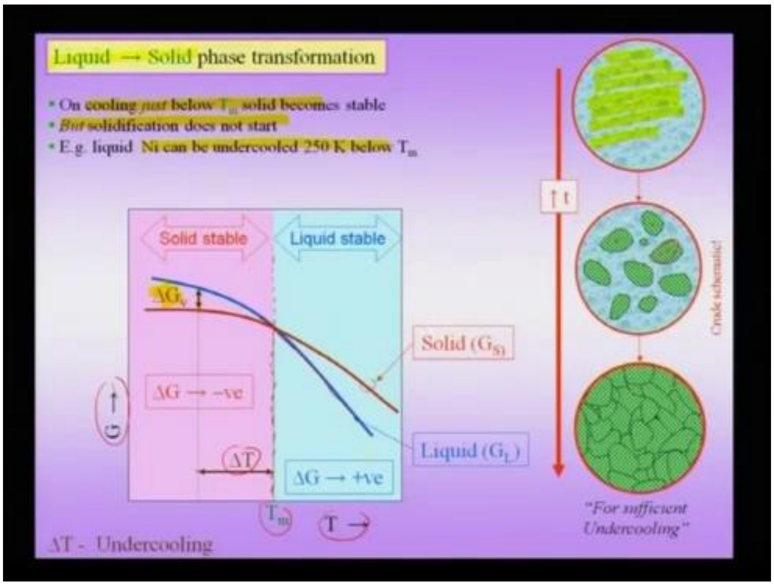

Liquid → Solid phase transformation

- On cooling *just* below T_m solid becomes stable
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Now, as you cool the material below the melting point, then at some under cooling delta T, which is shown here by, you would notice that, there might be some nuclear, which form which we had noted before and these nuclei actually, these nuclei would tend to grow to regions wherein I have crystals. At some point of time all this crystal of course, would grow and occupy the entire volume and all the liquid would have been transformed into a solid. Of course, we should note that these are schematic diagrams.

Now, if I track the free energy of the liquid and the solid, I would notice that this my Tm which I have drawn here, the vertical line here. Above the melting point, you see that the free energy of the liquid now, the blue curve is the free energy of the liquid curve, and the red curve is the free energy of the solid curve. And I am plotting my temperature versus Gibbs free energy, which means, these are negatively curved, these are curved the way they are.

Now, above the melting point the blue curve is lower than the red curve, which means the liquid is stable as compared to the solid, and therefore this system would prefer to remain in the liquid state. But below the melting point, you can see that the red curve is below the blue curve, and I am talking about melting point. I am talking about the melting point of a bulk crystal and still we are not talking about the melting point of a nano crystal, which we will take up very soon.

Now, you can see that below the melting point, and suppose I am at under cooling say for instance delta T, then I would notice that at this under cooling there is a benefit for the system, if it goes from the liquid state to the solid state. In other words, this is my bulk Gibbs's free energy driving force for system to solidify. But we noted, as we noted before that, even though there is a driving force, but the system actually does not solidify and we will understand it soon.

That means, on cooling just below Tm, the solid becomes thermo dynamically stable, but solidification does not start, and because of this nickel actually can be under cooled about 250 Kelvin below the bulk melting point, so there is under cooling possible. And of course, this under cooling is only possible if you avoid heterogeneous nucleation, and you have so far this kind of a large under cooling. And we have for now, we will, we have assumed that all the nucleation, we are observing is homogeneous nucleation.

To summarize this slide I am talking about a liquid to solid phase transformation, which implies that strain energy effects can be ignored, the liquid is stable above the melting point, the bulk melting point, the solid is stable above the below the melting point. And here again I am once again to emphasize a bulk melting point I am talking about here. Even though I have a melting point defined in heating in other words, if I am heating, then the metal melts at this melting point, when I cool it the melting point is not the same as a freezing point. In other words, solidification does not start and you need to under cool the system before solidification starts.

