

Microscopic Kinetic and Thermodynamics

Notes of the course

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Thermodynamics of equilibrium in condensed phases

1.1 Physical properties

When one thinks at the study of condensed matter, the first thing that might come to his mind is the evaluation of the properties of a material intended as its characteristics. That is indeed true to some extent, but still one question that the reader thinking at it should ask himself is: what is a material property? This question may seem daunting at first sight, nevertheless an incredible simple and elegant answer can be given to it in the following terms

Definition 1.1.1: Physical property

A physical property is a relation between two measurable quantities.

If one is not completely obscure to physics may find out that this definition fits for the description of quantities like the conductivity σ , connecting external field \mathbf{E} and density current \mathbf{J} , or elasticity constant K and so on. Therefore, this concept may seem to lead us in the right track to understand what a physical property is but to have the picture complete we shall need to define exactly what quantities can be related by such properties. We are going to classify them in **generalized forces** and **conjugate responses** which are related in the following way

Definition 1.1.2: Measurable quantities

We classify the measurable quantities between generalized forces ψ_i and conjugate response ξ_i which are related by the following relation

$$\psi_i d\xi_i = \delta w, \quad (1.1)$$

where δw is the differential of work per unit volume done on the system.

One can also see this definition, or distinction, on a more physical level by thinking at the generalized forces ψ as stimuli that, acting on the system, generates a response ξ . Exactly like pressure P generate

a variation of volume from the system dV that so create work PdV .

This framework also allow us to rewrite the first principle of Thermodynamics in a simpler manner since we have given a general form to the work δw on the system. In particular, using the Einstein implicit summation formalism, we will have

$$du = Tds + \psi_i d\xi_i, \quad (1.2)$$

where we can also think at the temperature as a generalized force with entropy as a response. Thus, we will write from now on X_i for all the generalized forces, including temperature, and Y_i for the responses having Eq. (1.2) written as

$$du = X_i dY_i, \quad (1.3)$$

that will work as our **generalized first principle of thermodynamics**.

During the course we will also see how this definition of physical property also allow us to distinguish two main categories: **equilibrium properties**, that appear in a system at equilibrium such as the spring constant, and **transport properties**, that appear do to irreversible thermodynamic such has the conductivity. The main difference between the two can be thought to be the fact that in one case the material is still, in the other case average currents are present that, even if are in a stationary state, create transport of matter inside the material.

Constitutive relation

Once defined what a physical quantity is in general we can go and see how they look like, which is something that can be done in a first approximation making the assumption that a linear relation between forces and response are present. In this way we can assume that a general way to write down such linear relation in general is the following

$$Y_i - Y_i^0 = \mathcal{K}_{ij}(X_j - X_j^0). \quad (1.4)$$

The latter is called **constitutive relation** and effectively relates forces with responses through the tensor \mathcal{K} which, therefore, contains all the physical properties. Obviously this is only a first order approximation used to evaluate the variation of the two quantities from a starting state $(\mathbf{X}^0, \mathbf{Y}^0)$, nevertheless still allow us to have a first simple way of looking at the physical properties. In fact, inside Eq. (1.4) we are able to write down the entries of \mathcal{K} simply using

$$\mathcal{K}_{ij} = \left. \frac{\partial Y_i}{\partial X_j} \right|_{X_j=X_j^0}, \quad \mathcal{K} = \begin{pmatrix} \nabla_k Y_1 \\ \vdots \\ \nabla_k Y_N \end{pmatrix}. \quad (1.5)$$

This tensor is the main object of interest in a first approximation and understanding its properties can lend us a huge help on a general ground. Luckily the definition we have given leave us a lot of space to work with and one can readily go and see easily how the following is true

Theorem 1.1.1: Symmetry of \mathcal{K}

The physical property tensor \mathcal{K} is a symmetric one, therefore we have

$$\mathcal{K}_{ij} = \mathcal{K}_{ji}. \quad (1.6)$$

Proof: We can consider the free energy function g , we know it's defined as the Legendre transform of the internal energy which in our generalized case makes us obtain the following

$$g = u - X_i Y_i, \quad dg = -Y_i dX_i. \quad (1.7)$$

Since g is assumed to be continuous we can use the Schwartz theorem and say that the order of the derivation doesn't matter having so that

$$\frac{\partial^2 g}{\partial X_i \partial X_j} = \frac{\partial^2 g}{\partial X_j \partial X_i}, \quad (1.8)$$

which, using Eq. (1.5), turns out as

$$\mathcal{K}_{ij} = \mathcal{K}_{ji}. \quad (1.9)$$

⊕

So, before even starting to look into the actual form of \mathcal{K} we already now that has certain symmetries, but it's also not so difficult to give a concrete form to this tensor by assuming the forces into play inside our system. In particular, we are going to assume that inside a solid state system the work is mainly given by the following expression

$$\delta w = \mathbf{E} \cdot d\mathbf{D} + \mathbf{H} \cdot d\mathbf{B} + \boldsymbol{\sigma} \cdot d\boldsymbol{\varepsilon}. \quad (1.10)$$

Where electric and magnetic work are presents along with the one given by the stress $\boldsymbol{\sigma}$ and strain $\boldsymbol{\varepsilon}$. The last two are symmetric rank two tensors that kind of generalize pressure and variation of volume. This allows us to see the various general force and responses that we need to relate, making us have a general form for the \mathcal{K} tensor that look as in Fig. (1.1). Inside that general form we can see how all the quantities are related to each others somehow. This means that the presence of an electric field not only can cause the creation of an electric polarization, generated by the on-diagonal blocks called **principal effects**, but also a magnetic one or a change in shape. These phenomenons are due to the presence of off-diagonal blocks, called **cross effects** or **interaction effects**, inside the tensor that relate the force also to non-conjugate responses. For this reason can be important to look at some of them, also to understand some important properties of these tensors.

c specific heat, $T(0)$. Relates the temperature and the heat transmitted to the solid per unit volume at constant \mathbf{E} , \mathbf{H} and $\boldsymbol{\sigma}$. It's important to notice that is a scalar quantity, the only one inside \mathcal{K} , and so can be also written as $T(0)$ ¹.

k dielectric constant, $T_S(2)$. Relates the polar vectors \mathbf{E} and \mathbf{D} , it's known from classical electromagnetism. Also, being on the diagonal one can see that needs to be symmetric $\mathbf{k} = \mathbf{k}^\dagger$, so it's a rank two symmetric tensor, $T_S(2)$ ², and as such has 6 independent components.

μ magnetic permeability, $T_S(2)$. Relate two axial vectors \mathbf{H} and \mathbf{B} , and it's also known from classical electromagnetism. The same consideration done on \mathbf{k} are valid also on him being on the diagonal.

¹To identify different type of tensor we will use the notation $T(n)$, which means tensor of rank n .

²If a tensor is symmetric the subscript S is used.

	T	E	H	σ
s	c/T	p	q	α
D	p'	k	λ	d
B	q'	λ'	μ	Q
ϵ	α'	d'	Q'	s

Figure 1.1: General form of the \mathcal{K} tensor that defines the constitutive relations inside the material. The different blocks are composed by tensors of different ranks and symmetries, but the overall structure needs to be symmetric.

s elastic compliance, $T_s(4)$. It generalizes Hooke's law relating stress with deformation which are rank two tensors, making it a rank four that write down the relation of the two as

$$\varepsilon_{ij} = s_{ijkl}\sigma_{kl}. \quad (1.11)$$

Also, in this case the tensor is symmetric since ε and σ are having so $s_{ijkl} = s_{klji}$, this make so that the total number of independent variables in the tensor are 21. The inverse of this tensor, \mathbf{c} , is called **elastic stiffness**.

p electrocaloric effect, $T(1)$. Describes how an external electric field can generate heat inside a material changing entropy and so temperature. Since \mathcal{K} is symmetric we need to have $\mathbf{p} = \mathbf{p}'$.

p' pyroelectric effect, $T(1)$. Describe the electric polarization generated by variation of the material's temperature.

q magnetocaloric effect, $T^{ax}(1)$. Describes the variation of temperature generated by an external magnetic field. Also, since we will have that $T\mathbf{q} = \mathbf{H}$ we will need \mathbf{q} to be a pseudo-vector, therefore the tensor is called an axial one³.

q' pyromagnetic effect. $T^{ax}(1)$. Describe Magnetization induced by temperature changes, and from symmetry we once again have $\mathbf{q} = \mathbf{q}'$.

³We will describe axial tensor with the upscript ax , mathematically are objects that are not invariant to parity transformations.

Symmetry is important

In the simple description of the constitutive relation that we give previously inside a simple linear approximation was already simple to grasp how the symmetry of \mathcal{K} helped us in the understanding of some phenomena. For example, we found out that if the \mathbf{p} entries are non-zero we have electrocaloric effect, and with it also \mathbf{p}' needs to be non-zero having so also the pyroelectric effect. Therefore, only by simple symmetry we see how several effects are related to each others, but we can go deeper and the way to do that rely on a simple but incredibly clever principle thought by Nuemann that assume the following.

Theorem 1.1.2: Nuemann principle

The symmetry of any physical property of a material can not be lower than the symmetry of its atomic-level structure.

Proof: This is not really a proof of the principle, it's more an explanation of the logic on which is based. The idea is that if I make a rotation to the system and the atomic structure doesn't change, due to symmetry, therefore I have the exact same material and interactions. This implies that, if the latter was true, also all the properties of the material should not have changed. Mathematically, this translates to the invariance of the mathematical object to the action of the group elements inside the point group of the crystal. ☺

To understand to what extent the utility of this principle we can look at some cases of application to some quantities. For example, let's imagine having a crystal with inversion as a symmetry and see what happens to rank ones tensors. Therefore, let's assume to have the tensor $\mathbf{p} = (p_x, p_y, p_z)$ if the system have inversion symmetry the following needs to be true

$$\begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} -p_x \\ -p_y \\ -p_z \end{pmatrix}. \quad (1.12)$$

This clearly makes so that the only possible solution to the equation to make the vector invariant is $\mathbf{p} = \mathbf{0}$, meaning that in a crystal with inversion symmetry no $T(1)$, or $T(0)$, properties can be present. This is already a powerful result that let us know which materials can possibly show some properties. Another interesting thing to see is looking at the presence of rotational symmetries which allow us to have the following result

Corollary 1.1.1

If a rotation symmetry is inside the point group of the crystal the $T(1)$ properties can only have non-zero entries only in the direction of the axis of rotation called **polar direction**.

Proof: Let the group C_n be a subgroup of the point group, and we assume that the rotation axes is in z direction, so that if we need to make a $T(1)$ invariant respect to the rotation we will require the following

$$\begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} \cos(2\pi/n) & \sin(2\pi/n) & 0 \\ -\sin(2\pi/n) & \cos(2\pi/n) & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} \cos(2\pi/n)p_x + \sin(2\pi/n)p_y \\ \cos(2\pi/n)p_y - \sin(2\pi/n)p_x \\ p_z \end{pmatrix}. \quad (1.13)$$

To solve the equation it's easy to see how $p_x = p_y = 0$ while only the component in the polar direction can be non-zero. ☺

The same principle can be applied to other rank tensors, and becomes really important for rank two ones \mathbf{T} where the requirement for respecting a certain symmetry \mathbf{R} simply becomes

$$\mathbf{T} = \mathbf{R}\mathbf{T}\mathbf{R}^{-1}. \quad (1.14)$$

Applied to general matrix using specific high symmetry point groups allows for a huge simplification of the independent components inside the tensor. The simplest, and probably most important, case is the one of a crystal with cubic symmetry, which bring the possibilities to one

Corollary 1.1.2

Inside a cubic crystal all the $T(2)$ properties are isotropic, therefore have only one independent component and can be written as $\mathbf{A} = A\mathbf{1}$.

I'm not going to do the computations, but in reality are really easy since you only need to impose two 90° rotations on different axis.

Note

This particular case forms also a counterexample to prove how the Neumann principle doesn't work backwards, meaning that it's possible how a physical property shows greater symmetry than the crystal itself. In fact, in this case the $T(2)$ becomes a scalar which is invariant under any type of rotational symmetry, while the cubic crystal has only C_4 at best.

Time symmetry

One last type of symmetry was left out by the latter discussion, in fact inside magnetic crystals the orientation of the magnetic moment may add another degree of symmetry. If we assume that all magnetic phenomena can be associated to the presence of moving charge, and so currents, then also the **time reversal symmetry** Θ becomes important. In particular one can call **i-tensors** the ones that are invariant under Θ and **c-tensors** the others we will have that the magnetic field is inside the latter, having

$$\mathbf{H}(-t) = -\mathbf{H}(t). \quad (1.15)$$

The same thing can be applied to the \mathcal{K} matrix and add also time-symmetry to the Nuemann principle. In particular the physical quantity needs to be compatible with the properties of the quantities that relates, for example let's consider \mathbf{X} and \mathbf{Y} both i or c-tensors we can write

$$\Theta\mathbf{Y} = \pm\mathbf{Y} = \pm\mathcal{K}\mathbf{X} = \Theta\mathcal{K}\mathbf{X}. \quad (1.16)$$

Which simply translates to no further restrictions to the properties of the physical quantities. Instead, if we have that \mathbf{X} and \mathbf{Y} are opposite time reversal tensors, in that case the relation between the two becomes

$$\Theta\mathbf{Y} = -\mathbf{Y} = -\mathcal{K}\mathbf{X} = \Theta\mathcal{K}\mathbf{X}. \quad (1.17)$$

This leads to the fact that $\Theta\mathcal{K} = -\mathcal{K}$ giving rise an increase of the symmetry inside the tensor. Also, if we assume that \mathcal{K} is a c-tensor in the specific case we are looking we obtain $\mathcal{K} = -\mathcal{K}$ saying to us that the tensor needs to be identically zero.

The properties that relate different time-symmetry tensors are, therefore, special and takes the name of **special magnetic properties**. Some examples of such properties are the magnetocaloric effect p_i , magnetoelectric polarization λ_{ij} and piezomagnetism Q_{ijkl} .

1.2 Unary heterogeneous systems

To start the approach to the thermodynamic study of material it's better to first approach simple systems, and in this field the simplest case that one can think of are **unary systems**. The latter are simply defined as systems where only one element is present, such as Carbon, Silicon or also more complicated ones such as water or SiO_2 . In fact, also system composed by molecules can be thought as unary as long as we work in a range where the smallest component is stable and no spontaneous dissociation appears.

Definition 1.2.1: Unary systems

A system said to be unary if is composed by only one main component, which can be a molecule or an atom, that is stable inside the working range of the analysis.

Our aim in working with this system is start to understand how they present themselves in nature in different ambient. Basically we will explain how to predict if a material at a certain pressure and temperature is in gases, solid or liquid state, comprehending how to read and construct a **phase diagram** for these simple cases.

For the readers that has never seen, or heard of, a phase diagram some examples for the cases of Carbon and Water are reported in Fig. (1.2). These type of plots are made to clearly show the state in which the material present itself in the selected region of phase space. In our case we selected the (P, T) representation, where is possible to see at what pressure and temperature the two materials are in a solid state or transform to a liquid one etc. Nevertheless, the real points of interest inside the graph are the lines that marks the boundaries between phases. They are called **coexistence lines** and are a special subspace of phase space where both phases can coexist at equilibrium. A condition that allow us to model what happens in that region and predict their form and, therefore, the boundaries that describe the phase diagram. At last, of great interest are also the points at the intersection of two lines, called **triple points**, where three states of matter coexist at the same time, which we will see is the maximum number of state that can coexist in a unary system.

Equilibrium conditions

To draw a phase diagram of a system we need to predict the positions of the coexistence line, finding out the subset of phase space where two, or more, phase of matter are in equilibrium with each other and

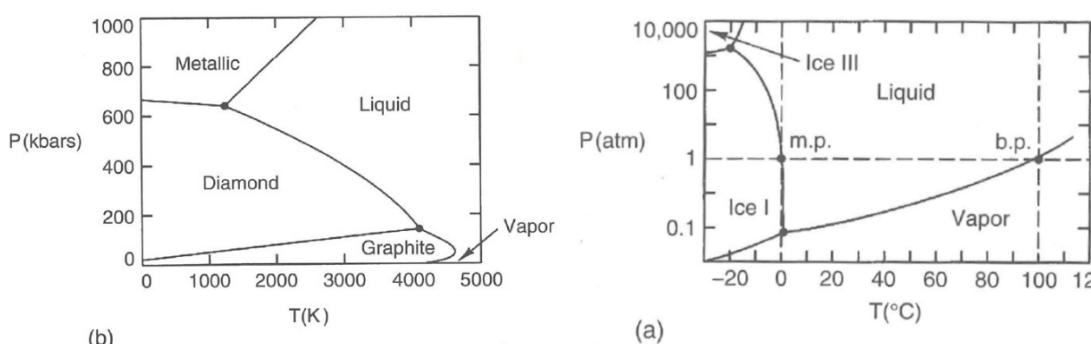


Figure 1.2: Phase diagrams of simple unary systems: Carbon(a) and Water(b). Both are reported in a P vs T graph, where we can clearly see the triple points and the coexistence lines.

can, therefore, coexist. To do that is needless to say that we need to define what being in equilibrium means, and in particular finding out the physical conditions that tells us when two phases of matter are in equilibrium with each others. In order to do that simple thermodynamic considerations allow us to arrive to the following results.

Theorem 1.2.1: Equilibrium conditions

Inside a unary system two phases α, β of matter can coexist at equilibrium, creating a heterogeneous system, only if the relation for **thermal**, **mechanical** and **chemical** equilibrium are satisfied, namely:

$$T^\alpha = T^\beta, \quad P^\alpha = P^\beta, \quad \mu^\alpha = \mu^\beta. \quad (1.18)$$

Proof: Let's imagine to start with the system composed by α and β being an open one inside an environment. After some time the studied system will evolve to an equilibrium state within the environment, which nevertheless will not depend on it. This is something that we can easily understand since, for the zeroth principle of thermodynamics, if we close the system when in equilibrium, basically eliminating the environment, the state of the α and β unary system will remain untouched. Basically the evolution of the open system leads to an equilibrium situation that is analogues to the case of a closed one, meaning that at equilibrium we can consider $\alpha \cup \beta$ as closed having that the following conditions must be true

$$U^\alpha + U^\beta = \text{const}, \quad V^\alpha + V^\beta = \text{const}, \quad N^\alpha + N^\beta = \text{const}. \quad (1.19)$$

Basically the total energy, volume and number of particle must remain constant in a closed system, as we know. Now, inside equilibrium we can also write down the first principle of thermodynamics, in the normal form, as follows

$$du = Tds - PdV + \mu dn. \quad (1.20)$$

Where u is the energy density, s the entropy per unit volume and n the number of mole. With this equation we can rewrite it to obtain the differential of the entropy as

$$ds = \frac{du}{T} + \frac{P}{T}dV - \frac{\mu}{T}dn, \quad (1.21)$$

this is really useful since being at equilibrium is implicitly saying to us that the entropy should be at a maximum. In fact, from classical thermodynamics we know that system evolves towards maximum entropy, so that the differential of the total entropy of the system must be zero at its maximum $ds^\alpha + ds^\beta = 0$. If we now use Eq. (1.21) and the relations Eq. (1.19) we can easily see that the following is true

$$\left(\frac{1}{T^\alpha} - \frac{1}{T^\beta} \right) du^\alpha + \left(\frac{P^\alpha}{T^\alpha} - \frac{P^\beta}{T^\beta} \right) dV^\alpha - \left(\frac{\mu^\alpha}{T^\alpha} - \frac{\mu^\beta}{T^\beta} \right) dn^\alpha = 0, \quad (1.22)$$

which can be respected only if the conditions in Eq. (1.18) are true. ☺

These conditions are essential for the study of the phenomenon of coexistence that we are interested in since gives us a mathematical way of imposing the presence of the phases we are interested in. Nevertheless, are not the only tools that we need to arrive at a solution. In fact, equilibrium conditions can be formulated also on the base of others quantities such as the different **thermodynamic potentials**. The major ones that we are going to use the most are reported synthetically inside Tab. (1.1), the latter is not a mathematical precise definition of them, which is obtained through Legendre transform, but that is outside the scope of the course. Between the different types of potential defined we will focus on a

Table 1.1: Table with the major thermodynamic potential giving their: definition, differential and major cases in which are used in a quick way.

Name	Definition	Differential	Utility
Hentalpy	$H = U + PV$	$dH = Tds + VdP + \mu dn$	isobare study, since $dH = \delta Q$.
Helmoltz ener.	$F = U - TS$	$dF = -SdT - PdV + \mu dn$	isocore-isotherm study.
Gibbs free ener.	$G = U - TS + PV$	$dG = -SdT + VdP + \mu dn$	isobare-isotherm study.

particular one, the **Gibbs free energy** G . The reasons for it are several, for example one can see from its differential how taking the Gibbs energy per number of mole, \bar{G} , is equal to the chemical potential

$$\mu = \left. \frac{\partial G}{\partial n} \right|_{T,P} = \left. \frac{\partial(n\bar{G})}{\partial n} \right|_{T,P} = \bar{G} \left. \frac{\partial n}{\partial n} \right|_{T,P} = \bar{G}. \quad (1.23)$$

Nevertheless, this is still not the major reason why we are interested in it. The main reason is that using that we can give another powerful equilibrium condition based on it.

Theorem 1.2.2: Gibbs' equilibrium condition

Every system, not at equilibrium, constrained to constant pressure and temperature will evolve in order to minimize the Gibbs free energy per unit mole, reaching an equilibrium where \bar{G} is at its minimum.

Proof: We can take the differential of \bar{G} , which is equal to μ , by using the total one and eliminating the part on the variation of the number of mole, having

$$d\mu = -SdT + VdP. \quad (1.24)$$

Now, this differential is exact only if we have a reversible transformation. In a non equilibrium situation the differential changes to an unknown form that still we know have Eq. (1.24) as upper limit. In fact, if one use the second principle of thermodynamics for a general transformation in the derivation of the differential will obtain

$$d\mu \leq -SdT + VdP. \quad (1.25)$$

Now, if we assume that the system is kept at constant P and T that relation becomes simply $d\mu \leq 0$, meaning that μ can only decrease as the system evolve reaching equilibrium when found its minimum. ☺

This equilibrium condition is really powerful to us, since all we need to do is found out the functions $\mu^i(P, T)$ for all the possible phases that we are interested into for our system and confront them. We will have that the one with the lower chemical potential will be the one that shows up in that position of the phase diagram, also if we have two phases with same μ than that means a coexistence line will pass on that point. This process is really simple and is clearly explained with the example given in Fig. (1.3) where all that was sad before is present.

As a last remark it could be interesting to understand how the values of μ can be computed inside a system, in particular using experimental results. The idea is starting from the differential Eq. (1.24)

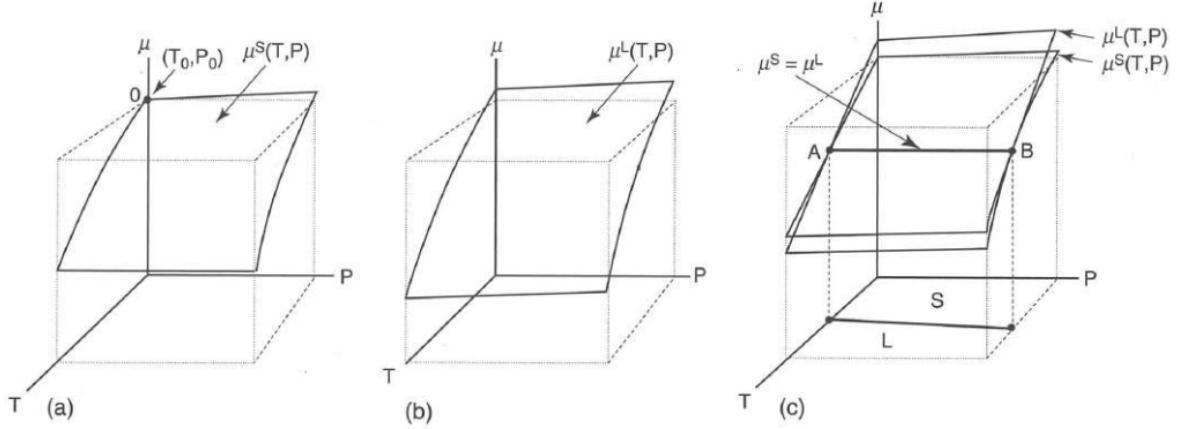


Figure 1.3: Graphical representation of the chemical potential for a solid phase(a), liquid phase(b) and the superposition of the two to see which one prevails on the other for the equilibrium phase(c). It's possible to see how in the part of the phase diagram where $\mu^S = \mu^L$ a coexistence line appear.

and try to write down expressions for S and V . To do that we need first to write down the differential of those two quantities, starting from S

$$dS = \left. \frac{\partial S}{\partial P} \right|_T dP + \left. \frac{\partial S}{\partial T} \right|_P dT. \quad (1.26)$$

We need to simplify it and the first thing that we can say is that μ is a continuous function, therefore the Schwartz theorem apply having

$$\left. \frac{\partial^2 \mu}{\partial P \partial T} \right|_T = - \left. \frac{\partial S}{\partial P} \right|_T = \left. \frac{\partial^2 \mu}{\partial T \partial P} \right|_P = \left. \frac{\partial V}{\partial T} \right|_P = V \alpha. \quad (1.27)$$

Where the definition of **thermal expansion coefficient** $\alpha = V^{-1} \left. \frac{\partial V}{\partial T} \right|_P$ was used. The remaining partial derivative in Eq. (1.26) is simply the **specific heat** at constant pressure c_P , having so that the final form is

$$dS = -V \alpha dP + \frac{c_P}{T} dT. \quad (1.28)$$

Analogous considerations can be done for the volume, using also the **bulk modulus** β having so that its final form will be instead

$$\frac{dV}{V} = -\beta dP + \alpha dT. \quad (1.29)$$

In this way both $V(P, T)$ and $S(P, T)$ can be computed since α, β and c_P can be easily obtained experimentally and then the differential can be integrated through known numerical routines. For example, one can easily compute a so-called **isobaric section**, basically a slice of phase diagram at constant pressure P_0 , using two consecutive integrations

$$S(T, P_0) = S(T_0, P_0) + \int_{T_0}^T \frac{c_p(T')}{T'} dT', \quad (1.30)$$

$$\mu(T, P_0) = \mu(T_0, P_0) - \int_{T_0}^T S(T') dT'. \quad (1.31)$$

Clausius-Clapeyron equation

Now we want to completely focus on the coexistence lines and try to describe them better. In particular our main goal is to find a way to predict their form so that we will be able to draw them on the phase diagram having so, directly, all the information needed. It is known that a solution to this is present in literature and comes with the name of **Clausius-Clapeyron equation**.

Theorem 1.2.3: Clausius-Clapeyron equation

A coexistence line between two phases α and β of a system has a slope in the P vs T plane that is given by the following relation

$$\frac{dP}{dT} = \frac{1}{T} \frac{\Delta H^{\alpha \rightarrow \beta}}{\Delta V^{\alpha \rightarrow \beta}}. \quad (1.32)$$

Proof: Since we are on a coexistence line we know that the equilibrium conditions of Eq. (1.18) must be valid, therefore $d\mu^\alpha = d\mu^\beta$ along with dT and dP , leading to

$$-S^\alpha dT + V^\alpha dP = -S^\beta dT + V^\beta dP \quad (1.33)$$

Rearranging and assuming that the study is done in an isobare condition, meaning that $dH = TdS$, we will have the wanted result.

$$\frac{dP}{dT} = \frac{1}{T} \frac{H^\beta - H^\alpha}{V^\beta - V^\alpha} = \frac{1}{T} \frac{\Delta H^{\alpha \rightarrow \beta}}{\Delta V^{\alpha \rightarrow \beta}}. \quad (1.34)$$



This is a really known equation that can tell us some interesting information about the system. For example, if we have the phase diagram of a transition from solid to liquid, we know that ΔH needs to be positive since the heat is transferred inside the material during melting. Therefore, if experimentally we have that the coexisting line has a positive slope, this means that the system is expanding, while it's becoming smaller if the slope is negative. The latter case is something that can be clearly seen in the phase diagram of water, which is known it's a peculiar case where the volume reduce going from solid to liquid.

The equation can also be solved exactly for some simple cases of which the most important is the case of liquid-gases coexistence lines where a really simple result can be found out.

Corollary 1.2.1 Vapor pressure curves

A coexistence line between a liquid and gases phases can be described analytically by the following equation

$$P = c \exp\left(-\frac{\Delta H}{RT}\right), \quad (1.35)$$

where c is a constant.

Proof: We can use Eq. (1.32) assuming that $\Delta V^{\alpha \rightarrow \beta} \approx V^{gas}$ since gases have much larger volume than liquid. Then by using the equation of perfect gas one can obtain the differential equation

$$\frac{dP}{P} = \frac{\Delta H}{R} \frac{dT}{T^2}, \quad (1.36)$$

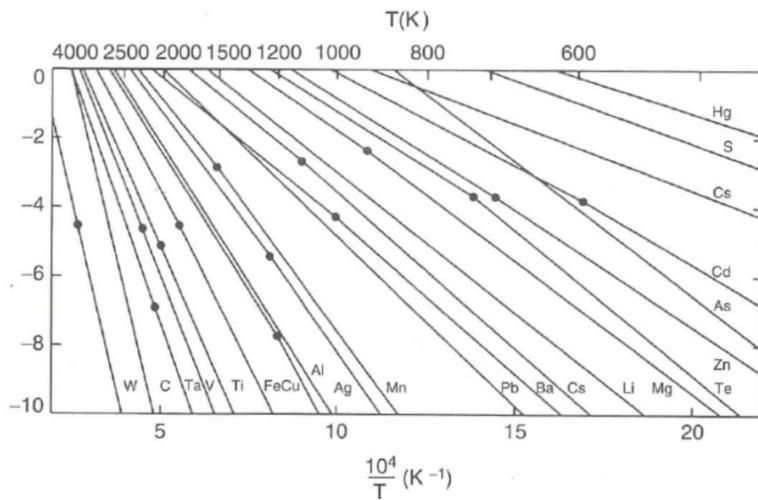


Figure 1.4: Compilation of vapor pressure for the elements with $\log P$ on the y-axis. A change in slope (marked by the dot) corresponds to the melting point, which is also a triple point here because of the coexistence with the vapor phase.

where ΔH has usually a small dependence on T and can therefore be assumed constant. Thus, the equation can be integrated directly giving the wanted result. \circlearrowright

This equation allow us to describe up to a good precision the wanted lines where gasses are involved. To make an example of how good of an approximation this is we can have a look to Fig. (1.4) where the coexistence lines all respect the exponential relation given by Eq. (1.35) being straight lines that changes slope on the melting point, in correspondence of a change in ΔH going from liquid-gass to solid-gass one.

Note

Fig. (1.4) also tells us that the difficulty in having sublimation instead of melting for a material is not in the different amount of heat that we need to give in the two processes, since the slopes changes really little, but only in the needs of a much higher temperature for the former process to even start.

1.3 Multicomponent homogeneous systems

Now we make our first step to increase the complexity of the system under study and let the possible number of components inside the system to increase. Thus, now two type of molecules or atoms can be present inside the material or solution allowing for a much larger phase space to consider. Nevertheless, to still keep the things simple we will assume a **homogeneous** phase, meaning that the system is composed by different elements in the same phase of matter. Therefore, we will not consider the possibility of having a solid with liquid or gas inside for the moment.

Definition 1.3.1: Multicomponent homogeneous systems

We will call a system multicomponent homogeneous if it's composed by different components, molecules or atoms, which are all in the same state of matter: solid, liquid or gass.

To make an example, the typical system one can think about is an **alloy**, a terminology used to indicate a solid mixture of two or more chemical elements. The latter is mainly used for metallic solids but can be

extended to all materials. An alloy can be homogeneous, in which case is also called a **solid solution**, where the dominant element is called **solvent**, and the others **solutes**.

To work with these systems we will focus on how the system is composed, looking at how the different elements interact with each other modifying the physical properties of the material. This basically means that a general function of state f' will now depend on the composition of the system in a way that will look like the following

$$f'(n_1, n_2, n_3, \dots, n_N; T, P) = f'(\mathbf{n}, T, P), \quad (1.37)$$

Where n_i is the number of mole of the i -th component. We can also notice that f has also dependence on the thermodynamical quantities T and P which, nevertheless, are often taken to be constant during experiments. In this context it comes really handy to define some important quantities that will be used extensively during the section.

Definition 1.3.2: Molar fraction

Taken the i -th component inside a multicomponent system we will define its molar fraction as

$$X_i = \frac{n_i}{\sum_j n_j} = \frac{n_i}{n_T}. \quad (1.38)$$

Basically we have normalized the number of mole of a component so to work with a simple quantity that allow to know in percentage how much of that component is present inside the material. For example, if $X_i = 1$ that means that only that component is present while 0 determines its absence. This normalization over n_T is really useful also for the physical quantities, which allow to make them depend on X_i rather than n_i . For this reason we will often work with molar functions.

Definition 1.3.3: Molar function

Taken a physical quantity f' we will define the molar function deriving from it the value

$$f = f'/n_T. \quad (1.39)$$

At last, it's important to remind to the reader the important difference that exist between **intensive** and **extensive** quantities inside a thermodynamic system. It's possible that the reader has already seen this exact definitions in other instances, but it will be useful to rewrite them inside the contest of multicomponent systems. In particular the reader should recall how the difference is usually settled at words as if the quantity is proportional or invariant to variations of the system sizes. Inside our description the size of the system is controlled by the number of moles of the components, therefore we can mathematically state the definition of extensive and intensive in the following way.

Definition 1.3.4: Extensive quantities

A thermodynamic quantity f' is said to be extensive if taken $\lambda > 0$ the following equality holds true

$$f'(\lambda \mathbf{n}, T, P) = \lambda f'(\mathbf{n}, T, P), \quad (1.40)$$

which mathematically means that is a homogeneous function of degree 1.

Definition 1.3.5: Intensive quantities

A thermodynamic quantity f' is said to be intensive if taken $\lambda > 0$ the following equality holds true

$$f'(\lambda \mathbf{n}, T, P) = f'(\mathbf{n}, T, P). \quad (1.41)$$

This ends the series of definitions, now we can start to study the properties of multicomponent systems.

Partial molar properties

Let f' being an extensive thermodynamic quantity that we are interested in studying for our multicomponent system. To approach this problem we may want to have a look to its differential

$$df' = \nabla_{\mathbf{n}} f' \cdot d\mathbf{n} + \frac{\partial f'}{\partial T} dT + \frac{\partial f'}{\partial P} dP, \quad (1.42)$$

which is usually written by taking P and T constant since in solid state those quantities are easier to be fixed during experiments. In this way we can fully characterize f' in terms of the partial derivatives respect to the number of moles of the components

$$\bar{f}_i = \left. \frac{\partial f'}{\partial n_i} \right|_{n_j \neq i, T, P}, \quad df' = \sum_i \bar{f}_i dn_i. \quad (1.43)$$

These derivatives are, therefore, really powerful and will become the main focus of the studies around the physical properties. For this reason we will give them the name of **partial molar properties** (PMP), and we will define them rigorously as follows.

Definition 1.3.6: Partial molar properties

Taken a physical quantity f' the partial molar property related to the i -th component of the system is defined to be

$$\bar{f}_i = \left. \frac{\partial f'}{\partial n_i} \right|_{n_j \neq i, T, P}, \quad (1.44)$$

which can also be seen as the application of the **partial molar operator** $\partial/\partial n_i$ to f' itself.

Thus, we can show effectively how powerful they can be by showing that the knowledge of \bar{f}_i can, not only, shows us how f' changes, but allows also for the function itself to be known without the need of integration. In particular, this result can be obtained in the following way.

Theorem 1.3.1: Determination's of physical quantities via PMPs

Given f' an extensive thermodynamic quantity then the following relation holds true

$$f'(\mathbf{n}, T, P) = \sum_i \bar{f}_i(\mathbf{n}, T, P) n_i. \quad (1.45)$$

Proof: Since f' is extensive is also a homogeneous function of degree 1, having $f'(\lambda \mathbf{n}, T, P) = \lambda f'(\mathbf{n}, T, P)$ of which we can take the derivative respect to λ from both sides. The right one simply

becomes f' , while the right one gets

$$\frac{df'}{d\lambda}(\lambda \mathbf{n}, T, P) = \sum_i \frac{\partial f'}{\partial (\lambda n_i)}(\lambda \mathbf{n}, T, P) \frac{\partial (\lambda n_i)}{\partial \lambda} = \sum_i \frac{\partial f'}{\partial (\lambda n_i)}(\lambda \mathbf{n}, T, P) n_i. \quad (1.46)$$

So, by setting the two parts equal to each others we have

$$\sum_i \frac{\partial f'}{\partial (\lambda n_i)}(\lambda \mathbf{n}, T, P) n_i = f'(\mathbf{n}, T, P), \quad (1.47)$$

where $\lambda = 1$ gives the wanted relation. \odot

Here we can start to see how the quantities expressed in molar terms can be powerful, even if someone may ask if we are not simply complicating things by the need now of determining N values of \bar{f}_i instead of simply f' . The reason for it is that some interesting properties can be found out for the PMPs that are general and will allow for their computations.

Corollary 1.3.1 PMPs are intensive quantities

Taken an extensive physical quantity f' its PMPs are all intensive ones.

Proof: We can start from Eq. (1.45) and from it apply the transformation $\mathbf{n} \rightarrow \lambda \mathbf{n}$, we will have

$$f'(\lambda \mathbf{n}, T, P) = \lambda \sum_i \bar{f}_i(\lambda \mathbf{n}, T, P) n_i = \lambda \sum_i \bar{f}_i(\mathbf{n}, T, P) n_i. \quad (1.48)$$

For the two expressions to be equal we need that $\bar{f}_i(\lambda \mathbf{n}, T, P) = \bar{f}_i(\mathbf{n}, T, P)$ making \bar{f}_i intensive quantities. \odot

This is interesting under a physical point of view since we can evaluate \bar{f}_i in systems without caring about the sizes and still having exact values for every possible compositions. Also, this means that we can imagine at \bar{f}_i like **properties of the single components** of the systems, so that do not depend on their quantities but only on their atomistic properties. Along with that, we can also see how every one of them influences the others since also a relation between the differentials can be found out.

