Microscopic Kinetic and Thermodynamics
Notes of the course

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Thermodynamics of equilibrium in condensed phases

1.1 Physical properties

When one think 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 matherial 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

$$\psi_i \mathrm{d}\xi_i = \delta w, \tag{1.1}$$

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 $\mathrm{d}V$ that so create work $P\mathrm{d}V$.

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

$$\mathrm{d}u = T\mathrm{d}s + \psi_i \mathrm{d}\xi_i, \tag{1.2}$$

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

$$\mathrm{d}u = X_i \mathrm{d}Y_i, \tag{1.3}$$

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

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

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

$$\mathcal{K}_{ij} = \left.\frac{\partial Y_i}{\partial X_j}\right|_{X_j = X_j^0}, \qquad \mathcal{K} = \begin{pmatrix} \boldsymbol{\nabla}_{\mathbf{k}} Y_1 \\ \vdots \\ \boldsymbol{\nabla}_{\mathbf{k}} Y_N \end{pmatrix}. \tag{1.5}$$

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

$$\mathcal{K}_{ij} = \mathcal{K}_{ji}. \tag{1.6}$$

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

$$g = u - X_i Y_i, \qquad \mathrm{d}g = -Y_i \mathrm{d}X_i. \tag{1.7}$$

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

$$\frac{\partial^2 g}{\partial X_i \partial X_j} = \frac{\partial^2 g}{\partial X_j \partial X_i}, \tag{1.8}$$

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

$$\mathcal{K}_{ij} = \mathcal{K}_{ji}. \tag{1.9}$$

😄

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

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

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 σ. 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.

[1]To identify different type of tensor we will use the notation $T(n)$, which means tensor of rank n.
[2]If a tensor is symmetric the subscript S is used.

	T	**E**	**H**	$\boldsymbol{\sigma}$
s	c/T	p	q	α
D	p'	k	λ	d
B	q'	λ'	μ	Q
$\boldsymbol{\varepsilon}$	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

$$\varepsilon_{ij} = s_{ijkl}\sigma_{kl}. \tag{1.11}$$

Also, in this case the tensor is symmetric since $\boldsymbol{\varepsilon}$ and $\boldsymbol{\sigma}$ are having so $s_{ijkl} = s_{klij}$, this make so that the total number of independent variables in the tensor are 21. The inverse of this tensor, **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 **q** to be a pseudo-vector, therefore the tensor is called an axial one[3].

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

[3] We 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 princple 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

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

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

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

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 ceratain symmetry $\mathbf{R}$ simply becomes

$$\mathbf{T} = \mathbf{R}\mathbf{T}\mathbf{R}^{-1}. \tag{1.14}$$

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 $\mathbf{\Theta}$** becomes important. In particular one can call **i-tensors** the ones that are invariant under $\mathbf{\Theta}$ and **c-tensors** the others we will have that the magnetic field is inside the latter, having

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

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

$$\mathbf{\Theta}\mathbf{Y} = \pm\mathbf{Y} = \pm\mathcal{K}\mathbf{X} = \mathbf{\Theta}\mathcal{K}\mathbf{X}. \tag{1.16}$$

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

$$\mathbf{\Theta}\mathbf{Y} = -\mathbf{Y} = -\mathcal{K}\mathbf{X} = \mathbf{\Theta}\mathcal{K}\mathbf{X}. \tag{1.17}$$

This leads to the fact that $\mathbf{\Theta}\mathcal{K} = -\mathcal{K}$ 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 is sad 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

