Microscopic Kinetic and Thermodynamics
Notes of the course

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Contents

1

Phase transformations

1.1 Discrete phase transitions

During the whole course we have mainly focus on the description of physical systems behaves inside a particular phase, allowing us to understand which phase is stable at certain conditions. Nevertheless, another important question that we want to answer is how the transition to one phase to another happens exactly. We have talked, when we faced phase diagrams, how certain materials are able to go from one state to another in particular situation in a qualitative way, here we aim in describing it mathematically using the tools obtained from equilibrium Thermodynamics and kinetics.

The first thing that we shall say is that a phase transformation happens when, due to variation of certain parameters such as temperature or external field, the system breaks some internal symmetry finding more advantages to restructure itself in a more or less ordered way. For this reason, we are going to describe such phenomena using a set of parameters ξ that mainly describes the order that is present inside the material, called **order parameters**. We have already seen some example of them in previous studies: like the long range order η and the fractional density X_i inside the study of the equilibrium inside a binary system. On a more general ground, during the study we will have to work with two main type of order parameters that we need to take into account, and we will define as follows.

> **Definition 1.1.1: Conserved and Non-Conserved order parameters**
>
> An order parameter ξ inside a system is conserved if it needs to be a constant inside a closed system, while non-conserved ones can change also if the system is closed.

It's easy to understand that in the examples we have already seen X_i is conserved, while η is not. These two types of parameters highly influences how the transition behaves since the free energy will depend on them, $G(\xi)$, and based on their variation the energy landscape will be modified. To be more precise, we can evaluate a general form for the variation of free energy inside a material due to order parameters' changes in the two cases.

> **Theorem 1.1.1: Variation for non-conserved ξ**
>
> Suppose that in a closed system composed of N moles of material n moles undergo a variation of a non-conserved order parameter from ξ_1 to ξ_2, where we assume $N \ll n$. The corresponding

change of free energy of the whole system is

$$\delta G_u = n[G(\xi_2) - G(\xi_1)] \approx nG'(\xi_1)\delta\xi, \tag{1.1}$$

where G is the molar free energy of the material.

Proof: The proof is really simple since the order parameter is non-conserved it can change as wants inside the closed system, and so we can assume tha all the $N - n$ moles remains in ξ_1 being unperturbed by the change of the others. In this way we can set the change of free energy in the whole system as

$$\delta G_u = (N - n)G(\xi_1) + nG(\xi_2) - NG(\xi_1) = n[G(\xi_2) - G(\xi_1)]. \tag{1.2}$$

Also, the approximation with the first derivative is only the first order term of the Taylor series setting $\delta\xi \equiv \xi_2 - \xi_1$. ☺

This shows how for non-conserved parameters the change totally relies only on the form of G itself, with a behavior that is totally analogous to the one of the normal system. In the case of conserved parameters the thing changes a little becoming more interesting.

Theorem 1.1.2: Variation for conserved ξ

Suppose that in a closed system composed of N moles of material n moles undergo a variation of a conserved order parameter from ξ_1 to ξ_2, where we assume $N \ll n$. The corresponding change of free energy of the whole system is

$$\delta G_c = n\{G(\xi_2) - [G(\xi_1) + G'(\xi_1)(\xi_2 - \xi_1)]\} \approx \frac{n}{2}G''(\xi_1)\delta\xi^2, \tag{1.3}$$

where G is the molar free energy of the material.

Proof: In this case the total order parameter inside the material could not change, still ξ can have local variation that can be compensated by the variation of the order parameter of the rest of the material. Meaning that, if n moles now have ξ_2 as order parameter then all the remaining $N - n$ one's needs to have $\xi_1 - \Delta$ to compensate as follows

$$(N - n)(\xi_1 + \Delta) + n\xi_1 = N\xi_1, \tag{1.4}$$

which gives $\Delta = n(\xi_1 - \xi_2)/(N - n)$ so that $N\Delta \approx n(\xi_1 - \xi_2)$. In this way we can write down the following variation

$$\delta G_c = (N-n)G(\xi_1+\Delta)+nG(\xi_2)-NG(\xi_1) \approx (N-n)[G(\xi_1)+G'(\xi_1)\Delta]+nG(\xi_2)-NG(\xi_1), \tag{1.5}$$

which gives exactly what we wanted. Then, to have the approximation we can write $\xi_2 = \xi_1 + \delta\xi$ and expand the value of $G(\xi_2)$ to the second order obtain the final result. ☺