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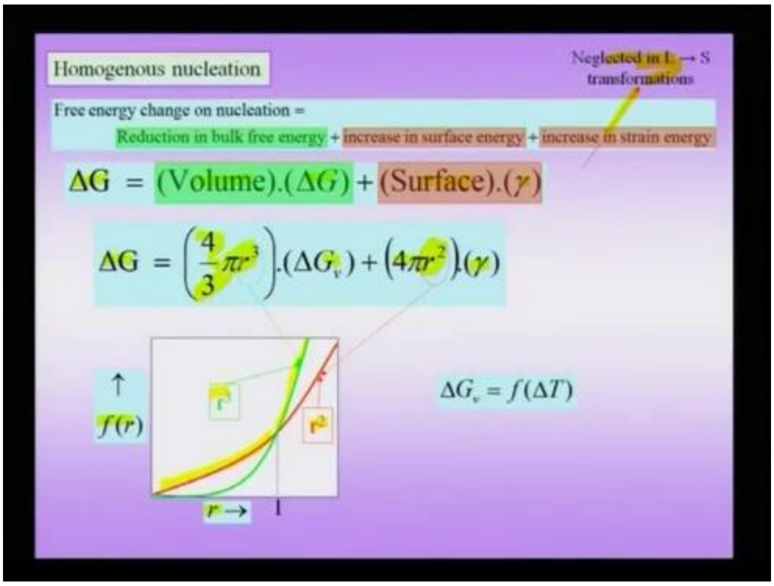

Homogenous nucleation

Neglected in L → S transformations

Free energy change on nucleation =

Reduction in bulk free energy + increase in surface energy + increase in strain energy

$$\Delta G = (\text{Volume}).(\Delta G) + (\text{Surface}).(\gamma)$$

$$\Delta G = \left(\frac{4}{3}\pi r^3\right).(\Delta G_v) + \left(4\pi r^2\right).(\gamma)$$

$$\Delta G_v = f(\Delta T)$$

Now, if to understand this effect of nucleation barrier, let me write down the free energies involved that means, there is a reduction in bulk Gibbs's free energy, there is an increase in surface energy, and there is also increase in strain energy. But for now we will ignore this increase in strain energy coming from because we are considering a liquid to solid transformation. So, the delta G for this transformation can be written as the volume of the material being transformed into delta G, and the surface area into gamma.

And suppose I assume that the nucleus or the second phase, which is forming is spherical, then I can write down the volume as 4 by 3 pi r cube and the Gibbs free energy is delta G v and the surface of this sphere will be 4 pi r squared into gamma, which is the interface energy between the solid and the liquid. Now, this delta G function has two terms, one is going as r cube and one is going as r square. We know that r cube terms will tend to dominate for larger values of r, while the lower power would dominate at the lower values of r.

That means, now if I am suppose I am just plotting f of r versus r, and I am tracking two functions r square and r cube, then r cube will be the dominant function above one, but r square is a dominant function similarly, r will also dominate over r square when I am below one. That means, the second odd second term r square is going to dominate at these smaller sizes, and at larger sizes the bulk free energy r cube term is going to dominate.

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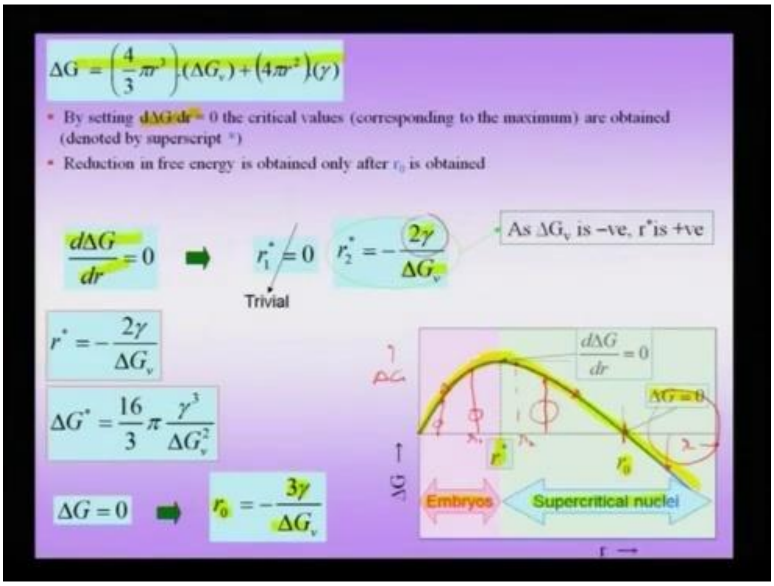