Corollary 1.3.2 Gibbs-Duhem equation

Taken an extensive physical quantity f' the differentials of the PMPs relates using this equation

$$\sum_i n_i d\bar{f}_i = 0. \quad (1.49)$$

Proof: Using Eq. (1.45) we can write down the differential of f' as follows

$$df' = \sum_i \bar{f}_i dn_i + \sum_i n_i d\bar{f}_i = df' + \sum_i n_i d\bar{f}_i, \quad (1.50)$$

where Eq. (1.43) was used to rewrite the differential. Then, by rearranging, the wanted relation is obtained. \odot

As a last remark we can also show that these molar quantities retains some of the same properties of the normal thermodynamical quantities. In particular, every thermodynamic potential posses a PMP counterpart defined in the same way as the normal one. For example, the Gibbs free energy $G' = H' - TS'$ can be written, by applying the partial molar operator

$$\bar{G}_i = \bar{H}_i - T\bar{S}_i, \quad (1.51)$$

which tells that all the known thermodynamic relations remains true, like

$$\bar{S}_i = - \left. \frac{\partial \bar{G}_i}{\partial T} \right|_{n_k, P}, \quad \bar{V}_i = \left. \frac{\partial \bar{G}_i}{\partial P} \right|_{n_k, T}. \quad (1.52)$$

Along with that, also the Maxwell relations or the differentials remains unchanged we only need to substitute the PMP's version of the quantity present in the normal relation. The only change between the normal and PMP cases worth noticing is the value of \bar{G}_i , which we have already seen that becomes μ inside a unary system and here things doesn't change since

$$dG' = -S'dT + V'dP + \sum_i \mu_i dn_i, \quad \mu_i = \left. \frac{\partial G'}{\partial n_i} \right|_{n_{k \neq i}, P, T} = \bar{G}_i. \quad (1.53)$$

Thus, everything related to the Gibbs free energy will become a relation using the chemical potential⁴.

Example 1.3.1

With these results we are able to already study some simple systems in an analytic form. For example, let's take a two component system and study the behavior of a molar function $f(X_1, X_2; T, P)$. Since we are using the molar version of f' we can also rewrite it differential that becomes

$$df = \bar{f}_1 dX_1 + \bar{f}_2 dX_2, \quad (1.54)$$

but we also know that $X_1 + X_2 = 1$ leading to $dX_1 = -dX_2$. Thus, we can find out the derivative of f as

$$\frac{df}{dX_2} = \bar{f}_2 - \bar{f}_1, \quad (1.55)$$

we only need to write down the two quantities. The idea is that we know from Eq. (1.45) that $f = \bar{f}_1 X_1 + \bar{f}_2 X_2$, so by substituting $X_1 = 1 - X_2$ we have

$$\bar{f}_1 = \frac{f - \bar{f}_2 X_2}{1 - X_2}. \quad (1.56)$$

Thus, by inserting it inside the derivative of f found previously we obtain a general simple relation for the physical quantity

$$f = \bar{f}_1 + (X_2 - 1) \frac{df}{dX_2}, \quad (1.57)$$

⁴Keep in mind that this happens only because we have decided to work at constant P and T for experimental simplicity, in a general situation we may keep constant other quantities and then G will no more be the potential of choice while another may become the right one whose PMP gives μ .

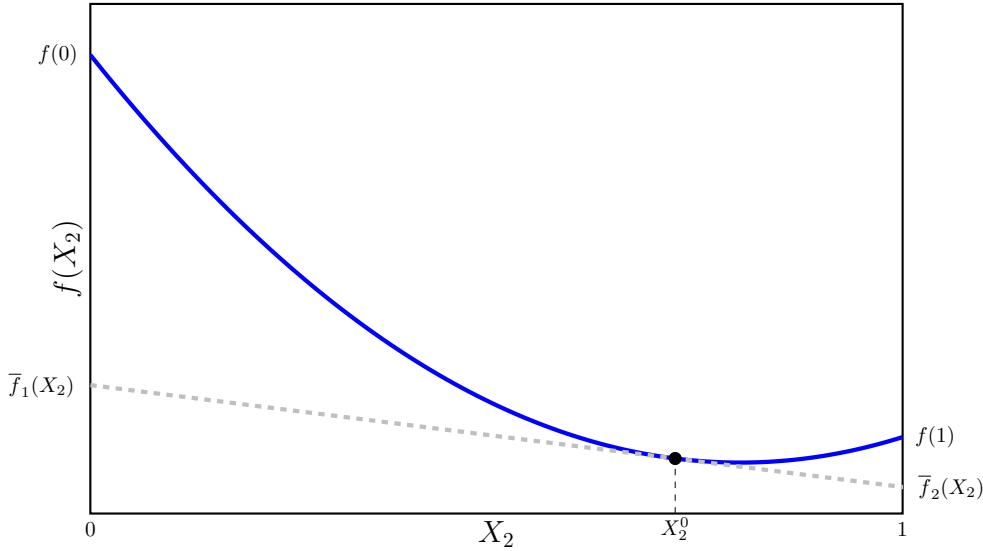


Figure 1.5: Illustration of the graphical method to compute the PMPs of a binary system in the case of a simple physical quantity. It's possible to see how the method basically select one point X_2^0 and then draw the tangent to f in that point finding the PMPs as the intercepts with the $X_2 = 0$ and $X_2 = 1$ axis.

same computations can be done for X_1 leading to the same results but with inverted subscripts. Basically, using really simple considerations we were able to obtain a general result for f that allow us to study the system simply, but most importantly gives us a geometric way of evaluating the PMPs. In fact the Eq. (1.57) can be rewritten in terms of \bar{f}_i and taken a fixed point X_2^0 one can see how it describes a line coming from the point to the intercept with the y-axis as is illustrated in Fig. (1.5).

Note

The result obtained not only showed us the power of PMPs but also that they are not independent of the material composition. In fact the values of \bar{f}_i changed based on the point X_2^0 taken. The only situation where they are independent is when f is linear in X_i , which is obvious since the PMPs are the derivative of f respect to X_i and so if it's linear the X_i dependence go away.

Mixing process

The next step is studying how the physical quantities changes due to the mixing of the various components. Thus, we can imagine to gradually insert an element inside the system and has the molar fractions changes look at how a certain f changes, and this can be written as

$$\Delta f_{mix} = \sum_i \bar{f}_i X_i - \sum_i f_i^\circ X_i = \sum_i \Delta \bar{f}_i X_i, \quad (1.58)$$

where f_i° represent \bar{f}_i evaluated in the point where $X_i = 0$. This has shown how the variation of the physical quantities can be directly expressed in terms of the PMPs, and in particular of what we will call the **PMPs of mixing** $\Delta \bar{f}_i$. For this reason we are interested in look also at the properties of these quantities, in particular it's easy to see that a version of Gibbs-Duhem equation can be written for them.

Theorem 1.3.2: Gibbs-Duhem equation for mixing

Taken an extensive physical quantity f' the differentials of the PMPs of mixing relates using this equation

$$\sum_i d(\Delta \bar{f}_i) X_i = 0. \quad (1.59)$$

Proof: We start by evaluating the differential of Eq. (1.58) in order to have, by using Einstein notation

$$d(\Delta f_{mix}) = d\bar{f}_i X_i + \bar{f}_i dX_i - df_i^\circ - f_i^\circ dX_i = \Delta \bar{f}_i dX_i. \quad (1.60)$$

Where we can see how f_i° being constant has null differential, while the normal G-D equation lead to $d\bar{f}_i X_i = 0$ having so

$$d(\Delta f_{mix}) = \Delta \bar{f}_i dX_i. \quad (1.61)$$

Nevertheless, we can also write down the differential of the mixing quantity by differentiating the last equality in Eq. (1.58) and having

$$d(\Delta f_{mix}) = d(\Delta \bar{f}_i) X_i + \Delta \bar{f}_i dX_i, \quad (1.62)$$

so to have equality between Eq. (1.61) and Eq. (1.62) the wanted relation needs to hold true.



Example 1.3.2

Also in this case we can look at an exercise to compute the PMPs of mixing given in a binary system once the enthalpy of mixing is given as $\Delta H_{mix} = aX_1X_2$. To do it we can use the same result obtained in the previous example and start with

$$\Delta \bar{H}_1 = \Delta H_{mix} - \frac{d(\Delta H_{mix})}{dX_2} X_2, \quad (1.63)$$

and using $X_1 = 1 - X_2$ we can arrive to the final result

$$\Delta \bar{H}_1 = aX_2^2, \quad \Delta \bar{H}_2 = aX_1^2. \quad (1.64)$$

Where for $\Delta \bar{H}_2$ we used the same exact approach described here, even if it's possible to evaluate it also by the value of $\Delta \bar{H}_1$. In fact, we can use the G-D equation to write down $d\Delta \bar{H}_2 = -X_1/X_2 d\Delta \bar{H}_1$ where, by using $X_2 = 1 - X_1$ and integrating we have

$$\Delta \bar{H}_1 = \int_0^{X_1} \frac{X'_1}{(X'_1 - 1)} 2a(X'_1 - 1) dX'_1 = aX_1^2. \quad (1.65)$$

Activity and solutions

The activity a_i of a system is a variable strictly related to the mixing phenomena described previously. In particular, we are going to define it mathematically in the following way.

Definition 1.3.7: Activity

The activity of a solution a_i evaluate the variation of free energy on the i -th component due to a mixing phenomena as

$$\Delta\mu_i = \mu_i - \mu_i^\circ = RT \ln a_i. \quad (1.66)$$

In this simple definition one can understand easily that for an **ideal solution** the activity will simply be $a_i = X_i$, also called **Raoult's law**. This result will also lead to other interesting forms for certain quantities in the idea case as

$$\Delta\bar{S}_i = -\left. \frac{\partial\Delta\mu_i}{\partial T} \right|_{n_k, P} = -R \ln X_i, \quad \Delta\bar{V}_i = \left. \frac{\partial\Delta\mu_i}{\partial P} \right|_{n_k, T} = 0. \quad (1.67)$$

We can so insert them inside the definition of the mixing thermodynamic potential and obtain some other results as

$$\Delta H_{mix} = 0, \quad \Delta G_{mix} = RT \sum_i X_i \ln X_i, \quad \Delta S_{mix} = -R \sum_i X_i \ln X_i. \quad (1.68)$$

Where we can recall for ΔS_{mix} a form totally analogous to the **Shannon entropy**.

Nevertheless, all of this was only an ideal case, we can also try to study the real one by inserting the non ideality inside a **activity coefficient** γ_i defined as

$$a_i = \gamma_i X_i. \quad (1.69)$$

If we insert this definition inside Eq. (1.66) we will have that two part of the variation appears

$$\Delta\mu_i = RT \ln X_i + RT \ln \gamma_i = \Delta\mu_i^{id} + \Delta\mu_i^{xs}, \quad (1.70)$$

where $\Delta\mu_i^{xs}$ is what changes from ideality. We can so use these coefficients to study the evolution of the chemical potential inside our system also because another G-D equation can be written for them.

Corollary 1.3.3 Gibbs-Duhem equation for activity coefficient

Taken an extensive physical quantity f' the differentials of the reactivity coefficients relates using this equation

$$\sum_i d(\ln \gamma_i) X_i = 0. \quad (1.71)$$

Proof: To demonstrate it one can take the differentials of $\Delta\mu_i$ and then use the relation Eq. (1.59) to obtain the wanted one, all the tedious mathematical details are left to the reader. ☺

Using this relation we can have a lot of information on the mixing properties of the material, for example is possible to demonstrate the **Henry's law** for dilute solutions

$$\lim_{X_i \rightarrow 0} a_i = \gamma_i^\circ X_i. \quad (1.72)$$

Where we have only seen the result in the context of binary systems, but I believe that is kind of general, meaning that in the case of really low solute, $X_2 \rightarrow 0$, the solvent, $X_1 \rightarrow 1$ shows ideal behavior with $\gamma_1 \rightarrow 1$, as shown in Fig. (1.6).

Another type of situation that we are interested in is a particular type of systems called **regular solutions** that are defined in the following way.

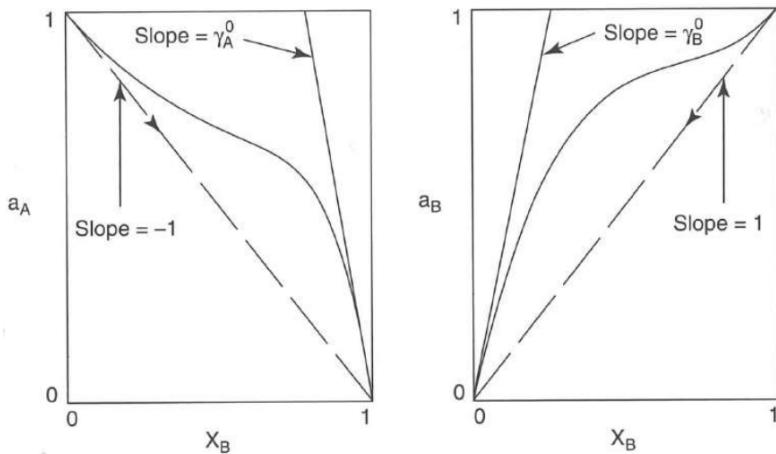


Figure 1.6: Illustration of the activity inside a binary system composed by the phases a and b , showing the expected behaviors of ideality in the diluted case.

Definition 1.3.8: Regular solutions

A solution is called regular if the following two conditions are respected:

1. The entropy of mixing is the same as for ideal solutions

$$\Delta S_{mix} = -R X_i \ln X_i. \quad (1.73)$$

2. The enthalpy of mixing is different from zero

$$\Delta H_{mix} = \Delta H_{mix}^{[xs]} \neq 0. \quad (1.74)$$

Some things can already be said for such systems, in fact we can easily say that the excess entropy of mixing, ΔS_{mix}^{xs} , is necessarily zero. Meaning that also the following is true

$$\frac{\partial \Delta H_{mix}^{xs}}{\partial T} = \frac{\partial \Delta G_{mix}^{xs} - T \Delta S_{mix}^{xs}}{\partial T} = \frac{\partial \Delta G_{mix}^{xs}}{\partial T} = -\Delta S_{mix}^{xs} = 0, \quad (1.75)$$

so the enthalpy of the solution shall not depend on the temperature. Thus, this also implies that the variation from ideality is given by the enthalpy change having

$$\Delta \mu_i^{xs} = \Delta \bar{H}_i, \quad (1.76)$$

and recalling $\Delta \mu_i^{xs} = RT \ln \gamma_i$ we can find out a general relation for the reaction coefficients

$$\gamma_i = \exp \left(\frac{\Delta \bar{H}_i}{RT} \right), \quad (1.77)$$

that can be really useful in some situations.

Example 1.3.3

To make an example of where the relation Eq. (1.77) can be really useful. Basically the simplest

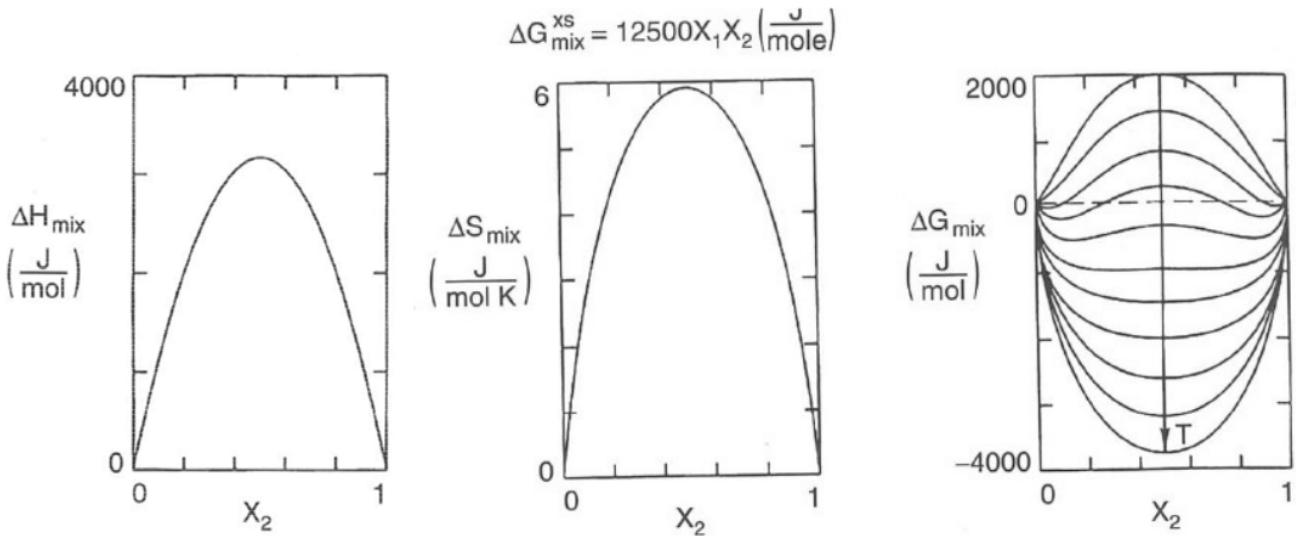


Figure 1.7: Computed values of mixing properties for the simple system given by the mixing enthalpy aX_1X_2 . It's possible to see how only the mixing free energy has a temperature dependence, and it's interesting that for some values of T a curve with two global minima is obtained.

model possible for a regular solution posses as excess enthalpy the quantity $H_{mix}^{xs} = aX_1X_2$, that we have already studied, and we know have $\bar{\Delta H}_i = aX_i^2$, so

$$\gamma_i = \exp\left(\frac{aX_i^2}{RT}\right). \quad (1.78)$$

This result also shows how $\lim_{X_i \rightarrow 1} \gamma_i$ does not depend on X_i so that for the dilute solution the Henry's law holds. Using the form of γ_i the values of ΔS_{mix} and ΔG_{mix} can be obtained as shown in Fig. (1.7).

Note

It's interesting to see how also inside the simple system defined in the Ex. (1.3.3) for certain values of T the solution ΔG_{mix} posses two global minima. This means that the system doesn't know on which minima should go, basically becomes a frustrated system which minimize the energy not only going into one of the minima, but different parts of the system can go in different minima generating different phases. This is the way in which heterogeneous systems originates in nature.

Atomistic model for binary systems

So far we have focused mainly on the general description of thermodynamic properties inside a general system. Now the aim is to look deeper into a specific system trying to create a microscopic atomistic model that describes the behavior of binary systems. Basically we will imagine to work with a system composed of two types of elements A and B that can occupy two different lattice sites α and β on the unit cell of the material. The goal is to describe how the atoms position themselves inside the lattice on average, and in general the possible scenarios are the three depicted inside Fig. (1.8).

To study which type of structure will be the one found out inside a material we will use a **quasi-**

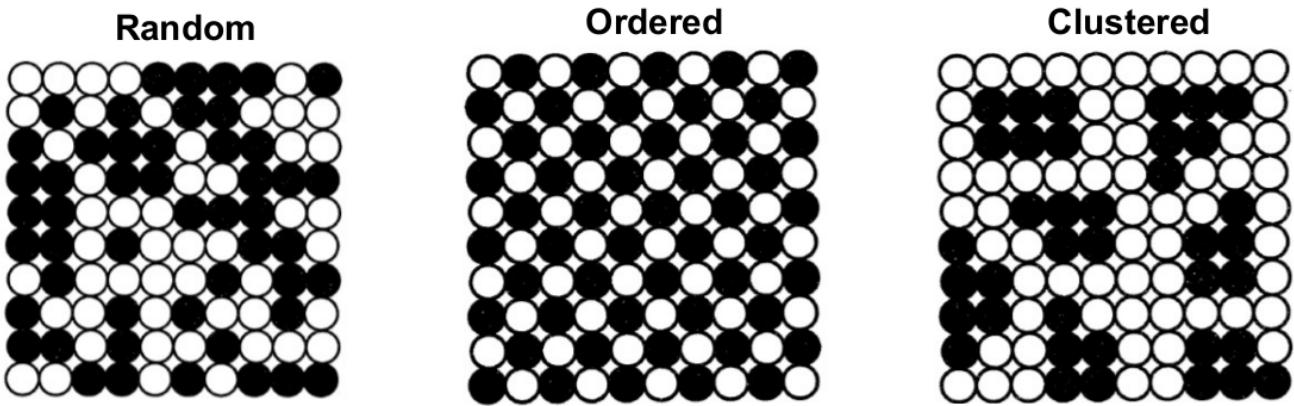


Figure 1.8: Illustration of the three possible type of distributions of the atoms inside a binary system, with the possibility of randomly placed atoms, ordered structure creating a known lattice and clustered systems.

chemical model, meaning that we will focus on the bonds that can be generated between nearest neighbours atoms, whose number if given by the coordination one Z , and their strength. To do so we will need to consider three types of bonds and the energy gain that they bring to the system: E_{AA} for $A - A$ bonds, E_{BB} for $B - B$ bonds and E_{AB} for $A - B$ bonds. Before entering the computations will be useful to define two **orders parameters** that will simply the treatment of the system

$$X_i = \frac{1}{2} (X_i^\alpha + X_i^\beta), \quad \eta = \frac{1}{2} (X_B^\alpha - X_B^\beta), \quad (1.79)$$

where X_i^j describe the molar fraction of atoms i inside the site j . It's important to notice that both the parameters are limited, in the sense that from the properties of molar fractions we can find out how

$$0 \leq X_i \leq 1, \quad -\frac{1}{2} \leq \eta \leq \frac{1}{2}. \quad (1.80)$$

Also, using some further mathematical consideration one can find out how $\eta \leq \min(X_B, X_A)$. In physical terms, one can understand how the two quantities are intrinsically different since inside a closed system the total number of atoms N is conserved along with also the two numbers of A and B atoms. This means that the value of X_A and X_B are **conserved quantities** inside closed systems, while η can still change being dependent also on the order with which the atoms position themselves inside the lattice. In particular, one can easily understand that if we call $P(B, \alpha)$ and $P(B, \beta)$ the probabilities of having a B atom in site α or β , and we assume N_B^j to be averages we can write $X_B^j = N_B^j/N = P(B, j)$ having

$$\eta = \frac{1}{2} (X_B^\alpha - X_B^\beta) = \frac{1}{2} [P(B, \alpha) - P(B, \beta)]. \quad (1.81)$$

Showing how η is zero only if I have the same probability of having B on one site or the other, therefore a **random lattice**, while will be maxed out if I'm sure that B atoms are on a specific site generating the maximum order inside the system, **ordered lattice**. We will also call the case when η is at one of the extreme a situation of **long range order** (LRO), so that global symmetries inside the lattice can be found.

Note

It's interesting to point out that even if η increasing means an increase in order that doesn't mean that there is also an increase in the symmetry. In fact, increasing order could mean also a decrease in the

symmetry. For example in the case of a bcc binary system, if a random lattice is present on average I have same probability of having A or B atoms on the diagonal, creating the pattern A/B – A/B – A/B – etc. If, instead, Order comes into play I have a structure of the type A – B – A – B – etc which has less symmetry.

Using these informations we can simply write down forms to describe the average number of different types of bonds present inside the material by using an equation of the type

$$N_{ij} = \frac{\text{number of bonds present}}{2} \times P(i, \alpha)P(j, \beta), \quad (1.82)$$

where the division by 2 is due to the fact that we don't want to count the same bond twice. In this way we can directly write down general forms for the number of bonds in the following way

$$N_{AA} = \frac{NZ}{2} X_A^\alpha X_A^\beta = \frac{NZ}{2} [(1 - X_B)^2 - \eta^2], \quad (1.83)$$

$$N_{BB} = \frac{NZ}{2} X_B^\alpha X_B^\beta = \frac{NZ}{2} [X_B^2 - \eta^2], \quad (1.84)$$

$$N_{AB} = \frac{NZ}{2} (X_A^\alpha X_B^\beta + X_B^\alpha X_A^\beta) = \frac{NZ}{2} (X_A X_B + \eta^2). \quad (1.85)$$

We can now set the number of atoms inside the system to the Avogadro number, to have all quantities referring to one mole, and then compute the energy of the system coming from the bonds

$$U = N_{AA}E_{AA} + N_{BB}E_{BB} + N_{AB}E_{AB}. \quad (1.86)$$

Still our main interesting is in how the two atoms mix inside the system, so we can write the mixing energy by using as a starting point the case where the two types of atom were separated in different systems having

$$\Delta U_{mix} = U - \frac{N_A Z}{2} E_{AA} - \frac{N_B Z}{2} E_{BB}. \quad (1.87)$$

By using the definitions in Eq. (1.83) and some algebra we can rewrite the mixing energy in a close form depending on the order parameters as

$$\Delta U_{mix} = N\Omega (X_A X_B + \eta^2), \quad \Omega = Z \left[E_{AB} - \frac{1}{2} (E_{AA} + E_{BB}) \right], \quad (1.88)$$

where Ω is called **interaction parameter**. This result is already showing us some interesting properties of the mixing inside a binary system. In particular, we can understand that the sign of Ω determines whether the energy variation from the mixing is negative or positive, and so if the process is favorable or not. Basically, it's possible to say that if the bond between $A - B$ is stronger than the average of the $A - A$ and $B - B$, meaning the energy is lower, the interaction parameter becomes negative and a structure with more $A - B$ bonds should appear, therefore an ordered lattice is more favorable. In the other case, atoms of same type would prefer to stay with same type driving the system into a clustered lattice situation.

Nevertheless, to describe better the thermodynamic of the system and the real form of the lattice at equilibrium, we shall work better with the Gibbs free energy of mixing

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}. \quad (1.89)$$

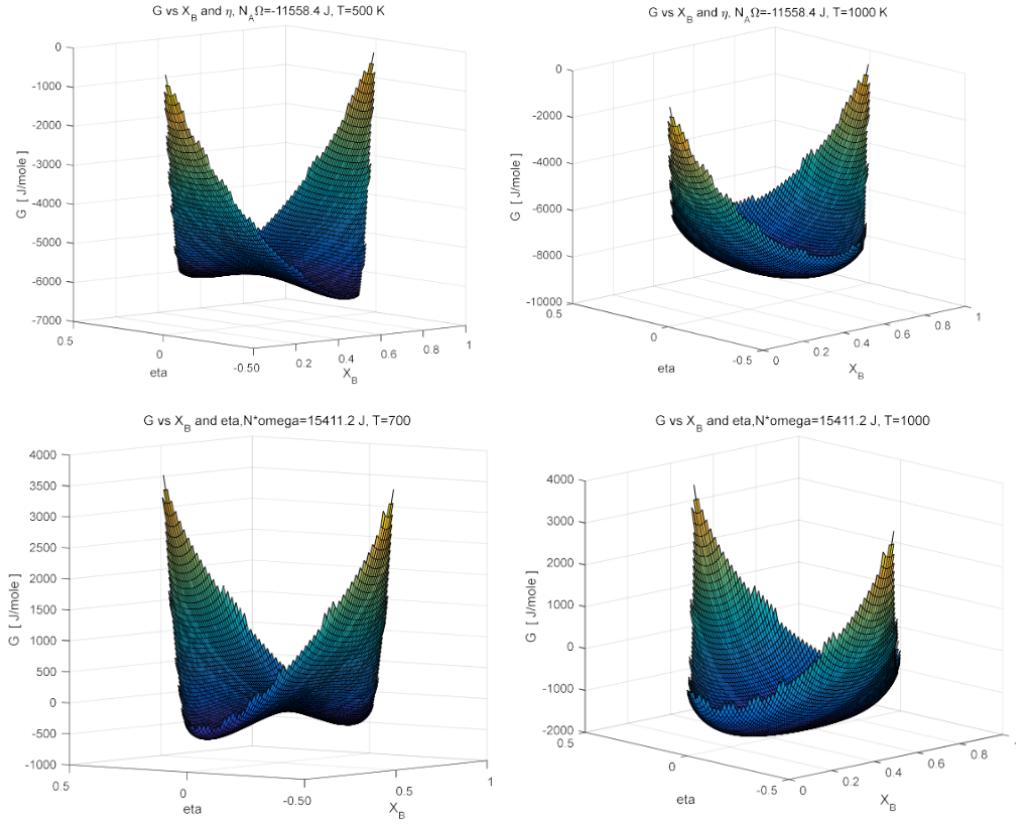


Figure 1.9: Graphical visualization of the ΔG_{mix} inside a binary system for different values of interaction parameter and temperature. In the top row negative Ω are plotted, while positive ones are shown in the bottom row.

To evaluate it we can first write down the form of the enthalpy of mixing which is easily obtained from Eq. (1.88) remembering that in solid state systems $\Delta V \approx 0$ so that

$$\Delta H_{mix} = \Delta U_{mix} + P\Delta V_{mix} \approx N\Omega(X_AX_B + \eta^2). \quad (1.90)$$

Then, for the entropy we can use classical thermodynamic and evaluate it using $\Delta S_{mix} = k_B \ln W$, where W are the possible dispositions of atoms A and B in the various lattice positions. By using some combinatory calculus one can arrive to the **Bragg-Williams-Gorsky configurational entropy**

$$\Delta S_{mix} = k_B \ln \left[\frac{(N/2)!}{N_A^\alpha N_B^\alpha} \frac{(N/2)!}{N_A^\beta N_B^\beta} \right] = -\frac{k_B N}{2} \sum_{i=A,B} \sum_{j=\alpha,\beta} X_i^j \ln X_i^j. \quad (1.91)$$

A form that shall recall to ourselves the Shannon entropy for a generic system. Thus, by inserting Eq. (1.91) and Eq. (1.90) inside Eq. (1.89) we have the final form

$$\Delta G_{mix} = N\Omega(X_AX_B + \eta^2) + \frac{k_B TN}{2} \sum_{i=A,B} [(X_i + \eta) \ln (X_i + \eta) + (X_i - \eta) \ln (X_i - \eta)]. \quad (1.92)$$

This form of the free energy describes the thermodynamic behavior of our system, and it's possible to see how the type of lattice that is going to appear is totally determined by the value of Ω and of the temperature. In particular, we can see how at low temperatures the leading term inside ΔG_{mix} is the first one, having a behavior analogous to the one that we hinted to describing the mixing energy. In fact,

Table 1.2: Qualitatively phase space description of a binary system with the four main regions discussed from Eq. (1.92) and their regimes.

Interaction par.	Temperature	η	X_B	Lattice
$\Omega < 0$	Low	± 0.5	0.5	Ordered
$\Omega < 0$	High	0	0.5	Random
$\Omega > 0$	Low	0	Two sol.	Clustered
$\Omega > 0$	High	0	0.5	Random

if $\Omega < 0$ the minimum of the free energy is obtained for η maximum, as can be seen plotted in Fig. (1.9), showing how the system is effectively driven to an ordered lattice. Instead, if $\Omega < 0$ the minima is present at $\eta = 0$ giving out a random distribution of atoms.

Nevertheless, the result Eq. (1.92) doesn't only show the simple behavior that we had already described previously since now temperature plays a role and if we go away from low temperatures other situations can appear. In fact, even if we have $\Omega < 0$ as we increase the temperature the minimum of the free energy moves from the maximum of η reaching zero at high T , showing how **thermal energy is able to destroy the order inside a system**. Instead, in the case of $\Omega > 0$ it's possible to see how the minimum is always placed at $\eta = 0$ for every possible value of T . Nevertheless, the real interesting parameter to look at in this situation is X_B , ΔG_{mix} can possess more than one minimum respect X_B at low temperature. This lead to an interesting situation where we can imagine having an isolated system with fixed X_A and X_B which due to temperature find itself in an unstable position with two possible minima at other molar fractions. The system would like to go into one of those minima, but it's not possible since the molar fractions are conserved becoming a **frustrated system**. In this situation the best way nature has to minimize the energy and solve the situation is to divide the system, having that different domains starts to appear inside the material that place themselves in either one of the two minima. Thus, the total number of atoms is conserved, but locally a minimum is obtained, creating also a heterogeneous system composed by zones more rich of A atoms or B atoms, a clustered lattice. The region of phase space that correspond to this two-phase situation takes the name of **miscibility gap** and is what gives the start to the study of heterogeneous systems. Still, also in this case temperature is able to destroy this phase since as T increase ΔG_{mix} moves the two minima close together bringing the equilibrium to the random lattice once again.

All of these considerations were based on simple numerical simulation to look at the form of ΔG_{mix} , nevertheless also an analytical solution can be found out by using simple function studying technique and is reported next. Still, we were able to describe all the thermodynamic behaviors of the system in question, looking at the different structures that appears at different temperatures, composition and interaction term. Thus, I have reported the main results about the phase space of the system inside Tab. (1.2).

Note

The Gibbs free energy of mixing in Eq. (1.92) is fairly general and interesting, for example we can see easily how in the case of a disordered system, $\eta = 0$, Eq. (1.92) becomes the free energy of a regular solution

$$\Delta G_{mix} = N\Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B) = \Delta H_{mix} - T\Delta S_{mix}^{id}. \quad (1.93)$$

Showing that a random binary system is in fact a regular solution, with both ΔH_{mix} and ΔS_{mix} symmetric respect to X_B .

Analytic solution

To study analytically the function in Eq. (1.92) we need to find out the minimum respect to η by taking the derivative and setting it to zero, having as a final result

$$4\Omega\eta = -k_B T \ln \frac{(X_B + \eta)(X_A + \eta)}{(X_B - \eta)(X_A - \eta)}. \quad (1.94)$$

This condition for the minimum already shows how solutions with $\eta \neq 0$ are possible only for $\Omega < 0$, so ordered systems exist only for negative interaction parameter as according to Tab. (1.2). Still, it's interesting to see how from this result we can expand near $\eta = 0$ to obtain the temperature were the transition from ordered to disordered appear in the case of $\Omega < 0$, given by

$$K_B T^C = -2\Omega X_A X_B, \quad T_{max}^C = -\frac{\Omega}{2k_B}, \quad \frac{T^C}{T_{max}^C} = 4X_A X_B. \quad (1.95)$$

Showing how the **critical temperature** can be found for every value of the system's composition but the one that maximize T^C needing the most energy to destroy the order is the case where $X_A = X_B = 0.5$, describing the most stable point. It's also possible to see that setting $X_A = X_B$ Eq. (1.94) transforms into

$$4\Omega\eta = -k_B T \ln \left(\frac{1+2\eta}{1-2\eta} \right)^2, \quad (1.96)$$

that at low T makes η tend to the value of ± 0.5 , therefore maximum order as expected. One can also take the second derivative of the free energy

$$\frac{\partial^2 \Delta G_{mix}}{\partial X_B^2} = -2N\Omega + \frac{k_B TN}{2} \left(\frac{1}{X_B + \eta} + \frac{1}{X_B - \eta} + \frac{1}{X_A + \eta} + \frac{1}{X_A - \eta} \right), \quad (1.97)$$

and see how it's always positive for $\Omega < 0$ at every temperature showing how only one minimum of ΔG_{mix} can exist in that case making the system stable in a homogeneous composition. Instead, in the case of $\Omega > 0$ we can look at the second derivative along the line $\eta = 0$ that describes the minimum in terms of order and find out

$$\left. \frac{\partial^2 \Delta G_{mix}}{\partial X_B^2} \right|_{\eta=0} = N \left[\frac{k_B T}{X_B X_A} - 2\Omega \right]. \quad (1.98)$$

This can change sign depending on T and the points where this happens are called **spinodal points**, while the locus on (X_B, T) space is called **spinodal line**, defined by setting Eq. (1.98) to zero. In this model the line will have the form of a parabola

$$k_B T^s = 2\Omega X_A X_B, \quad T_{max}^s = \frac{\Omega}{2k_B}, \quad (1.99)$$

this shows how the presence of two minima is possible giving rise to the formation of a heterogeneous system with regions on the two minima. The region of phase space in which this is present is called miscibility gap, as was already said, and the line $T^b(X_B)$ that describes the boundaries of that region is the **binodal line**. Therefore, for $\Omega > 0$ the equilibrium state below $T^b(X_B)$ is heterogeneous, while above homogeneous random as we had already seen.

1.4 Multicomponent heterogeneous systems

After the study of systems where only one component was allowed we jumped to the study of multiple components having still one phase now also this last constraint has been released. Therefore, we want to understand how a general system behaves at thermodynamic equilibrium and to do that we need to start with the conditions for equilibrium itself. In fact, having now a series of possible phases and components the conditions seen in Eq. (1.18) are no longer exact, and we need to expand them as follows.

Theorem 1.4.1: General equilibrium conditions

In a heterogeneous system composed by p phases and c components we have that at equilibrium for every α and β phases inside the system the following is true $\forall i \in \{0, \dots, c\}$ components

$$T^\alpha = T^\beta, \quad P^\alpha = P^\beta, \quad \mu_i^\alpha = \mu_i^\beta. \quad (1.100)$$

Proof: The proof is totally analogous to the one for the equilibrium conditions of the simpler case, the only difference is that now the differential of the internal energy contains more elements being

$$dU' = \sum_{\nu=1}^p \left(T^\nu dS'^\nu - P^\nu dV'^\nu + \sum_{i=1}^c \mu_i^\nu dn_i^\nu \right). \quad (1.101)$$

Applying the equilibrium conditions of an isolated system that in our case are

$$\sum_{\nu} dU'^\nu = 0, \quad \sum_{\nu} dV'^\nu = 0, \quad \sum_{\nu} dn_i^\nu = 0, \quad (1.102)$$

we can simply arrive to the wanted result. ☺

Basically, we need to keep in mind that more components are present and so, for two phases to be in equilibrium with each others we need that the chemical potentials of the different components are equal in both phases component by component.

The equilibrium conditions are the main general properties that are needed in order to study such systems. By keeping them in mind we can start to develop the theory of how this kind of general materials behave, understanding how the phases interacts with one another at equilibrium.

Gibbs' phase rule

In the construction of a phase diagram of a general system one may think that nothing is really known a priori due to the complexity of the system itself. Nevertheless, it's possible to find out some insight on at least the degrees of freedom that we have inside the diagram. In fact the equilibrium conditions gives large limitations on the possible thermodynamical variable that can change in certain regions of the phase diagram leaving us with the following result.