In this case the variation of the free energy do not simply depend on the form of G but also on the convexity of it. In particular, the variation of free energy due to order changes is mainly given by the second derivative. Meaning that if we are in a local maximum $G'' < 0$ and the system is **unstable** wanting to change to a minimum where $G'' > 0$ so that even if ξ changes the variation of energy is positive and the system is so **metastable**. Where we use the word metastable and not stable since it's
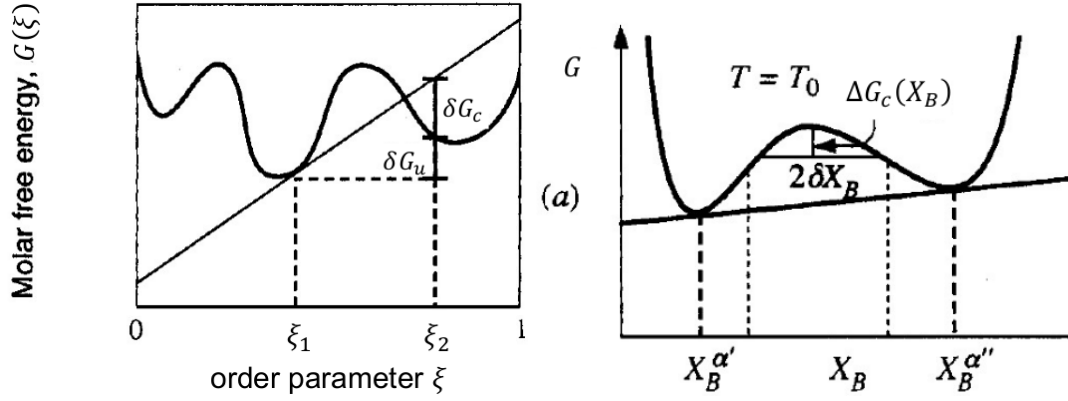
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Figure 1.1: Representation of a free energy landscape depending on order parameters with the opportune variations on the left, and a representation of a $G(X)$ with the spinodal points in evidence on the right.

not sad that the system will remain in that minimum forever, due to large variation of energy coming external factors, like thermal fluctuations, the system can jump to another valley and sit there for some time until another jump happens.

This description of how G changes due to order parameters is really general and profound, showing us not only how the free energy changes based on the nature on the parameter itself, but also suggest to us how that change happens. Let's focus a moment on Eq. (1.3) in the situation depicted on Fig. (1.1), the system will have two metastable state divided by an energy barrier which defines an unstable region. In particular, the unstable region is delimited by the ξ so that $G''(\xi) = 0$, where X_B is the order parameter in that case. We have already talk about points with such a property calling them **spinodal points**, basically the region inside the spinodal points is unstable meaning that it will natural evolve continuously to a minimum. Then, when it reaches a metastable position it will sit there and remain there until a sudden discontinuous change happens, and the system changes minimum to sit in. These two different behaviors define the two main types of phase transitions that we are going to touch called **continuous** and **discontinuous** phase transitions, which mainly differ in how quick the change happens and in the extension of the change, having that discontinuous transformations are usually locals while continuous are more global.

In this first section we will focus first on the discontinuous type describing the main, and simpler, possible forms of such transitions: like the formation of a water droplet in clouds. We will leave the continuous case to a further section.

Nucleation theory

Nucleation is an important phenomenon that consist in the spontaneous formation of cluster of components inside the material that will then grow over time through different mechanisms like coarsening. In particular, in the classical theory of nucleation the system goes through four different steps: an initial incubation where no cluster are formed over time, to then a steady-state situation where the number increase in time reaching a maxima where driving forces of nucleation start to reduce, and then the coarsening that will decrease the number generating bigger grains. Inside such a complex kinetic behavior we aim first in the description of the distribution of cluster inside cluster space $N_\nu(t)$, where N_ν is the number of cluster possessing ν monomers components inside them.

To start the study we can try to write down a form for the variation of free energy of the system in the formation of a cluster with ν components. We can assume that inside a matrix in state α and
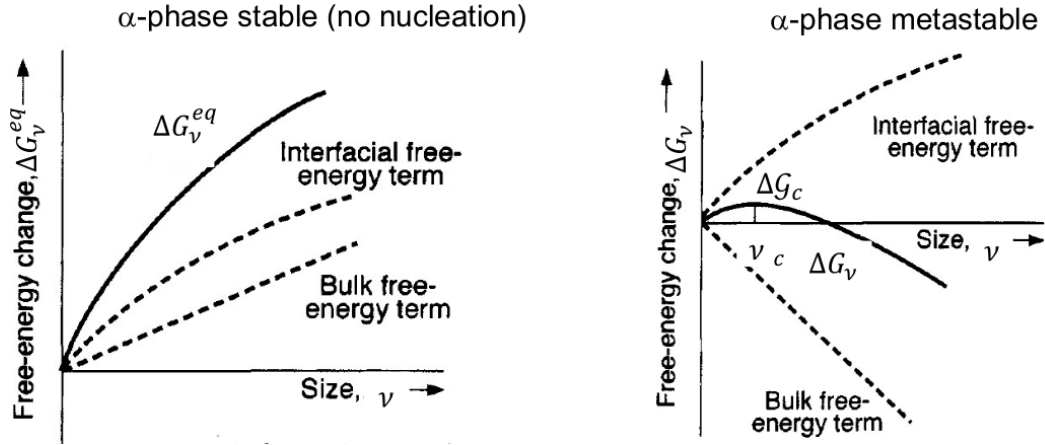
4

Figure 1.2: Graph of the variation of free energy due to nucleation as a function of cluster size, in particular on the left there's the case where the chemical potential of the α matrix phase is more favorable than the one of the β grain phase, and on the right the opposite.