$$\Delta G = \left(\frac{4}{3}\pi r^3\right)(\Delta G_v) + (4\pi r^2)(\gamma)$$

- By setting $d\Delta G/dr = 0$ the critical values (corresponding to the maximum) are obtained (denoted by superscript *)
- Reduction in free energy is obtained only after r_0 is obtained

$$\frac{d\Delta G}{dr} = 0 \Rightarrow \cancel{r_1^* = 0} \quad r_2^* = -\frac{2\gamma}{\Delta G_v}$$

Trivial

As ΔG_v is –ve, r^* is +ve

$$r^* = -\frac{2\gamma}{\Delta G_v}$$

$$\Delta G^* = \frac{16}{3}\pi\frac{\gamma^3}{\Delta G_v^2}$$

$$\Delta G = 0 \Rightarrow r_0 = -\frac{3\gamma}{\Delta G_v}$$

Now, suppose I plot this curve, the delta G curve, then you would notice that delta G curve goes up and down with r and this is now r versus delta G curve. So, I am plotting r versus delta G, and you see that the curve goes up and down, and now this implies that if I form a small nucleus, and now I am talking about a phase transformation from liquid to solid and I form a small nucleus of small radius r. Then, I see that the energy of the system actually increases over the liquid state.

If I form even larger nucleus, then or a even larger solid phase, then there is an even larger increase in the energy. If I go to even larger sizes, then I notice that there is though a reduction it is similar to this. And finally, of course, beyond a value r 0, there is actually a, if I grow a very large precipitate like this, then I very large for you might call a solid, then actually there is a reduction in the free energy. That means, if I have a liquid and I, there is a small r which forms, the energy of the system does not decrease, but actually increases.

So, even though we are talking about the, we are below the bulk freezing point or the bulk melting point to be more precise, the system does not benefit, if this small volume or small r actually becomes a solid, the energy of the system actually increases. Now, there are critical points in this curve, the maxima, the curve point r 0 below, which actually the curve goes down below 0, and we will we can actually find these numbers by taking this function of delta G which is shown here.

And actually differentiating this function d delta G by d r, and if you said d delta G by d r is equal to 0, then I would find this critical value and which is a maxima in the curve, and I can actually set this function delta, this delta G equal to 0 and I can find the value of r 0. Now, by doing, so we find that the by setting d delta G by d r equal to 0, and I find that r star, which is the value of r at the maxima or which is also called the critical nucleus size turns out to be 2 gamma by delta G.

That means, larger the interface energy, larger will be the r star. And what is this r star? r star is the maxima in the curve. What is the physical meaning of this r star? It implies for some reason suppose I suddenly form a solid of size r 1, then what will happen is that, this r 1 will shrink, and in other words this solid will actually remelt, it will not because that is the direction of decreasing free energy. But by some other chance suddenly some region of space you put a solid of radius, which is larger than r star here and I call this r 2, then the system actually can grow, the radius can grow by decreasing its free energy.

And now, I am not comparing my r 1 and r 2, the energies corresponding to that with the overall energy at the origin. I am just saying by chance suppose I put, I take a crystal of r size r 2 and put it into the melt or equivalently by some chance an r 2 forms in the melt and I am not explaining how it is forming, I just assume it forms, then such an r 2 can actually grow downhill in Gibbs free energy, while if I form an r 1, it will actually shrink and vanish.