Theorem 1.4.2: Gibbs' phase rule

In a system with p phases and c component the available degrees of freedom inside the system are given by the following relation

$$f = c - P + 2. \quad (1.103)$$

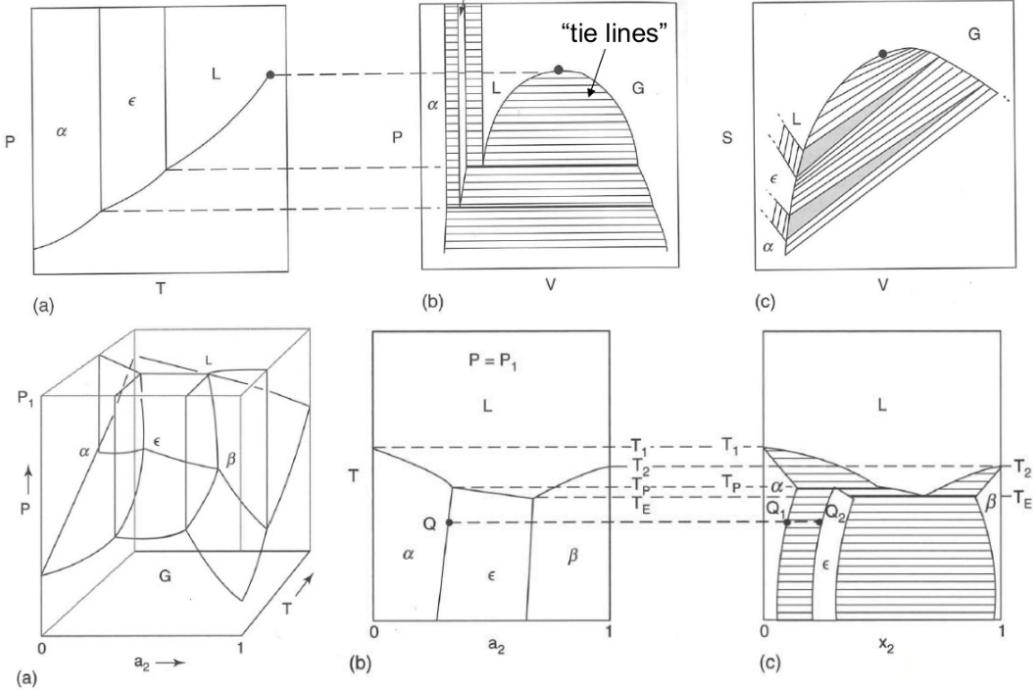


Figure 1.10: Examples of phase diagrams in different phase space for a two component, top, and a three component system, bottom. It's possible to see how the Gibbs' phase rule is respected perfectly in the T vs P phase space while modifications due to more freedom in the parameters are present in the others. In (b) of bottom row an isobaric section of (a) is represented.

Proof: We have, from Eq. (1.100), that T and P must be the same for all phases, so 2 variables are present. Then we also have the molar fractions X_i^j to be possible variable having exactly $(c - 1)p$ of them, one for every component in every phase with a -1 due to the condition

$$\sum_i X_i^j = 1, \quad \forall j \in \{1, \dots, p\}. \quad (1.104)$$

Then we have the chemical potentials, which sets further restrictions to the system where we need to have all $\mu_i^1 = \dots = \mu_i^p$ for every component giving us $c(p - 1)$ constraints which lead us to

$$f = 2 + (c - 1)p - c(p - 1) = c - p + 2, \quad (1.105)$$

as expected. \circlearrowright

This rule is telling us a lot on the phase diagram properties in general. In fact, we can understand that in a system with two components if I want to have two phases coexist the degrees of freedom available becomes simply one, meaning that the region with two phases coexisting is a line as we know. Instead, if we want three phases zero degrees of freedom are present becoming a point, that is what we already called triple point. If we wanted to go up with the number of phases the value of f will become negative, which is impossible, meaning that in a binary system only maximum three phases can coexist at once. The latter is a result that can be generalized really easily having that.

Corollary 1.4.1 Maximum coexisting phases

In a system with p phases and c component the maximum number of coexisting phases are $c + 2$.

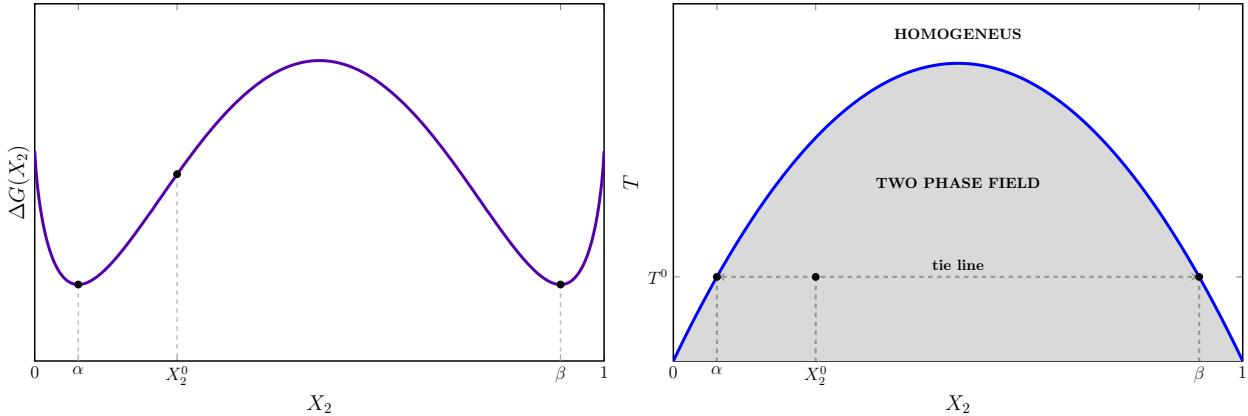


Figure 1.11: Illustration of a two phase system with miscibility gap, showing so a two phase field inside the phase diagram under the curve that describes the critical temperature of the system after which we have a homogeneous disordered phase.

Examples of this can be clearly seen inside Fig. (1.10) where phase diagrams of binary and ternary components are present, and we can see how in the formers the points find themselves in the connection of four phases the maximum number that can coexist.

It's also important to keep in mind that this result is valid as long as we represent the diagrams in the (T, P) phase space, if we change visualization to another space the diagram will change and also the degrees of freedom can. Looking at the figure (b) in the top row of Fig. (1.10) we can see an example, substituting the variable T with the volume V makes it so that the latter can change at equilibrium since no condition on him is present inside Eq. (1.100). Therefore, if we take a triple point and draw it on (P, V) it will become a so-called **tie line** horizontal to the x-axis that allow to have the coexistence of the phases also while the volume of the system can change. That can also be seen for the X_2 case in the ternary component system of the bottom row where coexistent of different phases can be present at different values of molar content while in the normal representation they were points.

Binary phase diagrams

Let's now focus a moment on a binary heterogeneous system, a situation that we have already seen during the homogeneous study founding out that for certain interaction parameters and temperatures a miscibility gap appeared bringing the system to form two different phases. We want now to describe some features of this separation of phases using the same conceptual model used before, having that the homogeneous system separates in a phase α that is more rich of atoms of type 1 and a β rich of type 2. Therefore, we are going to consider a system with a free energy of mixing as the one seen in Fig. (1.11), where it's possible to understand that the miscibility gap appear only in a certain range of temperature described by the parabola like shape found out in the phase diagram. The states inside that parabola forms the do called **two phase fields**, meaning that inside those states it's possible for the system to form two phases to lower the total free energy. What we want to understand now is what changes from states that are on the same tie line of the two phase field.

To answer that question we can take a system with a certain molar fraction X_2^0 as depicted in Fig. (1.11) and start thinking. The system will split, since it's in the two phase field, creating zones that are in a 1-rich state α and others in 2-rich state β . Nevertheless, the system has in total a major number of 1 type atoms since X_2^0 is lower than 0.5 meaning that it will be able to create a larger number of α zones.

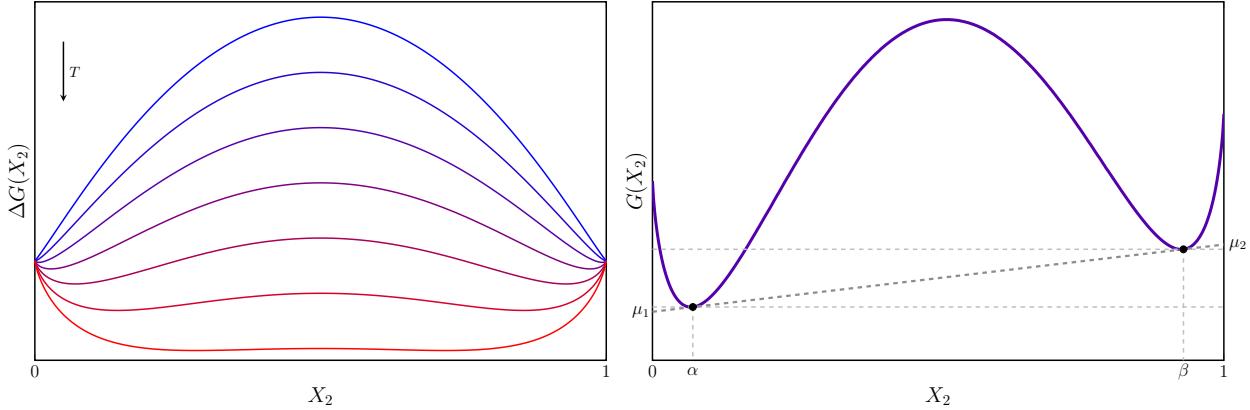


Figure 1.12: Representation of the mixing free energy at different temperatures on the left, and of the form of the normal free energy written as $G = \Delta G + \mu_2^0 X_2$ assuming $\mu_1^0 = 0$ on the left. It's possible to notice how the final form of G is asymmetric.

Meaning that systems on different position on the tie line will differ by the **relative extensions of the two phases**, where systems more close to α will have larger 1-rich zones while the other will have larger β phases rich of 2 type atoms. It's also possible to evaluate the weights a_α and a_β of the two phases inside a system by using the following relations

$$a_\alpha + a_\beta = 1, \quad a_\alpha X_2^\alpha + a_\beta X_2^\beta = X_2^0, \quad (1.106)$$

where X_2^i represent the molar fractions of the two minima. These relations form a system of equation that can be easily solved obtaining the simple solutions

$$a_\alpha = \frac{X_2^\beta - X_2^0}{X_2^\beta - X_2^\alpha}, \quad a_\beta = \frac{X_2^0 - X_2^\alpha}{X_2^\beta - X_2^\alpha} \quad (1.107)$$

In this way we can understand how much total volume of the system the two phases will take for themselves. One should also notice how these results are analogous at the one found out in classical mechanics to evaluate the on the two extreme of a lever, for this reason Eq. (1.107) are also referred to as **lever rules**.

Another important thing that we say is that by now we have always looked at the free energy of mixing, but it's also interesting to look at the normal free energy of the system depicted in Fig. (1.12). We know how the form of the free energy can be obtained from the mixing one by using the relation

$$G = \Delta G + \sum_i \mu_i^0 X_i, \quad (1.108)$$

with μ_i^0 the chemical potential of the i -th component in its separated form. This makes so that the final form of the free energy is no more symmetric with minima that are not the same of the free energy of mixing, in fact the added terms shift the minima in others point so that they don't really represent the equilibrium phases. In fact, if we use the **tangent construction** to evaluate μ_i of the two phases, by taking the tangents in the two minima, we would have that the results, $\mu_i(X_2^\alpha)$ and $\mu_i(X_2^\beta)$, would be at different height and so the equilibrium conditions of Eq. (1.100) are not respected. Nevertheless, we can overcome this problem in a simple way by using the so-called **Double tangent construction**.

Theorem 1.4.3: Double tangent construction

Let G be the Gibbs free energy of the system under study, to find out the minimum of ΔG we can search for two points on the curve that posses same derivative so that a tangent line connect them without crossing the graph.

Proof: More than a mathematical proof this is a reasoning. We know that the intercept of the tangent to a graph with the delimiting axis will give out the values of the chemical potential related to the two components inside the system. Therefore, using this construction we have found out two points that posses same intercepts, as depicted in Fig. (1.12), and so have the same chemical potential for the two components respectively, satisfying by construction the equilibrium conditions. ☺

Therefore, in this way the two real phases that are stable at equilibrium constituting the minima of ΔG are found graphically in a simple way analogous to the tangent construction present inside the homogeneous systems. Also, this construction works also if the system posses several Gibbs free energy of different type of phases that are contending with each other like: liquid state G^L , gases state G^g or different types of solid phases, bcc structure, fcc and so on. All of them can be present, and you can study the ones that are in equilibrium with each other by using as the real free energy

$$G(X) = \min\{G^L(X), G^g(X), \dots\}, \quad (1.109)$$

so that the construction remains the same, only changes that more phases can be in equilibrium together.

Note

I also wanted to point out that the double tangent construction also allows to understand that the points in the middle of the two that defines the tangent constitute a miscibility gap. Having so that a two phase field is present every time the double tangent is constructed. Thus, if the point is onto the far left or the far right of the curve the system will be in a homogeneous situation since no tangent can be constructed, meaning that no other state has same chemical potential and so can be in equilibrium with it.

Examples of binary phase diagrams

At last, we can show some examples of some standard phase diagrams of binary components that may allow comprehending better the concepts shown so far while seeing how much phase diagrams can tell us on the systems we are looking at. While looking at the different examples one can also keep in mind that the most of them can be reproduced using as models for the Gibbs energy of the different phases a regular solution like

$$G^L = \mu_1^{0,L} X_1^L + \mu_2^{0,L} X_2^L + RT(X_1^L \ln X_1^L + X_2^L \ln X_2^L) + \Omega^L X_1^L X_2^L, \quad (1.110)$$

$$G^\alpha = \mu_1^{0,\alpha} X_1^\alpha + \mu_2^{0,\alpha} X_2^\alpha + RT(X_1^\alpha \ln X_1^\alpha + X_2^\alpha \ln X_2^\alpha) + \Omega^\alpha X_1^\alpha X_2^\alpha. \quad (1.111)$$

Where the α phase usually represent a particular type of solid state. Therefore, by changing the values of $\mu_i^{0,j}$ and the interactions parameters Ω^j one should be able to obtain in good approximation all the examples we will show.

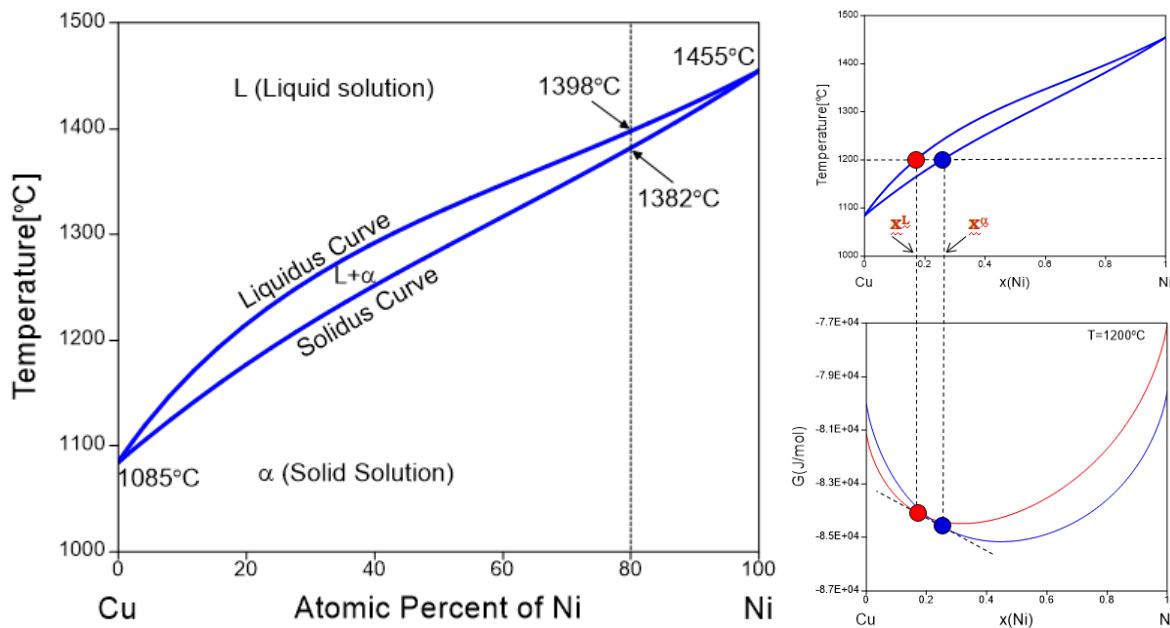


Figure 1.13: Phase diagram of Cu–Ni system on the left, with double tangent construction of it on the right for a certain fixed temperature reported on the image.

Isomorphous Systems. These are systems where the Two elements are completely soluble in each other in solid and liquid states. To have two atoms be able to achieve this type of solutions they need to possess some particular characteristics called **Hume-Rothery Rules**. The latter are empirical properties that have been observed through experiments, and shows that the atoms need to have:

- | | |
|-------------------------------|---------------------------------------|
| 1) similar radii, | 2) same crystal structure, |
| 3) similar electronegativity, | 4) solute should have higher valence. |

The most simple example that respect those conditions is Cu–Ni which forms a really simple system whose phase diagram is reported in Fig. (1.13). From the latter we can simply see how the system can change phase, going from an α solid phase to the liquid one passing through a double one where both liquid and solid exist. Nevertheless, no miscibility gap is present, meaning that there's not a portion of the phase space where the system splits in two phases that have different atomic percentage of the two components. In fact, we will give the following definition for an element to be soluble inside another.

Definition 1.4.1: Solubility of an element

Inside a multicomponent system, we will tell that one element has a solubility γ inside another element at certain temperature when, taken X the molar fraction of that element in the solution, the following is true

$$X < \gamma, \text{ homogeneous}; \quad X > \gamma, \text{ heterogeneous.} \quad (1.112)$$

Basically, an element is soluble inside another as long as the two form a homogeneous phase mixing together, but after a certain amount a miscibility gap can be found and the system separate in two forming a heterogeneous one. That is the phenomenon from which the miscibility gap takes the name. Also, this definition shows that the system Cu–Ni is effectively miscible over all phase space.

From this type of graph we can also take other types of information, for example the marginal lines

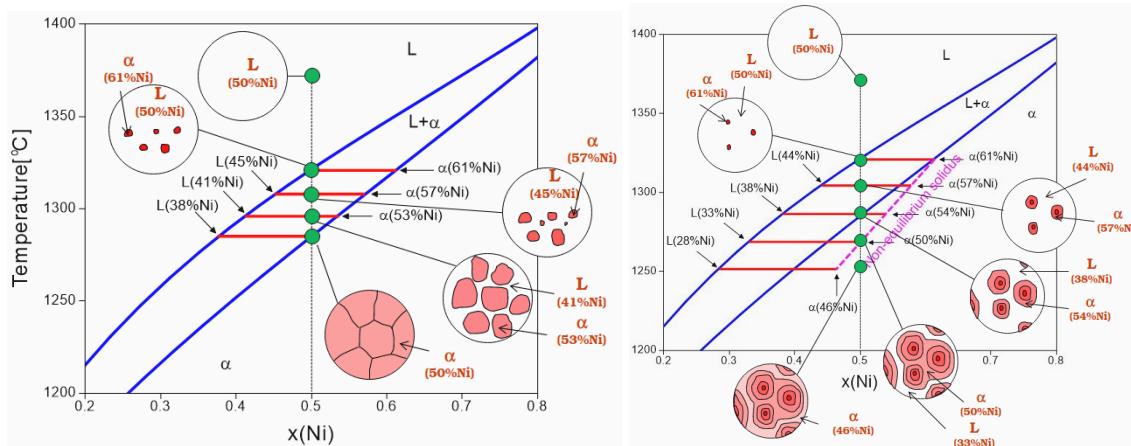


Figure 1.14: Illustration of the cooling of the system from the liquid phase to the solid one using a slow process, on the left, and a quick one where system has no time to reach equilibrium at every step, on the right.

describes the behaviors of the single elements. Therefore, giving us the values of the melting points of Cu and Ni being at 1085 °C and 1455 °C respectively. Then, we can also talk about the evolution of the system as it moves inside the phase space itself, trying to understand how the system will reach equilibrium as it gets cooled or heated. Understanding this can be non-trivial, and an example of this can be seen in Fig. (1.14) where a cooling evolution is showed for a slow and quick process. In the slow case the system has time to reach equilibrium at every step, entering the most favorable phase for that position in the phase space. Meaning that, from a starting liquid solution grains of solid phase with varying dimensions will start to form, and as we go down the weight a_α of the solid phase will start to increase following the **lever rule** having at the end only solid phases. One can also notice, from the labels in Fig. (1.14), that the percentage of Ni in the grains changes, that is due to the fact that as we go down in temperature also the position of the phase α changes moving from a higher molar fraction of Nickel to a lower one that becomes equal to the one present in the total system. Instead, in the case where the evolution goes fast the system has no time to reach equilibrium at every point, leading to the system **not completely following the phase diagram**, since it being a result of equilibrium thermodynamic can be incorrect when the processes are irreversible. In fact, in this situation as we cool down the system grains starts to form, but they are not able to form fast enough so that some liquid can remain confined inside a grain itself having so a mixture of liquid and solid also at lower temperatures respect to the expected one. This interesting phenomenon is also called **over-cooling**, and we will understand it better further in the course when we will talk about irreversible thermodynamic.

Eutectic Systems. This type of system are characterized by the presence of a particular triple point inside the phase diagram called **Eutectic point** connecting a liquid phase to a mixture of two solid phases. We have seen two example of compounds with such phase diagrams Cu–Ag and Pb–Sn, still we are going to focus on the latter and look at the evolution of the system during cooling as we have done for the isomorphous systems. In particular, the phase diagram we are interested in is shown in Fig. (1.15) where also various type of systems evolution were shown. The most interesting is the one where the cooling pass through the eutectic point, top left figure, there the system goes from liquid to two solid phases in one go. Also, this process happens in a specific way, generating the two phases one next to each others in a stripe form, as depicted in figure, that is typical of the eutectic systems. We can also see how the evolution of the system away from the point is totally analogous to the one described previously by the isomorphous case only that another phase appears inside the solid one once it's formed. At last,

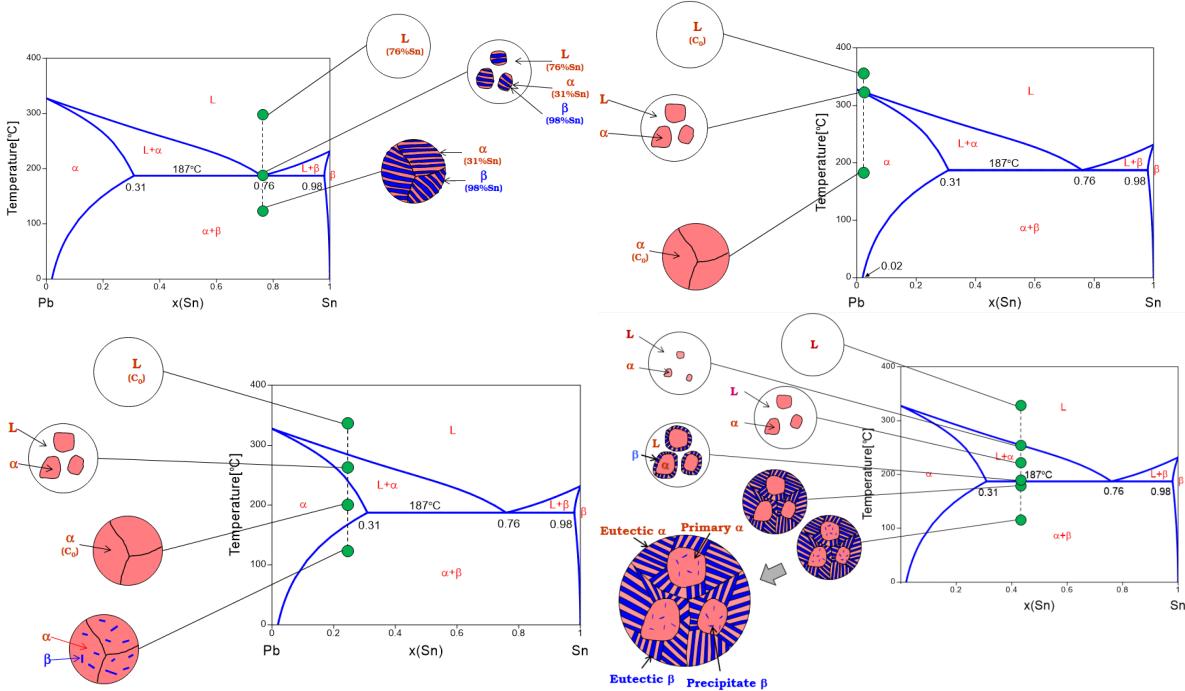


Figure 1.15: Illustration of the cooling of a Eutectic system in different points of the phase diagram, looking at positions near the eutectic point and away from it.

it's possible to see how near the eutectic point the system undergoes a cooling that brings to results similar to the one of the first case, but since it first needs to create a solution with both liquid and solid grains of only one type of phase the final striped form will start to generate around the grains. Meaning that the final form will be composed by grains with both phases in it surrounded by the stripe compound typical of eutectic points.

Eutectoid Systems. This type of systems are characterized by the presence of a triple point similar to the one of the eutectic systems, but it collects now a homogeneous solid phase to a heterogeneous one. This system is particular to begin with, from Fig. (1.16) we can see that it possess a phase called Cementite that exist only for a really narrow part of phase space. This type of phases are known in

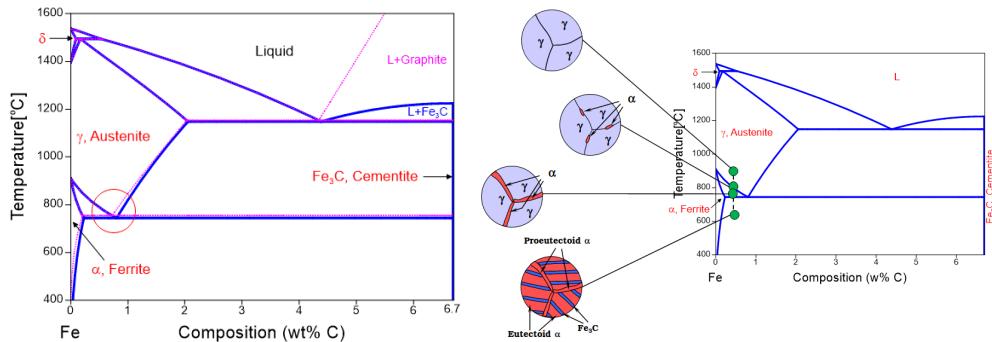


Figure 1.16: Phase diagram of Iron-Carbon system expressed in weight percentage of Carbon. On the left the phase diagram is shown along with the real equilibrium theoretical one in pink, the difference from equilibrium are present since the mixture is in reality a metastable state that take a long time to go into real equilibrium. On the right the cooling evolution near the eutectoid point is shown.

Table 1.3: Tables with all the possible type of binary systems known along with the peculiar points that characterize them inside the phase space. Also, a series of examples are reported in order to allow the reader to search for the respective phase diagram online. Notice how the ones that ends in "tectic" has liquid phase involved, while the ones in "tectoid" only posses solid phases in the equations.

Reaction	Symbolic equation	Schematic presentation	Example
Eutectic	$L \leftrightarrow \alpha + \beta$		Cu-Ag, Pb-Sn, Al-Si
Eutectoid	$\alpha \leftrightarrow \beta + \gamma$		Fe-C
Peritectic	$L + \alpha \leftrightarrow \beta$		Cu-Fe, Pb-In
Peritectoid	$\alpha + \beta \leftrightarrow \gamma$		Al-Cu
Monotectic	$L_1 \leftrightarrow L_2 + \alpha$		Cu-Pb, Al-In
Monotectoid	$\alpha_1 \leftrightarrow \alpha_2 + \beta$		Al-Zn
Syntectic	$L_1 + L_2 \leftrightarrow \alpha$		Na-Zn

physics as **line phases** since in the phase diagrams are basically lines meaning that they can exist only at really specific composition of the systems. Basically if we see Cementite in our system we perfectly know the Carbon weight percentage in it, which can be an interesting thing to know.

Instead, if we talk about the evolution of the system on cooling not so much changes respect to the eurectic systems. In fact, as the system pass through the eutectoid point the evolution bring to the formation of stripes as in previous case, but now they have different sizes for Fe and C due to the different percentage of the element in the overall material. The only real interesting thing that we can see here is when the system passes near the critical point and the intermediate solid phase, in this case $\gamma + \alpha$, needs to form in the system. That is interesting because we can see how the **new solid phase tend to form between the grain boundaries** of the γ phase, a behavior that is common for nucleation as we will see while studying kinetics.

Note

Another series of types of binary systems is present in nature, but they all differ mainly from the type of phases that the triple point inside the phase diagram connects and on the direction of the ramifications from the point. Therefore, very little changes respect to what was said in the previous three cases. Still, I will report on Tab. (1.3) the various possible type of systems with the different peculiar points on the phase diagrams for the ones that are more interested.

Example 1.4.1 (Growth of nanowire)

An interesting example of useful phase diagrams can be in the understanding of reality we can have a look at a really important application in the field of nanoscience, the growth of nanowire. Basically, from the phase diagram of Ge–Au, shown in Fig. (1.17), one can see how the two elements are highly immiscible at normal temperature, so that really the solubility of the two is basically zero. Nevertheless, at higher temperature the liquid phase is perfectly homogeneous, so that by heating up the mixture we can create a solution where the two elements are coexisting homogeneously. Still, when the liquid mixture is obtained we can increase the percentage of Germanium inside it bring the system inside the two phase field on the left, starting the nucleation

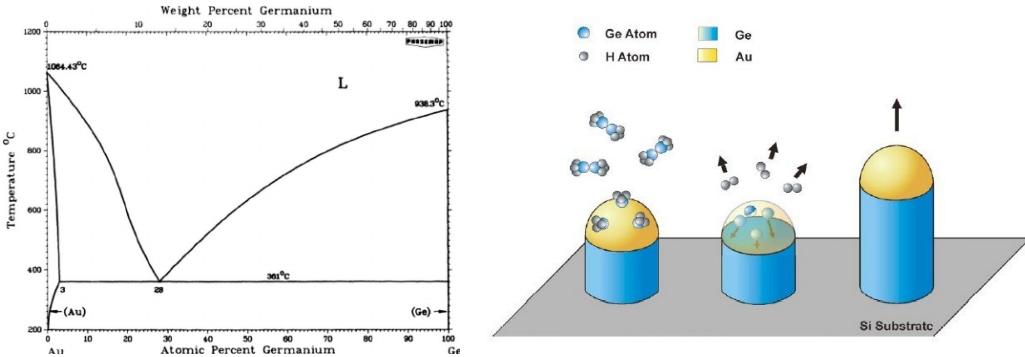


Figure 1.17: Phase diagram of Ge–Au mixture showing how the two elements are immiscible at normal temperature with a eutectic point at 28% of Germanium, on the left. Visualization of the Ge nanowire growth, on the right.

of Germanium inside the mixture. Knowing this we can simply take a substrate of Si and place liquid Ge–Au in small droplet on it as Germanium is inserted inside the chamber. In this way the Ge concentration will increase inside the droplet and Germanium start to nucleate inside it depositing onto the substrate under the droplet growing and forming the nanowire overtime.

Quick introduction to ternary phase diagrams

Inserting another component inside the system highly complicates the visualization of the phase diagram since a two-dimensional visualization is needed, but the presence of two independent, X_2 and X_3 , molar fractions makes a three-dimensional one more suited. The main way in which this can be overcome is usually by writing down the diagram at constant pressure and temperature so that the independent variables are only X_2 , X_3 , something not different from the constant pressure representation that was used in every binary phase diagram seen so far. Nevertheless, even fixed a point on (T, P) phase space the visualization is complicated since the values of X_2 and X_3 are not completely uncorrelated since if $X_2 = 0.2$ the other independent variable is confined to $X_3 \in [0, 0.8]$, so can't have all possible values. To overcome this problem a clever graphical representation of the phase diagram is used called **Gibbs triangle**, showed in Fig. (1.18), where the phase space is seen as an equilateral triangle. Inside this representation to find out the molar fraction X_i of a component of a point in phase space the following

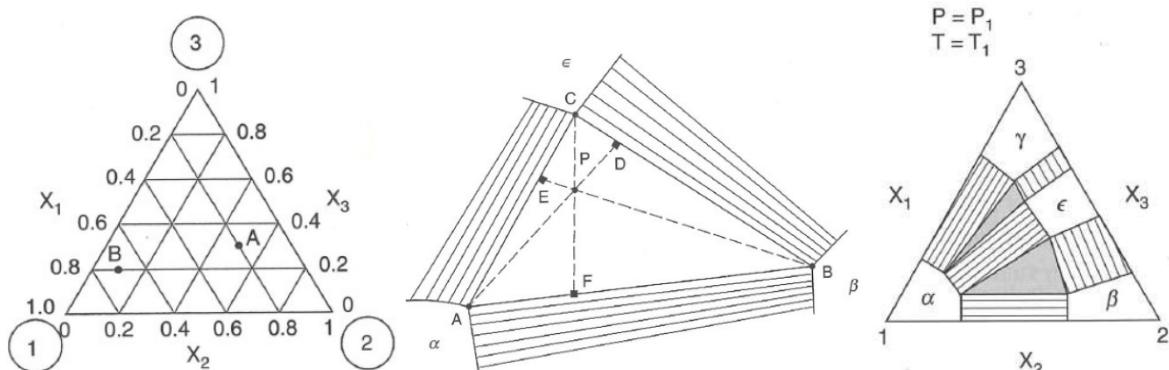


Figure 1.18: From the left: Gibbs triangle representation of the ternary systems' phase space, example of the lever rule in a three phase field portion of the phase space, and example of a ternary phase diagram.

procedure need to be used:

- 1) On the point, draw the line perpendicular to the median that begin from the vertex that correspond to the i -th component you are interested in;
- 2) See where it intersects the side of the triangle corresponding to X_i , the point found is its value.

In this way we are able to define the molar fraction of every point inside the system so that the sum of all X_i gives out 1.

Using Gibbs triangle we are, therefore, able to visualize in a simple two-dimensional way the phase diagrams of all ternary systems at constant T and P , where an example is given inside Fig. (1.18). In the latter we can also see how, due to the present of three component, ternary phase fields now appears along the binary phase ones, forming triangular shapes inside the phase diagram. We have already seen how to treat the binary phase field, in particular the weight of the two components inside the heterogeneous phase using the **lever rule**. It's possible to see how a form of the lever rule can be found also inside this more complex situation, where the weights of the three possible phases can be evaluated using the lengths of the lines that connects the points to the vertices corresponding to a determinate phase. In particular, using as reference Fig. (1.18), the following relations can be obtained

$$a_\alpha = PD/AD, \quad a_\beta = PE/BE, \quad a_\epsilon = PF/CF, \quad (1.113)$$

giving the relative extensions of the three phases inside the system we are studying. Obviously, this is only the tip of the iceberg since the complexity of the ternary phase diagrams goes far beyond this and a lot of other aspects could be described. Nevertheless, this is not a course purely on phase diagram study, and so the full description of ternary, along with quaternary and so on, case goes beyond its scope. For this reason we will stop to this simple description on the Gibbs' representation and the lever rule.

2

Kinetics: transport properties, diffusion

2.1 Irreversible Thermodynamics

When we talked about physical quantities we mentioned also the presence of a part of them called transport properties, where was said that they appeared in the study of irreversible phenomena. Such phenomena are can be thought simply as the kinetic evolution of the system in time when it's out of equilibrium. In fact, a system where transport of matter, energy or momenta is present inside it can't be in equilibrium and can be seen by some simple examples. Take two thermal reservoirs at temperatures T and $T + \Delta T$ that are in contact through a cave. A thermal current I_Q will be present between the two, and we know that a variation of entropy is generated in both of them as

$$\frac{dS_1}{dt} = -\frac{I_Q}{T + \Delta T}, \quad \frac{dS_2}{dt} = \frac{I_Q}{T}. \quad (2.1)$$

Thus, we can write down the total variation of entropy inside the system by taking the sum of the two and seeing how

$$\frac{dS}{dt} \approx \frac{I_Q}{T} \frac{\Delta T}{T} > 0, \quad (2.2)$$

meaning that the process is irreversible since a variation of entropy is created and the system is not in equilibrium as it happens. Also, this is only an example, but every single process that involve a current posses the same property, like charge current I_q . The power dissipated in the environment through Joule effect, in fact, generates entropy since we have

$$P = \Delta V I_q, \quad \frac{dS}{dt} = \frac{P}{T} = \frac{\Delta V}{T} I_q. \quad (2.3)$$

Where we can see how in both cases the entropy increase has a form composed by the product of a **flux**, like I_Q or I_q , by a gradient, which usually represent the **driving force** that in these cases were the electric force ΔV and the thermal gradient ΔT .

Therefore, if we aim at describing the kinetic properties of matter and how atoms move inside it, we will need to restate thermodynamics in order to account also for irreversible process.

Entropy production

The first thing we need to do is understand how entropy is created to its core, and to do it we are going to make a general construction to tackle the problem using already known results. Basically we

want to imagine that every non equilibrium system can still be seen as multiple ones that are in local equilibrium that interacting altogether locally generates entropy over time. Basically we are assuming something that we are going to call **local thermodynamic equilibrium** that we are going to formally define in the following way.

Definition 2.1.1: Local thermodynamic equilibrium

A general system is in local thermodynamic equilibrium if it can be divided in a series of smaller subsystems with thermodynamics fully defined by the values of the thermodynamic potential within the cell. Meaning that the generalized first principle is valid within the subsystem as

$$Tds = du - \psi_i d\xi_i, \quad (2.4)$$

where ψ_i are the thermodynamic potentials, and ξ_i are their conjugate responses.