chemical potential for component μ^α start to grow a cluster in state β which changes also the chemical potential of the ν monomers. Such a formation will so generate a simple variation of free energy to which we will need also to add the energy coming from the interface γA, where $A \propto V^{2/3}$ and $V \propto \nu$, meaning that naming η the constant of proportionality we have

$$\Delta G_\nu = \nu \left(\mu^\beta - \mu^\alpha \right) + \eta \nu^{2/3} \gamma. \tag{1.6}$$

It's form can be seen in Fig. (1.2), where we can see clearly how the starting bulk term completely determine the possibility of nucleation. In fact, when ν is small the term that leads the change in free energy is the surface one, which is always positive, meaning that cluster of small size will always be energetically unfavorable, while as ν increase $\mu^\beta - \mu^\alpha$ will start to lead. In this way we can understand that, if the difference in the chemical potential is negative, cluster starts to grow consistently only when they reach a certain critical value from which ΔG_ν starts to decrease

$$\left. \frac{\mathrm{d}\Delta G_\nu}{\mathrm{d}\nu} \right|_{\nu=\nu_c} = 0, \qquad\qquad \nu_c = -\left(\frac{2\eta\gamma}{3(\mu^\beta - \mu^\alpha)} \right)^3. \tag{1.7}$$

Therefore, we will have that in a first moment the cluster are not able to form for a long period of time due to the increase in free energy, but there is still a probability that due to thermal fluctuations, or other external factor, one cluster of size ν_c forms starting increasing its size naturally from there and forming the center of nucleation. Meaning that we are already able to understand the presence of the **incubation phase**, which can be overcome through probability fluctuations typical of a discontinuous phase transformation.

We can now start to model the process of formation of the grains overtime, and in order to do that we want to work inside the space of cluster size N_ν. Meaning that we want to find out a form for the flux $J_\nu(t)$ describing how many cluster goes at certain time from having ν components to $\nu + 1$. Such a quantity can be easily modelled by assuming that the probability of one monomer to enter the cluster over time is β_ν, while the probability for one to hoop out of it is α_ν having that

$$J_\nu(t) = \beta_\nu N_\nu(t) - \alpha_{\nu+1} N_{\nu+1}(t). \tag{1.8}$$

Using such a description allows us to find out some important information on the form of the distribution itself. For example, we can see what happens in a case where the system reaches an equilibrium, assuming that the α phase is stable, $\mu^\beta - \mu^\alpha > 0$, we can find out the following.

5

> ### Theorem 1.1.3: Equilibrium distribution
>
> When the matrix α phase is stable respect to the grain β one the system will evolve in time reaching an equilibrium where, still, a series of clusters are formed following the distribution given by
>
> $$N_v^{eq} = N \exp\left(-\frac{\Delta G_v}{k_B T}\right), \tag{1.9}$$
>
> with N the total number of atoms.

Proof: This demonstration was not done during the lectures. ☺

Such a result is really helpful for us since allows for the creation of a relation between the different probabilities α_v and β_v defined earlier. In fact, we can say that at equilibrium $J_v = 0$ for every value of v and so the following is true

$$\beta_{v+1} = \beta_v \frac{N_v}{N_{v+1}} = \beta_v \exp\left(-\frac{\Delta G_{v+1} - \Delta G_v}{k_B T}\right). \tag{1.10}$$

Still, such a distribution is not the one we are more interested in, in fact inside such an equilibrium distribution we have only the formation of small clusters due to fluctuations inside the material, the number larger cluster is zero inside such a quick descending distribution. The situation in the case where the α phase is metastable, with $\mu^\beta - \mu^\alpha < 0$, the situation changes since the system will undergo an irreversible transformation that through the stable phase that involves nucleation. Meaning that the final goal is to find out a way to describe the non-equilibrium distribution of clusters $Z_v(t)$, in particular focussing on the form of J_v still defined as before in a steady state situation.

> ### Theorem 1.1.4: Non-equilibrium steady-state flux
>
> When the matrix α phase of the material is metastable the system will undergo a nucleation that, passed the state of incubation, will grow in a steady state regime given by the flux in cluster size space J as
>
> $$J = N\beta_c \sqrt{\frac{\Delta G_c}{3\pi k_B T v_c^2}} \exp\left(-\frac{\Delta G_c}{k_B T}\right), \tag{1.11}$$
>
> where β_c is the probability of capture by the critical size cluster.

Proof: During such a demonstration we will assume the condition of constrained equilibrium allowing for the relation between the coefficients in Eq. (1.10) to be valid also in this particular case[1]. This allows us to write down that

$$J_v = \beta_v Z_v - \alpha_{v+1} Z_{v+1} = \beta_v N_v^{eq}\left(\frac{Z_v}{N_v^{eq}} - \frac{Z_{v+1}}{N_{v+1}^{eq}}\right), \tag{1.12}$$

then we can recall that in a steady-state situation we have $J_v = J_\omega$ for every v and ω, so that $J_v = J$. Then we will also assume that for small v also in Z_v the leading term will be the one given by the surface energy, which do not change from equilibrium and non-equilibrium case, meaning that the distribution