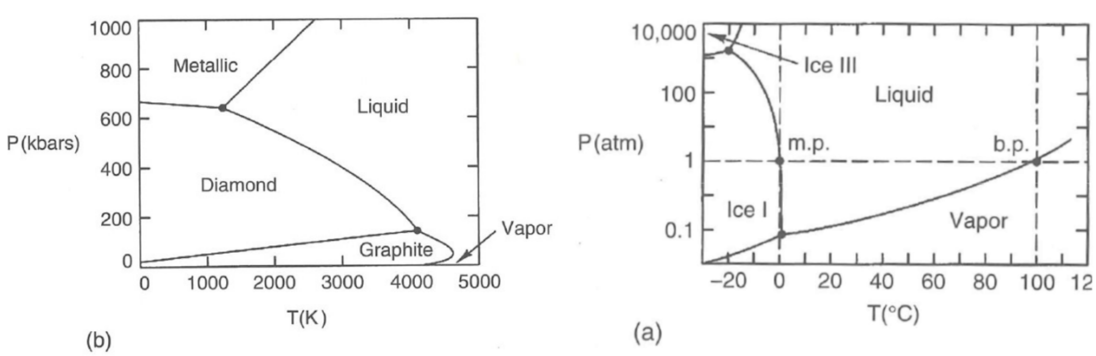


Figure 1.2: Phase diagrams of simple unary systems: Carbon(a) and Water(b). Both are reported in a P vs T graph, where we can clearly see the triple points and the coexistence lines.

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:

$$T^\alpha = T^\beta, \qquad P^\alpha = P^\beta, \qquad \mu^\alpha = \mu^\beta. \tag{1.18}$$

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

$$U^\alpha + U^\beta = const, \qquad V^\alpha + V^\beta = const, \qquad N^\alpha + N^\beta = const. \tag{1.19}$$

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

$$\mathrm{d}u = T\mathrm{d}s - P\mathrm{d}V + \mu\mathrm{d}n. \tag{1.20}$$

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

$$\mathrm{d}s = \frac{\mathrm{d}u}{T} + \frac{P}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}n, \tag{1.21}$$

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 $\mathrm{d}s^\alpha + \mathrm{d}s^\beta = 0$. If we now use Eq. (1.21) and the relations Eq. (1.19) we can easily see that the following is true

$$\left(\frac{1}{T^\alpha} - \frac{1}{T^\beta}\right)\mathrm{d}u^\alpha + \left(\frac{P^\alpha}{T^\alpha} - \frac{P^\beta}{T^\beta}\right)\mathrm{d}V^\alpha - \left(\frac{\mu^\alpha}{T^\alpha} - \frac{\mu^\beta}{T^\beta}\right)\mathrm{d}n^\alpha = 0, \tag{1.22}$$

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	$H = U + PV$	$\mathrm{d}H = T\mathrm{d}s + V\mathrm{d}P + \mu\mathrm{d}n$	isobare study, since $\mathrm{d}H = \delta Q$.
Helmoltz ener.	$F = U - TS$	$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}n$	isocore-isotherm study.
Gibbs free ener.	$G = U - TS + PV$	$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}n$	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, $\overline{G}$, is equal to the chemical potential

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

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 $\overline{G}$ is at its minimum.

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

$$\mathrm{d}\mu = -S\mathrm{d}T + V\mathrm{d}P. \tag{1.24}$$

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

$$\mathrm{d}\mu \leq -S\mathrm{d}T + V\mathrm{d}P. \tag{1.25}$$

Now, if we assume that the system is kept at constant P and T that relation becomes simply $\mathrm{d}\mu \leq 0$, 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)