Notice how small letters, like s , u , were used in the definition since we are focussing on densities and not on the total properties in the system. Also, notice how we are using Einstein convention.

This principle will be our key to use known results in the study of the more complex behaviors of irreversible processes. In particular, by assuming it on a system we can easily obtain a first result inside a general system as follows.

Theorem 2.1.1: General continuity equation

Inside a system in local thermodynamic equilibrium, where non-zero local entropy production $\dot{\sigma}$ is present the following continuity relation for the entropy is valid

$$\frac{\partial s}{\partial t} = \dot{\sigma} - \nabla \cdot \mathbf{J}_s. \quad (2.5)$$

Proof: The proof it's really easy, basically from classical mechanics we know how a conserved quantity c needs to respect the continuity equation

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{J}_c, \quad (2.6)$$

which tells us that the variation of c are given by the quantity that was entering minus the one going out. In the case of entropy here we have that in it is also being created by the system **locally**, assumption given by the local equilibrium. Thus, the variation in time of the entropy must account also for $\dot{\sigma}$ giving Eq. (2.5). ☺

Therefore, we are starting to account for the presence of source of entropy inside our system that can change the behavior of the whole solid, but one may ask what those sources are. We have already seen them in the previous discussion, in reality, seeing how currents are able to generate variations of entropy locally and that can be set on a general ground in the following way.

Theorem 2.1.2: Current generates entropy

Inside a system in local thermodynamic equilibrium the variation of entropy is generated through the presence of current inside a system, where the local generation of entropy $\dot{\sigma}$ is given by

$$T\dot{\sigma} = -\frac{\mathbf{J}_Q}{T} \cdot \nabla T - \mathbf{J}_i \cdot \nabla \xi_i. \quad (2.7)$$

Proof: We can start by writing down a form for the variation of entropy in time by using Eq. (2.4)

$$\frac{\partial s}{\partial t} = \frac{1}{T} \frac{\partial u}{\partial t} - \frac{1}{T} \psi_i \frac{\partial \xi_i}{\partial t}. \quad (2.8)$$

Then, we can use the normal continuity equations on the energy densities and on the conjugates responses having that

$$\frac{\partial s}{\partial t} = -\frac{1}{T} \nabla \cdot \mathbf{J}_u + \frac{1}{T} \psi_i \nabla \cdot \mathbf{J}_i, \quad (2.9)$$

with \mathbf{J}_i the flux related to quantity ξ_i . Then we can use the algebraic identity $A \nabla \cdot \mathbf{B} = \nabla(A\mathbf{B}) - \mathbf{B} \cdot \nabla A$ to obtain the following form

$$\frac{\partial s}{\partial t} = \mathbf{J}_u \cdot \nabla \left(\frac{1}{T} \right) - \mathbf{J}_i \cdot \nabla \left(\frac{\psi_i}{T} \right) - \nabla \cdot \left(\frac{\mathbf{J}_u - \psi_i \mathbf{J}_i}{T} \right). \quad (2.10)$$

We can then use once again Eq. (2.4) and taking its time derivative to notice how the last term is simply $\nabla \cdot \mathbf{J}_s$, so that by substituting Eq. (2.10) inside Eq. (2.5) we can find out that

$$\dot{\sigma} = \mathbf{J}_u \cdot \nabla \left(\frac{1}{T} \right) - \mathbf{J}_i \cdot \nabla \left(\frac{\psi_i}{T} \right). \quad (2.11)$$

Nevertheless, we can use the general first principle of thermodynamics to rewrite the flux of energy in a form that simplify the expression as

$$du = \delta Q + \psi_i d\xi_i, \quad \mathbf{J}_u = \mathbf{J}_Q + \psi_i \mathbf{J}_i, \quad (2.12)$$

that inserted in the previous result allow us to arrive at the form

$$\dot{\sigma} = \mathbf{J}_Q \cdot \nabla \left(\frac{1}{T} \right) - \frac{\mathbf{J}_i}{T} \cdot \nabla \psi_i. \quad (2.13)$$

Then by using the known relation $\nabla 1/T = -T^{-2} \nabla T$ we obtain the wanted result. \odot

Therefore, the presence of a current means that an irreversible process is happening and vice versa. For this reason will be useful to see some examples of possible currents that will probably appear in our studies like

$$\text{Heat,} \quad \mathbf{J}_Q, \quad -\frac{\nabla T}{T}, \quad \mathbf{J}_Q = -\kappa \nabla T; \quad (2.14)$$

$$\text{Charge,} \quad \mathbf{J}_q, \quad -\nabla \phi, \quad \mathbf{J}_q = -\rho^{-1} \nabla \phi; \quad (2.15)$$

$$\text{Matter,} \quad \mathbf{J}_i, \quad -\nabla \mu, \quad \mathbf{J}_i = -c_i M_i \nabla \mu. \quad (2.16)$$

Where along with the general known forms for the conjugated flux also the driving force was reported, and is possible to see how the latter is always a gradient so that the product of flux and force generate an **energy density dissipation**. Also, the relations known that connect the two is always linear relation with a transport property, like κ , ρ or $c_i M_i$, that connects force and response.

The result obtained is actually really great one that allows us to understand how the variation of entropy is effectively created inside a system. Nevertheless, something else can be actually sad about the variation of entropy. In particular, from second principle we know that in general the total entropy of the system always increase, so that is possible to have situations where the local entropy decrease but the one of the environment compensate having a total that is positive. Still, this situation can be really complex to tackle in a general situation so that we are going to make a really important assumption in order to make things easier.

Definition 2.1.2: Postulate of irreversible thermodynamic

In proximity of equilibrium, the local rate of entropy production is non-negative

$$\dot{\sigma} \geq 0. \quad (2.17)$$

Basically, we are ruling out the possibility of even having local increase of the order of the system if we are in a situation close to equilibrium. That is actually interesting since we can easily apply it to Eq. (2.7) to see that

$$T\dot{\sigma} = -\mathbf{J}_Q \cdot \frac{\nabla T}{T} = \frac{\kappa \nabla^2 T}{T} \geq 0, \quad (2.18)$$

meaning that the value of κ needs to be positive near equilibrium. This applies on every transport property, having that ρ and all M_i needs to be positive near equilibrium.

Linear irreversible thermodynamics

Now, we have seen how as in equilibrium thermodynamic we have generalized forces connected to conjugated responses here we have driving forces that are related to flows. Therefore, we might want to follow the same reasoning and find out a constitutive relation between the driving forces and the fluxes. In particular, recalling the general form obtained for the static physical quantities we can imagine that a flux \mathbf{J} do not only depend on its driving force but all of them give a contribution, having in general

$$\mathbf{J} = \mathbf{J}(\mathbf{F}), \quad \mathbf{F} = \left(\frac{\nabla T}{T}, \nabla \phi, \dots \right). \quad (2.19)$$

Then, we can make a linear approximation for this relation since we have already seen how some known forms for the fluxes linearly depend on the conjugated driving forces. Therefore, we can simply assume that a form for the general relation between the two quantities is the following

$$J_\alpha = \frac{\partial J_\alpha}{\partial F_\beta} F_\beta = \mathcal{L}_{\alpha\beta} F_\beta. \quad (2.20)$$

Defining, so, a general matrix \mathcal{L} that contains all the information on the transport properties of the system.

Also, we can now study this new matrix and see their properties in a way analogous to the one seen for the \mathcal{K} matrix seen for static properties. In particular the first thing that we can say is the following.

Theorem 2.1.3: Positivity of \mathcal{L}

In a near equilibrium situation the \mathcal{L} matrix is a positive one.

Proof: We can use the principle of irreversible thermodynamic to write down the following thing

$$T\dot{\sigma} = J_\alpha F_\alpha = \mathcal{L}_{\alpha\beta} F_\beta F_\alpha \geq 0, \quad (2.21)$$

which is valid for every value of F_α and F_β meaning that \mathcal{L} is positive. \odot

Still, the most important relations, as we have seen in the first part, concern the symmetry properties of the matrix, which are similar to the one of \mathcal{K} since the following result can be proven formally.

Theorem 2.1.4: Onsager's symmetry principle

The \mathcal{L} matrix is a symmetric one, and therefore the following is true

$$\mathcal{L}_{\alpha\beta} = \mathcal{L}_{\beta\alpha}. \quad (2.22)$$

Proof: The proof is complex and goes microscopically imposing the detailed balance on the fluxes near equilibrium. We haven't seen it during the course, and so I'm not going put it here for now. ☺

The same symmetric properties that is often present inside important physics matrices, if not all of them, is found out. We can also have a look at how this property can also be restated as

$$\frac{\partial J_\alpha}{\partial F_\beta} = \frac{\partial J_\beta}{\partial F_\alpha}, \quad (2.23)$$

which have a form similar to Maxwell's relations seen in equilibrium thermodynamics. Also, as we have seen for the \mathcal{K} matrix we can see how various blocks are present and we can have a little look at them really quickly

k thermal conductivity, $T_S(2)$. Relates temperature gradient and heat current, and from symmetry properties it's easy to see how

$$k_{\alpha\beta} = k_{\beta\alpha}. \quad (2.24)$$

σ electrical conductivity, $T_S(2)$. Relates electric potential and charge current, its inverse is the resistivity and also this is symmetric.

β, β' thermoelectric cross effects. Off diagonal term that relates the electric potential with heat current and temperature gradient with charge current. It's easy to see how from \mathcal{L} symmetry one can find out that since are off diagonal terms

$$\beta_{ij} = \beta'_{ji}. \quad (2.25)$$

D_i diffusivity, $T_S(2)$. It's the more general way of writing down $c_i M_i$ term for matter transport appearing in Fick's law, the real way of writing down \mathbf{J}_i . The appendix i describe the type of component is getting transported, and D_i has the same symmetry properties of the others diagonal terms.

Thermoelectric materials

To make an example of the use irreversible thermodynamic theory can have we can look at the properties of thermoelectric materials. The latter are systems that are able to generate potential gradients due to the presence of a thermal one, and vice versa. Basically, thermoelectric materials are systems that posses a non-zero β component inside the \mathcal{L} matrix, so that the constitutive relations of the heat and charge flux becomes coupled equations with

$$\mathbf{J}_Q = -k\nabla T - \beta'\nabla\phi, \quad \mathbf{J}_q = -\frac{\beta}{T}\nabla T - \sigma\nabla\phi. \quad (2.26)$$

This shows how the movement of the microscopic elements inside the material is intrinsically related to the flux of both charge and energy. In fact, the electrons are the main charge and heat transport carrier inside matter, meaning that a movement of heat inside a material often means that also charge is being transported. Nevertheless, we want to focus on the relation between the driving forces in this case and in particular in an equilibrium situation where the fluxes are zero meaning that $\mathbf{J}_q = 0$ and

$$\nabla\phi = -S\nabla T, \quad S = \frac{\rho\beta}{T}. \quad (2.27)$$

A linear relation between the two appears giving rise to the **Seebeck effect**, a really important phenomenon that tells us that a variation of temperature can generate a potential with an intensity dependent on S , called **thermopower**. This is a really important information that is used a lot in technological applications to measure temperature using instruments called thermocouples. Still, this is not the only interesting thing we can say about equations Eq. (2.26) since another situation can appear where, at non equilibrium, we have both transport of charge and heat but with a constant temperature in the system. This condition is called **Peltier effect** and describes how the presence of electrons moving in the system due to a potential gradient also generates a heat current even if no heat gradient is present in the material. Therefore, by placing ∇T to be null we can see how

$$\mathbf{J}_Q = \Pi \mathbf{J}_q, \quad \Pi = \beta' \rho, \quad (2.28)$$

where we can also see how a relation between Π and S is present. In fact, by using that ρ is a symmetric tensor and Eq. (2.25) we can easily see that

$$\Pi_{ij} = TS_{ij}, \quad (2.29)$$

which is an interesting relation first proven by lord Kelvin. Thus, all thermoelectric properties can be described by the value of S , which can be found out using particular transport models. We have, obviously, not seen those since can be really complex, especially if a semi-classical one is used, giving out directly the final results for **metal** and **semiconductor** respectively

$$S_{met} \approx \left(\frac{k_B}{e} \right) \frac{k_B T}{E_F}, \quad S_{sco} \approx \left(\frac{k_B}{e} \right) \frac{E_g}{k_B T}. \quad (2.30)$$

Where, we can understand that the constant in front gives out the order of magnitude for the value of S , which is $k_B/e \approx 87 \mu\text{V}/\text{K}$. Also, we can see how metals and semiconductors differ since S is much smaller in the formers than the others since usually $E_F \gg k_B T$ at room temperature, while $E_g \approx k_B T$. In addition, semiconductors can display both negative and positive thermopower, for electron and hole conduction respectively, so that in general the real value of the coefficient is a weighted mean of the two

$$S \approx \frac{\sigma_n S_n + \sigma_p S_p}{\sigma_n + \sigma_p}. \quad (2.31)$$

Where the subscript n is for electrons while p is for holes.

Seebeck and Peltier effects are extensively used for technological applications of several kinds. For example, the Peltier effect can be used to create efficient and simple refrigeration mechanisms where, by using an electric current you can induce a heat one between two objects that will then cool down. Also, similarly you can use heat to generate \mathbf{J}_Q that induces electrical transport to power other apparatus. This two type of applications are described schematically in Fig. (2.1), and are impactful in a lot of fields like

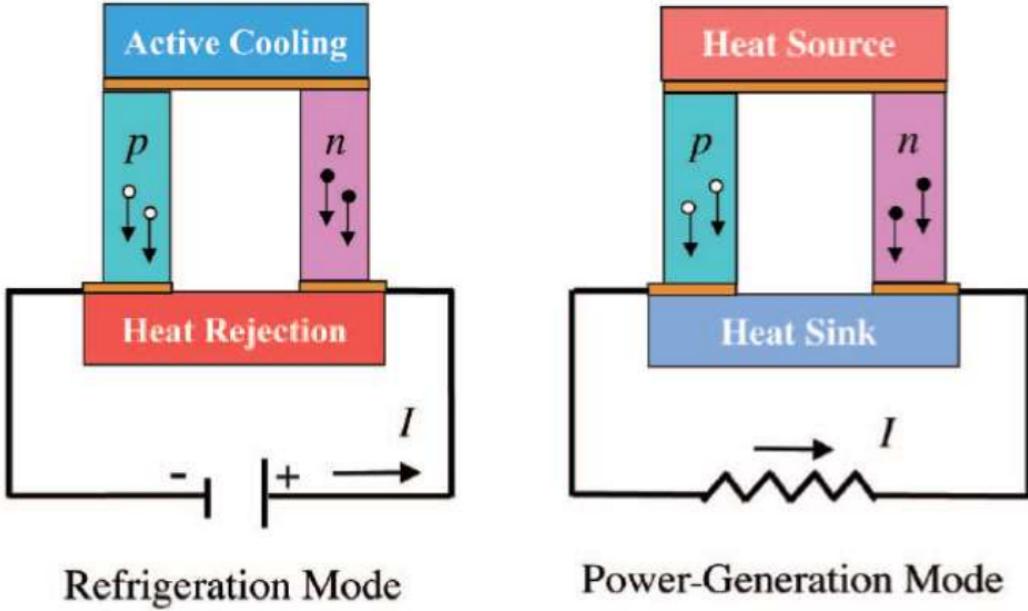


Figure 2.1: Diagram of a Peltier thermoelectric couple made of an n-type and a p-type thermoelectric material. Refrigeration and power generation modes are possible, depending on the configuration.

spacecraft engineering where Radioisotope Thermoelectric Generators(RTG) are widely used. Such devices bring a lot of advantages in general, like the fact that no moving parts are present giving: high reliability, no noise, no vibration or torque. Also, they are usually highly resistant to radiations and can be miniaturized. Therefore, it's of our interest to understand the characteristic that a material needs to have in order for it to be a good one to create such instruments. Thus, a figure of merit for thermoelectric materials is defined in the following way

$$ZT \equiv \frac{S^2 \sigma T}{\kappa}, \quad (2.32)$$

where σ is the electrical conductivity, while κ is the thermal conductivity. Still this is the definition for a device made of a single material, while it's possible to have one made out of both n and p type conductors do that a more general definition that takes that into account would be

$$ZT \equiv \frac{(S_n - S_p)^2 T}{\sqrt{(\rho_n \kappa_n)^2 + (\rho_p \kappa_p)^2}}. \quad (2.33)$$

Using this definition we can also see the efficiency of the machine that we are going to build by using the following relation

$$\eta = \frac{T_H - T_C}{T_H} \left(\frac{\sqrt{1 + ZT_M} - 1}{\sqrt{1 + ZT_M} + T_C/T_H} \right), \quad (2.34)$$

where T_H , T_C and T_M are hot, cold and mean temperature in the system. Where we can see how the term in front has the form of the Carnot efficiency, meaning that the two are related and that $\eta \rightarrow \eta_c$ for $ZT \rightarrow \infty$. Therefore, we are looking for materials that possess ZT high as possible in order to increase our efficiency closer as we can to the thermodynamic limit.

In order to maximize the value of ZT we can look at Eq. (2.32) and see how the best thing is to have low thermal conductivity but great electrical one. Still this is not so easy to achieve since we know

that two contributions are present inside κ , electrical and phononic one, and the former is related to σ by the **Wiedenmann-Franz law**

$$\kappa = \kappa_E + \kappa_P, \quad \kappa_E = L\sigma T, \quad (2.35)$$

where L is a constant called Lorentz number. Therefore, the best we can do is to get κ_P as low as possible meaning that we aim at having the smallest phonon free path since we know that

$$\kappa_P = \frac{1}{3}v_s C \lambda_P, \quad (2.36)$$

where v_s is the velocity of sound. In general, we can imagine that a really low value of λ_P would be as the interatomic distance so that an estimate of κ_P would be $0.25 \text{ W m}^{-1} \text{ K}^{-1}$. But, even if κ_P would be really low the thermopower needed in order to achieve a value of $ZT = 1$ is really high. In particular, by using an idea zero phonon conductivity model we would obtain $S = \sqrt{L}$ which means $160 \mu \text{V K}^{-1}$. In this optic the better type of material we can aim for are semiconductors with narrow-bandgap which posses high mobility, in order to maximize the value of S by the fact that hole and electron coefficients add up.

2.2 Driving forces and fluxes for diffusion

We know how materials are formed by atoms placed in symmetric positions in space in order to form an ordered lattice, but this is entirely true only in theory. In fact, real materials present a large series of defects, wanted and unwanted, that locally destroy the symmetry and change materials properties. One of the most important types of defects that exist are impurities, where atoms of types different from the ones of the normal materials are present inside the structure. In particular, we want to focus on the situation where those atoms are smaller than the principle one having so that they enter interstitial sites where they can move between larger atoms, like in Fig. (2.2). A practical example of such a phenomenon is the diffusion of Carbon inside Iron, or Hydrogen in a general material. Such movements are able to give the material particular properties or drive it to different equilibrium respect the one we imagine. Therefore, we want to focus on the study of atoms movements inside the material to create a good model for diffusion processes to then apply them into material modelling.

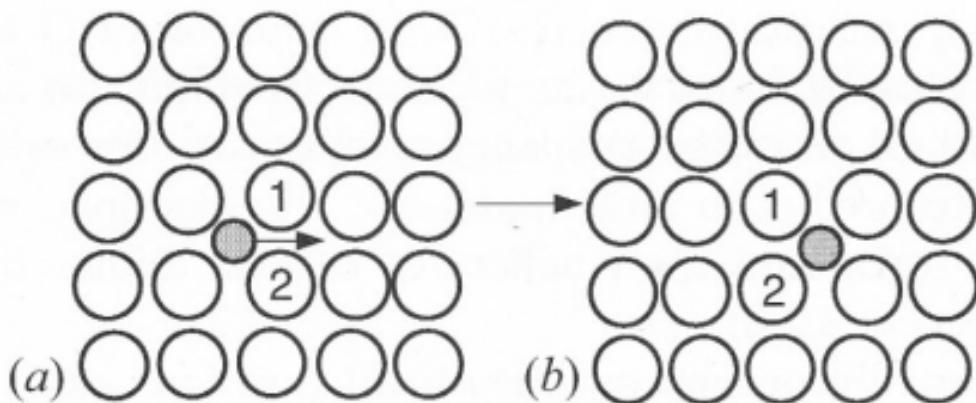


Figure 2.2: Example of diffusion of an interstitial atom inside a general simple lattice.

In order to do that we shall focus on the description of the flux of particles of i -th type, \mathbf{J}_i , inside the material, and we have seen that is related to the gradient of chemical potential. Still, we can see more in depth how they are related by defining a really important quantity called **mobility** as follows.

Definition 2.2.1: Mobility

The mobility of atoms of type i , M_i , inside a material is constant of proportionality between the average particle velocity and the gradient of chemical potential

$$\langle \mathbf{v}_i \rangle = -M_i \nabla \mu_i. \quad (2.37)$$

Then, from this definition one can easily see how the flux and chemical potential are related since \mathbf{J}_i is given by the density of that type of atoms c_i multiplied by the average velocity, having

$$\mathbf{J}_i = c_i \langle \mathbf{v}_i \rangle = -c_i M_i \nabla \mu_i. \quad (2.38)$$

Which is the relation we have seen in the previous part when talking about the \mathcal{L} matrix. Still, we can work the expression a little more and see how in reality we can collect the flux at the gradient of concentration using the following result.

Theorem 2.2.1: Fick's law

Inside a material, if the interstitial moving atoms are much less compared to the solvent atoms so that the system can be approximated to a dilute solution we can write the flux of atoms as

$$\mathbf{J}_i = -k_B T M_i \nabla c_i = -D_i \nabla c_i, \quad (2.39)$$

where D_i is also called **diffusion constant**.

Proof: Since the system can be thought of a dilute solution the Henry's law can be used so that the chemical potential is

$$\mu_i = \mu_i^0 + k_B T \ln(\gamma_i^0 X_i) = \mu_i^0 + k_B T \ln\left(\gamma_i^0 \frac{N_i}{V} \frac{V}{N_T}\right) = \mu_i^0 + k_B T \left[\ln\left(\frac{\gamma_i^0}{\langle c \rangle}\right) + \ln c_i \right]. \quad (2.40)$$

We can see how in this relation $\gamma_i^0 / \langle c \rangle$ is a constant, so that by taking the gradient we have that a relation between μ_i and c_i is obtained as

$$\nabla \mu_i = \frac{k_B T}{c_i} \nabla c_i. \quad (2.41)$$

Then by substituting it inside Eq. (2.38) the wanted relation is obtained, with also the important equality

$$D_i = k_B T M_i, \quad (2.42)$$

which is also called **Nernst-Einstein relation**. 😊

Substitutional diffusion

To be able to model the flux of a certain atomic species inside a material we need first to unravel the possible mechanisms that allow it to move in the first place. We have already discussed how one simple

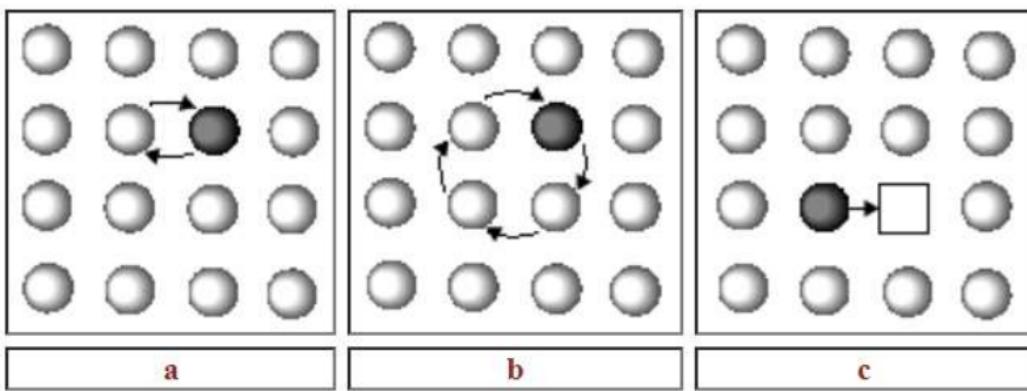


Figure 2.3: Representation of the three main possible diffusion mechanism, in order: direct exchange, cyclic exchange, and vacancy diffusion.

way in which an atom can move inside a solid is by moving in the interstitial positions inside the lattice. Nevertheless, this is valid only if the species we are looking at is small enough, and that is not the case for the majority of diffusion mechanisms inside a material. In particular, we now want to focus on the situation where no interstitial occupancy is present, and obviously also double occupancy of a site, and see how atoms of different types can move inside the lattice.

A lot of research was done in the past by several physicists working especially in the world of metallurgy, and to this day we know three main possible mechanisms that allow atoms to diffuse inside a lattice described in Fig. (2.3). We can see how three mechanisms are described, where the atoms can exchange positions with one another, either with a **direct exchange** with one another or with a **cyclic exchange**, or by moving inside particular point defects called **vacancies**. The latter, in particular, result in being the most important mechanism of the three, able to describe a lot of physical phenomena. To understand this we need first to address the fact that before 1939 the only mechanism that was thought possible was the direct exchange so that a lot of constraints for the diffusion were present. For example, if we have an alloy formed by two atomic species the only possibility for the species to move respect to each other was to exchange places, so that for an atom of type A going in a direction one of type B was going in the opposite having

$$\mathbf{J}_A + \mathbf{J}_B = 0. \quad (2.43)$$

A really important scientist called Kirkendall showed how this identity was indeed not true, so that the fluxes of the two species inside an alloy could have different modules.

Kirkendall took an ingot of Brass, an alloy composed by Cu and Zn, with a series of Molybdenum wires attached to it and then coat the structure with an outer layer of Copper. Then, he took the system to a temperature of 785 °C and waited looking at how atoms will diffuse in the Copper. In fact, the main point was that at that temperature and concentration the Brass phase was stable, so that Zn atoms would travel in the outside part creating brass at lower concentration while also Cu atoms will travel inside to form Brass. Mo wires instead remained attached to the core during this process, since were not miscible, allowing to see if the core volume would change or not. If only the direct exchange mechanism was present then outside Zn flux would be the opposite of inward Cu one, meaning that the core should have remained the same in volume, but the experiment showed the situation in Fig. (2.4). In order to explain such a result the only possibility is to insert inside the computations the presence of a third species that is traveling inside the material, so that the relation Eq. (2.43) would have a larger degree of freedom. Thus, Kirkendall proposed that vacancies inside the material would actually work as the third species

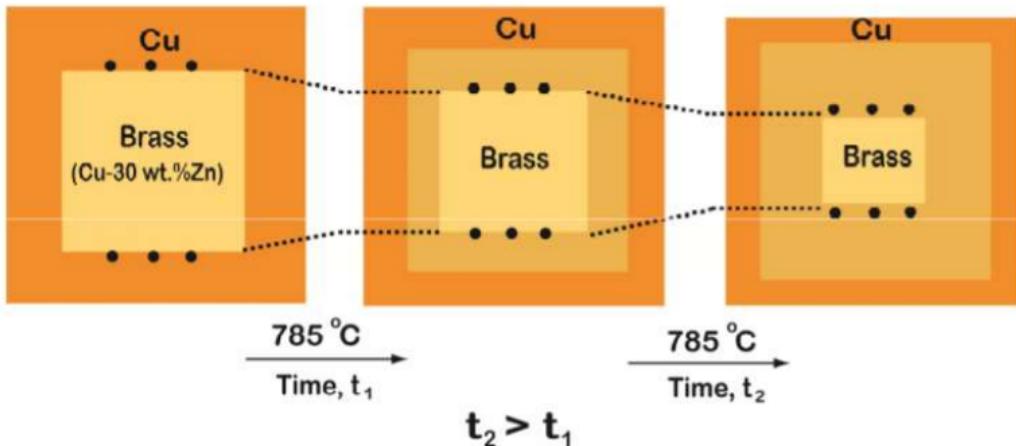


Figure 2.4: Results of the Kirkendall experiment showing how the Brass core becomes smaller due to different values of the fluxes for the two different atomic species.

so that fluxes relation would be

$$\mathbf{J}_A + \mathbf{J}_B + \mathbf{J}_V = 0, \quad (2.44)$$

allowing for what is now called the **Kirkendall effect** to happen. Therefore, the presence of vacancies inside a material is of a major importance in the description of the diffusion processes that are able to modify the concentration of atomic species inside it, as we will see.

Note

The diffusion of atoms inside a material is called substitutional diffusion since we can think of the phenomenon just described as atoms of different species respect the expected one are present inside the lattice, forming substitutional defects. Then those defects start to move inside the material varying the concentration of the several species, so in this optic we imagine defects as a type of atom so a particular substitutional defect.

Network constraint

To study the evolution of atomic concentration inside a material we will need to make more formal the observation seen inside the previous discussion and see how they apply mathematically. In particular, we have seen how the main point reside on the fact that the fluxes are constrained due to continuity effect along with the nature of the direct exchange mechanism. This can be said in a more formal way using the following result

Theorem 2.2.2: Network constraint

Inside a material with C different components we have that if we assume that the volume of the system is fixed and the site can be singly occupied or vacant, then the total number of entities must be locally conserved:

$$\sum_{i=1}^{c+1} dN_i = 0. \quad (2.45)$$

Where the $c + 1$ count also the vacancies as a component.

That result is of a major importance in the theoretical study of the diffusion processes since we can easily see how allows for the theoretical derivation of the constraint described in the Kirkendall effect. In fact, by recalling how the flux is defined one can easily write down the following

$$\mathbf{J}_i = \frac{\partial^2 N_i}{\partial A \partial t} \mathbf{n}, \quad \sum_{i=1}^{c+1} \mathbf{J}_i = 0, \quad (2.46)$$

where \mathbf{n} is the normal vector to the surface A over which we are evaluating the flux. Nevertheless, this is not the only use we have for such an expression, we can also see how the network constraint also implies that an arbitrary chemical potential can be used as a reference for the others. Basically, we can select a component j and use Eq. (2.45) to rewrite its differential using the others, so that

$$dN_j = - \sum_{i \neq j} dN_i, \quad (2.47)$$

which can be substituted inside the form of the Gibb's free energy in order to have

$$G = \sum_{i=1}^{c+1} \mu_i dN_i = \sum_{i \neq j} (\mu_i - \mu_j) dN_i. \quad (2.48)$$

This is telling us that we can choose one chemical potential of our choice, set it to zero, and scale the others based on that to work with basically one component less. Also, Eq. (2.48) shows how also the conjugates forces that relates to the dN_i quantities, and so the fluxes, can be rescaled in terms of a component. Meaning that we can simply write the driving forces using the relation

$$\mathbf{F} = -\nabla (\mu_i - \mu_j), \quad (2.49)$$

simply the rescaled chemical potential gradient.

As a last remark, we can also see another interesting result. In particular, using the network constraint we can see how the \mathcal{L} matrix posses more symmetry than what we expect having that the following is true.

Corollary 2.2.1 \mathcal{L} symmetry

In a system where the network constraint is valid we have that the following holds

$$\sum_{i=1}^{c+1} \mathcal{L}_{ij} = 0 = \sum_{i=1}^{c+1} \mathcal{L}_{ji}. \quad (2.50)$$

Proof: The proof is simple, we can simply use the definition of the matrix and the relation Eq. (2.46) to obtain

$$\sum_{i=1}^{c+1} \mathbf{J}_i = \sum_{i=1}^{c+1} \sum_{j=1}^{c+1} \mathcal{L}_{ij} \mathbf{F}_j = \sum_{j=1}^{c+1} \left(\sum_{i=1}^{c+1} \mathcal{L}_{ij} \right) \mathbf{F}_j = 0, \quad (2.51)$$

since this must hold for an arbitrary value of the forces the element between parenthesis needs to be zero, and the Onsager's symmetry gives out the wanted result. \square

Substitutional diffusivity

Now, it's time to use what we have seen so far to create a mathematical simple model for diffusion. In particular, we are going to use a binary alloy and see how a model for diffusion can be obtained giving out a value for the diffusivity D_i of a certain atomic species.

Theorem 2.2.3: Diffusivity in a binary alloy

Inside a dilute binary alloy, with concentration gradient, the diffusivity of a component can be written as

$$D_i = k_B T \begin{cases} \left(\frac{\mathcal{L}_{11}}{c_1} - \frac{\mathcal{L}_{12}}{c_2} \right) \left(1 + \frac{\partial \ln \gamma_1}{\partial \ln c_1} + \frac{\partial \ln \langle V \rangle}{\partial \ln c_1} \right), & i = 1 \\ \left(\frac{\mathcal{L}_{22}}{c_2} - \frac{\mathcal{L}_{21}}{c_1} \right) \left(1 + \frac{\partial \ln \gamma_2}{\partial \ln c_2} + \frac{\partial \ln \langle V \rangle}{\partial \ln c_2} \right), & i = 2 \end{cases}. \quad (2.52)$$

Proof: We know that in a binary alloy the total atomic species that we need to count are three, one of which are the vacancies. Therefore, we can use the result of the network constraint and set the chemical potential of the vacancies as the reference, having $\mu_V = 0$, and work on the other two. We can so use the Gibbs-Duhem equation in this situation and divide the relation for the volume V to have

$$c_1 d\mu_1 + c_2 d\mu_2 = 0, \quad d\mu_1 = -\frac{c_2}{c_1} d\mu_2, \quad (2.53)$$

where $d\mu_V = 0$ since μ_V was set to the constant value of zero. Then, we can use the constitutive relations $\mathbf{J} = \mathcal{L}\mathbf{F}$ to write down a form for the fluxes inside the material in a general way as

$$\mathbf{J}_1 = -\mathcal{L}_{11}\nabla\mu_1 - \mathcal{L}_{12}\nabla\mu_2, \quad \mathbf{J}_2 = -\mathcal{L}_{21}\nabla\mu_1 - \mathcal{L}_{22}\nabla\mu_2. \quad (2.54)$$

We can then take the flux for the first atomic type and substitute the gradient of μ_2 in order to obtain

$$\mathbf{J}_1 = -\left(\mathcal{L}_{11} - \frac{c_1}{c_2} \mathcal{L}_{12} \right) \nabla\mu_1. \quad (2.55)$$

Then, the Henry's law form for the chemical potential can be used so that we can explicitly write down the gradient as

$$\mu_1 = \mu_1^0 + k_B T \ln(\gamma_1 X_1) = \mu_1^0 + k_B T \ln \left(\gamma_1 \frac{N_1}{V} \frac{V}{N_T} \right) = \mu_1^0 + k_B T (\ln \gamma_1 + \ln \langle V \rangle + \ln c_1). \quad (2.56)$$

We will assume that γ_1 and $\langle V \rangle$ will depend on position by the value of c_1 so that we can evaluate the gradient simply as

$$\nabla\mu_1 = \frac{k_B T}{c_1} \left(1 + \frac{\partial \ln \gamma_1}{\partial \ln c_1} + \frac{\partial \ln \langle V \rangle}{\partial \ln c_1} \right). \quad (2.57)$$

By substituting inside Eq. (2.55) and confronting with Fick's law $\mathbf{J}_i = -D_i \nabla c_i$ we are able to obtain the wanted result. The procedure is analogous for the other component. ☺

In this way we are able to describe the evolution of the species by using Fick's law, seeing how the fluxes goes in the directions opposites to the gradient of concentration. Meaning that atoms goes in the direction where they are less and the two of them can have different velocities, since the difference between the two is compensated by the vacancy flux. Also, often Eq. (2.52) is simplified since the

diagonal components of \mathcal{L} are generally larger than the off-diagonal once and $\langle V \rangle$ is usually nearly constant meaning that for the case of the first component one can write

$$D_1 \approx \frac{k_B T \mathcal{L}_{11}}{c_1} \left(1 + \frac{\partial \ln \gamma_1}{\partial \ln c_1} \right). \quad (2.58)$$

Where the term with γ_1 represent the level of non ideality of the solution. Also, another specific case is when the second type of atoms 1^* is taken as an isotope of the other one, so that the solution is surely ideal and the diffusivity becomes

$$D_1^* = k_B T \left(\frac{\mathcal{L}_{11}}{c_1} - \frac{\mathcal{L}_{11^*}}{c_{1^*}} \right), \quad (2.59)$$

which is also called **self diffusivity**. Usually also the off-diagonal term \mathcal{L}_{11^*} it's pretty small having that at last the approximation of D_1 can be stated in terms of the self diffusivity as

$$D_1 \approx D_1^* \left(1 + \frac{\partial \ln \gamma_1}{\partial \ln c_1} \right). \quad (2.60)$$

Meaning that the diffusion properties of a species can be seen as the one for its diffusion in itself plus the non ideality of the solution in which is present.

All of these equations have implicitly used a system of reference attached to the crystal lattice, the C-frame, since we have always considered the movements of the atoms relatives to the atomic positions themselves. It is also possible, and useful, to restate the theory using the system of reference of the laboratory where the volume of the sample is fixed in space called the V-frame, and is defined by assuming the ends of the sample at rest, not moving, and so fixed volume. In this frame of reference it's possible to see some results, like the relative velocity given by

$$\mathbf{v}_C^V = (D_1 - D_2) \bar{V}_1 \nabla c_1. \quad (2.61)$$

Another important property that can be seen of the movements inside the V-frame is that the two components of a binary alloy present the same diffusivity, called **interdiffusivity** defined as

$$\tilde{D} = c_1 \bar{V}_1 D_2 + c_2 \bar{V}_2 D_1. \quad (2.62)$$

So, the diffusivity in this situation is the same for both the species, but the fluxes can still be different due to different concentration gradients.

Vacancies in equilibrium

We have seen how vacancies are probably the most important point defect that we need to focus on in order to describe the diffusion mechanism inside a material. For this reason is interesting to see how effectively they appear and how many of them are present. The latter, in particular, can be addressed in a simple way by using equilibrium thermodynamic in order to see the molar fraction of vacancies that minimize the free energy of a system. Giving rise the result reported next.