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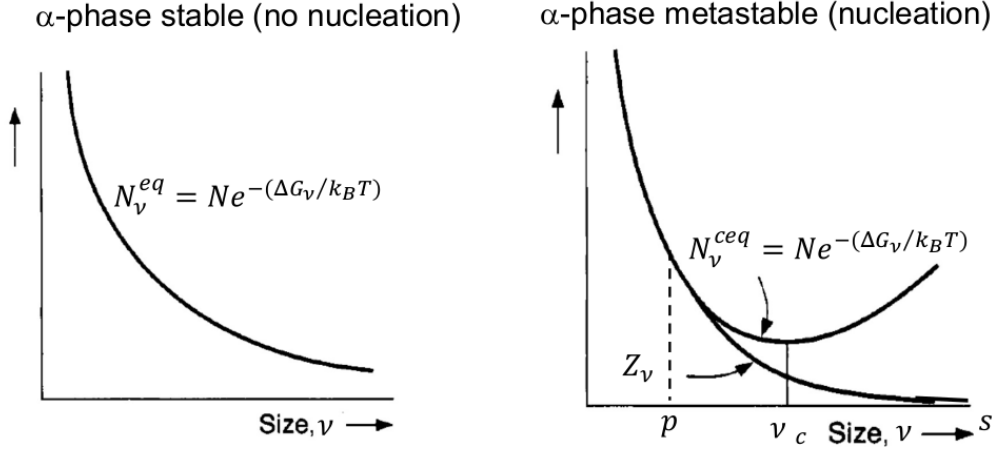[1]Probably better to look up on the internet for such a piece of theory.

α-phase stable (no nucleation)   α-phase metastable (nucleation)

$$N_v^{eq} = Ne^{-(\Delta G_v/k_B T)}$$

$$N_v^{ceq} = Ne^{-(\Delta G_v/k_B T)}$$

Z_v

Size, v ⟶ p v_c Size, v ⟶ s

Figure 1.3: Plot of the equilibrium and non equilibrium distribution in the two cases where α is stable and metastable in order to guide better the demonstration of the results.

remains the same. While for larger sizes the distribution needs to drop respect to what N^{eq} predict, since the exponent would have a positive term inside after v_c, having that we assume the form

$$Z_v = \begin{cases} N_v & v \leq p < v_c \\ 0 & v \geq s > v_c \end{cases}.$$

(1.13)

Where p and s are integer values chosen in order for Z_v to fit better to the equilibrium distribution as in Fig. (1.3). In this situation we can write down the following thing

$$\frac{J}{\beta_v N_v} = \left(\frac{Z_v}{N_v^{eq}} - \frac{Z_{v+1}}{N_{v+1}^{eq}} \right),$$

(1.14)

which can be summed up over all the possible grain sizes in order to obtain a telescopic series

$$\sum_{v=p}^{s} \frac{J}{\beta_v N_v} = \frac{Z_p}{N_p} - \frac{Z_{s+1}}{N_{s+1}} = 1,$$

(1.15)

since $Z_{s+1} = 0$ and $Z_p = N_p$. Therefore, we can write a simple form for J as a summation that can be approximated remembering that β_v needs to have a maximum at v_c since is the size at which caching becomes favorable

$$J = \left[\sum_{v=p}^{s} \frac{1}{\beta_v N_v} \right]^{-1} \approx \left[\frac{1}{\beta_c N} \sum_{v=p}^{s} e^{\Delta G_v/k_B T} \right]^{-1}.$$

(1.16)

In this situation we can approximate the sum for an integral and also expand ΔG_v around v_c since is its maximum and the main contribution is near there, having

$$\Delta G_v \approx \Delta G_c + \frac{(v - v_c)^2}{2} \frac{\partial^2 \Delta G_v}{\partial v^2} \bigg|_{v=v_c} \qquad \frac{\partial^2 \Delta G_v}{\partial v^2} \bigg|_{v=v_c} = -\frac{2}{9} \eta \gamma v_c^{-4/3} = -\frac{2}{3} \frac{\Delta G_c}{v_c^2}.$$

(1.17)

Then we can simply insert inside the summation and integrate as

$$\sum_{v=p}^{s} e^{\Delta G_v/k_B T} \approx e^{\Delta G_c/k_B T} \int_p^s dv \exp\left(-\frac{2}{3} \frac{\Delta G_c}{v_c^2 k_B T} \frac{(v - v_c)^2}{2} \right) \approx e^{\Delta G_c/k_B T} \sqrt{\frac{3\pi k_B T v_c^2}{\Delta G_c}},$$

(1.18)

7

where we have expanded the extreme of the Gaussian integral to cover the whole domain since the tails give a small contribution. Then by inserting such result inside the form of J we obtain the wanted result. 😊

Now, this is an interesting result that describes the evolution of the nucleation inside the material in the **steady-state phase** where the number of cluster with greater size increase linearly in time since J is constant. Also, we can see how inside J all the contribution are given by ν_c, since is effectively the most important term, but still the factor $\sqrt{\bullet}$, called **Zeldovich factor**, is giving us corrections to consider also the surrounding contribution. In fact, if we didn't expand ΔG_ν to first order but zeroth we will have had a 1 in its place, instead a number ~ 0.1 is given. At last, we shall understand that the only term that we don't know how to write down inside J is the form of β_c, which still can be described using a series of model resumed shortly inside the slides.

