Phase Transformation in Materials
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Lecture – 25
Heterogeneous Nucleation

Today, we are going to discuss about heterogeneous nucleation and I am going to take examples; both from the liquid to solid and solid to solid transformations. Just to show you that how we can drill such a kind of problems; in a both physical as well as mathematical manner as I have told you in the class in the last; previous class also that heterogeneous nucleation is more close to the practical problems in the industry or even normal solidification conditions.

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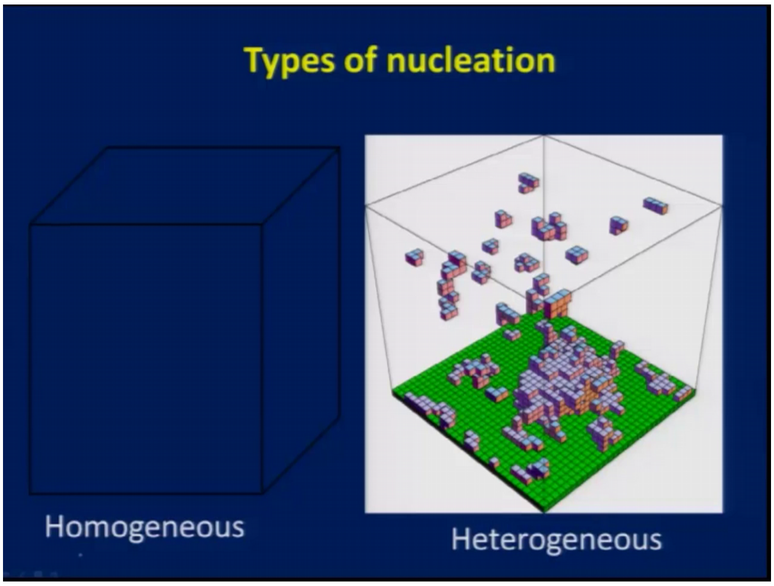
Types of nucleation

There is always presents of impurities in the liquid or in the solid impurities can be just like an oxide or a surface or the mold wall or it can be even some chemical in homogeneities or in defect structure like a dislocations or a boundary or an edge.

So, these are evidently present in all the systems that is why nucleation will be predominately heterogeneous type because it is very easy to nucleate a parent new phase inside a parent phase when there is an impurity present. So, just to give you some examples that heterogeneous nucleation is basically preferential means this nucleation events will happen on certain sets of particles which will offer better tendency for nucleation and this is very evident in this picture where you see there only few places where the solid phase which is shown like a pink cover is forming on this cube.

They are not uniformly distributed. So, in the literature people normally think that when we have an impurity or a mould wall the way nucleation can happen is what is known as a cap cycle; cap on a substrate.

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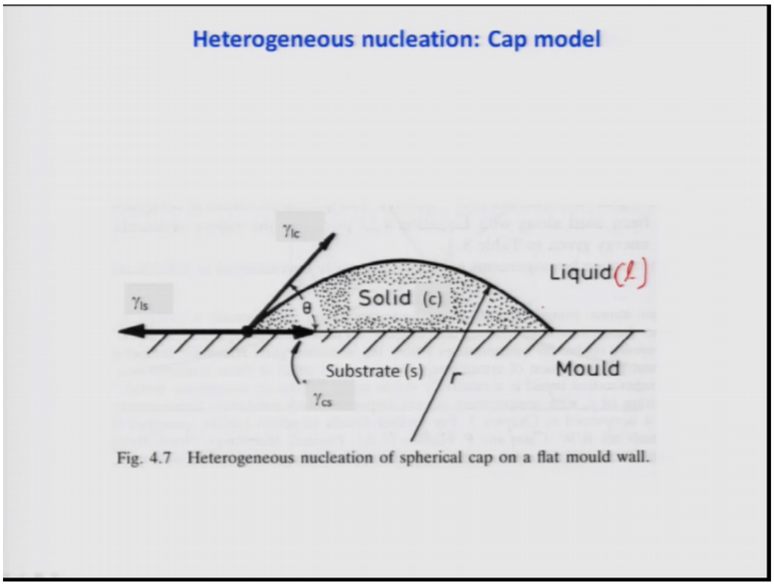

Heterogeneous nucleation: Cap model

Fig. 4.7 Heterogeneous nucleation of spherical cap on a flat mould wall.