Theorem 2.2.4: Vacancy presence

In a material composed by N_A atoms and N_V vacancies, if we have $N_V \ll N_A$, we have that at equilibrium the molar fraction of vacancies is

$$X_V = \exp\left(-\frac{G_V^f}{k_B T}\right) = \exp\left(\frac{S_V^f}{k_B}\right) \exp\left(-\frac{H_V^f}{k_B T}\right), \quad (2.63)$$

where G_V^f is the variation of free energy needed in order to form the vacancy in the crystal.

Proof: We can write down the free energy of the system by adding to the free energy of the single component the increase of entropy given by using Bragg-Williams-Gorsky configurational entropy once again, and having

$$G = N_A \mu_A^0 + N_V G_V^f + k_B T \left[N_A \ln\left(\frac{N_A}{N_A + N_V}\right) + N_V \ln\left(\frac{N_V}{N_A + N_V}\right) \right]. \quad (2.64)$$

From this we use the fact that $N_V \ll N_A$ and evaluate the chemical potentials of the two components having

$$\mu_A = \frac{\partial G}{\partial N_A} \approx \mu_A^0, \quad \mu_V = \frac{\partial G}{\partial N_V} \approx G_V^f + k_B T \ln X_V. \quad (2.65)$$

At equilibrium, we need $\partial G / \partial N_V = 0$ meaning that we can obtain the wanted relation by simply setting $\mu_V = 0$ and inverting it. ☺

It's interesting because the value of X_V can be experimentally measured by differential diffractometry at different temperatures, where the variation of the volume can be obtained and then the one that comes from thermal expansion can be omitted by evaluating the lattice constant using diffraction. Still, X_V can be computed and so by doing a logarithmic fit one can obtain the value of H_V^f which can be useful for some other investigations, also the general values are around 0.65 eV.

Still, this result is leaving behind some questions. In fact, it seems strange that the vacancies can have a constant value at equilibrium if still a constant flux is present inside the material which would lead to elimination of them in time. It's not easy to imagine how vacancies traveling inside a material at a constant speed would at the end arrive at the surface where they will simply become a surface defects eliminating one vacancy. For this reason having a constant value of X_V is implying that center of creation of vacancies needs to be present inside the material, and can be seen how this is actually true the source being **dislocations**.

Dislocations in crystals

Dislocations are line defects inside materials that are created due to external pressure pushing the sides of the sample in an uneven way moving the lines of atoms in different positions. The best way to understand the latter description is by using the **Burger's circuit** construction for the definition of such defects in a structure. Basically the idea is to draw a cyclic rectangular line on the surface of the material, and in case no defects are present the cycle will close, otherwise the vector missing completing the line is called **burger vector** and define the entity of the dislocation alongside with the direction. An example of that is shown in Fig. (2.5) where the two major types of dislocations are depicted by the drawing of

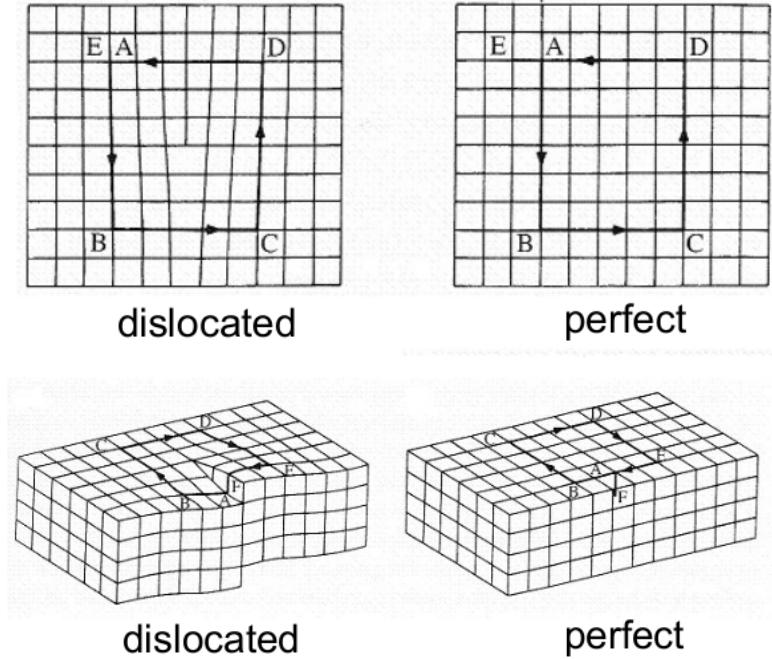


Figure 2.5: Construction of Burger's vectors in two different types of dislocations: edge dislocations on top, and screw one on the bottom.

the Burger circuit, still in reality the situation is more complex than that having dislocations that are a mix of those two but it's good to have an image of how they look like.

Nevertheless, we are interested in the description of how such line dislocations can be thought as creators of vacancies, and to understand that we need to talk about how dislocations can move inside a crystal. In fact, dislocations are able to change positions inside a lattice by using two main movements: **glide**, and **climb**. The former is a simple situation where a shear pressure is applied to the lattice and in the direction of the Burger's vector so that the dislocation start gliding on the side of the material, as its possible to see in Fig. (2.6). Still, such movements isn't able to produce vacancies, it's more important for the possibility of eliminating defects bringing dislocations to the edge of the material recreating symmetry in the bulk. The real movement that we are interested in is so the climb one. We can see, always from Fig. (2.6), how the climb movement instead of moving the dislocation to the side is able to bring it up or down in extension. In particular, the way in which this happens requires for atoms around the dislocation to move in order to position themselves into the dislocations, to increase the extent, or out of it, decreasing it. In both cases for the atoms to move in other positions we need that vacancies are involved, in fact if atoms would swap places with another one nothing would happen. Therefore, if the dislocation increase in extent an atom from the symmetric lattice need to enter the dislocation line leaving behind a vacancy, **generating them**, instead if we have a decrease an atom need to go into a vacancy, **destroying them**. Basically, through the climbing mechanism the **dislocations can be seen as both sources and sink of vacancies**, giving rise to a non-conservative motion that involves atomic diffusion.

We have so seen how effectively vacancies can be created inside a material understanding how effectively is possible that a constant fraction of them is present at equilibrium. Still, dislocations posses also other properties that influences the diffusion inside the material. In particular, is possible to understand that due to the variation of lattice near the defect also a pressure gradient is created that tries to separate the part under the dislocation and unite the one above it. That pressure gradient, called **Cottrell**

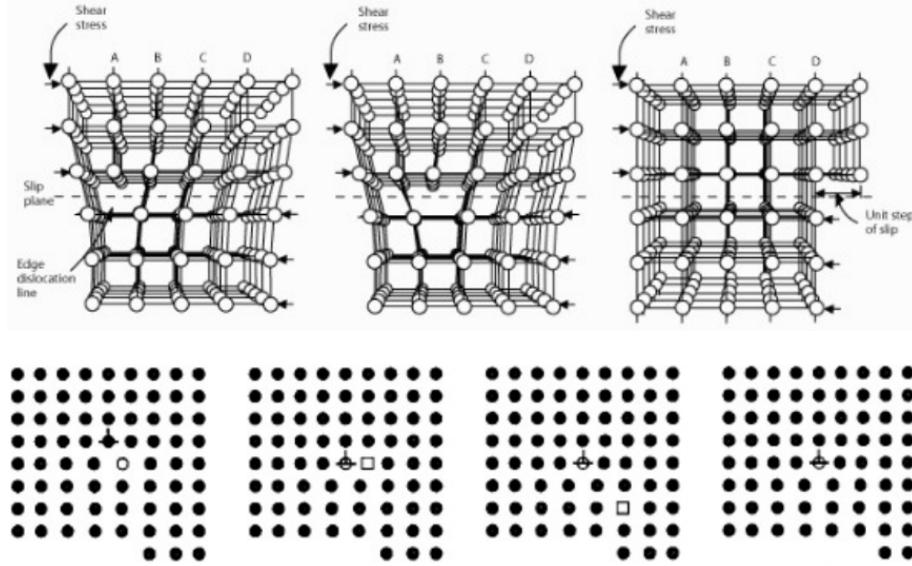


Figure 2.6: Graphical representation of the two types of dislocations movements: glide movement on top, climb movement on the bottom. In particular, the climb movement bring the dislocation down in this case.

atmosphere at equilibrium, is felt by the atoms in the surroundings creating variation in the flux that can be inserted using the following expression

$$\mathbf{J}_i = -D_i \left(\nabla c_i + \frac{c_i \Delta \bar{V}_i}{k_B T} \nabla P \right), \quad (2.66)$$

where $\Delta \bar{V}_i$ is the local variation of the volume occupied by the i -th species due to the dislocation. This can be also described by the substitution of the chemical potential as the designed one to generate the flux to an **elastochemical** one that is defined as

$$\Phi_i = \mu_i + \Delta \bar{V}_i P, \quad (2.67)$$

and use that in the computations. This idea of redefining the potential to include effects inside the diffusion mechanism is a really valid one that we are going to use also further in the course. For this reason we will anticipate the form for the diffusion potential inside an ionic crystal, where the electrostatic forces between atoms needs to be taken into account for diffusion giving rise to

$$\Phi_i = \mu_i + q_i \phi. \quad (2.68)$$

Where ϕ is the electrical potential present in the crystal and the total potential is so-called **electrochemical diffusion potential**.

2.3 Diffusion equation and atomic models

We have already discussed how diffusion can be model on a macroscopical base using non equilibrium thermodynamics obtaining interesting result both for the forms of the fluxes and of the diffusion constant. Now, we want to look at a more microscopic level trying first to describe how we can understand the motions of atoms looking at their density $c(\mathbf{x}, t)$ inside the material.

We have seen in the previous section how the flux of particles \mathbf{J} can be described by using the density of atoms inside the material via Fick's first law, Eq. (2.39). Still, we can also try to describe the density of atoms inside the system, in fact the function c describing the number of atoms inside the material will need to respect some continuity condition such as Eq. (2.5). These two conditions taken together allow us to obtain a really powerful tool in order to study the evolution of density inside materials.

Theorem 2.3.1: Second Fick's law

Inside a multicomponent material the density $c_i(\mathbf{x}, t)$ of the i -th component respect the following differential equation

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i. \quad (2.69)$$

Proof: We can write down the continuity equation for the densities assuming that source or sink terms \dot{n}_i are negligible, since the vast majority of the time this is the case, so that we have

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{J}_i = \nabla \cdot (D_i \nabla c_i). \quad (2.70)$$

In general D_i should be a tensor, still we are going to think at it as a simple scalar which in general can be assumed to depend on position through the density, as $D_i(c_i)$. Meaning that the diffusivity can be expanded using Taylor as

$$D_i \approx D(\langle c_i \rangle) + (c_i - \langle c_i \rangle) \left. \frac{\partial D_i}{\partial c_i} \right|_{\langle c_i \rangle}, \quad (2.71)$$

where $\langle c_i \rangle$ is the average value of the density inside the material and was chosen as the expansion point for simplicity. Inserting that expansion inside the continuity equation we get

$$\nabla \cdot (D_i \nabla c_i) = D(\langle c_i \rangle) \nabla^2 c_i + \left. \frac{\partial D_i}{\partial c_i} \right|_{\langle c_i \rangle} (\nabla^2 c_i + \nabla c_i \cdot \nabla c_i), \quad (2.72)$$

but the second term is often neglected since the diffusivity has a general low dependence on the density, obtaining the wanted result. \ominus

This equation allow us to describe the density of atoms inside the material in every moment in time given some initial conditions. To make an example, in 1D it's easy to see how if you take as a boundary condition for the density $c_i(x, t \rightarrow 0) = n_i \delta(x)$ than the following function is the solution

$$c_i(x, t) = \frac{n_i}{\sqrt{4\pi D_i t}} e^{-\frac{x^2}{4D_i t}}. \quad (2.73)$$

Where n_i is the total number of atoms so that c_i will be the number of atoms divided by a lenght, and one can easily see how that expression satisfy both the partial differential equation and the boundary conditions. From it, we can see how the atoms will start centered in the origin and then will start to spread from it inside the material. In particular one can see how the average displacement of the atoms will be equal to the spread of the Gaussian itself σ which can be easily computed using the known formula

$$G(\mu, \sigma) = \frac{C}{\sqrt{2\pi}\sigma} e^{-\frac{(x-\mu)^2}{2\sigma^2}}, \quad \sigma = \sqrt{2D_i t}. \quad (2.74)$$

Meaning that the average displacement will be proportional to \sqrt{t} , which is typical for diffusion phenomena showing how the process is slow needing much more time to spread the atoms as the dimensions of the system increase.

This result is general also when we look at higher dimensions, since it's possible to see that the same boundary condition and solution can be used even in 2D or 3D so that the solution is a simple product of the 1D one

$$c_i(\mathbf{r}, t) = \frac{n_i}{(4\pi D_i t)^{d/2}} e^{-\frac{r^2}{4D_i t}}. \quad (2.75)$$

Where d is the dimensionality of the system, and we can see how the Dirac delta form for $t \rightarrow 0$ is still respected along with the differential equation. Also, the form of the average displacement is closer to the naive 1D case, but we can find out a more general form by evaluating it explicitly as

$$\langle R^2(t) \rangle = \frac{\int_{\mathbb{R}^+} \int_{\Omega} r^2 c(r, t) r^2 d\Omega dr}{\int_{\mathbb{R}^+} \int_{\Omega} c(r, t) r^2 d\Omega dr} = 2dD_i t, \quad (2.76)$$

which is consistent with Eq. (2.74). This result is telling us that doesn't matter the dimension, the evolution of the displacement in a diffusive process only depend on the nature of the process itself and scales in time as \sqrt{t} , usually slow.

Therefore, using these results we were able to already describe some interesting properties of the diffusion process in a material having some important quantitative results. Still, this is only the beginning this model can be highly refined by using several considerations that will allow for it to be of great precision.

Note

The Gaussian form of the solution is interesting not only for the description of the evolution in time itself, but also on an experimental point of view. In fact, if one is able to evaluate $c(x, t)$ as function of position and time can see how

$$\ln c_i = \text{const.} - \frac{x^2}{4D_i t}, \quad (2.77)$$

meaning that by making a linear fit in a $\ln c_i$ vs x^2 plot at a certain time will allow us to estimate D_i experimentally.

Diffusion and random walk

Another way to approach the modelling of diffusion is describing it using the mathematical model of the **random walk**. We can consider the atom moving by performing a series of possible jumps in space defined by the vectors $\{\mathbf{r}_i\}$, where every jump can be done with a frequency Γ . This means that after a certain time t the number of jumps performed would be $\langle N_t \rangle = \Gamma t$ and the distance travelled by the atom would be

$$\mathbf{R}(t) = \sum_{i=1}^{\Gamma t} \mathbf{r}_i, \quad R^2(t) = \sum_{i=1}^{\Gamma t} r_i^2 + 2 \sum_{i=1}^{\Gamma t-1} \sum_{j=1}^{\Gamma t-i} \mathbf{r}_i \cdot \mathbf{r}_{i+j}. \quad (2.78)$$

Where also the square of the displacement was reported since our aim is to evaluate the mean square displacement of the average walker inside the diffusion process and confront it with the previous model.

Therefore, by taking the average of R^2 it's possible to see how its value will take the form of

$$\langle R^2(t) \rangle = \Gamma t \langle r^2 \rangle + 2 \left\langle \sum_{i=1}^{\Gamma t-1} \sum_{j=1}^{\Gamma t-i} \mathbf{r}_i \cdot \mathbf{r}_{i+j} \right\rangle = \Gamma t \langle r^2 \rangle + 2\Pi(t), \quad (2.79)$$

where Π is the time correlation function between the jumps, describing how much the jumps influence one another. Now, in the case of a pure random walk, the jumps are totally uncorrelated with a uniform probability of going in every possible direction. Meaning that $\Pi = 0$ and average displacement takes a form analogous to the one already seen

$$\langle R^2(t) \rangle = \Gamma t \langle r^2 \rangle, \quad (2.80)$$

showing how the evolution is still proportional to $t^{1/2}$ as expected from diffusion.

We can now confront the model just obtained, Eq. (2.79), and the more macroscopic description given by the solution of the diffusion equation, in Eq. (2.76), and see how we can retain a form for the diffusivity.

Theorem 2.3.2: Microscopic diffusivity

Inside an atomistic model the diffusion can be thought as a random walk with frequency of jump Γ , so that macroscopically the density can be described using Fick's law with a diffusivity given by the microscopic properties as follows

$$D = \frac{\Gamma \langle r^2 \rangle f}{2d}, \quad f = 1 + \frac{2\Pi(t)}{\Gamma t \langle r^2 \rangle}, \quad (2.81)$$

where $\Pi(t)$ is the time correlation function for the jumps.

Proof: At first, we can see how Eq. (2.79) can be recast in a simpler form analogous to the one in Eq. (2.76) by using

$$\langle R^2(t) \rangle = \Gamma t \langle r^2 \rangle f, \quad f = 1 + \frac{2\Pi(t)}{\Gamma t \langle r^2 \rangle}. \quad (2.82)$$

Which can be confronted with the mean square displacement of the macroscopic diffusion model to see that

$$D = \frac{\Gamma \langle r^2 \rangle f}{2d}, \quad (2.83)$$

having our final result. ☺

Therefore, by simple consideration on the microscopic nature of the diffusion mechanism we were able to connect the diffusivity to the rate of jump inside the lattice. All we have to do now is describe how such rate can be expressed quantitatively, and then the whole model would be complete.

Thermally activated jumps

We now consider a statistical model to evaluate the transition rate of the jump between the different main states inside the material, starting from a minimum and jumping to a maximum, called transition state, to then go into another minimum, as depicted in Fig. (2.7). In particular, we are going to make some important assumption in order to work out the model:

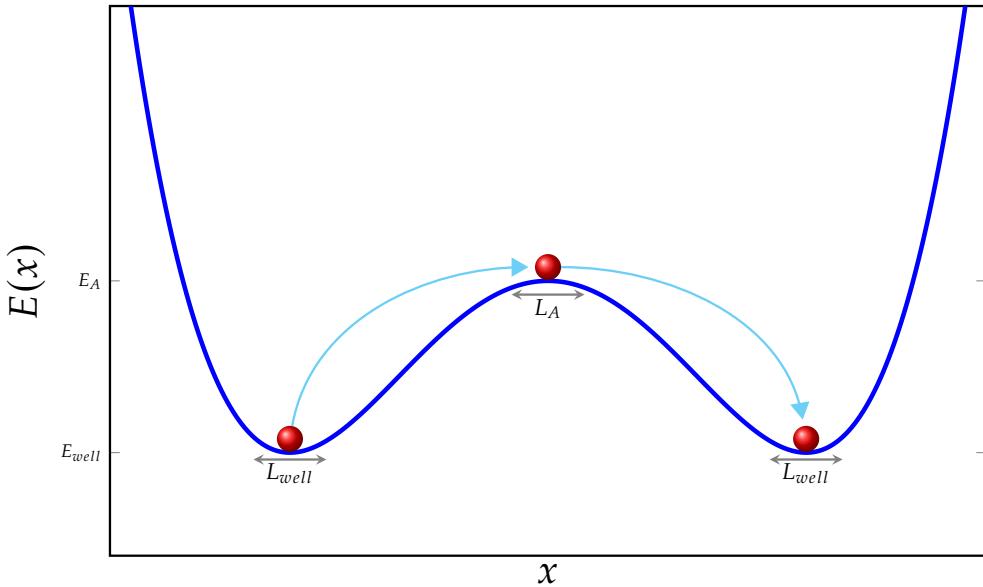


Figure 2.7: Representation of the energy landscape of a possible system under study in the context of thermally activated processes. Where the path followed by the atom is in 1D and is described by the directions of the arrows.

- 1) Single particles in a potential energy with harmonic wells,
- 2) Thermal equilibrium described by classical partition function,
- 3) Quantum tunneling is negligible.

Using this assumption is possible to create a microscopic model that allow us to obtain a quantitative evaluation of the transition rate that is given by the following result.

Theorem 2.3.3: Thermally activate transition rate

A thermal activated process inside a system where quantum tunneling is negligible posses a transition rate that can be expressed with the form

$$\Gamma = z\nu \exp\left(-\frac{E^m}{k_B T}\right), \quad \nu = \frac{1}{2\pi} \sqrt{\frac{\beta}{m}}. \quad (2.84)$$

Where E^m is called **migration energy**, defined as the difference between the energy of the minimum of the starting point and the transition point energy, while β is the first order coefficient of the Taylor expansion on the minimum and z the numbers of neighboring sites.

Proof: From the assumption we can evaluate the value of the medium time for a transition to happen as the quantity

$$\tau_{cross} = \frac{L_A}{\langle v \rangle}, \quad \langle v \rangle = \frac{\int_{\mathbb{R}^+} v e^{-\frac{mv^2}{2k_B T}} dv}{\int_{\mathbb{R}^+} e^{-\frac{mv^2}{2k_B T}} dv} = \sqrt{\frac{2\pi m}{k_B T}}, \quad (2.85)$$

where a Maxwell-Boltzmann distribution for the velocities was used in the computations of the mean. So, the value of $1/\tau_{cross}$ will give us the probability of a particle to cross the energy barrier in the unit time, now to complete the probability of transition we need the probability of having a particle to be ready to jump, which can be given by

$$P_A = \frac{N_A}{N_T} = \frac{N_A}{N_A + N_{well}} \approx \frac{N_A}{N_{well}} = \frac{Z_A}{Z_{well}}. \quad (2.86)$$

Where Z_A and Z_{well} are the partition functions of the well and transition state of the one-particle system, also we assumed that the number of particle in the minimum are much larger than the one in the transition state. Now, the value of the partition function can be evaluated by assuming that the minimum has an energy that can be approximated using $E(x_{well}) = E_{min} + \beta(x - x_{well})^2$ while the maximum is nearly constant in the L_A distance having that

$$\frac{Z_A}{Z_{well}} = \frac{\int_{-L_A/2}^{L_A/2} e^{-\frac{E(x)}{k_B T}} dx}{e^{-\frac{E_{min}}{k_B T}} \int_{-L_{well}/2}^{L_{well}/2} e^{-\beta \frac{(x-x_{well})^2}{k_B T}} dx} \approx L_A e^{-\frac{E_A - E_{min}}{k_B T}} \sqrt{\frac{\beta}{2\pi k_B T}}. \quad (2.87)$$

Where we also assumed that the integral over the well could be extended to the all domain in order to count also for the tails and have an analytic form for the solution. Therefore, we can so define Γ' as the following quantity

$$\Gamma' = \frac{P_A}{\tau_{cross}} = \frac{Z_A}{Z_{well}} \frac{1}{\tau_{cross}} = \nu e^{-\frac{E_m}{k_B T}}, \quad (2.88)$$

which represent the transition rate in a specific direction in space, since the model was in 1D, in reality the hopping can happen in all the possible directions of neighboring sites. Assuming that the probability of going in equivalent sites near the well has same Γ' rates we need to sum all them up in order to obtain the total one, finding out the final result as claimed. ☺

We can see how the transition rate obtained in this particular one particle model is interesting, having a frequency multiplied by an exponential factor that goes down as the potential barrier needed to overcome the jump increases. Such a form allows us to give a simple and strong physical interpretation to the result, where the particle in equilibrium **vibrates on the minimum** with a changing intensity over time such that has a **non-zero possibility of vibrate with enough strength in order to overcome the barrier and hope**. Meaning that, in average, all particles stay in an equilibrium position for a time $1/\Gamma$ before hopping to another minimum inside the lattice due to thermal vibrations. Also, it's possible to see how the latter posses a typical amplitude $\nu \propto m^{-1/2}$ as expected from classical vibrations, meaning that also the **mass of the atom** gives a contribution, so that different isotope of the same element have different diffusive behaviors. This phenomenon created what takes the name of **isotope effect**.

Such a model is so able to describe the on a first principle base the very nature of the hopping as a statistical process, giving a quantitative evaluation of the transition rate that is at the very core of really important mechanism such as chemical reactions, not only atoms' diffusion. For this reason such theory, called **transition state theory**, is of great interest not only on a theoretical point of view and has been refined over time to also include the presence of many particles inside the system, relaxing the single particle assumption. We have not the time to undergo the study of such a complex theory, nevertheless we are going to make use of its result so that we are going to use the following form for the transition rate.

Corollary 2.3.1 Many-body case

If we relax the condition of a single particle inside the system imagining to have a many-body interacting one, the transition rate take the following form

$$\Gamma = z\nu \exp\left(-\frac{G^m}{k_B T}\right) = z\nu \exp\left(\frac{S^m}{k_B}\right) \exp\left(-\frac{H^m}{k_B T}\right). \quad (2.89)$$

Basically the energy of migration is exchanged with the free energy of migration. We can so use such a model for the transition rate to give out a final form that we can use for the diffusivity constant, since by inserting Eq. (2.89) into Eq. (2.81) we can obtain

$$D = \frac{z \langle r^2 \rangle f}{2d} \nu \exp\left(\frac{S^m}{k_B}\right) \exp\left(-\frac{H^m}{k_B T}\right). \quad (2.90)$$

Which is the final microscopic form for the diffusivity where we can see how such a complex parameter depend on sever factors. The **geometry** of the system defined by the neighboring sites, z , the dimensionality and the correlation, d and f . Then, **vibrations** with their general value of ν and **migration entropy** give a contribution, which in general is not too high having that often such factor are kept constant to reference values with right order of magnitude. At last, the most important contribution is given by the **migration enthalpy** which is generally the factor that influences the most the value of D , having not only a strong dependence on temperature, showing how the process is **thermally activated**, but also since its value can be high.

Example 2.3.1 (Vacancy diffusion)

A simple example of application of such an equation is the case of diffusion of vacancy inside a fcc lattice. We know how $z = 12$ inside such a geometry and the distance between neighbors is $a/\sqrt{2}$, where a is the lattice constant, meaning that $\langle r^2 \rangle = a^2/2$. If we assume that the jumps are uncorrelated for the movement of a vacancy inside a lattice then we can easily see how the final form for the diffusivity is

$$D_V = a^2 \nu \exp\left(\frac{S_V^m}{k_B}\right) \exp\left(-\frac{H_V^m}{k_B T}\right). \quad (2.91)$$

Such an equation gives us a lot of information, especially since we can experimentally evaluate D at different temperatures so that by fitting $\ln D$ vs $1/T$ we can estimate H_V^m which can be compared to first principle DFT computations of such value.

Inside such systems we can also rephrase the motion of vacancies in terms of motions of atoms inside the material, since as a vacancy move also an atom follows along. Therefore, we can simply think at the jumping rate of atoms as the one of vacancy multiplied by the probability of having vacancies to move in, so that

$$\Gamma_A = \Gamma_V \frac{N_V}{N_T} = \Gamma_V X_V. \quad (2.92)$$

We know analytic expressions for both of the quantities, so that we can write down the general form of the diffusivity but still we need first to say that in reality the diffusion of atom is not totally uncorrelated. In particular, we have that an atom jumping into a vacancy leaves behind another one, so that the probability of jump back into the other vacancy is higher than to wait for another one to show up, creating a correlation factor of $f \approx 1 - 2/z$. Using that and Eq. (2.63) we can so

obtain the following form

$$D_A = f a^2 \nu \exp\left(\frac{S_V^m + S_V^f}{k_B}\right) \exp\left(-\frac{H_V^m + H_V^f}{k_B T}\right) = D_A^0 e^{-\frac{E}{k_B T}}, \quad (2.93)$$

where S_V^f and H_V^f are the entropy and enthalpy of formation for the vacancy inside the material. It's also good to see how in general $D_A^0 \approx 0.1 - 1.0 \text{ cm}^2 \text{s}^{-1}$, in good agreement with the typical values of $a \approx 3 \text{ \AA}$, $\nu \approx 1 \times 10^{13} \text{ s}^{-1}$ and $S_V^m + S_V^f \approx 2k_B/\text{atom}$.

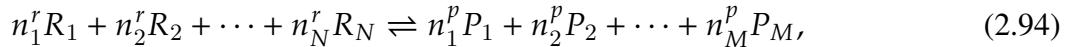
Note

Such a model can effectively be tested in experiment using different types of setups, some examples are on slides, allowing for the evaluations both H_V^m and H_V^f , which are incredibly important for testing theoretical first principle computations. In particular, it's also interesting to see how such values are highly correlated to other ones, like formation enthalpy is correlated to cohesive energy, since stronger are the bonds in the material the more difficult create a vacancy is. Another interesting one is the fact that migration enthalpy is related to the bulk modulus, which tells us how difficult is to move an atom in the material, and it makes sense since H_V^f tells us the variation of the energy in the material when a vacancy travels inside it moving atoms on the way.

Diffusion in ionic materials

One of the most interesting application of diffusion in modern times is the understanding of how ions move inside materials, since ions are able to transport charge allowing for the creation of batteries. In fact, modern Lithium batteries uses Li ions as charge transports from anode to cathode making them diffuse inside liquid electrolyte, which allow for quick diffusion but at the risk of highly flammable batteries that can work only in a short range of temperatures. This lead to a lot of effort to substitute the organic electrolyte into a solid one making Li diffuse inside a material. We shall see how this is possible and how would also allow for high performance batteries to be created.

In order to understand it we shall need first to address the study of a general reaction inside the material. For example take the following situation



where n_i^r and n_i^p are the mole of all the reactant needed and product created. We can have a look at the thermodynamic of such a reaction and describe its chemistry finding out a really important result.

Theorem 2.3.4: Van't Hoff equation

In every reaction is possible to define an equilibrium constant K_{eq} that describes the if the reaction is more favored in the direction of reactants or products, defined as

$$K_{eq} = \frac{\prod_{i=1}^M \gamma_i^p X_i^p}{\prod_{j=1}^N \gamma_j^r X_j^r} = \frac{\prod_{i=1}^M a_i^p}{\prod_{j=1}^N a_j^r}, \quad (2.95)$$

where the molar fractions are the one when the system is in thermal equilibrium. Such a constant

is related to the free energy of the unmixed system, and at equilibrium we have that

$$\Delta G^0 = -RT \ln K_{eq}, \quad K_{eq} = \exp\left(-\frac{\Delta G^0}{RT}\right). \quad (2.96)$$

Proof: We can start by writing down the form of the ΔG^0 in a simple known way by using the form

$$\Delta G^0 = \sum_{i=1}^M n_i^p \mu_i^{p0} - \sum_{i=1}^N n_j^r \mu_j^{r0}. \quad (2.97)$$

Then, we know that in the case where the various reactants and product start mixing forming a solution we can use another known form for the Gibbs free energy that looks like this

$$\Delta G = \sum_{i=1}^M n_i^p \left(\mu_i^{p0} + RT \ln a_i^p \right) - \sum_{i=1}^N n_j^r \left(\mu_j^{r0} + RT \ln a_j^r \right) = \Delta G^0 + RT \ln K. \quad (2.98)$$

Where K is not equal to K_{eq} since the molar fractions can be different from the two, and the equilibrium in the reaction is reached only when the number of products and reactants are so that $K = K_{eq}$. To find out such a value we can simply impose the equilibrium inside the solution by assuming that $\Delta G = 0$ and finding out the wanted results. ☺

This is a powerful result that allow us to see a lot of information on the reaction itself only by looking at the equilibrium constant. In particular, it's possible to see how if $K < K_{eq}$ then $\Delta G > 0$ and the products will decompose to generate reactants, instead for $K > K_{eq}$ the reactants will generate products.

The Van't Hoff equation will be able to give us key information for describing the concentration of defects inside ionic crystals. In fact, the real difference from the diffusion in a normal or ionic material is the presence of atoms that carries a charge since anions and cations are present in equal amount inside the latter. Therefore, we can't really have the simple formation of vacancies inside ionic material since would mean that by eliminating a charge the total material would no more be neutral and that cannot be. Such a constraint make so that the type of defects present inside such materials needs to be more complex to maintain the total charge having that typically are of two types: **Schottky**, where an anion and a cation leaves the structure together leaving two vacancies but no accumulated charge, **Frenkel**, a cation takes an interstitial position leaving a vacancy in its place. Thus, our next task will be, understand how much of such complex defects are present in the material and to do it we will use also a powerful notation that will help us in the reasoning.

Definition 2.3.1: Kroger-Vink notation

We can write down a point defect inside an ionic crystal by using the form X_S^C , where the various letters have the following meanings:

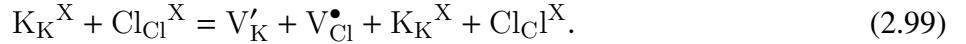
X is the element inside the defect, if a vacancy is present the letter V can be used or the symbol □;

S is the site that the defect has taken place in, can be used the name of the atom that has substituted for example;

C is the effective charge that the defect has inserted inside the system. For example, if a Cl^{+1} is

substituted by a vacancy its like having a negative charge more inside the material so that the defect is written as V'_{Cl} where the apostrophe indicates -1 . To write $+1$ a dot is used instead, and an X is for 0 .

Using it we can write down chemical like equations for the generation of defects, for example we can easily write down how a Schottky one is generated inside KCl as



This equation describes a situation where two atoms, one of Cl and one of K, moves inside the material up to the surface leaving behind a Schottky defect as in Fig. (2.8). Therefore, we can now study the thermodynamic of this reaction using the Van't Hoff equation, than we can understand how K_K^X and Cl_{Cl}^X appears in both side of the equation meaning that we can simplify them. Thus, we only need to care of the a coefficients for the cation vacancies a_{CV} and anion vacancies a_{AV} that we can write explicitly since their concentration is really low, having a dilute solution with $\gamma_i \approx 1$, meaning

$$a_{CV} = X_{CV} = [V'_K], \quad a_{AV} = X_{AV} = [V'_{\text{Cl}}]. \quad (2.100)$$

In this way the value of K can be computed really easily finding out an analytic form for the Van't Hoff equation connecting the concentration of vacancy to the free energy of formation, where recalling that for charge conservation $[V'_K] = [V'_{\text{Cl}}]$ we get

$$K_{eq} = [V'_K][V'_{\text{Cl}}] = \exp\left(-\frac{G_S^f}{2k_B T}\right), \quad [V'_K] = [V'_{\text{Cl}}] = \exp\left(-\frac{G_S^f}{2k_B T}\right). \quad (2.101)$$

The density of vacancies inside an ionic material can so be found in this way, having that the rate of hopping for self diffusion becomes slightly different respect to the one in normal solid

$$D_K = g f a^2 v \exp\left(\frac{S_V^m + S_V^f/2}{k_B}\right) \exp\left(-\frac{H_V^m + H_V^f/2}{k_B T}\right). \quad (2.102)$$

Which is analogous to Eq. (2.93), but the energy of formation is reduced by a factor of two, since double the vacancies needs to be created to maintain charge, also g is the geometric factor that account for the lattice geometry in the fcc was 1. A totally analogous computation can be done to study also the Frenkel defects, only that now instead of generating two vacancy you create an interstitial atom and a vacancy, both helping diffusion.

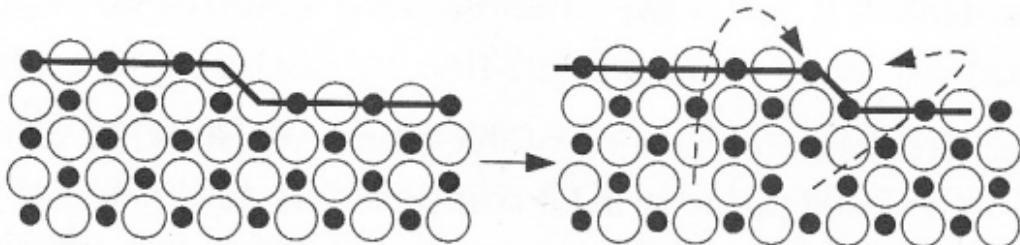


Figure 2.8: Graphical description of the creation of a Schottky defect inside an ionic crystal, where a cation and an anion travels up into the surface.

Boosting ionic diffusion via doping

The real power of ionic crystal is not only contained in the decrease of the contribution inside the exponential of the diffusion constant inside the material, but the real power is the possibility of increasing the number of vacancies by using doping. In fact, the conservation of charge need to work not only inside the generation of vacancies but also when other elements with different oxidation number enters the material. Meaning that, if I dope KCl with Ca the latter will substitute K in the lattice, but we will have that K^+ will transform in Ca^{2+} leading the material to naturally form vacancies to compensate.

Theorem 2.3.5: Doping of KCl

By doping KCl with $CaCl_2$ a concentration of vacancies inside the material is inducted having the following amount

$$[V'_K] = \frac{[Ca_K^\bullet]}{2} \left(1 + \sqrt{1 + \frac{4[V'_K]_{pure}^2}{[Ca_K^\bullet]^2}} \right), \quad (2.103)$$

where $[V'_K]_{pure}$ is the concentration of vacancies that is normally present in the crystal.

Proof: We can write down the equation for the creation of vacancies as

$$[Ca_K^\bullet] + [V_{Cl}^\bullet]_{pure} = [V'_K], \quad (2.104)$$

where we shall also remember how inside the pure crystal we need $[V_{Cl}^\bullet]_{pure} = [V'_K]_{pure}$. Then, by using Van't Hoff equation we can write down the value

$$[V_{Cl}^\bullet]_{pure} [V'_K]_{pure} = e^{-\frac{G_S^f}{k_B T}} = [V_{Cl}^\bullet] [V'_K] = [V'_K] ([V'_K] - [Ca_K^\bullet]), \quad (2.105)$$

which can be transformed in the wanted result after some algebra steps. ☺

This result shows how the concentration of vacancies depends on the fraction $\eta = [V'_K]_{pure} / [Ca_K^\bullet]$ that describes also the regime of doping we are working in. In particular, if $\eta \gg 1$ we are in a **intrinsic regime** and the number of vacancies is nearly the same as the of the pure material, meaning that the diffusion coefficient is still described by Eq. (2.102). Instead, the **extrinsic regime** is described by $\eta \ll 1$ and the number of vacancies transforms into a constant number $[V'_K] \approx [Ca_K^\bullet]$ so that no more exponential dependence on the G_S^f is present inside D_K . This would lead to a great increase in the diffusivity of the material inside the extrinsic regime, where we are also able to highly slow down the decrease of D_K as temperate goes up since the enthalpy of formation at the exponential vanishes.