So, r star is that critical radius above which actually the crystals will tend to grow right. And we will note very soon that, this r star itself actually lies in the nano scale we will note that very soon. Now, and this r star scales as gamma that means, larger the interfacial energy, larger will be the size of that r star, which actually can grow downhill in Gibbs's free energy.

Now, this, and how does this r star actually arise, and how does the solidification take place? is that the liquid is exploring all kind of configurations because now this is a liquid, it atoms are mobile and all kind of configurations are being explored, and some region of the liquid you would actually observe that, atoms are coming in a precise configuration. Suppose, I am talking about aluminum crystal, which looks like an FCC aluminum crystal right, this is occurring by what you might call a random statistical fluctuation.

Now, this if that region wherein, you found an crystal of aluminum, which looked like a crystal of aluminum in terms of its atomic arrangement. If, it is below the value of r star, then such a crystal would actually shrink away, and if it is above r star, then such a crystal would actually grow and lead to solidification, then it will grow to a stable regime, and actually will lead to solidification.

Now, in some sense we will note later on that, this is actually not very surprising and this is what you would expect. But additionally we can actually calculate the value, which is known as r 0, which is said, got by setting delta G equal to 0. And we can actually obtain the value beyond which of course, the whole system is actually lowering its energy, but needless to say r 0 as a much larger value than r star. So, in realistic systems, you would not expect crystallite sizes of r 0 to form, you would rather expect crystallite size of slightly larger than r star to form my random fluctuations.

Now, the r which are smaller than r star are called embryos in other they are the unstable things, which will just vanish and those which are larger than r star are called super critical nuclei and the r star it is also is called the critical nucleus size. Therefore, I need to at least put an r star before which my system would grow and give me my phase transformation.

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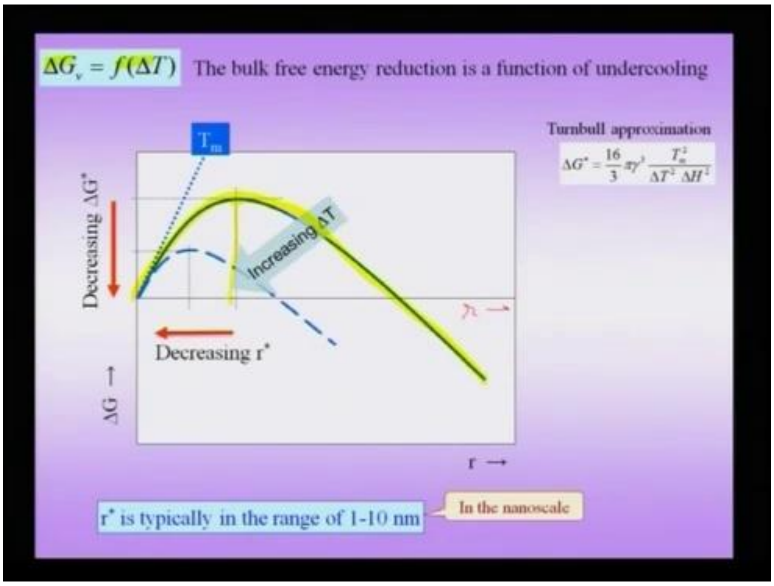

$\Delta G_v = f(\Delta T)$ The bulk free energy reduction is a function of undercooling

Turnbull approximation

$\Delta G^* = \frac{16}{3}\pi\gamma^3 \frac{T_m^2}{\Delta T^2\,\Delta H^2}$

r^* is typically in the range of 1-10 nm

In the nanoscale

Now, obvious it is needless to say that the delta G v, which I have used as a function in this function near delta G v, which is the reduction in free energy per unit volume, is a function of the under cooling and larger than under cooling. Now, suppose I plot my delta G versus r curves, and now this is my the previous curve which I showed you, delta G versus r curve, but now for different under cooling. Now, if I start with a normal under cooling like this, I notice that I get a curve wherein I have a certain value of r star.