Before going into the next topic, we shall first make some remarks for the result that we have obtained right now. In particular, we shall say that the nucleation that we have described is generally called **homogeneous nucleation** and is characterized by the creation of the clusters out of atmosphere with no preferential position on where to appear. In this type of nucleation the result Eq. (1.11) is telling us a lot on the velocity of the process, and its value depends strongly on ΔG_c giving us the following insights

1. $\Delta G_c \propto \gamma^3$ and in incoherent interfaces $\gamma \approx 0.5\,\mathrm{Jm}^{-2}$, while in coherent is lower by at least a factor of three. Therefore, in most situations homogeneous nucleation is possible only for coherent interfaces;

2. $\Delta G_c \propto (\mu^\beta - \mu^\alpha)^{-2}$ shows how J can increase suddenly due to temperature variations that modify the driving force;

3. One can estimate the value of ΔG_c to have an idea by using $J \approx 1\,\mathrm{cm}^{-3}\mathrm{s}^{-1}$ along with $\beta_c \approx 10^12$ and a Zeldovich factor of 0.1 to find $\Delta G_c \approx 76 k_B T$;

4. In the case of solid-solid nucleation we shall include inside the free energy also a strain term that is often described using the volumetric density of bulk free energy Δg_B. Basically, to the normal energy of the bulk inside the system a Δg_ϵ term due to the strain caused by the generation of solid clusters inside a solid appears, a term that can be neglected if the nucleation happens inside a liquid or a gas for obvious reasons.

Such information can be important in the study of the phenomena in a general way, in particular we shall remember the notion of volumetric density of free energy Δg since we are going to use it in future topics.

Example 1.1.1 (CNT-Exercise)

At the end of the topic the prof showed a really simple exercise to understand how much the steady-state flux depends on the free energy seeing how also small variations can cause rapid increases. The assumption is that in a system with an atomic fraction of B atoms of $X_B = 0.3$ homogenized at $1200\,\mathrm{K}$ and quenched to $800\,\mathrm{K}$ has a β-phase nucleation rate of $10^6\,\mathrm{m}^{-3}\mathrm{s}^{-1}$. We want to increase the density of B atoms in order to bring the flux at $10^{21}\,\mathrm{m}^{-3}\mathrm{s}^{-1}$ knowing that

$$\Delta g_B = [-100(X_B - 0.3) - 9]10^7\mathrm{Jm}^{-3}, \qquad\qquad \gamma = 75\,\mathrm{Jm}^{-2}. \qquad (1.19)$$

We can so write down the total variation of free energy of the system by using the following

equation

$$\Delta G = \frac{4\pi}{3} r^3 \Delta g_B + 4\pi r^2 \gamma, \tag{1.20}$$

which can be maximized to found out ΔG_c at the value of

$$r_c = -2 \frac{\gamma}{\Delta g_B}, \qquad\qquad \Delta G_c = \frac{16\pi}{3} \frac{\gamma^3}{\Delta g_B^2}. \tag{1.21}$$

Knowing that we can insert everything in the known formula for J and find out that in order to increase the flux by 15 orders of magnitude we only need to increase X_B by a 0.03, so that ΔG_c becomes half.

Heterogeneous nucleation

The next important case that we shall address is the case where the nucleation happens in some preferential points inside the system generating **Heterogeneous nucleation**. In particular, we will focus on the case where the cluster prefer to form in the interface's region, meaning that a surface is already present and so the formation of the grain can be more favorable due to variations of surface free energy. We will not go into the theoretical treatment of this particular phenomenon, but still we will need to address two cases: the creation of clusters in a grain boundary, where a solid-solid interface is present, and the film deposition, where the interface where the grain forms is a solid-gas one.

In the first case we can have that the clustering begins in the interface between two solid phases α generating a grain that changes the free energy thanks to the variation of chemical potential of the grain's β phase and the interface free energy variation. In the case without grain in the middle the interface posses an energy that is given by $\gamma^{\alpha\alpha}$, but it's possible that the $\alpha - \beta$ interface has a better surface free energy $\gamma^{\alpha\beta}$ having that the formation of clusters to substitute the $\alpha - \alpha$ interface is really favorable. Also, the shape that the cluster will take depends on how favorable such substitution is, giving a general form of a lens as in Fig. (1.4) with the angle given by a known result.
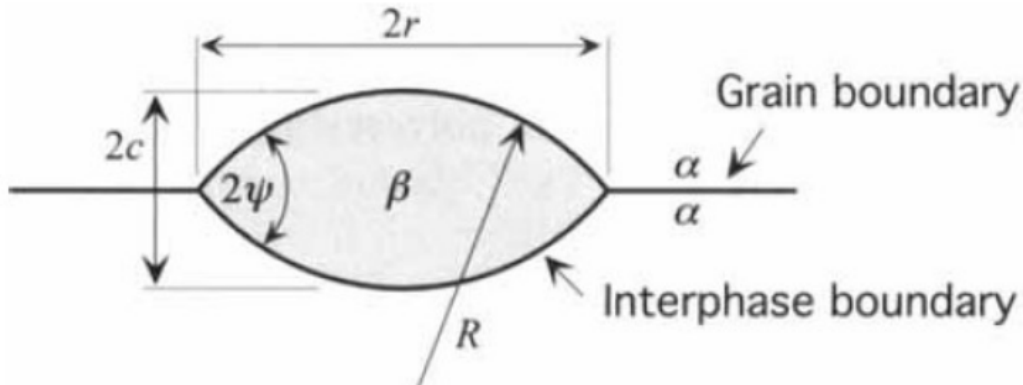