Using this property we are able to construct doped material that posses wanted behaviors for the diffusion of Li^+ to perform as a good electrolyte in a large range of temperatures. In this way, the problem of flammability of the liquid components would be solved at its core leaving also a lot of room for improvements. For example, solid state batteries will actually be much more compacts allowing them to be stacked in order to obtain much more power from them and higher durability. Such a technology would not only advance batteries, but can be implemented inside all the different devices that uses electrolytes such as fuel cells, for example, which would lead to the creation of high performance engine that could have high working temperatures quickening all the needed reactions.

Note

Just to make a little note, a really promising material in application seems to be pure Zirconia, ZrO_2 , which shows a cubic fluorite structure at room temperature if doped with Yttria Y_2O_3 . In this situation not only the thermal and mechanical properties of the material are highly increased, but we are doping it with substitutional cations, Y^{3+} , that have a lower valence than Zirconium, Zr^{4+} , inducing generation of vacancies.

2.4 Interfaces in materials

So far we have seen how much important the defects are to describe diffusion inside a solid state system, focussing on how defects allow it in the first place. Still, we want now to look at a different type of defects that highly influences the diffusion and are **interfaces**. Basically, real materials are not a simple single block of atoms bonded together, but it's usually composed by chunks of the same material oriented in different directions, called **grains**, and the regions of space that separate them are the interfaces. We want to look into the description of such objects to see effectively their characteristic and how they influence the diffusion.

At first, we shall say that different types of interfaces exist depending on which type of material separates, like: crystal-vapor, crystal-liquid and crystal-crystal, that are possible to see in Fig. (2.9). All of them are interesting and differ not only in the type of phase they connect. For example, it's possible to understand that the local degrees of freedom of such interfaces vary from one to another: in the first two types, in fact, having that liquid and vapor are isotropic then the interface is locally uniquely defined by the normal to the direction in which the interface point, which can be settled by two angles, so two degrees of freedom. On the other side, the crystal-crystal interface is more complex, since we need not only to describe the direction of the cut done by the interface, but also to describe the relative orientation of the two crystals in that position of space. A thing that can be done by imagining the two rotated respect one another, so that we can use the three Euler angle to define it, for a total of 5 degrees of freedom. In our study, we are going to account mainly for a specific type of interface that is defined as follows.

Definition 2.4.1: Grain boundaries

A Homophasic interface between crystals with same structure and composition is called grain boundaries.

Such a defect can be easily seen how describes a specific type of crystal-crystal interface, meaning that we will work in the most complex case with 5 macroscopic variable to work with.

Even after this simple description of what an interface is it's already possible to point out why they



Figure 2.9: Simple image of crystal-liquid/vapour and crystal-crystal interface in order to graphically guide their description of the difference in the degrees of freedom.

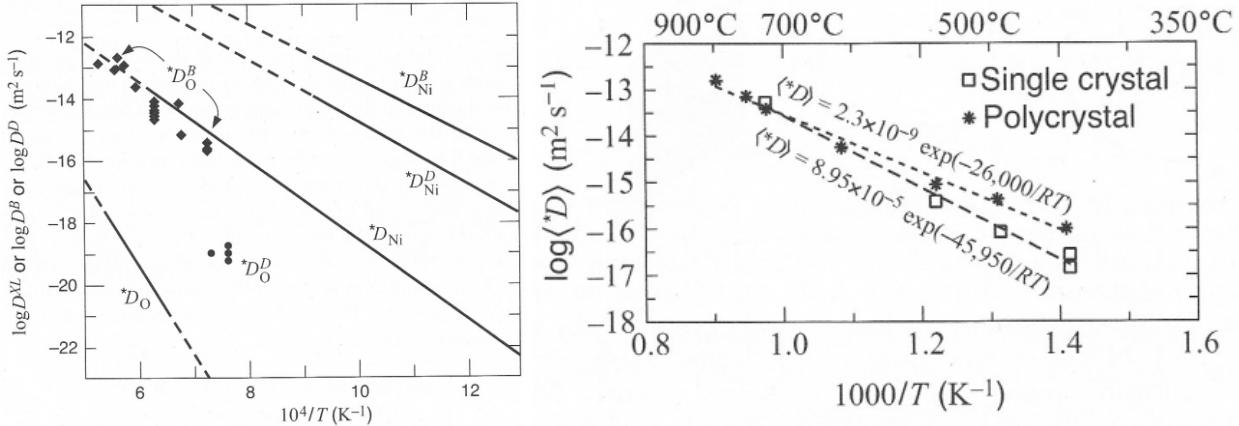


Figure 2.10: Experimental data on the diffusivity value inside NiO, with data for pure self-diffusion, $*D$, diffusion near boundaries, D^B , and diffusion near dislocation, D^D , on the left. Then, on the right, data on the average value of the diffusivity in a pure single crystal vs a polycrystal which posses interface.

play a role in diffusive processes. In fact, interfaces can be seen as microscopically as regions of free space inside the material, where the atoms are able to jump from one position to another without the need of breaking bonds with all neighbors or moving all the atoms to pass through. Meaning that, the energy barrier that the processes posses is much lower near such defects, highly boosting the transition rate and, therefore, the diffusivity D . Experimental data, shown in Fig. (2.10), confirm these simple thoughts showing how the diffusivity of material has a great boost of also several order of magnitudes around interfaces. Nevertheless, the average total value of the diffusivity, D^{eff} , does not change too much from a single crystal to one composed of grain boundaries and the reason is the following.

Theorem 2.4.1: Effective diffusivity

Inside a polycrystal where the normal diffusivity is D^{cry} and it's value on the boundaries is D^B we will have that the total effective diffusivity is

$$D^{eff} = D + \frac{3\delta}{d_G} D^B, \quad (2.106)$$

where d_G is the grain size and δ the boundary thickness.

Proof: D^{eff} is a weighted average between the pure D^{cry} and D^B , where the weights are the relative extent of the volume where the two types of diffusion are active. Meaning that if we account that $V_B \ll V_{cry}$ we can write $V_T \approx V_{cry}$ and the weights are

$$w_{cry} = \frac{V_{cry}}{V_{cry}} = 1, \quad w_B = \frac{V_B}{V_{cry}}, \quad (2.107)$$

where we can think at a grain as a sphere of diameter d_G surrounded by an interface of thickness δ . In this way we can write

$$V_B = \pi d_G^2 \delta, \quad V_{cry} = \frac{\pi}{6} d_G^3, \quad (2.108)$$

where we shall also take into account that the same interface is shared between two boundaries so that the total weight looks like the following

$$w_B = \frac{V_B}{2V_{cry}} = \frac{3\delta}{d_G}. \quad (2.109)$$



Basically, due to the much smaller extensions of the interfaces inside the material the average diffusivity changes only partially respect to the incredible increase between D and D^B . Still, the result is quite good, especially at lower temperatures since the exponent of D^B is much smaller allowing for an enhancing of the total diffusion by also orders of magnitudes.

By such simple considerations we have already seen how interfaces can be a key point in the description of diffusion inside materials, giving a great boost to the performance overall. For this reason we aim into describing on a more precise level the main properties of such a defect, understanding how they are formed and modelling their evolution.

Note

*Inside the description of surfaces during the course there was also another division between the category of crystal-crystal, defined by the way in which the interfaces are composed. In particular, they are divided between **sharp**, meaning that atoms form a precise line that divides the two boundaries creating a small interface tens of nanometers long, and **diffused**, where the interface is not really well-defined since the two phases that are connecting are kind of fused one into the other generating an interface that can be hundreds of nanometers in length.*

Surface free energy

As in every physical system the best way to see how a system evolves into generating an interface or to see how an interface is structured is to look at the energy. In this case it's easy to understand how creating an interface costs energy, since the creation of grains means that a series of bonds inside the material needs to be broken for the creation of **surfaces** that delimits the grain boundaries. Therefore, the idea is to focus on the increase of energy counted inside a specific quantity defined as follows.

Definition 2.4.2: Surface free energy

We define the surface free energy γ as the work needed to create a unit of area inside the wanted material

$$dw = \gamma dA, \quad (2.110)$$

where dw is the differential of work and dA the one of the area.

Basically, the idea is to compute the total free energy change ΔG due to interface, which will depend on γ along with several factors, and minimize it in order to obtain the form in which such interfaces form inside the material.

In particular, it's possible to evaluate experimentally or numerically the value of γ for several types of interfaces by taking a material, separate it and then change the relative angle of orientation between the two pieces. In this way one can find a general increase in the free energy as the angle increases, due to the less coherence between the two parts making the creation of bonds more difficult. Such a phenomenon is well explained inside Fig. (2.11), where it's possible to see how in the coherent interface

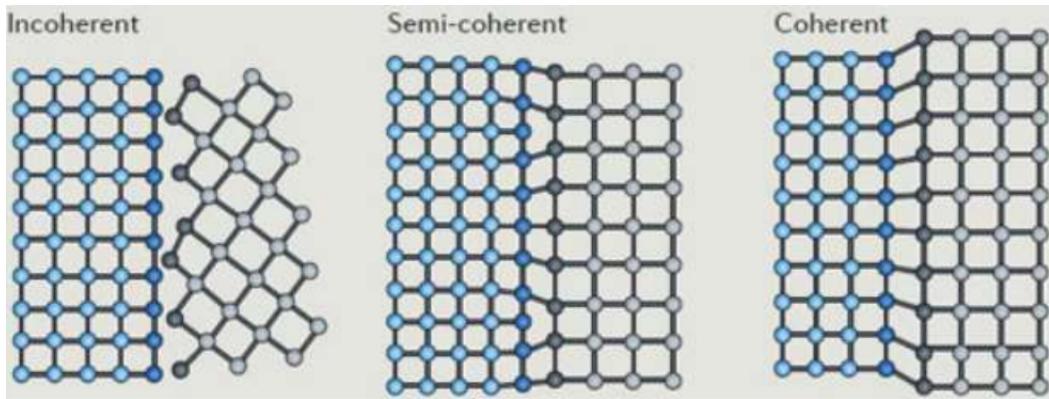


Figure 2.11: Example of incoherent, coherent and semi-coherent interface, all of them increase the energy of the system but the value of γ is less to the far right and increase going to the left due to the less number of bonds.

the system is only deformed but all the bonds still holds like in the normal crystal minimizing γ , but maximizing the **strain energy** σ . Instead, as we go into the incoherent interface the opposite occur, the system is not deformed but a lot of bonds are broken, maximizing γ while minimizing σ . Therefore, to understand the form that the interface would have in the end we shall minimize the total increase in energy due to its formation keeping in mind that will have a form of the type

$$\Delta G \approx \gamma A + \sigma V. \quad (2.111)$$

Using it we can understand how the minimization of the energy will bring to a coherent or incoherent interface depending on the extension of the structure variation. Meaning that, if the grain that is formed is small it will have a low V and a larger A , bringing to a situation where it's better to minimize γ having a coherent interface. While, as the dimensions increase V grows faster respect to A bringing to a preference for incoherent formation minimizing σ .

Still, this is only an approximation and works only in the contest of tiny grains of particle size, when it comes to describing grain boundaries the volume variation becomes not important due to the fact that the grains are often of similar composition inside the material. This means that in general the main contribution is still given by γ inside ΔG and our main focus will be in minimizing it.

Interface motion

A lot of different internal and external factor can cause interfaces to move or change on a morphological level. For example, the presence of an intrinsic difference in the free energy of the phases that compose the interface, like a crystal-liquid interface where $G_{cry} < G_{liq}$. Leading to an intrinsically lower energy barrier for atoms to move from liquid to crystal generating a flux of particles. Another possibility is the presence of external stress that generates fluxes of particles inside the material in order to deform it, indirectly changing the grains form and so the interfaces. Still, the main mechanism that we want to discuss here is the one of **capillary forces** which are forces formed by the presence of γ gradients on the interface itself. For example, the presence of two material with different γ on a surface generate a force that tend to mix the two of them in order to smooth γ out, a phenomenon called **Marangoni effect**.

In order to study such a behavior we need to first talk about how to better describe the interface and in particular of the really useful concept of curvature. In particular, we will define the curvature of a surface in a simplified way as follows.

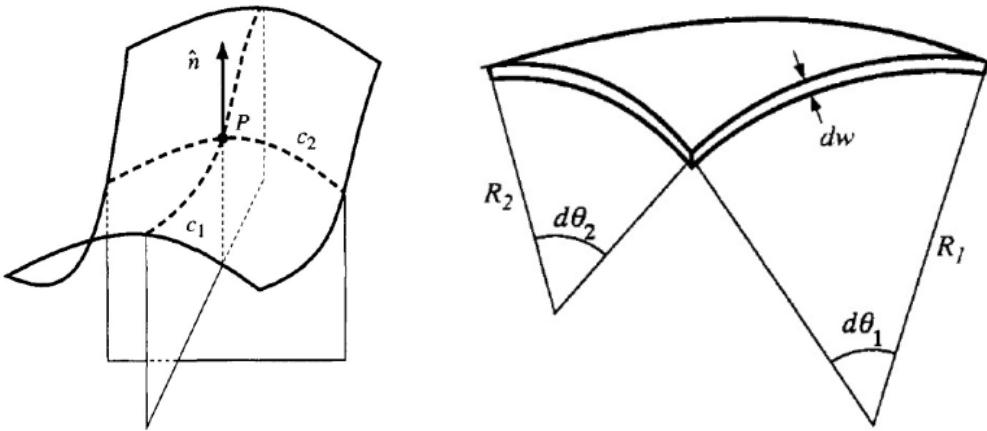


Figure 2.12: Graphical representation of a generic surface curvature and of the geometrical construction for the connection between the variation of volume and area.

Definition 2.4.3: Curvature

Inside a surface, the curvature κ in a particular point of the surface is defined as the sum of the curvature on the two main principle axis taken as

$$\kappa = \kappa_1 + \kappa_2 = \frac{1}{R_1^c} + \frac{1}{R_2^c}, \quad (2.112)$$

where R_i^c are the radii of the osculating circles that defines the curvature on the principle axis.

Such definition allow us to use the curvature inside our computations in order to link two important quantities inside the study of interfaces: area and volume changes. In particular, we can show that the following relation holds.

Theorem 2.4.2: Curvature property

Inside a generic object we can connect the variation of volume to the variation of surface area by the following relation

$$\frac{dA}{dV} = \frac{1}{R_1^c} + \frac{1}{R_2^c} = \kappa. \quad (2.113)$$

Proof: We can imagine transforming the variation of volume dV in a simple increase of the two osculating radii of a quantity dw , as shown in Fig. (2.12). In this way we easily write down the variation of area and volume as

$$dA = (R_1 + dw) d\theta_1 (R_2 + dw) d\theta_2 - R_1 d\theta_1 R_2 d\theta_2 = (R_1 + R_2) dw d\theta_1 d\theta_2, \quad (2.114)$$

$$dV = R_1 d\theta_1 R_2 d\theta_2 dw, \quad (2.115)$$

which can be used to compute the derivative seeing how the wanted relation holds. \odot

Already, by using such a result, it's possible to see how the increase of energy due to interface expansion can be restated in a more simpler form inquiring volume expansion, like

$$dw = \gamma dA = \gamma \kappa dV. \quad (2.116)$$

Such a form is also similar to the one of the work done on the mechanical pressure on the system. In fact, at equilibrium the mechanical work $\Delta P dV$, where ΔP is the pressure difference across the interface, needs to be equal to the one done by the surface tension funding out the **Gibbs-Thomson equation**

$$\Delta P = \gamma \kappa = \gamma \left(\frac{1}{R_1^c} + \frac{1}{R_2^c} \right). \quad (2.117)$$

This is a great result of classical thermodynamics that is really useful, and from our discussion was obtained really simply. Also, it's possible to understand how in the case we are working with a **spheric object** $R_1^c = R_2^c$ having $\kappa = 2/R^c$. At last, it's important to keep in mind that in the case we have a hollow inside the material the number of surfaces that increase as the volume changes are two, since the external one expands but also the one inside the hollow. Meaning that for a **hollow object** the surface tension needs to be multiplied by a factor of 2.

We want now to focus on a grain boundary surface where no hollow is present and the variation of volumes are created by atoms, or particles, of dimensions Ω can travel from one point to another through a flux. In this optic we can simply model that flux by setting as driving force the chemical potential biased by the presence of the surface energy as

$$\Phi = \mu + \gamma \kappa \Omega. \quad (2.118)$$

In this way we can see how an undulating surface will have some positions where the contribution given by γ is positive or negative depending on the curvature. Bringing to the creation of a flux of particles that will smooth out the differences in curvature, meaning that the final equilibrium interface will result in a **smooth surface** with zero $\nabla \Phi$. Thus, using some simple considerations we are able to describe really easily surface tension γ will act inside the material smoothing the surfaces present in the interfaces, and this is only the beginning. In fact, from Eq. (2.117) we can also grasp how γ will also have a role in the description of the pressure around the material, something that can be seen as follows.

Theorem 2.4.3: Curvature and vapor pressure

At equilibrium the vapor pressure around a system depends on both γ and κ as

$$P^{eq}(\kappa) = P^{eq}(0) \exp \left(\frac{\kappa \gamma \Omega}{k_B T} \right). \quad (2.119)$$

Proof: We can assume that the chemical potential explicit dependence on the pressure of the material is given by the relation

$$\mu(P) = \mu(P^0) + k_B T \ln(P/P^0), \quad (2.120)$$

and the potential of the gas phase outside the system is given by $\mu(P^{eq}(\kappa))$, while the one inside it is $\mu(P^{eq}(0)) + \gamma \kappa \Omega$. Meaning that at equilibrium we can set them equal and obtain the wanted relation. ☺

Basically, not only the curvature generate an atomic flux on the surface to smooth it out, but it also creates a gradient of pressure around the material that generate a flux of gasses particle in the same direction having two concurring mechanisms that smooth out the material. Also, the transport through gasses is much faster for obvious reasons.

Another important consequence that we will need in the next studies is the influence that curvature posses in the composition around a β particle immersed in an α matrix. Basically, we can imagine to work inside a system composed by two types of atoms A and B and having a two phase field where

grains of α and β compositions appear inside the material. We can use an argument analogous to the one of the vapor pressure in order to describe the fraction of B atoms in the A -rich α matrix near a β grain.

Theorem 2.4.4: Curvature and composition

Around a B -rich β grain inside an A -rich α matrix the equilibrium value of X_B is given by

$$X_B^{eq}(\kappa) = X_B^{eq}(0) \exp\left(\frac{\kappa\gamma\Omega}{k_B T}\right). \quad (2.121)$$

Proof: The proof is totally analogous to the one before, only that to describe μ we need to assume the validity of the Henry's law and write

$$\mu_B^\alpha(\kappa) = \mu_B^\alpha(0) + k_B T \ln\left(X_B^{eq}(\kappa)/X_B^{eq}(0)\right), \quad (2.122)$$

and then set the equilibrium as

$$\mu_B^\alpha(\kappa) - \mu_B^\alpha(0) = \mu_B^\beta(\kappa) - \mu_B^\beta(0) = \kappa\gamma\Omega. \quad (2.123)$$



This is a really important result that will play an important role in the description of the coarsening process, as we will see, since it will promote the formation of larger grains instead of a lot of smaller ones. In fact the idea is that larger grains have a minor concentration of B atoms around respect to small ones, having that a flux due to concentration gradient is created bringing atoms from smaller grains to larger ones slowly consuming the small in favor of a bigger grain. This also means that in terms of free energy we will have that the smaller grain will have higher values of Φ , since κ is greater, as can be seen in Eq. (2.118). The equilibrium concentration of the α and β phases will so change based on the dimensions of the grain, changing also the phase diagram of the grain itself.

Note

It's interesting to note how the surface tension is also important in the description of capillary effect such as the liquid that naturally rise inside a small tube. Where, after a simple description, it's possible to describe the height of the liquid column through the simple formula

$$h = \frac{2\gamma \cos \alpha}{\rho g r},$$

where α is the contact angle, ρ the density of the liquid, γ the surface tension and r the radius of the capillary. On slides the description is a little more accurate.

Coarsening of microstructure

With the study of curvature we have seen how the grains inside the material will evolve in order to minimize κ preferring the formation of bigger grains from the slow evaporation of smaller one. This process has a big relevance in the study of material structure and atomic diffusion inside it, and for this reason we want to create a model that allow us to predict how the grains are distributed inside the

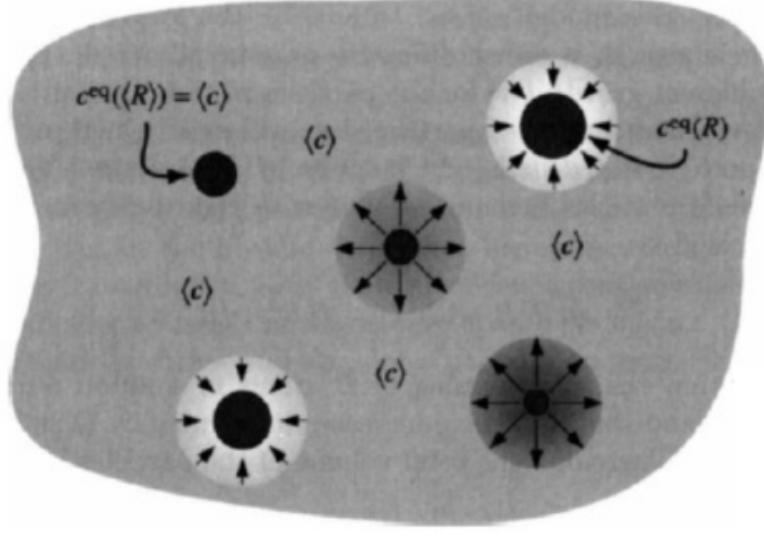


Figure 2.13: Model used to describe the coarsening phenomenon inside a material, shows spherical grains inside a uniform concentration matrix where bigger ones attracts atoms while the smaller gave them away.

material. In particular, we will focus on the description of $f(R, t)$ the **particle size distribution** inside the material, where R will be the grain radius assuming that all of them have a spherical shape.

The idea to model the process is to assume that the material at equilibrium is composed by several spherically shaped grains with composition β with an equilibrium concentration of atoms B that depends on their shape as

$$c^{eq}(R) = c^{eq}(\infty) \exp\left(\frac{2\gamma\Omega}{k_B T R}\right) \approx c^{eq}(\infty) \left(1 + \frac{2\gamma\Omega}{k_B T R}\right). \quad (2.124)$$

Where we have used Eq. (2.121) substituting the value of the curvature of a sphere $2/R$. Such particles are inside an α matrix that is assumed to have a constant average concentration $\langle c \rangle$, so that a gradient of concentration appear near every grain since c smoothly change from the average to $c^{eq}(R)$

$$\nabla c \approx \frac{c^{eq}(R) - \langle c \rangle}{R} \mathbf{n}. \quad (2.125)$$

Such a gradient generates a flux of B components, $\mathbf{J} = \tilde{D} \nabla c$, that increase or decrease the grain size depending on the size of it. In particular, if the grain is large the equilibrium concentration is smaller bringing material to it, while if R decrease the concentration rise making the B components go away as depicted in Fig. (2.13). Therefore, inside this simple construction we can describe how the grains grows inside the material by describing how the radius evolve over time in the following way

$$\frac{dR}{dt} = J\Omega = \tilde{D}\Omega \frac{c^{eq}(R) - \langle c \rangle}{R}. \quad (2.126)$$

This expression is already interesting, but it's not complete since we don't know how to write down $\langle c \rangle$. Nevertheless, a form for such an average can be found easily arriving at the following result.

Theorem 2.4.5: Growth rate

Assuming the total volume of the grains is constant the rate of change of the grains sizes takes the

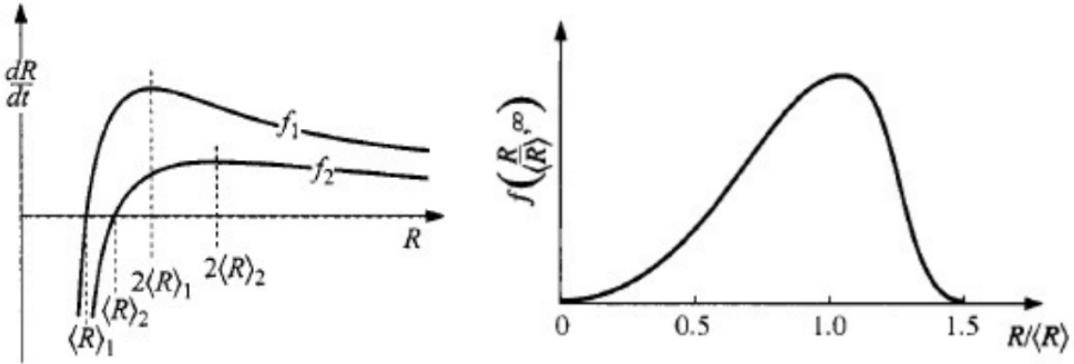


Figure 2.14: Graph of the rate of growth of the grains inside the GSW theory as a function of the particle size for two different types of grains, on the left. A graph of the solution of the continuity equation for the size distribution at equilibrium on the right.

following form

$$\frac{dR}{dt} = \frac{2\tilde{D}\gamma\Omega^2 c^{eq}(\infty)}{k_B T R} \left(\frac{1}{\langle R \rangle} - \frac{1}{R} \right). \quad (2.127)$$

Proof: If the total volume of the grains remain constant we can write down a simple condition as follows

$$\sum_{Grain} R^3 = \text{const}, \quad \sum_{Grain} R^2 \frac{dR}{dt} = 0. \quad (2.128)$$

In which we can substitute Eq. (2.126) and using Eq. (2.124) inside it we will have

$$\sum_{Grain} \tilde{D}\Omega \frac{R^2}{R} \left(\langle c \rangle - c^{eq}(\infty) - c^{eq}(\infty) \frac{2\gamma\Omega}{k_B T R} \right) = 0. \quad (2.129)$$

We can rewrite the expression by manipulating it in the following way

$$\left(\sum_{Grain} R \right) \tilde{D}\Omega (\langle c \rangle - c^{eq}(\infty)) = \sum_{Grain} c^{eq}(\infty) \frac{2\gamma\Omega}{k_B T R} = N_G c^{eq}(\infty) \frac{2\gamma\Omega}{k_B T R}, \quad (2.130)$$

then we can then remember how $\langle R \rangle = \sum_{Grain} R / N_G$ meaning that we simply obtain an evaluation for the average as

$$\langle c \rangle = c^{eq}(\infty) \left(1 + \frac{2\gamma\Omega}{k_B T \langle R \rangle} \right). \quad (2.131)$$

Substituting it inside the expression of dR/dt gets us the wanted result. \odot

This equation shows to us quantitatively when the grains will start to increase or decrease in size, seeing how they increase when $R > \langle R \rangle$ and vice versa. Also, if we plot it, as in Fig. (2.14), we can see how its form has a maximum for every grain type that is reached at $R = 2\langle R \rangle$ and then reaches a plateau as the dimensions grows further.

At last, we shall describe how to work out a form for $f(R, t)$ and in order to do that we can still focus on the fact that the number of particle inside the system needs to be conserved. Meaning that

the volume of the grains has to be conserved in the structure having that the continuity equation can be written out having

$$\frac{\partial f}{\partial t} = -\frac{\partial J}{\partial R} = -\frac{\partial}{\partial R} \left[f(R, t) \frac{\partial R}{\partial t} \right]. \quad (2.132)$$

Where we have used the definition of flux as $\mathbf{J} = n\mathbf{v}$ with n the density of material and \mathbf{v} the average velocity, in our case the density is the distribution of grains volume and the velocity the growth rate. Such an equation allow us to know how the distribution evolves over time, meaning that the initial form of $f(R, 0)$ can be taken as wanted and then evolves following Eq. (2.132) since it goes into equilibrium. An example of this is shown in Fig. (2.14) where the equilibrium form of f is shown for a starting configuration given by a Gaussian. The latter shows how the most probable dimension of a grain is $1.13 \langle R \rangle$ with a cut-off radius of $R_{co} = 1.5 \langle R \rangle$ after which no grains are presents. That distribution also allows us to describe the evolution of the front over time, meaning that in time R_{co} evolves, and we can see how such evolution goes on as follows.

Theorem 2.4.6: Cut-off radius growth

The biggest possible size of grains inside a material grows with time following the simple equation

$$\langle R(t) \rangle^3 - \langle R(0) \rangle^3 = \frac{8\tilde{D}\gamma\Omega^2 c^{eq}(\infty)}{9k_B T} t = K_D t. \quad (2.133)$$

Proof: Taking the distribution in Fig. (2.14) it's possible to take the average of the size as $2R_{co}/3$ so that we can write down

$$\frac{dR}{dt} \Big|_{R=R_{co}} = \frac{2\tilde{D}\gamma\Omega^2 c^{eq}(\infty)}{k_B T R_{co}} \left(\frac{3}{2R_{co}} - \frac{1}{R_{co}} \right) = \frac{\tilde{D}\gamma\Omega^2 c^{eq}(\infty)}{k_B T R_{co}^2}. \quad (2.134)$$

Then, we can take R_{co}^3 and take its derivative to obtain the value

$$\frac{dR_{co}^3}{dt} = R_{co}^2 \frac{dR}{dt} \Big|_{R=R_{co}} = \frac{\tilde{D}\gamma\Omega^2 c^{eq}(\infty)}{k_B T}, \quad (2.135)$$

which can be integrated obtaining a form for the wanted value which then needs to be averaged over the f distribution to obtain the final result. ☺

This is the final result for this model for the coarsening or **Ostwald ripening** phenomenon in the contest of **Greenwood-Lifshitz-Slyozov-Wagner theory**, which is a diffusion limited theory. Meaning that all the velocity at which the grains' growth is dictated by the diffusion velocity inside the matrix. It's also possible to take into account a situation where diffusion in the matrix is really fast and the slow step is the transfer of material inside and outside the grains across the interface. This case is called source limited, the concentration of the matrix is really uniform thanks to fast diffusion, and Eq. (2.133) can be rewritten as

$$\langle R(t) \rangle^2 - \langle R(0) \rangle^2 = K_S t. \quad (2.136)$$

Note

Just a little notice, during the lecture another really cool effect was just introduced called **Rayleigh instability**, which describes how a wire tend to not be stable as the temperatures rise up, or the thickness goes down. Basically, if I take a gold nanowire with a certain thickness we have a certain

temperature after which will start to ripe and transform in a series of nanosphere with a certain spacial ordering given by λ . Also, the ripening temperature goes down as the thickness goes down having that a copper nanowire with 30 nm in diameter will be completely formed by spheres at 400 °C but a 40 nm one not.

3

Phase transformations

3.1 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 3.1.1: 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 3.1.1: 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

$$\delta G_u = n[G(\xi_2) - G(\xi_1)] \approx nG'(\xi_1)\delta\xi, \quad (3.1)$$

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

$$\delta G_u = (N - n)G(\xi_1) + nG(\xi_2) - NG(\xi_1) = n[G(\xi_2) - G(\xi_1)]. \quad (3.2)$$

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

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 3.1.2: 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

$$\delta G_c = n\{G(\xi_2) - [G(\xi_1) + G'(\xi_1)(\xi_2 - \xi_1)]\} \approx \frac{n}{2}G''(\xi_1)\delta\xi^2, \quad (3.3)$$

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

$$(N - n)(\xi_1 + \Delta) + n\xi_1 = N\xi_1, \quad (3.4)$$

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

$$\delta G_c = (N - n)G(\xi_1 + \Delta) + nG(\xi_2) - NG(\xi_1) \approx (N - n)[G(\xi_1) + G'(\xi_1)\Delta] + nG(\xi_2) - NG(\xi_1), \quad (3.5)$$

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. \smile

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

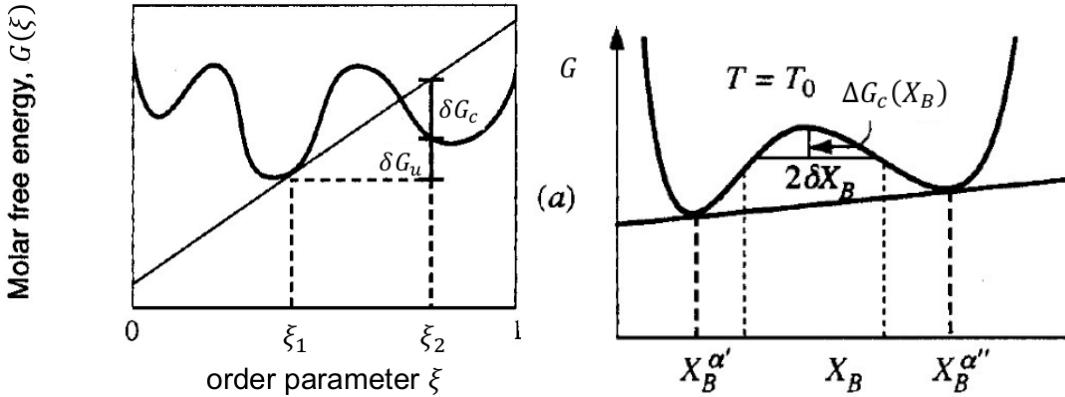


Figure 3.1: Representation of a free energy landscape depending on order parameters with the opportune variations on the left, and a representation of a $G(X)$ with the spinodal points in evidence on the right.

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. (3.3) in the situation depicted on Fig. (3.1), 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 $N_v(t)$, where N_v is the number of cluster possessing v 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 v components. We can assume that inside a matrix in state α and

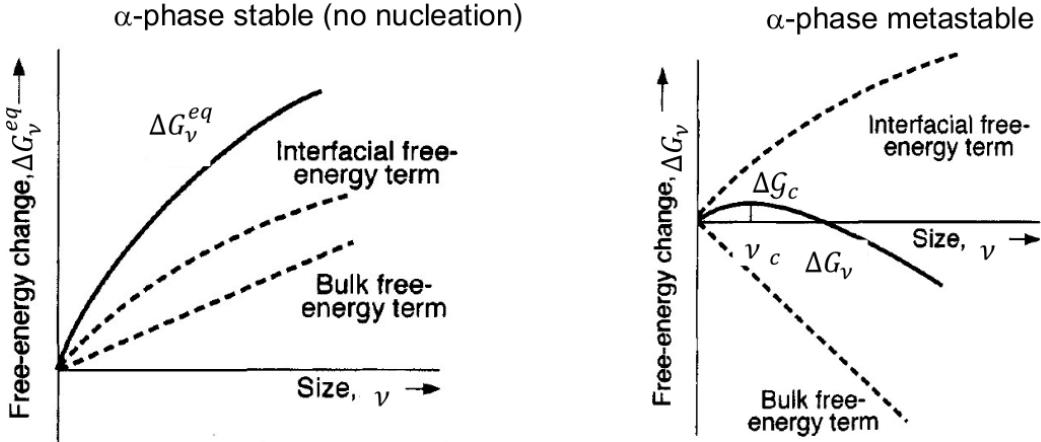


Figure 3.2: Graph of the variation of free energy due to nucleation as a function of cluster size, in particular on the left there's the case where the chemical potential of the α matrix phase is more favorable than the one of the β grain phase, and on the right the opposite.

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

$$\Delta G_\nu = \nu (\mu^\beta - \mu^\alpha) + \eta \nu^{2/3} \gamma. \quad (3.6)$$

It's form can be seen in Fig. (3.2), 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

$$\frac{d\Delta G_\nu}{d\nu} \Big|_{\nu=\nu_c} = 0, \quad \nu_c = - \left(\frac{2\eta\gamma}{3(\mu^\beta - \mu^\alpha)} \right)^{3/2}. \quad (3.7)$$

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

$$J_\nu(t) = \beta_\nu N_\nu(t) - \alpha_{\nu+1} N_{\nu+1}(t). \quad (3.8)$$

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.

Theorem 3.1.3: 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

$$N_v^{eq} = N \exp\left(-\frac{\Delta G_v}{k_B T}\right), \quad (3.9)$$

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_ν and β_ν defined earlier. In fact, we can say that at equilibrium $J_\nu = 0$ for every value of ν and so the following is true

$$\beta_{\nu+1} = \beta_\nu \frac{N_\nu}{N_{\nu+1}} = \beta_\nu \exp\left(-\frac{\Delta G_{\nu+1} - \Delta G_\nu}{k_B T}\right). \quad (3.10)$$

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 $Z_\nu(t)$, in particular focussing on the form of J_ν still defined as before in a steady state situation.

Theorem 3.1.4: 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

$$J = N \beta_c \sqrt{\frac{\Delta G_c}{3\pi k_B T v_c^2}} \exp\left(-\frac{\Delta G_c}{k_B T}\right), \quad (3.11)$$

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. (3.10) to be valid also in this particular case¹. This allows us to write down that

$$J_\nu = \beta_\nu Z_\nu - \alpha_{\nu+1} Z_{\nu+1} = \beta_\nu N_\nu^{eq} \left(\frac{Z_\nu}{N_\nu^{eq}} - \frac{Z_{\nu+1}}{N_{\nu+1}^{eq}} \right), \quad (3.12)$$

then we can recall that in a steady-state situation we have $J_\nu = J_\omega$ for every ν and ω , so that $J_\nu = J$. Then we will also assume that for small ν also in Z_ν 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

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

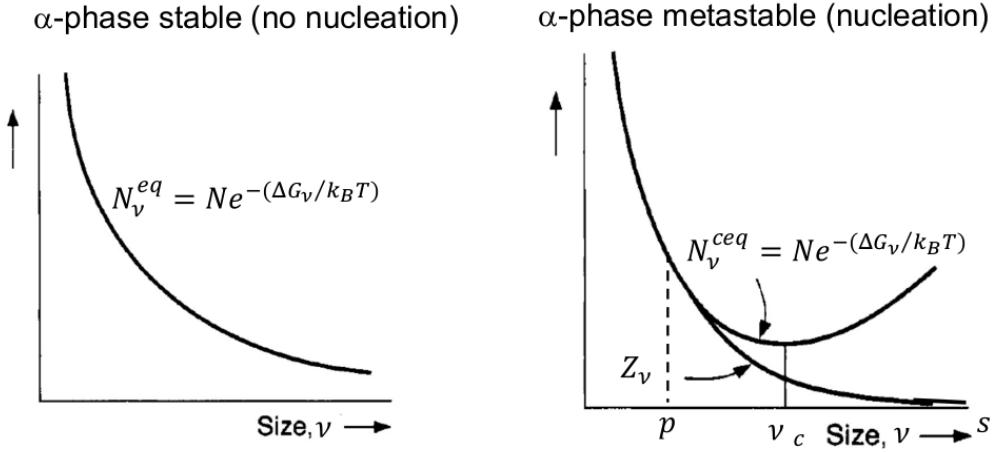


Figure 3.3: Plot of the equilibrium and non equilibrium distribution in the two cases where α is stable and metastable in order to guide better the demonstration of the results.