Substrate means a oxide or a nucleation or a mould wall or anything. So, first we are going to consider the case of a solid phase forming from the liquid and this nucleation happens on a substrate. So, I have marked here substrate as a symbol s solid as a symbol c liquid; obviously, will be such a symbol l and here you see that substrate is known a mould, it can be mould wall or it can be solid particles of side particles in the mould surface.

So, therefore, the solid which is forming from the liquid is forming like a cap on these and few important things before you get into the mould to explain it in details that the interfacial energies which will given as a solid liquid gamma solid. So, a crystal liquid gamma l c and the gamma c this is substrate and solid substrate and sorry crystal and sub solid in the substrate they are actually meeting at the point at which this solid newly from solid is touching the substrate and at the meeting point these energies are balanced and to balance it you need to have a contact angle and that contact angle is given as a theta.

Basically any heterogeneous nucleation when something forms on a substrate there has to be a contact and the contact is defined by an angle that angle is known as theta. So, now, I if go back to the board and just use the same methodology which I have used in the last class for the homogenous nucleation I will explain you. So, I derived some few mathematical formula; in case I do not forget that is what I am going to use this charts.

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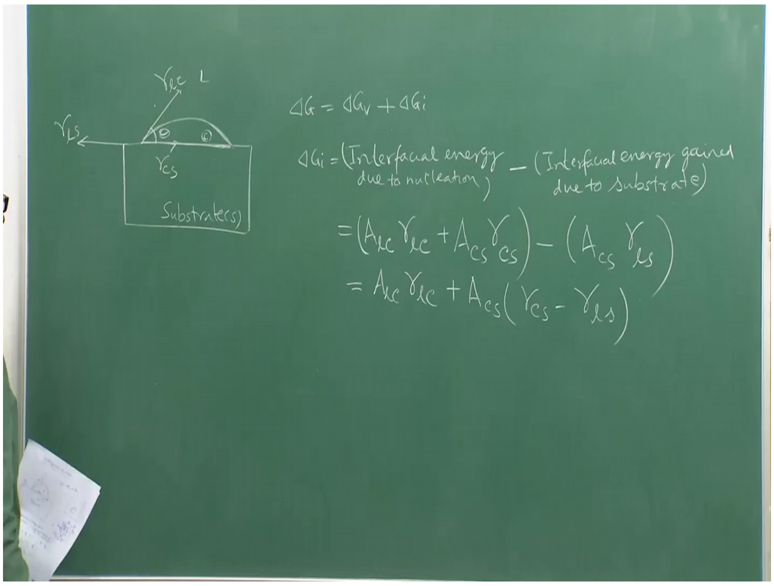

$$\Delta G = \Delta G_v + \Delta G_i$$

$$\Delta G_i = (\text{Interfacial energy due to nucleation}) - (\text{Interfacial energy gained due to substrate})$$

$$= (A_{lc}\gamma_{lc} + A_{cs}\gamma_{cs}) - (A_{cs}\gamma_{ls})$$

$$= A_{lc}\gamma_{lc} + A_{cs}(\gamma_{cs} - \gamma_{ls})$$

So, first of all; you see here that the module which I have used is looks like this, if I have a substrate like that this is substrate and we have a solid phase which is known as crystal forming out of the liquid and as I said interfacial energies are balanced at this point 3 interfacial energies this is gamma c s this is gamma l s liquid solid and this is gamma c l or l c liquid l and the crystal which is formed.

And this balance is basically leading to a contact angle theta. So, what you see here as you know delta G has 2 parts; one is the volumetric part other one is your surface energy related parts which we can defined as a interfacial part that is better actually because there are different types of surface energies here. So, first let us calculate what is delta G i for calculation of delta G i; that means, the part free energy part which is responsible for the interfaces we need to look at this picture carefully initially the substrate was in contact to the liquid.

So, therefore, the interface between substrate as liquid was present and as soon as these crystal when nucleates on the substrate these interface which was there initially between substrate of the liquid is now no longer represent. So, suppose therefore, these energy is recovered the energy surface energy because of the substrate on the liquid which was there earlier the formation of the solid nucleolus has basically happens in such way that this energy which is there earlier was link over or this energy is basically taken back by the; to the system.

On the other hand 2 new surfaces are created what are these one is between the liquid and the crystal other one is between the crystal and the substrate, right. So, liquid in the crystals basically forming an interface along these curved surface and solid on this substrate has forming a interface between along these things. So, basically there earlier sub surface which are between substrate and the liquid is now replaced why the crystal and the substrate so; that means, what; that means, we can write down the energies basically interface the energy; it has been energy due to a nucleation minus interfacial energy gain interfacial energy gain due to substrate that is what is the gain because of the nucleation.