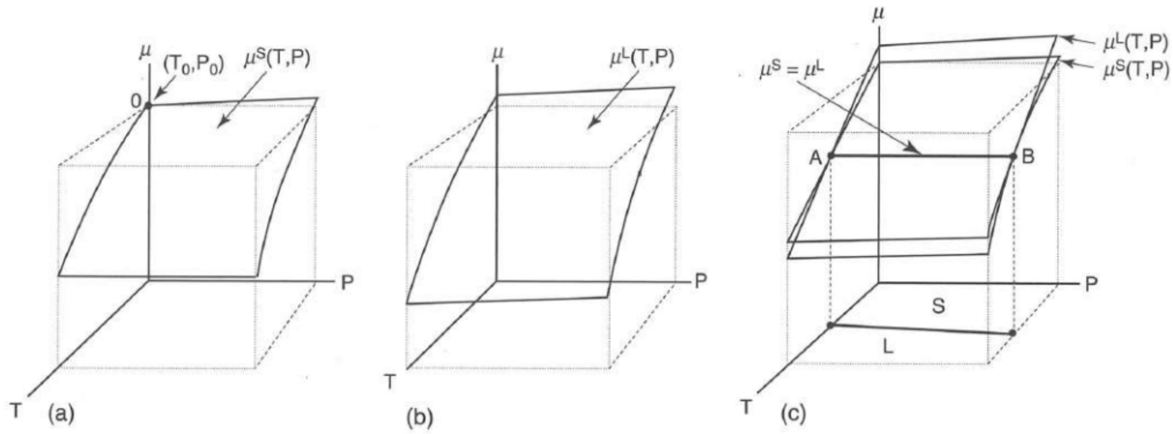


Figure 1.3: Graphical rapresentation of the chemical potential for a solid phase(a), liquid phase(b) and the superposition of the two to see which one prevails on the other for the equilibrium phase(c). It's possible to see how in the part of the phase diagram where $\mu^S = \mu^L$ a coexistence line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

$$\mathrm{d}S = \left.\frac{\partial S}{\partial P}\right|_T \mathrm{d}P + \left.\frac{\partial S}{\partial T}\right|_P \mathrm{d}T. \tag{1.26}$$

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

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

Where the definition of **thermal expansion coefficient** $\alpha = V^{-1}\,\partial V/\partial T\big|_P$ 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

$$\mathrm{d}S = -V\alpha \mathrm{d}P + \frac{c_P}{T}\mathrm{d}T. \tag{1.28}$$

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

$$\frac{\mathrm{d}V}{V} = -\beta \mathrm{d}P + \alpha \mathrm{d}T. \tag{1.29}$$

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

$$S(T,P_0) = S(T_0,P_0) + \int_{T_0}^{T} \frac{c_p(T')}{T'}\mathrm{d}T', \tag{1.30}$$

$$\mu(T,P_0) = \mu(T_0,P_0) - \int_{T_0}^{T} S(T')\mathrm{d}T'. \tag{1.31}$$

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 renown 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 givne by the following relation

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{1}{T}\frac{\Delta H^{\alpha\to\beta}}{\Delta V^{\alpha\to\beta}}. \tag{1.32}$$

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

$$-S^\alpha \mathrm{d}T + V^\alpha \mathrm{d}P = -S^\beta \mathrm{d}T + V^\beta \mathrm{d}P \tag{1.33}$$

Rearranging and assuming that the study is done in an isobare condition, meaning that $\mathrm{d}H = T\mathrm{d}S$, we will have the wanted result.

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{1}{T}\frac{H^\beta - H^\alpha}{V^\beta - V^\alpha} = \frac{1}{T}\frac{\Delta H^{\alpha\to\beta}}{\Delta V^{\alpha\to\beta}}. \tag{1.34}$$

😄

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 its 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 e 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

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

where c is a constant.

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

$$\frac{\mathrm{d}P}{P} = \frac{\Delta H}{R}\frac{\mathrm{d}T}{T^2}, \tag{1.36}$$

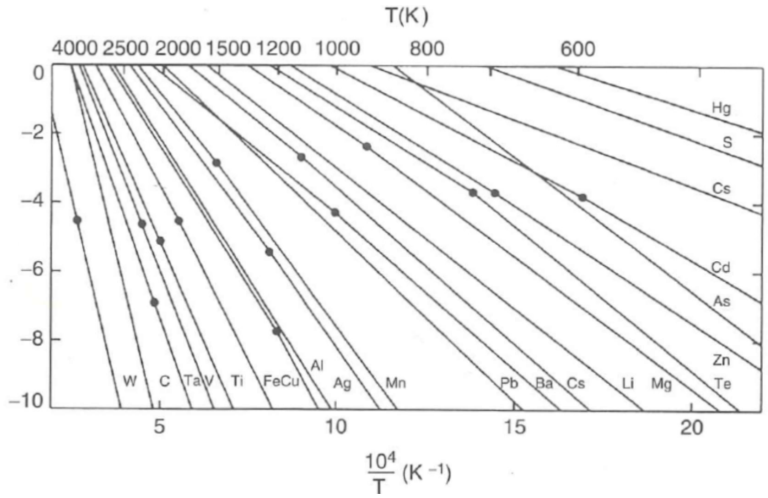


Figure 1.4: Compilation of vapor pressure for the elements with $\log P$ on the y-axis. A change in slope (marked by the dot) corresponds to the melting point, which is also a triple point here because of the coexistence with the vapor phase.