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

$$Z_v = \begin{cases} N_v & v \leq p < v_c \\ 0 & v \geq s > v_c \end{cases}. \quad (3.13)$$

Where p and s are integer values chosen in order for Z_v to fit better to the equilibrium distribution as in Fig. (3.3). In this situation we can write down the following thing

$$\frac{J}{\beta_v N_v} = \left(\frac{Z_v}{N_v^{eq}} - \frac{Z_{v+1}}{N_{v+1}^{eq}} \right), \quad (3.14)$$

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

$$\sum_{v=p}^s \frac{J}{\beta_v N_v} = \frac{Z_p}{N_p} - \frac{Z_{s+1}}{N_{s+1}} = 1, \quad (3.15)$$

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

$$J = \left[\sum_{v=p}^s \frac{1}{\beta_v N_v} \right]^{-1} \approx \left[\frac{1}{\beta_c N} \sum_{v=p}^s e^{\Delta G_v/k_B T} \right]^{-1}. \quad (3.16)$$

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

$$\Delta G_v \approx \Delta G_c + \frac{(v - v_c)^2}{2} \left. \frac{\partial^2 \Delta G_v}{\partial v^2} \right|_{v=v_c} \quad \left. \frac{\partial^2 \Delta G_v}{\partial v^2} \right|_{v=v_c} = -\frac{2}{9} \eta \gamma v_c^{-4/3} = -\frac{2}{3} \frac{\Delta G_c}{v_c^2}. \quad (3.17)$$

Then we can simply insert inside the summation and integrate as

$$\sum_{v=p}^s e^{\Delta G_v/k_B T} \approx e^{\Delta G_c/k_B T} \int_p^s dv \exp \left(-\frac{2}{3} \frac{\Delta G_c}{v_c^2 k_B T} \frac{(v - v_c)^2}{2} \right) \approx e^{\Delta G_c/k_B T} \sqrt{\frac{3\pi k_B T v_c^2}{\Delta G_c}}, \quad (3.18)$$

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_v 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. (3.11) 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 $\gamma \approx 0.5 \text{ Jm}^{-2}$, 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 $J \approx 1 \text{ cm}^{-3}\text{s}^{-1}$ along with $\beta_c \approx 10^{12}$ and a Zeldovich factor of 0.1 to find $\Delta G_c \approx 76k_B T$;
- [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_e 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 3.1.1 (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 K and quenched to 800 K has a β -phase nucleation rate of $10^6 \text{ m}^{-3}\text{s}^{-1}$. We want to increase the density of B atoms in order to bring the flux at $10^{21} \text{ m}^{-3}\text{s}^{-1}$ knowing that

$$\Delta g_B = [-100(X_B - 0.3) - 9]10^7 \text{ Jm}^{-3}, \quad \gamma = 75 \text{ Jm}^{-2}. \quad (3.19)$$

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

equation

$$\Delta G = \frac{4\pi}{3} r^3 \Delta g_B + 4\pi r^2 \gamma, \quad (3.20)$$

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

$$r_c = -2 \frac{\gamma}{\Delta g_B}, \quad \Delta G_c = \frac{16\pi}{3} \frac{\gamma^3}{\Delta g_B^2}. \quad (3.21)$$

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 prefers 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 possesses 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. (3.4) with the angle given by a known result.

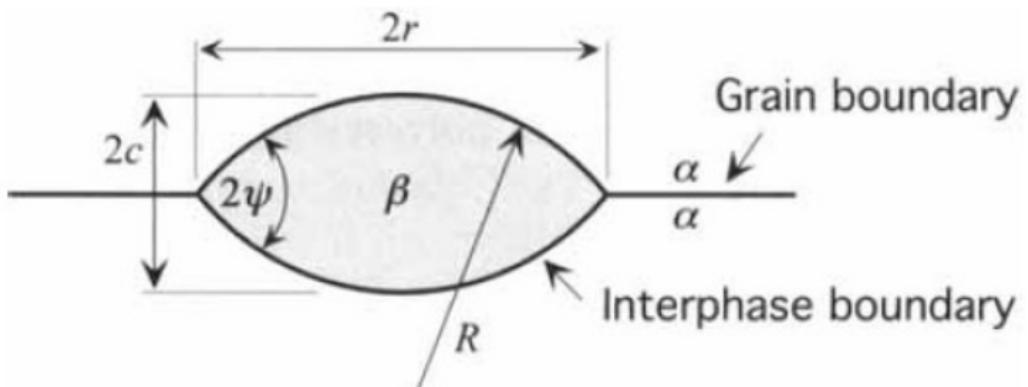


Figure 3.4: Representation of a heterogeneous nucleation in the solid-solid interface, important to see how the cluster formed takes the shape of a lens with an angle that depends on the surface tensions.

Theorem 3.1.5: 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

$$\gamma^{\alpha\alpha} = \gamma^{\alpha\beta} \cos \psi. \quad (3.22)$$

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 3.1.6: 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

$$\Delta G^{GB} = \left(\frac{2\pi R}{3} \Delta g_B + 2\pi R^2 \gamma^{\alpha\beta} \right) (2 - 3 \cos \psi + \cos^3 \psi). \quad (3.23)$$

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

$$V = \frac{2\pi R}{3} (2 - 3 \cos \psi + \cos^3 \psi), \quad A = 4\pi R^2 (1 - \cos \psi), \quad (3.24)$$

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

$$\Delta G^{GB} = V \Delta g_B + A \gamma^{\alpha\beta} - \pi r^2 \gamma^{\alpha\alpha}, \quad (3.25)$$

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

$$\frac{\Delta G_c^{GB}}{\Delta G_c^H} = \frac{1}{2} (2 - 3 \cos \psi + \cos^3 \psi), \quad (3.26)$$

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

$$n^{GB} = n \frac{\delta}{D} \quad J^H = \frac{n^{GB}}{n} \exp \left[-\frac{\Delta G_c^{GB} - \Delta G_c^H}{k_B T} \right], \quad (3.27)$$

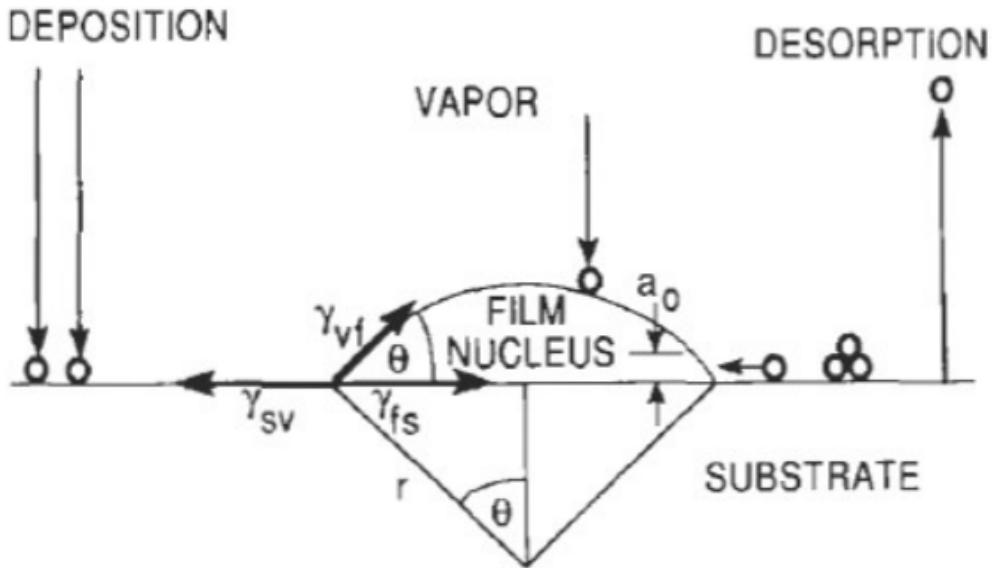


Figure 3.5: Representation of the nucleation on a solid-gas interface showing how the cluster formed is elongated due to surface effect generating a more uniform film.

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. (3.5), 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 3.1.7: 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

$$\gamma^{sv} = \gamma^{fs} + \gamma^{vf} \cos \theta. \quad (3.28)$$

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 3.1.8: 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

system takes the form

$$\Delta G_c = \frac{16\pi\gamma_{vf}^3}{3\Delta g_B^2} \frac{2 - 3\cos\theta + \cos^3\theta}{4}. \quad (3.29)$$

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

$$\Delta G = \pi(2 - 3\cos\theta + \cos^3\theta) \left(\frac{r^3\Delta g_B}{3} + r^2\gamma^{vf} \right), \quad (3.30)$$

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

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.

3.2 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. (3.6), where the material starts from an ordered

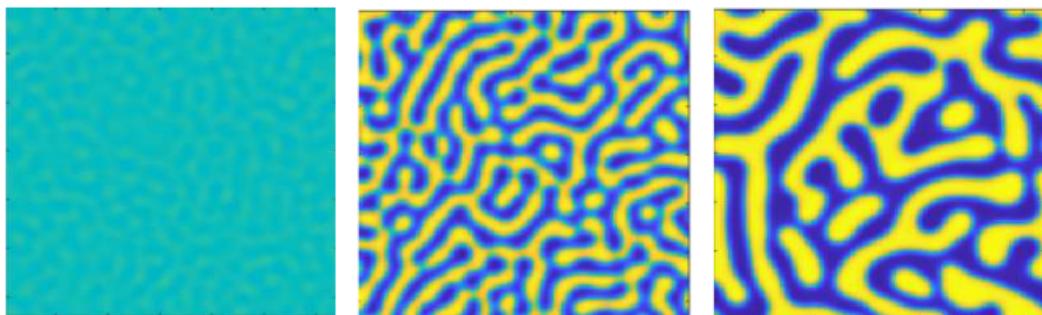


Figure 3.6: Result of a simulation to represent a phase transition in a binary alloy showing in different colors different densities that can be interpreted as the order parameter of the system.

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 its gradient, allowing us to write down a Taylor expansion of it near the value of $\nabla\xi = 0$

$$f(\xi, \nabla\xi) = f^{hom}(\xi) + \frac{\partial f^{hom}}{\partial \nabla\xi} \cdot \nabla\xi + \frac{\partial^2 f^{hom}}{\partial \nabla\xi^2} \nabla\xi \cdot \nabla\xi. \quad (3.31)$$

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

$$f(\xi, \nabla\xi) = f^{hom}(\xi) + K \nabla\xi^2. \quad (3.32)$$

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. (3.32) 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 3.2.1: Interface properties

Inside a continuous phase transformation where the local free energy can be written as in Eq. (3.32) the width of the domain interfaces and the surface free energy are given by

$$\delta = \sqrt{\frac{K}{\langle f^{hom} \rangle}}, \quad \gamma = 2\sqrt{K \langle f^{hom} \rangle}. \quad (3.33)$$

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

$$F = \int_V \left[f^{hom}(\xi) + K \left(\frac{d\xi}{dx} \right)^2 \right] dV, \quad (3.34)$$

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 multiplying and dividing for $A\delta$, where A is the area of the interface and δ the width

$$F = A\delta \left[\langle f^{hom} \rangle + K \left\langle \left(\frac{d\xi}{dx} \right)^2 \right\rangle \right]. \quad (3.35)$$

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

$$F \approx A \left[\langle f^{hom} \rangle \delta + \frac{K}{\delta} \right]. \quad (3.36)$$

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.

Now that we know how the interfaces and the free energy look like we can focus on the dynamics of the system. In particular, is possible by working on the total free energy of the system to define a particular quantity that help us to study the evolution of a general order parameter.

Theorem 3.2.2: Generalized diffusion potential

Inside a continuous phase transformation where the local free energy can be written as in Eq. (3.32) a generalized chemical potential can be defined describing the local evolution of the order parameter

$$\Phi(\mathbf{r}) = \frac{\partial f^{hom}}{\partial \xi} - 2K\nabla^2 \xi. \quad (3.37)$$

Proof: We can write down the total free energy of the system as in Eq. (3.34) and then try to minimize it by taking its functional derivative. Therefore, we can set $\xi \rightarrow \xi + d\xi$ to find out the following form for the variation

$$\delta F = \int_V \left[\frac{\partial f^{hom}}{\partial \xi} \delta \xi + 2K \nabla \xi \cdot \nabla (\delta \xi) \right], \quad (3.38)$$

then we can use the vector identity $\nabla \xi \cdot \nabla(\delta \xi) = \nabla \cdot (\delta \xi \nabla \xi) - \delta \xi \nabla^2 \xi$ alongside Gauss theorem to have

$$\delta F = \int_V \left[\frac{\partial f^{hom}}{\partial \xi} - 2K \nabla^2 \xi \right] \delta \xi dV - \int_{\partial V} \delta \xi \nabla \xi \cdot d\mathbf{A}. \quad (3.39)$$

The integral over the area gives no contribution in the thermodynamic limit since the volume to area ratio becomes so large that the volume part is the only one that matters. Now, the form obtained show a way to evaluate the variation of free energy inside a material by integrating the local change of energy due to a small $\delta \xi$ variation of the order parameter, and that defines exactly the generalized diffusion potential

$$\delta F = \int_V \left[\frac{\partial f^{hom}}{\partial \xi} - 2K \nabla^2 \xi \right] \delta \xi dV = \delta F = \int_V \Phi(\mathbf{r}) \delta \xi dV. \quad (3.40)$$

(3.40)

The form of Φ tells us how the parameter will change locally since if the potential is positive then the parameter will tend to lower its value, while if its negative will increase. Generalized potential is so really powerful in the study of evolution of phase transitions, but still it's not the full story. We can have a better insight on the dynamic by modelling the flux of the system in the case where ξ is a conserved parameter like concentration of B type atoms c_B . In that case a really important result can be obtained as follows.

Theorem 3.2.3: Cahn-Hilliard equation

Taking a binary system we can study the evolution of the concentration of B atoms by treating it as a conserved order parameter so that it's evolution is given by the following differential equation

$$\frac{\partial c_B}{\partial t} = \tilde{D} \left[\nabla^2 c_B - \frac{2K}{f''} \nabla^4 c_B \right], \quad (3.41)$$

where f'' defines the second derivative of f^{hom} respect to the order parameter.

Proof: We can write down the flux of density by using the generalized potential $\Phi(\mathbf{r})$ as driving force, so that the following relation holds true

$$\mathbf{J} = -M \nabla \Phi, \quad \frac{\partial c_B}{\partial t} = -\nabla \mathbf{J}, \quad (3.42)$$

where the second condition holds since c_B is conserved. Then, it's possible to demonstrate that the mobility M is related to the interdiffusivity by the following relation

$$M = \frac{\tilde{D}}{\frac{\partial^2 f^{hom}}{\partial c_B^2}} = \frac{\tilde{D}}{f''}, \quad (3.43)$$

which shows how since M is always positive if the system is unstable, meaning $f'' < 0$ in the spinodal regime, then the interdiffusivity is negative. A negative diffusivity means that the flux will be created in order to increase the gradient of concentration instead of bringing it down, generating the domains as we predicted. We can so bring all together in order to write down

$$\frac{\partial c_B}{\partial t} = \nabla \cdot \{ M \nabla [\nabla^2 c_B - 2K \nabla^4 c_B] \}, \quad (3.44)$$

where we can assume that M does not change much in space allowing us to substitute it with a space average $M_0 = \langle M \rangle$ that can be substituted with $M_0 = \tilde{D}/f''$ having the final result. \heartsuit

Now, this is something interesting, we have a partial differential equation that can be used in order to predict the evolution of the system density over time that contains the effect given by the generation of interfaces. In fact, if we bring the interface term to zero, $K = 0$, the equation return to be exactly the diffusion one that we have seen when talking about evolution of concentration in material. The second term adds a lot of information to the model allowing it to evolve through a phase transition if the system finds himself unstable generating domains with different order parameters. To see how this is the case we can simply look at the evolution of a concentration in 1D that posses a perturbation inside it and see how perturbation evolves. We will imagine that a general uniform concentration $c_B = (c_B^\alpha + c_B^\beta)/2$ is perturbed by a sine wave

$$c_B(x, t) = c_B + \varepsilon(t) \sin(kx), \quad (3.45)$$

meaning that the uniform distribution will possess a series of domains with concentrations $c_B - \varepsilon$ and $c_B + \varepsilon$ separated by a distance given by the wavelength $\lambda = 2\pi/k$. If we insert such a solution inside the Cahn-Hilliard equation we can write down a differential equation for ε that gives out the following result

$$\frac{d\varepsilon}{dt} = -\tilde{D} \left(k^2 + \frac{2Kk^4}{f''} \right) \varepsilon, \quad \varepsilon(t) = \varepsilon(0) \exp \left[-\tilde{D} \left(k^2 + \frac{2Kk^4}{f''} \right) t \right]. \quad (3.46)$$

Where we can see how the perturbation will grow over time only if the term at the exponential is positive and that can be possible only if f'' is negative so that also $\tilde{D} < 0$. In such a situation the system is unstable and a small perturbation can grow exponentially over time. Also, one can see how the evolution depends also on the value of k , having that have a critical value $k_c = \sqrt{-f''/2K}$ over which the exponential return negative. This means that only perturbation, and so domains, with spatial width $\lambda < 2\pi/k_c$ are possible inside the material, and in particular the one with $k = k/\sqrt{2}$ will be the most present since that is the value of wave vector that maximize the exponent.

This Fourier analysis allowed us to see how a system becomes unstable as quick as the second derivative of the free energy becomes negative. So that the system finds itself in the spinodal area and the decomposition of the system in stable domains goes quickly with domain sizes growing exponentially in time, starting by a situation where the system is all homogeneous to then form a lot of small islands surrounded by interface domains to then generate grains with different spatial extent. This phenomenon is therefore known as **spinodal decomposition** since happens in the spinodal region of the phase space, and as the system cross the spinodal points having $f'' > 0$ it stops leaving its place to discontinuous processes.

As a last remark we have discussed the effect of strain inside such a model. Basically, we shall also include the fact that atoms are bounded one to another in a way that generating interfaces creates also a strain in the material. This increase the free energy of the system by a term that we can define as follows

$$F^{el} = \alpha_c^2 Y \int_V (c_B - c_0)^2 dV, \quad (3.47)$$

which uses a harmonic approximation approach and α_c is called Vegard's parameter computed as $a^{-1}da/dc$, quantifying the deformation due to concentration variation, and Y is the Young modulus orientation-dependent elastic parameter. If we account for this term inside Eq. (3.34) and still minimize as we did before the Cahn-Hilliard equation will have an added term as

$$\frac{\partial c_B}{\partial t} = \tilde{D} \left[\left(1 + \frac{2\alpha_c^2 Y}{f''} \right) \nabla^2 c_B - \frac{2K}{f''} \nabla^4 c_B \right]. \quad (3.48)$$

That is interesting since it is telling us that the strain inside the material is making it more stable, setting the condition in order to have a positive exponent and make the perturbations grow exponentially from $f'' < 0$ to

$$f'' < -2\alpha_c^2 Y. \quad (3.49)$$

This is interesting, not only because influences generally the growth of domain, but because Y depends on the crystallographic direction and so such a condition can change depending on where the interface is created. In this way we can have an **isotropic pattern** for the phase transformation, happening when α_c is small or Y is nearly isotropic, or an **anisotropic pattern**, arising for large α_c and strongly anisotropic Young moduli.

Note

It's interesting to see how the role of interfaces inside such a phenomenon is really important and can't be neglected because in the first part of the transformation, when the domains start to form, the system is basically only composed by interfaces. For this reason we need to be able to account them in the model, without that term we will miss the whole physics of the material.

Allen-Chan equation

Another interesting situation is the case where the order parameter that is changing inside the phase transformation is not a conserved one. For example, take the long range order parameter $\eta(\mathbf{r}, t)$ and imagine that the phase transition affect a transformation that brings material from an order state to a disordered one creating an **order-disorder transformation**. Such transformation can be modelled in an analogous way to the precedent ones, having that the order parameter will evolve using the following result.

Theorem 3.2.4: Allen-Chan equation

The time evolution of a non conserved order parameter inside a material can be described using the following partial differential equation

$$\frac{\partial \eta}{\partial t} = -M_\eta \left\{ \frac{\partial f^{hom}}{\partial \eta} - 2K_\eta \nabla^2 \eta \right\}, \quad (3.50)$$

where M_η and K_η are the same constant as in the previous case.

Proof: Such a demonstration is trivial since the only difference respect to the conserved parameter case is that no continuity equation is present. That mean how the following relation is true

$$\frac{\partial \eta}{\partial t} = -M_\eta \Phi(\mathbf{r}), \quad (3.51)$$

where we can substitute the definition of the generalized chemical potential to obtain the final result. ☺

As before, we can see how also in this case the system is unstable to certain types of perturbations. In particular if we take as perturbation the same form as before, in a 1D model, and make an assumption on the free energy

$$\eta(x, t) = \varepsilon(t) \sin(kx), \quad f^{hom} = f_0^{hom} \left(\frac{1}{4} - \eta^2 \right)^2, \quad (3.52)$$

we can see how inserting it inside Eq. (3.50) giving out

$$\frac{d\varepsilon}{dt} = M_\eta(f_0^{hom} - 2K_\eta k^2)\varepsilon(t). \quad (3.53)$$

The same equation obtained in Eq. (3.46) having so a result that has an exponential form and is unstable if the coefficient $f_0^{hom} - 2K_\eta k^2$ is positive. Therefore, we can see how in this case we have that the coefficient is higher as k is smaller, having a maximum at 0, showing no preferential wavelength that will grow faster than the other. Instead, we can see how a critical wavelength is still present at $k = \sqrt{f_0^{hom}/2K_\eta}$ meaning how during the phase transition ordered structure that are small will disappear leaving space for the larger ones that will grow in order exponentially.

4

Electrochemical Energy Conversion

4.1 Introduction to electrochemistry

In this part of the course we want to put into practice the concepts obtained during the theoretical study of the kinetic inside a material and understand how to use it in practice. Our main focus will be the creation and conservation of energy inside batteries or, as chemists call them, **electrochemical cells**. Therefore, we will start with a simple introduction to the main concepts needed in this study.

The concept behind a battery is trivial in some sense, basically only three things needs to be present to have a working device: two or more electrodes, an electrolyte, and an external circuit. The idea is the one of using redox reactions between the electrodes, usually composed by metals or semiconductors, to make electron travel inside the circuit. In practice, let's imagine using two bars of Zn and Cu as electrodes putted inside a liquid, the two of them can give rise to a total cell reaction where electrons travel from Zinc to Copper as follows



where the subscripts tell the phase in which the atom is present. Basically, what is happening is that two different reactions are performed inside the system: one where the Zinc loses two electrons giving rise to the positive ion, and one where ionic Copper takes those two electrons. Therefore, the former is an **oxidation** reaction, while the latter is a **reduction** one, generating a distinction to keep in mind.

Definition 4.1.1: Oxidation-Reduction

Inside an electrochemical cell the element is reducing if is gaining electrons in the process, while is oxidizing if is loosing electrons.

Also, during the course we will call the element that undergo oxidation as **anode**, while the one reducing will be the **cathode**. Still, the aim of our device is creating this reaction and using the electrons that are generated in the process. So that the point is, we connect the anode and cathode with a circuit, so that electrons will start to spontaneously flow from one to the other generating the following semi-reactions



This process will so generate a current in the circuit, meaning that a voltage, called **cell potential**, is present between the two electrodes giving us energy that we can use. That is all great but as the reaction

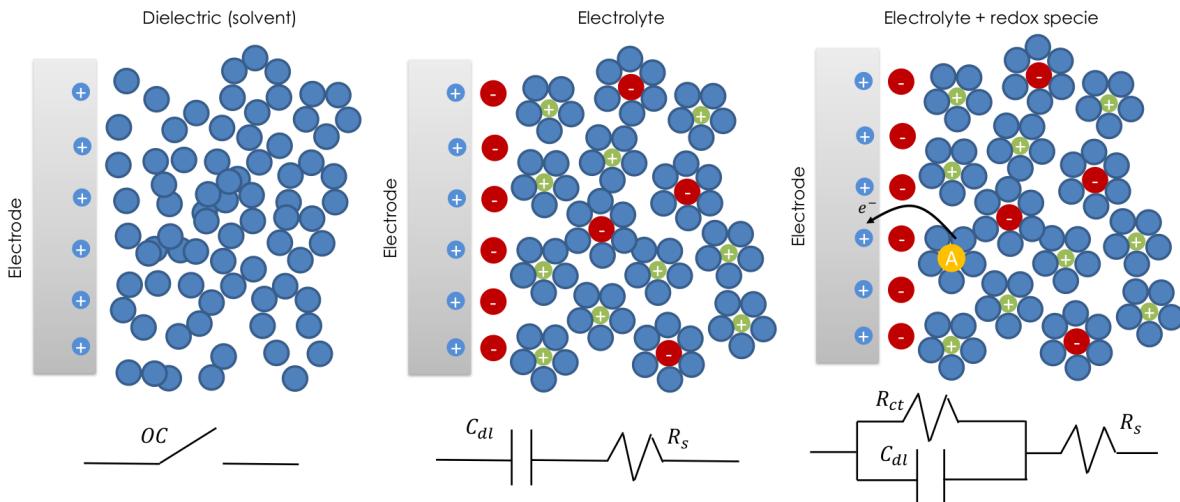


Figure 4.1: Graphical explanation of how an electrolyte works in practice, showing how the presence of ions inside it allows for the charge to move in the solution making species travel from anion to cathode making the reaction continue. Also, every step can be represented as a different circuit.

goes on the density of Zn^{2+} around the anode will reach saturation slowing down the reaction, a problem that can be easily eliminated by using the electrolyte. In fact, as we can see in Fig. (4.1), the electrolyte has the task of letting the ions generated move inside the system. For example, if a salt is present in the solution, the latter will split generating positive and negative ions which will travel to the cathode and anode respectively. That will give rise to a system that looks like a capacity, where the ions move as long as the charge around the electrodes is not compensated, but if inside the electrolyte we place also the redox species, Cu^{2+} , they will not only move to the electrodes but will react with those keeping the reaction going. For this reason the choice of the electrolyte is really important, since the diffusion properties of ions inside it will be key to the output power that we can have.

The final result that we obtain by this construction is a device that is able to generate a voltage and a current density inside the circuit attached to it. Still, the voltage and the current generated are not really as we might expect them to be. Usually, current and potential are linearly related via Hom's law, but here the relation between current density and cell potential is not, showing also the equilibrium point with no current $\mathbf{J} = 0$ at $\Delta V \neq 0$, as we can see in Fig. (4.2). Such a peculiar behavior can be described by the fact that simply the potential generated by the cell is not simply given by electrostatic interactions but a complex series of interfaces and chemical phenomena enters to play arising two questions: how to define the potential in electrochemistry, and what properties are affecting the current-potential characteristic? Both of the questions will be answered during this last part of the course, but we will try to give a simple explanation for the second one right now.

First, we should consider how inside the I-V characteristic showed in Fig. (4.2) the current density increase suddenly to then reach a plateau. That is our range to work with it, basically having a constant supply of current is exactly what we want from a battery, also if we would to go further the current will start to grow exponentially. That is due to reaching a value of the potential in the cell that is able to generate redox also inside the electrolyte oxidizing it, and is something that we want to avoid. Therefore, we will focus on the first part of the curve in the first quadrant, as showed in the figure on the right of Fig. (4.2). Inside that window we can identify two main regions to work with:

Non-Faradic. The first part where no current is present since the charge is accumulating near the electrodes as a capacitor charging. Possible presence of small capacitive current;

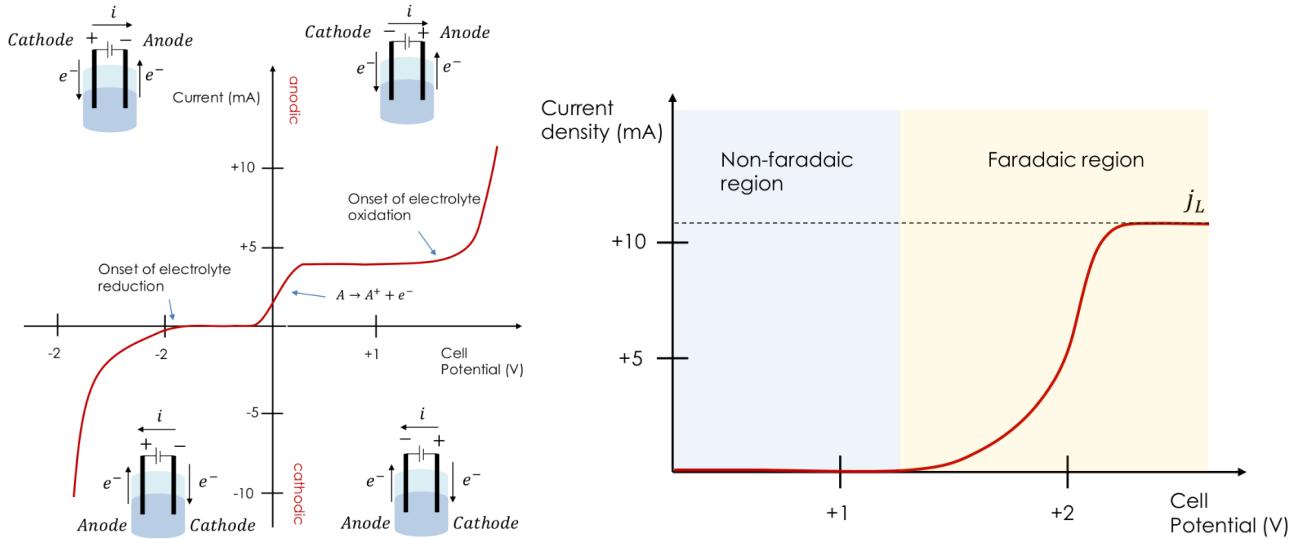


Figure 4.2: Graphics of the characteristic of a general electrochemical cell, with a close up on the first, and most important, quadrant. In the first quadrant we can see how the current will reach a plateau in the last part, that is due to the presence of diffusion inside the system that limits the speed at which the electrons can be emitted.

Faradic. The current becomes proportional to the reaction rate and starts to grow rapidly.

The latter region is the interesting one, and we can see how the first part, called **activation control**, shows an exponential growth of the current since the reaction starts and the electrons are generated with speeds proportional to the potential. Meaning that in this region a lot of factors, like: catalytic properties of the surface, area, adsorption, and concentration of species, are all important to the determination of the power supplied. Then, a rapid growth happens, and the constant current is reached in a situation called **mass-transport control**. The latter is a region of the graph where J is dictated by the velocity of diffusion inside the electrolyte, since the electrons goes much faster than the ionic species needed to make the reactions the numbers of electrons per unit time that pass through the circuit is limited by the flux of ions. Therefore, the current in the two regions can be described by

$$J_{ac} = nFk_{ct}c_x, \quad J_{mt} = nFDc_b, \quad (4.3)$$

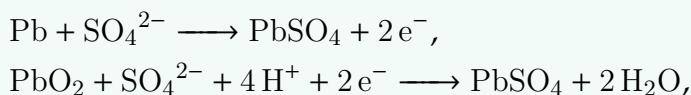
where F is the charge inside one mole of electrons, and n the moles generated. Then, also the region in between, called **Mixed control** can be easily described using these two results since it's a mixture of the two often approximated with

$$\frac{1}{J} = \frac{1}{J_{ac}} + \frac{1}{J_{mt}}. \quad (4.4)$$

In this way we can understand how the choice of the electrolyte is really important, since its diffusion properties will determine the current density generated in the electrochemical window of the device.

Example 4.1.1 (Lead-Acid Battery)

A good example of battery that we can look at just a moment is the Pb one, where the anode and cathode are created by bars of pure Pb and PbO_2 with an acid electrolyte. The reaction that happens inside the system are



Then, imagine that we use the battery for an hour at a constant current of 20 A, we can compute the amount of lead needed to sustain such power supply. The charge that is transported is $Q = It$, where we know both of them having that 72 000 C is effectively transported from anode to cathode, meaning $n_e = Q/F = 0.746$ mol. Therefore, we can compute the moles of lead needed to generate such amount of electrons by using the first semi-reaction and see how

$$n_{Pb} = n_e/2 = 0.373 \text{ mol} = 154.5 \text{ g},$$

not a small amount due to the high weight of lead. For that reason the Lithium batteries seems better, Li is lighter needing less weight for the same amount of power.

Note

The most used types of electrolytes are liquid where salt is inserted in order to generate ions that can freely move inside. In this way a high mobility is achieved, but a large research is present in this field, especially to create efficient solid state electrolytes with high enough diffusivity to work nicely and also reduce the problematics related to using liquids, such as safety due to flammability. By now some solid state devices are used but since D increase with temperature are mainly used for particular application where we need to work in hot systems.

Thermodynamics of an electrochemical cell

After this long introduction we can try to dig in the thermodynamics of the system and try to set up the basis for the discussion of specific devices. The first thing that we need to define is the concept of reversibility, which in electrochemistry is slightly different from the one we expect. The idea is that when performing an electrochemical reaction we can evaluate the value of the voltage between electrodes in the equilibrium state V_0 and then, if the reaction is **reversible**, we are able to promote either the forward and reverse reaction by applying a positive or negative bias to the system. In this sense we can give a really simple and general definition for the reversibility of a reaction as follows.

Definition 4.1.2: Microscopic reversibility

Infinitesimal change in a driving force causes the reaction to reverse direction.

This definition is intrinsically different from the real thermodynamic definition of reversible, but we can see how they are related somehow. In particular, a chemical reaction that is irreversible in this sense is also thermodynamically irreversible, but if it is reversible is not sad to be reversible in the real sense. Still, in general all of this is thought in terms of reaction rates for reversible reactions, having that if the rate of advancing K_a and going back k_b are nearly equal is reversible, if instead $k_a \gg k_b$ than is irreversible. Basically, you only need to think in terms of k in a reaction to say if it is reversible or not.

Knowing that we can start by thinking about the main quantities that will play a role inside the thermodynamic of the system, and since I would not like to stay here and describe one by one a series of tedious definition I will report the table given in the slides in Tab. (4.1). With the latter we can go into the thermodynamic of the system and see how the flux that defines the direction of the reaction looks like in this context. Let's take the chemical potential of component i to write down the following

Table 4.1: Table with definition of all the types of variables we are going to use in this study and so on.

Term	Symbol	Unit	Definition	Use
Electrochemical potential	$\bar{\mu}_j^\alpha$	J/mol	partial molar Gibbs free energy of a given species j in phase α	defines criteria for equilibrium; differences in $\bar{\mu}_j^\alpha$ drive the transport, transfer, and reactivity of both charged and uncharged species
chemical potential	μ_j^α	J/mol	partial molar free energy of a given species j in phase α neglecting electrostatic contributions	differences in μ_j^α describe driving force for reactions between uncharged species and the direction of diffusive transport
electric potential	ϕ	V	electric work needed to move a test charge to a specific point in space from a reference point (often at infinite distance) divided by the value of the charge	defines direction of electron transport in metals; gradient gives electric field; used to calculate electric potential energy
electrode potential	E_{we}	V	free-energy change divided by the electron charge associated with moving an electron (and any associated ion/solvent movement/rearrangement) from a reference state (often a reference electrode) to the working electrode	indicates oxidizing or reducing power of an electrode; related to the Fermi level of electrons in electrode
solution potential	E_{sol}	V	free-energy change divided by the electron charge associated with moving an electron (and any associated ion/solvent movement/rearrangement) from a reference state (often a reference electrode) into the bulk of a solution via a redox reaction	indicates oxidizing or reducing power of electrons involved in electrochemical redox equilibria; related to "Fermi level" of the electrons in solution and equivalent to the solution reduction potential
overpotential	η	V	generally, the difference between the applied electrode potential and the electrode potential when in equilibrium with the target electrochemical reaction	$\eta \cdot F$ gives the heat released, above that required by thermodynamics, per mole of electrons to drive an electrochemical process at a given rate; $F = 96485 \text{ C} \cdot \text{mol}^{-1}$

relation as the flux of that component

$$\mathbf{J}_i = - \left(\frac{c_i D_i}{RT} \right) \nabla \mu_i, \quad (4.5)$$

where the chemical potential of a specie in solution will be defined as

$$\mu_i = \frac{\partial G}{\partial n_i} = \mu_i^0 + RT \ln(a_i), \quad a_i = \gamma_i(c) c_i. \quad (4.6)$$

Basically, the potential the same as we have already seen, with the activity coefficient present. Still, this definition does not take into account the electrostatic effect presents, that we can insert by using the potential per mole in phase α called ϕ^α .

Definition 4.1.3: Electrochemical potential

The chemical potential of the i -th component of an electrochemical system needs to take into account also the electric potential per mole in the phase α in which is present, ϕ^α , giving

$$\bar{\mu} = \mu_i + z_i F \phi^\alpha, \quad (4.7)$$

where z_i is the charge number on the specie we are looking at.

That is the real potential we are going to use, so that the condition on the equilibrium of the system is given in terms of $\bar{\mu}$ and not simple μ . For this reason even if all the electrochemical potential of the species are equal still we can have differences in electrical potential, generating potential differences even at equilibrium called cell potential. Also, it's interesting to see how inside the definition of Eq. (4.7) we have how the chemical potential describe the short-range interactions while the electrical part counts for the long range since

$$\mu_i \propto r^{-6}, \quad z_i F \phi^\alpha \propto r^{-1}. \quad (4.8)$$

Therefore, we can have one component that wins on the other in specific situations, but still the two are strictly related. In particular, the real measurable quantity is $\bar{\mu}$ it's not possible to evaluate μ or ϕ separately since the measure of a potential always imply the creation of an interface during the measurement having both in the final result.