So, how we can write down that that can basically write down this is the interfacial energy nucleation is basically has 2 parts one between crystal and liquid on the crystal and the substrate. So, therefore, the surface of the area between crystal and the liquid multiplied by interfacial energy between crystal and the liquid that is see l c plus basically interfacial energy between interfacial energy between crystal and the substrate multiplied by surface energy or interfacial energy between crystal in substrate that is the energy because of nucleation minus the gain energy that is again A c s the surface area remain same multiplied by gamma substrate liquid substrate.

Now, I am clear that is the actually energy balance because of the nucleation of these new phase on the substrate now we can actually write down this very clearly gamma a and c gamma l c plus as you see here a c a c is common if I can take out that. So, become gamma c s minus gamma l s right. So, and we can think of this one a little bit different way like remove this tau we can think of this construction like this.

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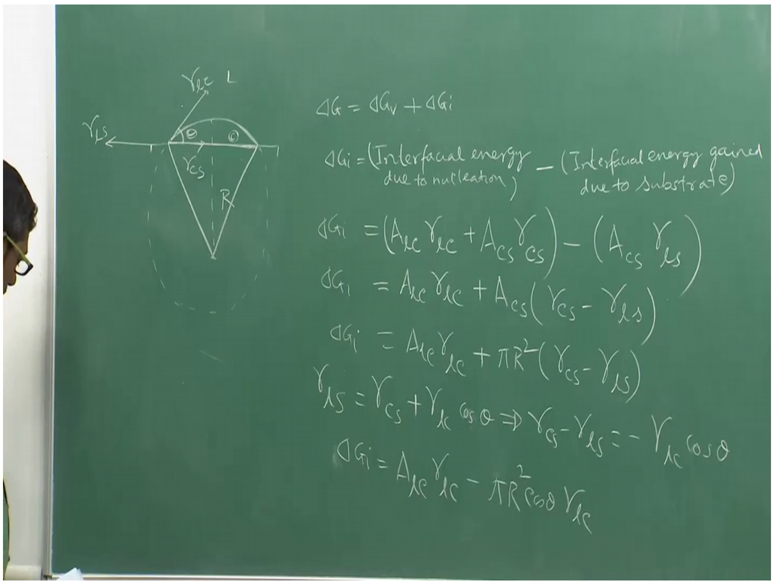

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$$\Delta G_i = A_{lc}\gamma_{lc} + A_{cs}(\gamma_{cs} - \gamma_{ls})$$

$$\Delta G_i = A_{lc}\gamma_{lc} + \pi R^2(\gamma_{cs} - \gamma_{ls})$$

$$\gamma_{ls} = \gamma_{cs} + \gamma_{lc}\cos\theta \Rightarrow \gamma_{cs} - \gamma_{ls} = -\gamma_{lc}\cos\theta$$

$$\Delta G_i = A_{lc}\gamma_{lc} - \pi R^2 \cos\theta\, \gamma_{lc}$$

We can think of this is a sphericals cap of a largest sphere of radius r you can always draw a largest sphere I am just doing a part of it.

So, that is the sphericals cap of a largest sphere of radius r now I can actually write down this as like this a l c gamma l c say a c is says what a c is this surface area that is nothing, but pi R square if I is these one gamma c s minus gamma l s that is basically my delta G i all right now as I know as I told you that these the interfacial energies that is gamma l s gamma l c and gamma c s; I actually balance at these point both vertical and horizontal components of balance if I simply considered the horizontal components I can write down gamma l c; oh sorry; gamma l s; these one is equal to gamma c s plus gamma l c cos theta.

That is very clear because of the energy balance you can see the cos component of these plus this one will be equal to the gamma l s at this point now I can actually use this expression to convert this terms c s minus l s. So, c s gamma c s minus gamma l s gamma c s minus gamma ls which is nothing, but minus gamma l c cos theta; so, if I plus in that into the delta G i delta G i will become A’s l c gamma l c minus pi R square cos theta gamma l c. So, that is; what is my interfacial energy term we will see how to calculate surface area l c later.