Figure 1.4: Representation of a heterogeneous nucleation in the solid-solid interface, important to see how the cluster formed takes the shape of a lens with an angle that depends on the surface tensions.

> **Theorem 1.1.5: Young's equation solid-solid**
>
> The shape of a grain in a solid-solid interface is defined by $\gamma^{\alpha\alpha}$ and $\gamma^{\alpha\beta}$ and is given by
>
> $$\gamma^{\alpha\alpha} = \gamma^{\alpha\beta} \cos \psi. \tag{1.22}$$

Where one can grasp a lot of information, for example if $\gamma^{\alpha\alpha} = 0$ means that we don't have the interface at all not having heterogeneous nucleation at all with $\psi = \pi/2$ so that the grain are spherical as in the homogeneous case. Instead, if $\gamma^{\alpha\alpha} = 2\gamma^{\alpha\beta}$ the angle is flat meaning that the interface catalyze the reaction so well that a continuous film around the interface is created. Also, we can evaluate the increase in free energy that such a grain can generate in the system by looking at the following result.

> **Theorem 1.1.6: Grain free energy solid-solid**
>
> If a nucleation starts on a solid-solid interface the increase of free energy of the system takes the form
>
> $$\Delta G^{GB} = \left(\frac{2\pi R}{3} \Delta g_B + 2\pi R^2 \gamma^{\alpha\beta} \right) \left(2 - 3\cos\psi + \cos^3\psi \right). \tag{1.23}$$

Proof: We can proof it by using that fact that the volume and the area of the lens figure formed can be computed using

$$V = \frac{2\pi R}{3}(2 - 3\cos\psi + \cos^3\psi), \qquad A = 4\pi R^2(1 - \cos\psi), \tag{1.24}$$

where R is the radius of the grain. Then we can evaluate the variation of energy due to the creation of a β bulk and the increase of the interface along with the elimination of the $\alpha - \alpha$ one as

$$\Delta G^{GB} = V \Delta g_B + A\gamma^{\alpha\beta} - \pi r^2 \gamma^{\alpha\alpha}, \tag{1.25}$$

then we can use the fact that $r \approx R\sin\psi$ along with Young's equation to obtain the final result. ☺

One can see how such a form is similar to the one of the homogeneous case, having that we can see that the first term is exactly equal to $1/2$ the homogeneous energy while the angular term is what really defines if the heterogeneous nucleation is preferred or not. Such a term is also called **wetting factor**, and we can see how the following is true

$$\frac{\Delta G_c^{GB}}{\Delta G_c^H} = \frac{1}{2} \left(2 - 3\cos\psi + \cos^3\psi \right), \tag{1.26}$$

this term shows how the energy is basically always less in the heterogeneous case, in fact one can see how since $\gamma > 0$ the wetting term is always contained in $[0, 1]$. Meaning that the nucleation phenomena is generally more favorable at the grain boundaries and becomes analogous at the homogeneous case only if the interface is coherent, as we have already anticipated previously. At last, it's possible to give an estimate of the steady-state rate of growth of the heterogeneous nucleation by using the homogeneous result and the density of boundary sites as follows

$$n^{GB} = n\frac{\delta}{D} \qquad\qquad \frac{J^{GB}}{J^H} = \frac{n^{GB}}{n} \exp\left[-\frac{\Delta G_c^{GB} - \Delta G_c^H}{k_B T} \right], \tag{1.27}$$
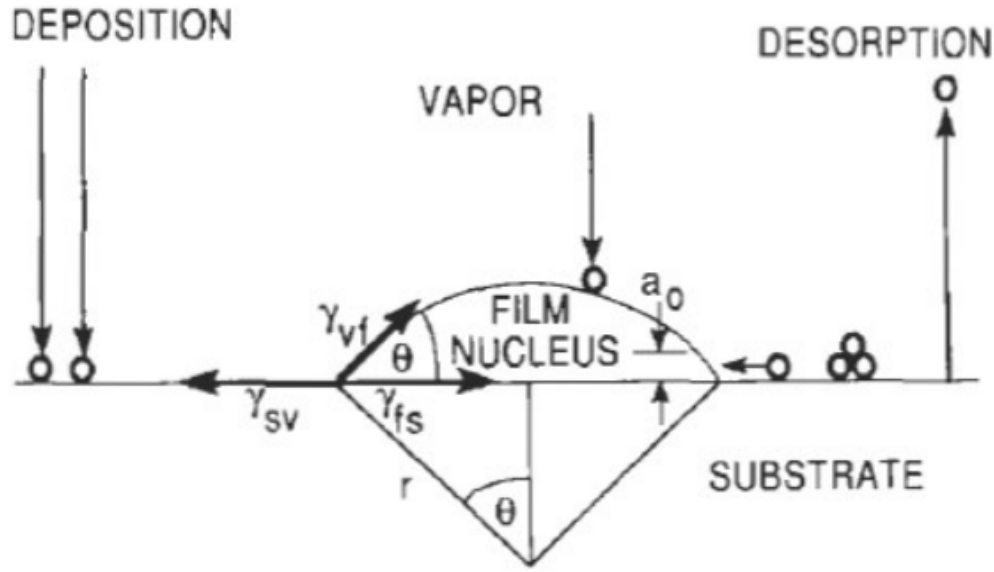
Figure 1.5: Representation of the nucleation on a solid-gas interface showing how the cluster formed is elongated due to surface effect generating a more uniform film.