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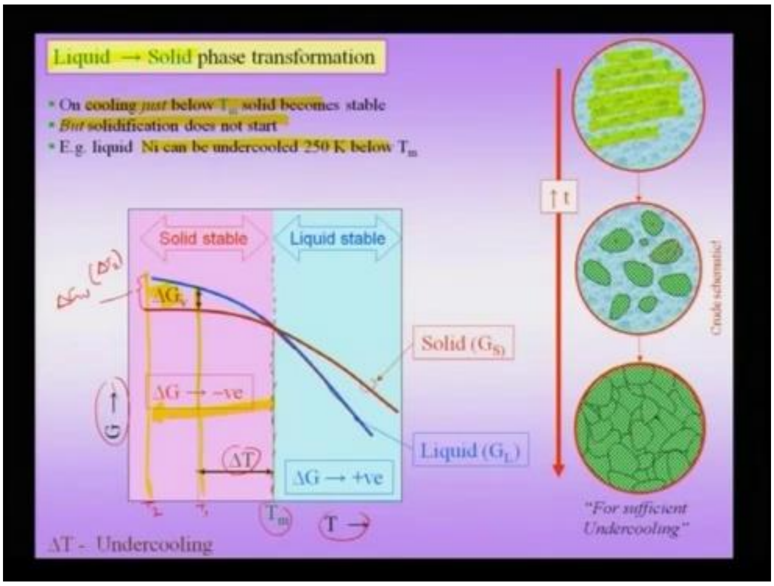

Liquid → Solid phase transformation

- On cooling *just* below T_m solid becomes stable
- *But* solidification does not start
- E.g. liquid Ni can be undercooled 250 K below T_m

ΔT - Undercooling

"For sufficient Undercooling"

Now, suppose I under cool this system even further which means, I am now somewhere here in the curve instead of being somewhere here in the curve. I am under cool my system even further and I am somewhere here in the curve. So, I under cool my system even larger; that means, I have a larger delta G v supposing my phase transformation. Now, this is my new delta G v at a larger under cooling delta T 2. If, this is my T 2 and this is my T 1.

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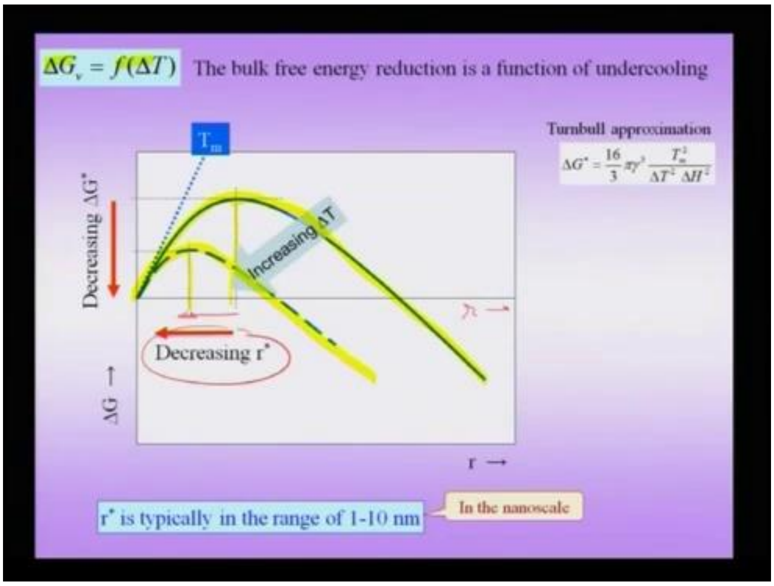

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r^* is typically in the range of 1-10 nm — In the nanoscale

And therefore, at a larger under cooling, you would notice that, the delta G versus r plot actually, sees has a maxima at a lower value of r star. That means, that with increase in delta T, which is under cooling my r star decreases. So, r star decreases with increase in under cooling. Therefore, what happens r star decreases implies that I need to form those r star kind of nucleus, which is smaller and smaller that means, if I under cool only by about 5 degree Celsius, then I need to assemble, which is this large. While suppose I cool it under cool it even further, then I need to assemble a much smaller crystal.