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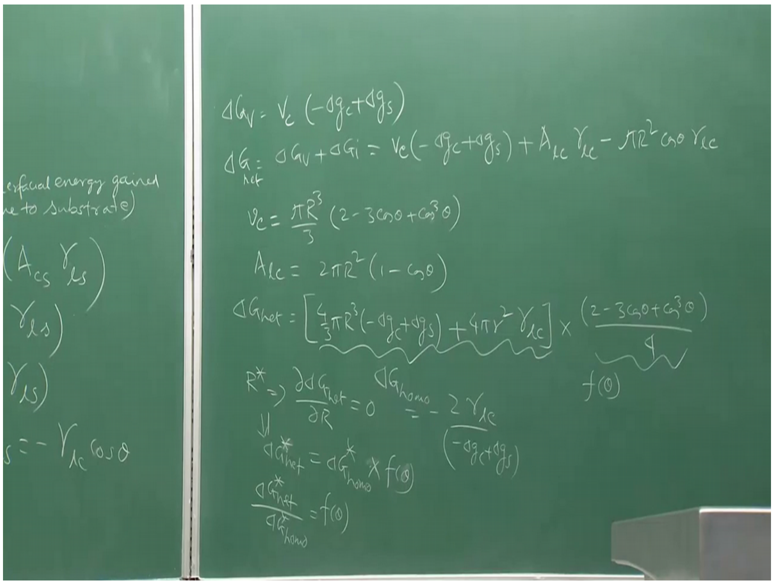

So, that I can easily get converted; now what about the delta G V part delta G V is a volume part; so, therefore, this must be the free energy multiplied by the volume of this spherical cap. So, that is nothing, but V c that is the volume of these crystal which is formed here multiplied by these 2 term; minus chemical energy plus stain energy that you have seen earlier. So, therefore, total energy is delta G V plus delta G i that is equal to V c multiplied by minus delta c and intentionally making this one minus in the books they are not given is obvious because the stable energy is always a positive part (Refer Time: 12:27) energy chemical free energy is basically is a negative as so high.

But in case if you what is both of them; poss you know same sign is not going to crate problem; only when you are going to calculate the values, you will see the negative (Refer Time: 12:41) and the picture and delta G i is this a l c gamma l c minus pi R square cos theta gamma l c. So, that is; what is basically my final equation. Now what I need to know what I need to know from the geometry construction is the surface area between this crystal and the substrate that is what is gamma l c that is no, no; that is accept A l c the crystal and the sorry the surface area between these 2 between the crystal and the liquid this is the surface area the cap surface area and the volume.

Now geometrically this is done in the book you do not need to do it you can do it V c also the value of this one is simply this I am not doing it because this is geometrically possible to do it you. So, try I have also try it and you can do it second is that A l c that is equal to basically twice pi R square 1 minus cos theta correct now once you put it everything there you will get a delta G star or basically this is; let us write down this is heterogeneous is better this is homogenous one was dealt G homogeneous. So, therefore, delta G heterogeneous is equal to basically it will be like 4 third pi I r cube G c plus G; G s plus 4 pi R square gamma l c multiplied by a factor twice minus 3 cos theta plus cube theta by O.

Is better you do this mass yourself the final mass final mass means from delta heterogeneous by putting all this values and get this equation. So, what do a get you get that this is basically nothing, but delta G homo geneous nucleation. So, therefore, the factor which is coming into picture when you do the calculation for heterogeneous nucleation is the 2 minus 3 cos theta plus cos q theta by 4 that is the main difference which make heterogeneous nucleation. So, potentially important in the actual applications the factor is basically is nothing, but relate to the contact angle.

So, that for you see this is nothing, but a function of a theta and you always in the books which I this as f theta because that is the factor which governs most of the heterogeneous nucleation aspects in the liquid on the solid also; so, that is simple by using this gap model which is very model and which is basically energetically favorable model we can actually get down into nucleation aspects. So, one can actually do kinds of things you can you know that this is already lead to R. So, therefore, r star can be calculated simply integrating this formula with respect to R; sorry, it can be differentiating it. So, that is nothing, but del by putting delta G heterogeneous by del r make it 0 and you can then calculate delta G star heterogeneous the various of height of the barrier height of the barrier height of the barrier height of the nucleation.

That all this things can be easily calculated there is that is part of very simple this will be all coming into same this will be equal to a get twice gamma l c preferred by this one minus G c plus G s correct and delta G heterogeneous also will be coming as a function of a theta basically this will be coming exactly same as delta G star homogenous and multiplied by f theta. So, therefore, we can clearly see that nucleation barrier is basically I can again write down for your reference. So, that the height of the barrier for the heterogeneous nucleation is basically functions of f theta when you compare with homogenous nucleation will see all this things later part of it.