where δ is the grain boundary thickness and D the average grain diameter.

Now we can work with the case where the growth happens in a solid-gas interface, in this situation what happens is that three different surface free energies appears, since also the interface formed by the cluster and the gas will have a specific γ. In this situation is also possible to predict the form of the generated cluster that is given by the form seen in Fig. (1.5), where we can see how the different surface tensions generate forces due to Marangoni effect giving at the cluster a more homogeneous form. The latter can be, once again, described using a clever result that connects the angle θ to surface tensions.

Theorem 1.1.7: Young's equation solid-gas

The shape of the cluster on a solid-gas interface is defined by the three surface tensions inside the system and is given by

$$\gamma^{sv} = \gamma^{fs} + \gamma^{vf} \cos \theta. \tag{1.28}$$

Knowing that, we can have a look at how the cluster will look like in various cases. For example, if $\gamma^{sv} < \gamma^{fs} + \gamma^{vf}$ then the angle is greater than zero, so the atoms on the surface are more attracted to each other than the substrate forming various islands with same form. Instead, if the surface tensions are equal the angle is null giving out that the atoms prefer to attach to the substrate forming a perfect layer that grows homogeneously, also in autoepitaxy we set $\gamma^{fs} = 0$. At last, the case where $\gamma^{sv} > \gamma^{fs} + \gamma^{vf}$ posses a behavior similar to the one before generating a homogeneous film, but the strain energy increase as the layer growth giving rise to phenomena of strain release by separation in island during the growth. Then, to complete the analogy to the previous case we can have a look to the free energy change inside the system due to the cluster formation.

Theorem 1.1.8: Grain free energy solid-solid

If a nucleation starts on a solid-gas interface the increase of free energy at the critical size of the

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system takes the form

$$\Delta G_c = \frac{16\pi\gamma_{vf}^3}{3\Delta g_B^2}\frac{2 - 3\cos\theta + \cos^3\theta}{4}. \tag{1.29}$$

Proof: One can compute the total energy change that comes from the cluster by using the same approach as before obtaining

$$\Delta G = \pi(2 - 3\cos\theta + \cos^3\theta)\left(\frac{r^3\Delta g_B}{3} + r^2\gamma^{vf}\right), \tag{1.30}$$

then we can maximize it and obtain the final result. ☺

Once again one can see how this value is equal to the homogeneous nucleation one multiplied by a wetting factor that is always less than unity. Meaning that, again, the creation of nuclei inside a system is more favorable near an interface.

> **Note**
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> *The fact that clusterization is more favorable near interfaces is an important fact in experimental techniques, in fact a lot of methods utilize them to achieve results. The simplest example is the physical vapor deposition, where a homogeneous thin film of material is constructed on a substrate inside a high vacuum chamber by vaporize a material so that the atoms from it travels in vacuum deposit on the surface of the substrate. In this way, by using the right materials, we can construct the film as described by the nucleation on solid-gas interface.*

1.2 Continuous phase transitions

In order to address the behavior of a system during a continuous phase transition we can imagine to work in a situation like the one of an unstable binary material. In that case we have that the system wants to generate areas in two different phases and since it's unstable as it is the process that will go through in forming them is a continuous transformation that naturally generates gradients of concentration inside the material. On a more general level we can say that the concentration is the order parameter ξ inside the material and the transformation is naturally generating a gradient $\nabla\xi$ inside the system that we want to study. A great example of this is shown in Fig. (1.6), where the material starts from an ordered
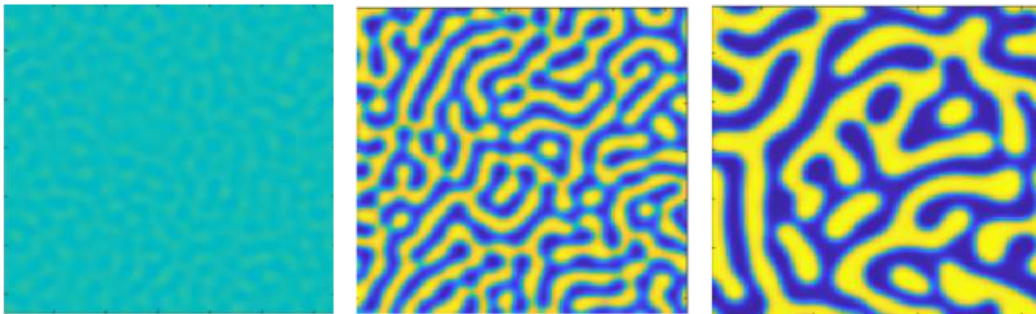

Figure 1.6: Result of a simulation to represent a phase transition in a binary alloy showing in different colors different densities that can be interpreted as the order parameter of the system.

situation with uniform density to then naturally create domains generating disorder.