And remember these crystals are arising out of random fluctuations and therefore, there is a better chance of hitting on a smaller crystal rather than a larger crystal arising out of random fluctuation. That implies that, if I under cool more, there is a better chance that my solidification would actually takes place. Now, this r star, which is the critical nucleus size is typically in the range of 1 to 10 nano meter and therefore, it is its own right actually a nano crystal.

Now, we will see the implications of this very soon when you are talking about melting of nano crystals. So, in other words to summarize this whole process, we are talking about transformations, which are of the first order transformation, which involves nucleation and growth. And we are also talking out the fact that melting point is only in heating, and cooling actually we need to under cool the system. The reason we need to under cool the system is because the interface energy plays an important role and is going to oppose your phase transformation.

And in addition to what you might call the strain energy, which is involved in solid to solid phase transformation and because I have to under cool, the reason I have to under cool the system is that only, then actually I get a benefit in terms of my forming a smaller nucleus, which actually can grow downhill in Gibbs's free energy and this process as I told you is arising out of a random fluctuation.

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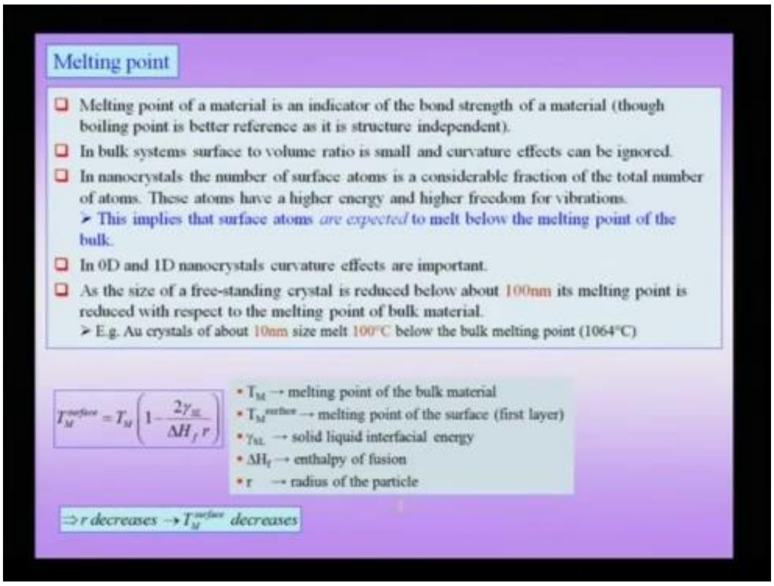

Melting point

- ☐ Melting point of a material is an indicator of the bond strength of a material (though boiling point is better reference as it is structure independent).
- ☐ In bulk systems surface to volume ratio is small and curvature effects can be ignored.
- ☐ In nanocrystals the number of surface atoms is a considerable fraction of the total number of atoms. These atoms have a higher energy and higher freedom for vibrations.
  - ➢ This implies that surface atoms *are expected* to melt below the melting point of the bulk.
- ☐ In 0D and 1D nanocrystals curvature effects are important.
- ☐ As the size of a free-standing crystal is reduced below about 100nm its melting point is reduced with respect to the melting point of bulk material.
  - ➢ E.g. Au crystals of about 10nm size melt 100°C below the bulk melting point (1064°C)

$$T_M^{surface} = T_M\left(1 - \frac{2\gamma_{SL}}{\Delta H_f\, r}\right)$$

- T_M → melting point of the bulk material
- $T_M^{surface}$ → melting point of the surface (first layer)
- γ_{SL} → solid liquid interfacial energy
- ΔH_f → enthalpy of fusion
- r → radius of the particle

$\Rightarrow r$ *decreases* $\rightarrow T_M^{surface}$ *decreases*

Therefore, we understood some of the essential aspects of what you might call a phase transformation, and especially melting in bulk crystals. And we can now turn our attention to melting point of nano crystals.