Fine; so, that is the important part of the mathematics which you need to know as a part of your as a part of your discussions; remember this functions we need to look at in details. So, that is what we will do now how this functional looks like and to do that let me just erase this part because that function is going to make the all difference of the homogeneous-heterogeneous nucleation compare to homogeneous nucleation that f theta because f theta comes everywhere the ratio of the heights of the barrier from nucleation as well as the now in the total function of the free energy.

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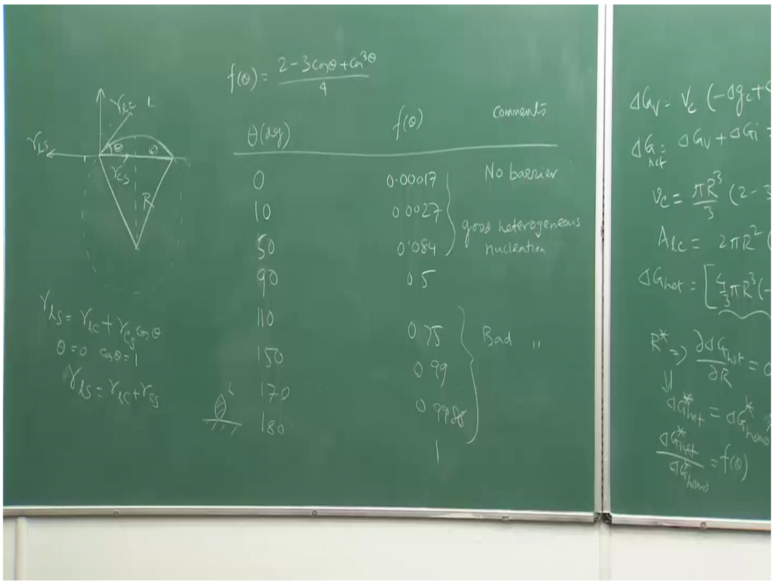

So, let me just write down the values of a theta I have calculated; it is from the book and take out at this things. So, f theta s 2 minus 3 cos theta plus cos cube theta by 4. So, these are the values of theta will decrease and this is the value of f theta and these are my comments which I will write now. So, as you see here when the angle is 0 degree, what is the meaning of 0 degree; that means, it is a complete weighting; that means, this solid see which is shown on the surface will be completely going to in a substrate.

That’s only possible when the solid possible when let us write down this equation gamma l s is equal to gamma l c plus gamma c s cos theta the cos theta one theta 0 degree means cos theta equal to basically that is means that theta is equal to 0 cos theta is equal to 1 and; that means, gamma l s is equal to gamma l c plus gamma c s energetically this is completely balanced for that f theta value will be very small, basically; this is 00017 that is means no barrier is present the barrier height is basically very small we can see this is basically 10 to the power minus 4 times homogenous nucleation barrier because this f theta multiplied by homogeneous nucleation will gives you barrier will give you provide you that is the nucleation barrier.

So, if you this 10 degree that is its little bit higher if it is twenty degrees still little bit higher, but quite a bit higher sorry and 50; 50 is how much then there is factoring this; now this is actually 50, 90 degree is become 0.5; 90 degree theta means is basically like this; this is 90 degree so; that means, what there is a contract angle us going to be changing 100 and 110; it will be 0.75; 150 that is equal to 0.99; 170 0.9988 and maximum angle perceiving is 180.

180 means what it will be hanging? Hanging on the like a point contract if I draw it properly 180 corresponding to it just like a if you put a marketing on a glass the situation that is the basically point is equal to 1. So, as you clearly see this is no barrier; barrier is same when it is hanging on the substrate the crystal is hanging on the substrate from the liquid; that means, barrier from homogenous heterogeneous nucleation is same that is not difference, but when it is 0 degree that is no barrier.

So, what I can tell these are the situations of good heterogeneous; heterogeneous nucleation and these are actually bad heterogeneous nucleation saturations the worst will be one which theta is equal to 180 degrees. So, simply by looking at a values of theta different values of theta you can actually design; then nucleating assigns in the industry as you know when you want to there are many examples which will; I will discuss you in the as a time goes by first example of such a kind of situation is the sending of rain basically.