To study such a phenomenon we should not focus our attention only on the domain that are forming inside the material, but an important contribution to the free energy is given by the interfacial regions. The latter are the region of space where the system goes from one domain to another, so the position where $\nabla\xi$ is effectively large and non-zero. In fact, such interfaces have a large role in the creation of the new phases since their number is really large in the first part of the transformation driving it at its core. Still, the presence of a gradient needs to generate an increase of $G(\xi)$ due to the fact that the minima of the free energy are represented by the order parameter in the domain, ξ_α and ξ_β. This means that, for ξ in between those two, present in the wall domain composing the interfaces, necessarily has higher free energy overall increasing it. Therefore, one may ask why they exist and are not reduced to the minimum, and the reason for it can be understood by making the example of magnetic domain in a ferromagnetic material. We know how the gain in energy inside a magnetic domain is due to **exchange interaction** between spins that prefers to have aligned spin minimizing the energy and increase it otherwise. In this situation having two domains with opposite spins one next to the other highly increase the energy, so that the presence of a gradient that smooth out the interaction is favorable. The question then becomes, how large should such interface be in order for it be effectively be energetically favorable giving rise to the generation of the domains, and how do they evolve? That's the question we are going to answer right now.

Cahn-Hilliard equation

To start modelling the evolution of the system during a phase transition we need to write down a form for the free energy focussing on the local free energy, that we will call f^{hom}. We will assume that such a function will depend on the order parameter and it's gradient, allowing us to write down a Taylor expansion of it near the value of $\nabla\xi = 0$

$$f(\xi, \nabla\xi) = f^{hom}(\xi) + \frac{\partial f^{hom}}{\partial \nabla\xi} \cdot \nabla\xi + \frac{\partial^2 f^{hom}}{\partial \nabla\xi^2}\nabla\xi \cdot \nabla\xi. \tag{1.31}$$

We can simplify such a form by noticing that if we change variable $\xi \rightarrow -\xi$ also the gradient change sign having that the first order term will modify the energy of the system. That is an absurd since a simple change of variable can't change the physics of the system having that the first derivative respect to the gradient needs to be zero. We can then define K as the second derivative term to end up with the following form

$$f(\xi, \nabla\xi) = f^{hom}(\xi) + K\nabla\xi^2. \tag{1.32}$$

The two terms present behaves so that the first wants to eliminate interfaces since works simply as the local free energy, meaning that has minima for the values of ξ corresponding to the domains and increase as the order changes. Instead, the second term goes against that pushing for the creation of larger interfaces so that $\nabla\xi$ is more extended but lower in absolute value along the material. In fact, if no interface would be present the gradient between two domains would have $|\nabla\xi| \rightarrow \infty$ rising a lot the value of the second term.

Therefore, the Eq. (1.32) will allow us to model the behavior of the system in general giving us insights on the form of the interfaces. As a matter of facts, it's possible to use such a form to arrive at the following simple result.

> **Theorem 1.2.1: Interface properties**
>
> Inside a continuous phase transformation where the local free energy can be written as in Eq. (1.32) the width of the domain interfaces and the surface free energy are given by
>
> $$\delta = \sqrt{\frac{K}{\langle f^{hom} \rangle}}, \qquad\qquad \gamma = 2\sqrt{K \langle f^{hom} \rangle}. \qquad (1.33)$$

Proof: We can write down the total energy in the proximity of an interface by integrating the local free energy so that

$$F = \int_V \left[f^{hom}(\xi) + K \left(\frac{\mathrm{d}\xi}{\mathrm{d}x}\right)^2 \right] \mathrm{d}V, \qquad (1.34)$$

where we assumed that the interface is only in direction x so that the gradient is present only in that component. We can then average the quantity over the volume of the interface by multipling and dividing for $A\delta$, where A is the area of the interface and δ the width

$$F = A\delta \left[\langle f^{hom} \rangle + K \left\langle \left(\frac{\mathrm{d}\xi}{\mathrm{d}x}\right)^2 \right\rangle \right]. \qquad (1.35)$$

The width of the interface can then be set to $\delta \approx \mathrm{d}x / \mathrm{d}\xi$ having that the final form of the energy is

$$F \approx A \left[\langle f^{hom} \rangle \delta + \frac{K}{\delta} \right]. \qquad (1.36)$$

By minimizing this value one can find the wanted value of the width that minimize the free energy and then by substitute it inside F and dividing it by A also γ can be computed. ☺

This is the result we expected after the previous description of the energy. In fact, we can see that as the parameter K, related to the gradient term, increase the width of the interfaces inside the material, while the average value of f^{hom} decrease them, exactly as we said before.