The new definition of $\bar{\mu}$ can be put at use in a really simple way. For example, we can imagine taking a metal and apply a potential on it so that the electrochemical potential difference of the electron in two different positions of the material becomes

$$\Delta\bar{\mu}_e = \bar{\mu}_e^\alpha - \bar{\mu}_e^\beta = \mu_e^\alpha - zF\phi^\alpha - \mu_e^\beta + zF\phi^\beta = -zF\Delta\phi. \quad (4.9)$$

Where we assumed that the chemical potential of the single electron remained equal inside the metal. Using this result we can see how the flux of electron can be written as

$$\mathbf{J}_e = -\left(\frac{c_e D_e}{RT}\right) \nabla \bar{\mu}_e = zF \left(\frac{c_e D_e}{RT}\right) \nabla \phi = R \nabla \phi, \quad (4.10)$$

the Hom's law was simply found. Still, this is only a trivial application what we want to do is studying what happens when two metals touching each others in equilibrium. Where we can easily see how the following becomes true.

Theorem 4.1.1: Interface potential

When two metals M_1 and M_2 are in contact with each others a potential difference appear at equilibrium in the interface of the two solid phases given by

$$\Delta\phi^{M_1-M_2} = \frac{\Delta\mu_e^{M_1-M_2}}{zF}. \quad (4.11)$$

Proof: That is incredibly easy, you only need to recall how the equilibrium condition in this case become $\bar{\mu}_e^{M_1} = \bar{\mu}_e^{M_2}$ so that you place them equal and obtain the result. ☺

Therefore, using the electrochemical potential is really helpful in the study of how the chemistry of the system mix with its electrical properties. For this reason it's the main quantity that we are going to study inside batteries, and we can predict cells behaviors with that.

Interface at equilibrium

To understand how the electrochemical cell works properly we need first to develop a way to study how solid liquid interface works in general, since the cell is composed by two metal electrodes inside a liquid electrolyte in general. We have already seen what happens with solid-solid interface, but now we aim to look more into the equilibrium of a reduction reaction like



In such an equation we can easily find out the potential difference generated by the transport of electrons at equilibrium by the following important result.

Theorem 4.1.2: Nernst equation

The electrode potential generated by a redox reaction at equilibrium E , depend both on ambient condition and chemical properties of the system through the relation

$$E = E_{O/R}^0 + \frac{RT}{nF} \ln(a_O/a_R), \quad (4.13)$$

where $E_{O/R}^0$ is also called standard electrochemical potential.

Proof: we can start by setting the equilibrium by doing the following operation

$$\Delta\bar{\mu}_e = \bar{\mu}_R^s - (n\mu_e^M + \mu_O^s) = 0, \quad (4.14)$$

where the up scripts s and M tells us if the element is in the electrolyte solution or in the solid component. Then, by using the definition of electrochemical potential and the fact that $z_R = z_O - n$ with $z_e = -1$ we can obtain

$$z_O F(\phi^s - \phi^M) = (\mu_R^s - \mu_O^s) - n\mu_e^M, \quad (4.15)$$

where the contributions from electrostatics, chemistry of the solution and the one of the solid were divided. We can now use the fact that $\mu_i = \mu_i^0 + RT \ln a_i$ to retain the following form

$$-\frac{z_O}{n}(\phi^s - \phi^M) = -\frac{\mu_R^{0,s} - \mu_O^{0,s}}{nF} + \frac{\mu_e^M}{F} + \frac{RT}{nF} \ln(a_O/a_R). \quad (4.16)$$

Here we can finish the job by defining the two main variables in the Nernst equation as follows

$$E = -\frac{z_O}{n}(\phi^s - \phi^M), \quad E_{O/R}^0 = -\frac{\mu_R^{0,s} - \mu_O^{0,s}}{nF} + \frac{\mu_e^M}{F} = -\frac{\Delta G^0}{nF}. \quad (4.17)$$

This also shows how the standard potential is also related to the form of the free energy difference. ☺

That is a powerful result, but still works only at equilibrium and understand when interfaces are at equilibrium may not be so easy. We can generally say that if the charge transfer kinetics is very fast we can be in Nernstian conditions since the superficial activity rapidly equilibrates before mass.

Now, we can imagine to level up and take into account a full cell composed by two electrodes in an electrolyte solution, so that two redox happens one for M_1 and one for M_2 . Now, in order to work better with our system we are going to assume that the electrolytes solutions are separated by a porous material that allows still for charge equilibrating still avoiding the contamination of reactants. In this way the electric potential in the solution ϕ^s is constant so that by writing the $\Delta\bar{\mu}$ for both reaction and sett equilibrium we obtain Eq. (4.15) for both metals which can be summed up in order to obtain

$$-z_{O2}F(\phi^M - \phi^{M2}) = \frac{z_{O2}}{z_O}(\mu_R^s - \mu_O^s) - z_{O2}\mu_e^M - (\mu_{R2}^s - \mu_{O2}^s) + z_{O2}\mu_e^{M2}. \quad (4.18)$$

By assuming that $\mu_e^M = \mu_e^{M2}$ we can obtain a form of the potential between the electrodes, that is generated by the cell, depending on the chemical properties of the two semi-reactions present inside the cell. In particular, if we define the cell potential E_{cell} to be that potential energy difference we can transform Eq. (4.18) into

$$E_{cell} = E_{right} - E_{left}. \quad (4.19)$$

Meaning that if we know the variation of the potential at the interface for the single reactions we can compute the total one. In particular, we can also have a look at how this knowledge can be used inside in order to evaluate the free energy difference of the reaction as follows.

Theorem 4.1.3: Gibbs and electrode potential

inside an electrochemical cell the variation of free energy of the system is proportional to the electrode potential following the relation

$$\Delta G = -nFE_{cell}. \quad (4.20)$$

Proof: For a generic reversible reaction in a closed system the maximum amount of work that can be extracted from the cell is $\Gamma = -W_{chem}$. If that work is extracted through heat dissipation we can say that the chemical work is equal to the electrical one, which is given by the simple relation

$$W_{el} = nFE_{cell}. \quad (4.21)$$

Which is the work done on every moving charge present, completing the result. ☺

That is great, since that tells us that if $E_{cell} > 0$ than the reaction is spontaneous. Meaning that only by looking at the components used in the cell and their reduction potentials, since the energies E are referred to the reduction reaction $\mu_R - \mu_O$, we can tell not only what E will be, but also in which direction it will point.

The fact that the potential is strictly related to the free energy allows us also to write down another important relation that generalize Nernst equation and probably is the real version for physicist.

Theorem 4.1.4: Generalized Nernst equation

Consider a generic reaction at equilibrium $n_{R_1}R_1 + \dots \longrightarrow n_{P_1}P_1 + \dots$ we can write down the electrode potential of the cell using

$$E_{cell} = E_{cell}^0 + \frac{RT}{nF} \ln \left(\frac{\prod_i a_{R_i}}{\prod_i a_{P_i}} \right). \quad (4.22)$$

Proof: Basically we know how the change in free energy can be written up using the chemical potentials as

$$\Delta G = \sum_i n_{P_i} \mu_{P_i} - \sum_i n_{R_i} \mu_{R_i}. \quad (4.23)$$

Then we can recall the form of the chemical potential $\mu = \mu^0 + RT \ln a$ to obtain directly the final form by dividing by $-nF$. ☺

That will allow to compute the cell potential also in the case of more complex reactions, which is really important for applications. Still this formula imply that we know the values of the reduction potential of all the elements in the reaction, meaning that we need to understand how to evaluate them. The latter is not a trivial task, since if we want to evaluate the potential at an interface directly I need to insert in the system a third element, a voltmeter, which creates a new interface modifying the properties. The idea is, therefore, to place the electrode of which we want to evaluate the potential, called **working electrode** (WE), inside a cell where the other electrode is a standard reference, **reference electrode** (RE). So that, we can evaluate E_{cell} by simply measuring the one between electrodes and then obtain the final result

$$E_{WE} = E_{cell} + E_{RE}. \quad (4.24)$$

In order for such measurement to be precise we will need for the RE to possess the properties of an **ideal non-polarizable electrode**, meaning that the value of E_{RE} does not depend on the bias applied to the system. The latter usually comes from a third electrode called **counter electrode** (CE), from which a current is inserted in the circuit in order to flow from CE to WE, RE is only used for potential measurement. Therefore, to construct a good RE, that has a constant potential not varying with change in the applied current, is often composed by a metal wire in a solution containing a redox couple providing:

- 1** Reversible reaction with fast kinetics, allowing the use of Nernst equation;
- 2** Essentially constant composition;
- 3** Ionic conduction to close the electrochemical circuit.

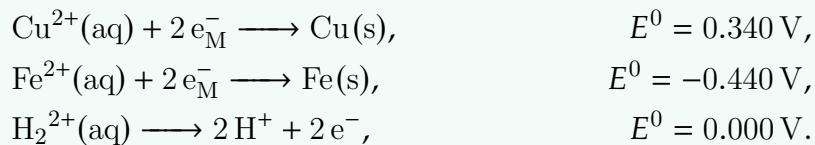
A good example of such reference electrodes is the hydrogen one, which is generally used as standard having a potential set to $E^0 = 0 \text{ V}$.

Note

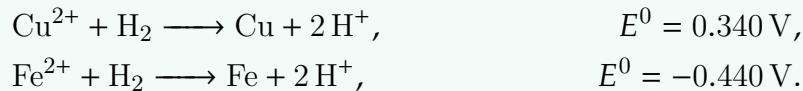
He also showed a particular type of diagram that can be used in order to study redox reaction called Pourbaix diagram, which simply is a phase diagram for the reduction of one electrode in the cell as a function of pH of the solution and equilibrium potential, E_{cell} .

Example 4.1.2 (Cu/Fe-H cell)

We have made a simple example taking looking at the values of the potential generated by a Cu-H cell and a Fe-H cell. To do that you need to look at an online table and search for the semi-reaction to find out how



Combining them we can find out the cell potentials for the two complete electrochemical reactions as



Meaning that the reduction of Copper is spontaneous, while the one of Iron requires energy since naturally it will oxidase.

4.2 Electrode's Kinetics

We will now focus on the study of the kinetics of the electrochemical reactions happening on the electrodes boundaries. In particular, we will first start searching for a way to describe the transport of charge

inside the system to then go into the mass transport phenomena. In this optics it will be quite useful to first recall some quantities that will be used inside the discussion.

Consider a general reduction reaction happening at an electrode, which can be written in the following form



We will describe the rates at which a reaction take place by using the flux v of electrons' moles that travels through the electrode surface. In this way we can describe also the current density on the surface by

$$J = nFv, \quad (4.26)$$

where n is the number of mole of electrons involved in the reduction reaction. Also, we know how both sides of the reaction are characterized by a transition rate k_f and k_b for the forward and backward direction, respectively. Such rates can be related to the flux easily by using the components surface density $C_i(x, t)$ and focus on the density at the surface as follows

$$v_f = k_f C_O(0, t) = \frac{i_f}{nFA}, \quad v_b = k_b C_R(0, t) = \frac{i_b}{nFA}, \quad (4.27)$$

where the surface was assumed to be at the position $x = 0$. If we connect this results we are already able to write down a form for the electrical current present in the system as

$$i = i_f - i_b = nFA[k_f C_O(0, t) - k_b C_R(0, t)]. \quad (4.28)$$

We only need to find a form for the quantities inside the equation, and that is basically what we are going to do in this section.

Nevertheless, to be ready for that we shall also recall how we already know how k can be computed by the use of transition state theory

$$k = k_0 \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) = \kappa \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right). \quad (4.29)$$

Where ΔG^\ddagger is the height of the barrier that separates the two states involved in the reaction, and the quantity κ is called transmission coefficient expressing the probability to decay from the transition state to products.

Butler-Volmer model

To study the kinetics of electrons in the system we start from a standard condition of equilibrium in a one-electron single step reaction, which we approximate as in Fig. (4.3). In that figure two conditions are depicted, a first one where we are in equilibrium so that the minima sits at the same height having so the same ΔG^\ddagger and therefore same rate, leading to $J = 0$. Then, we have the case where an external bias is applied and the energy of the electrons falls setting the reactants at lower potential generating a variation in the forward and backward barriers that can be estimated as follows

$$\Delta G_c^\ddagger = \Delta G_{0,c}^\ddagger - \alpha F(E - E^0), \quad \Delta G_a^\ddagger = \Delta G_{0,a}^\ddagger + (1 - \alpha)F(E - E^0).$$

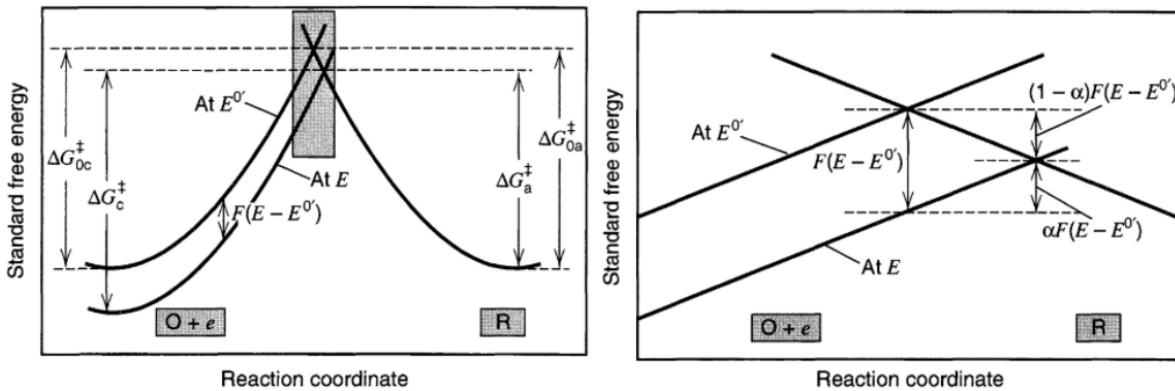


Figure 4.3: Approximation of the potential energy landscape inside a general reaction for some reaction coordinates. We are basically assuming that the reactants and products are minima in the energy and approximating the surrounding potential using second order Taylor expansion, so that the potential barrier is given by the interception of the parabolas.

Where α can be seen as an asymmetric factor, called transfer coefficient, that can range from zero to unity. Using these relations allows us to write down a form for the rates by inserting them inside Eq. (4.29) to obtain

$$k_c = \kappa \frac{k_B T}{h} e^{-\frac{\Delta G_{0,c}^\ddagger}{RT}} \exp\left(-\frac{\alpha F(E - E^0)}{RT}\right), \quad (4.30)$$

$$k_a = \kappa \frac{k_B T}{h} e^{-\frac{\Delta G_{0,a}^\ddagger}{RT}} \exp\left(-\frac{(\alpha - 1)F(E - E^0)}{RT}\right). \quad (4.31)$$

Knowing all of that we are able to obtain a really important result that is able to tell us the entity of the current inside our system as follows.

Theorem 4.2.1: Butler-Volmer equation

The current flowing through the interface of an electrode, performing a general redox reaction, inside a well stirred solution is given by the equation

$$i = i_0 \left[e^{-\alpha \frac{F\eta}{RT}} - e^{-(\alpha - 1) \frac{F\eta}{RT}} \right]. \quad (4.32)$$

Where i_0 is the equilibrium current at the cathode and anode, while η measure the bias applied as the difference between the cell potential and the standard one.

Proof: From Eq. (4.30) and Eq. (4.31) we can see how, since the system was supposed to be in equilibrium without bias, meaning $E = E^0$, the rates have the properties of $k_c(E = 0) = k_b(E = 0)$. This brings us to write down that

$$k^0 = \kappa \frac{k_B T}{h} e^{-\frac{\Delta G_{0,c}^\ddagger}{RT}} = \kappa \frac{k_B T}{h} e^{-\frac{\Delta G_{0,a}^\ddagger}{RT}}, \quad (4.33)$$

which substituted back into the equation and inserted inside Eq. (4.28) gives the result

$$i = FAk^0 \left[C_O(0, t)e^{-\alpha \frac{F(E - E^0)}{RT}} - C_R(0, t)e^{-(\alpha - 1) \frac{F(E - E^0)}{RT}} \right]. \quad (4.34)$$

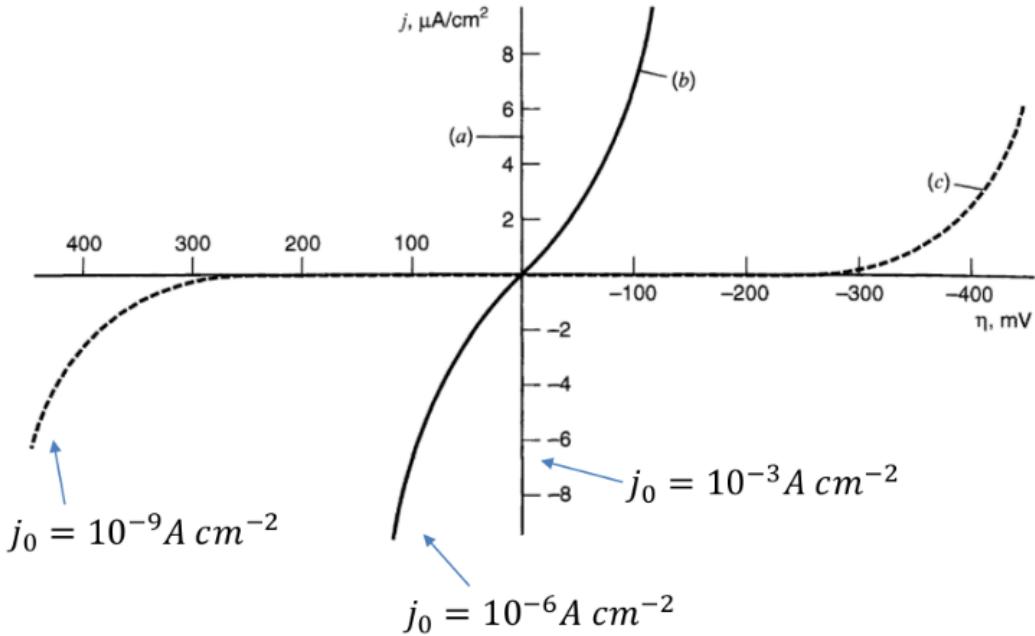


Figure 4.4: Graphic of the net current inside the cell as a function of the overpotential for different values of the exchange current, showing how the value of i_0 gives a great contribution to the overall current.

Now, in the equilibrium we have that $i = 0$ meaning how $i_c = i_a = i_0$ taking the name of **exchange current**, which can be found out easily from previous equation. In fact, by assuming equilibrium mass transfer is much faster than charge one surface concentration in electrode is equal to bulk one $C_0(0, t) = C_{O,b}$, so that we can write down

$$i_0 = FAk^0 c_{O,b} e^{-\alpha \frac{F(E_{eq} - E^0)}{RT}}. \quad (4.35)$$

Since the system is at equilibrium we can use also Nernst equation in order to express the value of E_{eq} as a function of concentration so that we can rewrite i_0 as

$$\frac{C_{O,b}}{C_{R,b}} = \exp \left[\frac{F}{RT} (E_{eq} - E_0) \right], \quad i_0 = FAk^0 C_O^{1-\alpha} C_R^\alpha. \quad (4.36)$$

Inserting it inside the previous equation of i and defining the **overpotential** η as the difference $E - E_0$

$$i = i_0 \left[\frac{C_O(0, t)}{C_{O,b}} e^{-\alpha \frac{F\eta}{RT}} - \frac{C_O(0, t)}{C_{O,b}} e^{-(1-\alpha) \frac{F\eta}{RT}} \right], \quad (4.37)$$

then in a stirred solution we also can assume that the surface concentration is equal to bulk one even out of equilibrium having that the frictions simplifies obtaining the right equation wanted. ☺

This equation is the key to understand how we can act on the variables of the system in order to boost the kinetics of the reaction. In particular, we can see how increasing both the external bias or the temperature can have huge effect on the reaction itself due to the exponential dependence. Also, one can see how the value of the exchange current posses a really important role since we can see from Fig. (4.4) how a lower i_0 gives a more **sluggish kinetics**. Where, a kinetics is more sluggish if you need a higher potential in order to obtain any net current at all inside the system.

Knowing such form for the current we can use it in order to perform some interesting computations regarding the kinetics properties. In particular, we can extract information about α and i_0 thanks to low

and large η regime. In the former case we have that a Taylor expansion leads us to the linear form

$$i = -R_{ct}\eta, \quad R_{ct} = \frac{i_0 F}{RT}, \quad (4.38)$$

the resistance R_{ct} is called **charge-transfer resistance** and represent the impedance to charge transport intrinsic in the solution. Then, we can look at the case where $\eta \gg 1$, so that one of the two terms in the Butler-Volmer equation dominate so that we can easily write down

$$i = i_0 e^{-\alpha \frac{F\eta}{RT}}, \quad \eta = \frac{RT}{\alpha F} \ln i_0 - \frac{RT}{\alpha F} \ln i. \quad (4.39)$$

Therefore, the potential linearly depends on the logarithm of the current giving rise to the form $\eta = a + b \ln i$ also called **Tafel theory**. The two constants inside such equation can be obtained with ease in experiments allowing us to estimate the values of both α and i_0 .

Mass transfer kinetics

Butler-Volmer model allowed us to see how the kinetics of the system depends also on the surface concentration at the electrodes $C_i(0, t)$, which changes over time due to mass transport inside the material. Thus, we can't limit ourselves to the simple study of charge transport but to obtain a satisfying result we shall account also for the mechanisms of migration, convection and diffusion of material that can limit the flux of ions in the cell. In order to create such a model we are going to suppose to work in Nernstian conditions, so that equilibrium is present and the potential is given by Nernst equation, and we will also assume that the reaction is governed mass transport. Meaning that the rate at which the electroactive species is brought to the surface defines the current density

$$J = nFv_{nt}, \quad (4.40)$$

where v_{nt} is the flux of matter inside the electrolyte. Nevertheless, that is only the beginning of the model what we need to do now is to find out a more precise way to describe it.

The best way to model the flux of particle we can use a general form given by the sum of the contribution given by the three main processes mentioned before

$$v_i(x) = -D_i \frac{\partial c_i}{\partial x} - \frac{z_i F}{RT} D_i c_i \frac{\partial \Phi}{\partial x} + c_i v(x). \quad (4.41)$$

Where we have, in order, diffusion, migration and convection contribution, and v represent the velocity of the solution in a certain point. Obviously such an equation is really complex, therefore we usually need to simplify it by setting ourselves in a situation where one or two contributions can be neglected such as:

Diffusion. Introducing stirring;

Migration. Addition of a concentrated supporting electrolyte;

Convection. Avoiding vibrations or stirring.

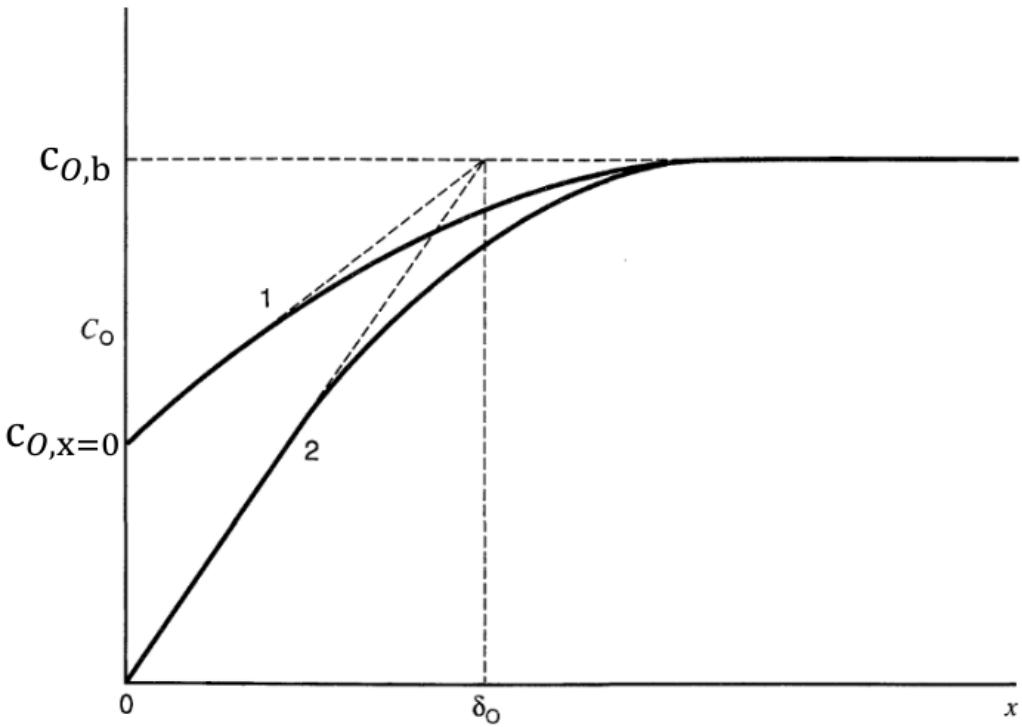


Figure 4.5: Representation of the concentration gradient approximation to understand what δ effectively looks like and how the concentration is.

Therefore, we can choose to use one or more trick in order to eliminate the related processes. Thus, we are going to imagine to work in a diffusion limited process so that v_i is defined simply by Fick's first law and the current density becomes

$$J = nFv_d = nFD \left. \frac{dC_O}{dx} \right|_{x=0}. \quad (4.42)$$

Where the derivative is evaluated at the interface and in a stirred solution we can assume that the bulk concentration is stable in the middle of the solution, meaning that C_O is constant at $C_{O,b}$ for x large enough. In this way we can approximate the derivative simply as a difference of the kind

$$J \approx nFD \frac{C_{O,b} - C_O(x=0)}{\delta}, \quad (4.43)$$

where δ is a constant that needs to be tuned in order to optimize the approximation called **Nernst Diffusion Layer thickness** and can be seen in Fig. (4.5). From that we can see how the diffusion is quicker the smaller δ is or the more negative the potential becomes. Still, it's quite difficult to know the value of δ so that its value is usually combined with the diffusivity defining the **mass-transfer coefficient** $m_i = D_i/\delta_i$. This relation can be used in order to describe the limiting behavior that the mass transport has on the kinetics of the reaction by seeing the following result.

Theorem 4.2.2: Limiting current

Inside an electrochemical cell where mass transport is driven by diffusion the system posses a limiting current given by

$$J_L = nFm_O C_{O,b}. \quad (4.44)$$

Proof: Since electrons travels at higher speeds respect to diffusion of ions in the solution, the rate of the reaction is limited for high value of the overpotential by the maximum flux of ions possible in the electrolyte. In particular, we have seen how Eq. (4.43) gives a way to estimate the rates inside the system for both O and R transfer, where the latter can be expressed by changing the constants and remembering how the electrode is positioned on the right and the solution on the left, so you need to invert the concentrations

$$J = nFm_R(C_{R,x=0} - C_{R,b}). \quad (4.45)$$

In both equations we can see how the maximum possible value that we can obtain is when the density of element on the surface of the electrode is zero, $C_{O,x=0} = 0$. That is the maximum flux that we can obtain, giving rise also to the maximum possible current inside the system. ☺

This relation can also be used in order to rewrite the concentrations of the elements in the solution in a simpler way. In particular, if you use the previous relation alongside with the form of the limiting current we can obtain that

$$C_O(x = 0) = \frac{J_L - J}{nFm_O}, \quad \frac{C_O(x = 0)}{C_{O,b}} = 1 - \frac{J}{J_L}, \quad (4.46)$$

which will be really useful in further descriptions. In particular, using such relations one can see how a value for the cell potential can be found out by assuming how the initial concentration of reduced specie is zero $C_{R,b} = 0$. This assumption inserted inside Eq. (4.45) allows us to obtain $C_{R,x=0} = J/nFm_R$ which inserted inside Nernst equation, alongside with Eq. (4.46), to obtain

$$E = E^0 - \frac{RT}{nF} \ln \frac{m_O}{m_R} + \frac{RT}{nF} \ln \left(\frac{J_L - J}{J} \right). \quad (4.47)$$

Such equation shows interesting behavior since all the quantities inside it are easy to evaluate experimentally, still only works if at the start of the reaction only one element is present in the solution. Nevertheless, we can see how at a certain value of the current $J = J_L/2$ the equation simplifies a lot, having

$$E_{1/2} = E^0 - \frac{RT}{nF} \ln \frac{m_O}{m_R}, \quad (4.48)$$

which value is often taken equal to E^0 since $m_O/m_R \approx 1$ in most of the cases. Therefore, that value is often used in order to rewrite the total equation substituting it, giving the final general form of the equation

$$E = E_{1/2} + \frac{RT}{nF} \ln \left(\frac{J_L - J}{J} \right). \quad (4.49)$$

In reality is possible to describe a model also for the case where both reduced and oxidized species are present inside the solution at time zero. In that case is important to take into account that two different limiting currents are present inside the material, one in the cathodic and one in the anodic direction as

$$J_{L,c} = nFm_O C_{O,b}, \quad J_{L,a} = -nFm_R C_{R,b}. \quad (4.50)$$

Which comes out from the same theory used previously to find Eq. (4.44), meaning that the relations Eq. (4.46) are valid also for C_R . In this way we can substitute everything inside the Nernst equation to gain the final general result

$$E = E^0 - \frac{RT}{nF} \ln \frac{m_O}{m_R} + \frac{RT}{nF} \ln \left(\frac{J_{L,c} - J}{J - J_{L,a}} \right). \quad (4.51)$$

This is a more general result that can be used, which also posses a peculiar property. In fact, is possible to see by this equation how the potential at equilibrium, $J = 0$, gives out exactly Nernst equation $E^0 + RT \ln(C_{O,b}/C_{R,b})/nF$.

All of this theory is great but is only an approximation frozen in time to estimate the limiting current. In reality, the value of J_L can change overtime due to changes in the concentration of the species inside the solution, but more importantly by the variation of the concentration gradient inside it due to diffusion processes. In particular, we can describe such a process by using the following result.

Theorem 4.2.3: Cottrell equation

If the reaction is Nernstian the limit current density decreases with time, following the equation

$$J_L = nFC_{O,b} \sqrt{\frac{D}{\pi t}}. \quad (4.52)$$

Proof: If the reaction is Nernstian, the concentration at the electrode surface immediately adjusts to the equilibrium value, but its gradient slowly shifts due to diffusion. The thickness of the Nernst diffusion layer is then time-dependent

$$\delta(t) = \sqrt{\pi Dt}, \quad (4.53)$$

which can be substituted inside Eq. (4.43) to obtain the result. Inside it, we assume $C_{O,b}$ is constant in time since if the solution is stirred it gets homogeneous in the bulk really quickly, the problem is only the gradient at the boundary. ☺

Note

As it was said the presence of convection allows us to assume $C_{O,b}$ constant over time inside Eq. (4.52), but it also generates one other thing. Basically, since the bulk concentration is homogeneous, the presence of convection is also limiting the diffusion in decreasing the gradient, meaning that when it is flattened to a certain point it can go any further since it needs to change the part of solution that has constant concentration thanks to convection. For this reason, in presence of convection $J_L(t)$ will not decrease indefinitely with time, but will reach a plateau.

Microscopic theories for charge transfer

So far so good, nevertheless all the theory described right now are of a phenomenological type, focussing on describing the phenomena using a series of constant that we need to compute experimentally, like k^0 or α . Now we want to relax such condition creating a more fundamental model for charge transfer inside the solution that can limit the number of constant that we are using. Thus, we are going to describe a famous model called **Marcus model** which is able to find a form of the transition rate dependent only on one phenomenological constant that can be also modelled via first principles.

We are interested in study the exchange of one electron from the electrode, so a metal, to the oxidation molecule inside the solution. The latter, is going to be modelled as a metallic sphere with a certain dipole and dielectric constant, which can interact with the electrode in two main ways: **outer sphere**, where the molecule is separated from the surface by a layer of solvent so that the e^- needs to travel by tunneling effect, or **inner sphere**, where a strong interaction is present so that the molecule is close to the surface leading to the exchange. We are not going to pick one of the two cases, since both

will be described by the model, as we will see, which simply focus on the transfer of the charge making the following four assumptions:

Isoenergetic process. the electron must move from an initial state (on the electrode or in the reductant, R) to a receiving state (in species O or on the electrode) of the same energy;

Franck-Condon. Basically no change in the atomic configuration happens, meaning that the nuclei remains still since electronic processes are much faster respect to atomic ones;

Fixed position. The reactant O has fixed position with respect to the electrode;

Quadratic G. Standard free energies of O and R, G_O and G_R , depend quadratically on the reaction coordinate, q .

Keeping in mind such approximations we are able to find out a general way to write down the transition rate for the reaction in general as follows.

Theorem 4.2.4: Marcus result

Inside an electrochemical cell where the four conditions before mentioned are satisfied, the transition rate for the charge transfer process is given by

$$k = \kappa Z \exp \left[-\frac{\lambda}{4RT} \left(1 + \frac{\Delta G^0}{\lambda} \right)^2 \right], \quad (4.54)$$

where κ is usually taken as 1, Z is a function of an electrostatic and collisional term, and λ is the so-called reorganization energy accounting for both inner and outer interactions.

Proof: the free energy is approximated to a quadratic form, therefore we can write down

$$G_O(q) = \frac{k}{2}(q - q_O)^2, \quad G_R(q) = \frac{k}{2}(q - q_R)^2 + \Delta G^0, \quad (4.55)$$

where k is a proportionality constant and ΔG^0 is the usual potential bias $F(E - E^0)$. Having both this values we can put them in a system and find out the point where the two curves intersect giving rise to the approximated transition state. Such a computation gives rise to the result

$$q^\ddagger = \frac{q_R + q_O}{2} + \frac{\Delta G^0}{k(q_R - q_O)}, \quad (4.56)$$

which can be used in order to evaluate the potential barrier for the oxidation process as $G_O(q^\ddagger) - G_O(q_O)$ which gives rise to

$$\Delta G^\ddagger = \frac{k(q_R - q_O)^2}{8} \left[1 + \frac{2\Delta G^0}{k(q_R - q_O)^2} \right]^2 = \frac{\lambda}{4} \left[1 + \frac{\Delta G^0}{\lambda} \right]^2. \quad (4.57)$$

Therefore, we have a form for the potential barrier which depends on the form of the reorganization energy. The latter can be evaluated by taking into account the inner and outer components' contribution

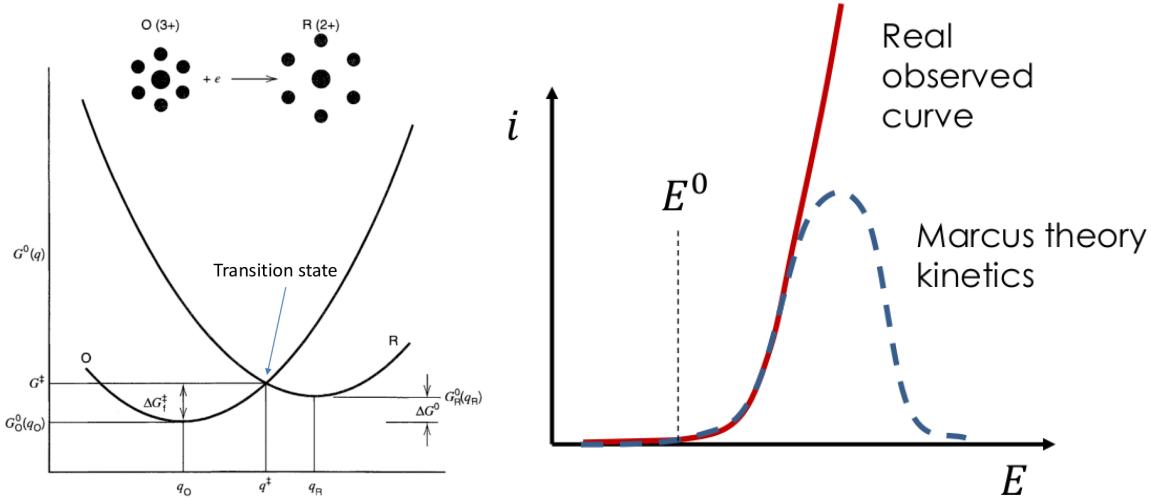


Figure 4.6: Representation of the energy landscape of the reaction in the Marcus approximation, on the left, and the graph of the result model obtained versus the experimental result, on the right.

to the reorganization of the species O and the solvent $\lambda = \lambda_i + \lambda_o$. Both of them can be modelled, the latter is given by the sum of normal vibration modes of reactants

$$\lambda_i = \sum_j \frac{k_j}{2} (q_{O,j} - q_{R,j})^2. \quad (4.58)$$

The latter, instead, is computed by calculating the ion-solvent electrostatic interaction for reactant and products, assuming the solvent as a dielectric continuum and the reactant a sphere of radius a_O

$$\lambda_o = \frac{e^2}{8\pi\varepsilon_0} \left(\frac{1}{a_O} - \frac{1}{R} \right) \left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s} \right). \quad (4.59)$$

Where R is twice the distance of molecule and surface of electrode, while the dielectric constants are the one of the molecule and of the electrode. Knowing this we can insert that value inside the known form of the transition rate in order to obtain the wanted relation. ☺

This model is really great, showing how depending on the ratio $\Delta G^0/\lambda$ the reaction will actually change its velocity. In particular, we can see how for biases so that $\Delta G^0 < -\lambda$ we got $k \propto \Delta G^0$ reaching a maximum in $\Delta G^0 = -\lambda$ and then having $k \propto 1/\Delta G^0$ for higher values. This is a really strange behavior since experimentally the so-called **inverted region** is not seen, as we increase the potential the reaction speeds up and that was the reason because the model took some time to be accepted by the community. The reason why this happens are basically two: the first is that **O are not still**, basically as E is increase the molecule interact more with the electrode lowering the distance R and so increasing λ , and **More levels are involved**, the model we have described assumed that the electron transferred is taken from the higher level inside the electrode, the Fermi level, that is true only in practice since as we increase the potential the electrons in lower levels can be exited and transferred too.