In the rain, sitting is very important thing in the many parts of the world where the amount of rain is basically is small and so, if you want to see it rain what you people do is that they sprinkle silver halide crystals at the crystal halide or crystal chloride crystals on these on these on the upper part of the atmosphere and this silver halide crystals with the hexagonal crystal structure, they allow the rain droplets will perform directly from the cloud idea is exactly same to design heterogeneous nucleation agent, you must try to make f theta to the as small as possible. So, that is what the good heterogeneous nucleation think will happen that is why the barrier height delta G will be reduce substantially and to do that you need to theta as small as possible.

If it is 5 degrees, 2 degrees, if it is better; 10 degree is not bad is basically, 2.7 to multiplied 10 to the power minus 3 of times of the heterogeneous nucleation barrier homogenous nucleation barrier does not bad, but making it very close to 0 like 2 degrees or 5 degrees or even 7 degree is also good. So, this is what is use similar example of the in the in the cloud setting; similar example is basically using ferrosilicon in the steel casting or the addition of the silicon or it is basically in cast iron casting ferrosilicon you know is basically add it in cast iron to make nucleation happen and they are actually known as you know cool ends in the in the area industry people say in a cool end.

You know cool end is nothing you put it in the mold. So, that they actually allow you to have many heterogeneous nucleation points in the solid. So, the grain size can be controlled. Similarly, there are examples of you know when you want to cast spherical graphite iron spherical graphite iron has the spherical separate graphite in a austenitic matrix or it can be politic matrix, but important aspect is to have large number of graphite spherical graphite particles inside these sample inside these you know materials. So, due to increase the graphite nucleation people normally add into the melt synthetic graphite because graphite is a very high mainly temperatures. So, they will never melt in the in the cast iron melt cast iron melts about 12 point to 39 degrees Celsius temperature.

So, in that melt, if I had pure graphite crystalline graphite particles the graphite particles with the act is heterogeneous nucleation to nucleate graphite or graphite and nucleating graphite or graphite theta will be very small because graphite will have perfect match with you; with the crystal which will you forming from the liquid. So, therefore, theta will be very low theta will be close to 1; actually in those cases, it will little bit distortion in the surface possible because of the thermal because with the temperature differences between the solid graphite is forming on a graphite particles.

So, and the barrier is very small; that means, what if I add synthetic graphite into the melt of graphite iron what I am going to do is create large number of heterogeneous nucleation sites and. So, that graphite size and shape size basically and the number density in the sample can be increased and there is what is important in spherical graphite iron. So, in that way one can actually do the microcrystalline engineering as a part of the phase transformation and this is very very natural way of doing things. Now in the next, I am going to take examples of different type heterogeneous nucleation even that is you see on this screen.

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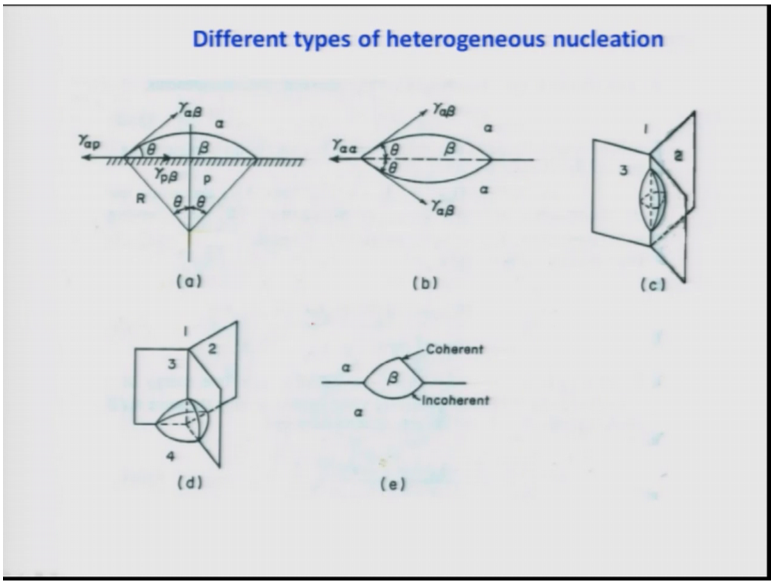

Different types of heterogeneous nucleation

You can have distortion is basically solid and solid you can have this scab modeling again solid and solid, but equations will remain same. So, I do not need to derive only thing it will change is this gamma values gamma alpha p gamma alpha beta gamma p p beta because p is a basically already present something some substrate or precipitate or whatever and beta is the phases is nucleating from the alpha you can also have a nucleation the grain boundaries you can also have nucleation the grain edges or grain corners. So, we will see it how we can deal this kind of situation in the next lecture.