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. 😄

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

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

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

$$X_i = \frac{n_i}{\sum_j n_j} = \frac{n_i}{n_T}. \tag{1.38}$$

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

$$f = f'/n_T. \tag{1.39}$$

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 sad to be extensive if taken $\lambda > 0$ the following equality holds true

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

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

Definition 1.3.5: Intensive quantities

A thermodynamic quantity f' is sad to be intensibe if taken $\lambda > 0$ the following equality holds true
$$f'(\lambda\mathbf{n}, T, P) = f'(\mathbf{n}, T, P). \tag{1.41}$$

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

$$\mathrm{d}f' = \nabla_{\mathbf{n}} f' \cdot \mathrm{d}\mathbf{n} + \frac{\partial f'}{\partial T}\mathrm{d}T + \frac{\partial f'}{\partial P}\mathrm{d}P, \tag{1.42}$$

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

$$\overline{f}_i = \left.\frac{\partial f'}{\partial n_i}\right|_{n_{j\neq i}, T, P}, \qquad \mathrm{d}f' = \sum_i \overline{f}_i \mathrm{d}n_i. \tag{1.43}$$

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
$$\overline{f}_i = \left.\frac{\partial f'}{\partial n_i}\right|_{n_{j\neq i}, T, P}, \tag{1.44}$$
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 $\overline{f}_i$ 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

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

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

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

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

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

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

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 $\overline{f}_i$ 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 $\mathbf{n} \longrightarrow \lambda\mathbf{n}$, we will have

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

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

This is interesting under a physical point of view since we can evaluate $\overline{f}_i$ in systems without caring about the sizes and still having exact values for every possible compositions. Also, this means that we can imagine at $\overline{f}_i$ 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

$$\sum_i n_i\mathrm{d}\overline{f}_i = 0. \tag{1.49}$$

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

$$\mathrm{d}f' = \sum_i \overline{f}_i\mathrm{d}n_i + \sum_i n_i\mathrm{d}\overline{f}_i = \mathrm{d}f' + \sum_i n_i\mathrm{d}\overline{f}_i, \tag{1.50}$$

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

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 appling the partial molar operator

$$\overline{G}_i = \overline{H}_i - T\overline{S}_i, \tag{1.51}$$

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

$$\overline{S}_i = -\left.\frac{\partial \overline{G}_i}{\partial T}\right|_{n_k,P}, \qquad \overline{V}_i = \left.\frac{\partial \overline{G}_i}{\partial P}\right|_{n_k,T}. \tag{1.52}$$

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 $\overline{G}_i$, which we have already seen that becomes μ inside a unary system and here things doesn't change since

$$\mathrm{d}G' = -S'\mathrm{d}T + V'\mathrm{d}P + \sum_i \mu_i \mathrm{d}n_i, \qquad \mu_i = \left.\frac{\partial G'}{\partial n_i}\right|_{n_{k\neq i},P,T} = \overline{G}_i. \tag{1.53}$$

Thus, everything related to the Gibbs free energy will become a relation using the chemical potential[4].

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

$$\mathrm{d}f = \overline{f}_1 \mathrm{d}X_1 + \overline{f}_2 \mathrm{d}X_2, \tag{1.54}$$

but we also know that $X_1 + X_2 = 1$ leading to $\mathrm{d}X_1 = -\mathrm{d}X_2$. Thus, we can find out the derivative of f as

$$\frac{\mathrm{d}f}{\mathrm{d}X_2} = \overline{f}_2 - \overline{f}_1, \tag{1.55}$$

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

$$\overline{f}_1 = \frac{f - \overline{f}_2 X_2}{1 - X_2}. \tag{1.56}$$

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

$$f = \overline{f}_1 + (X_2 - 1)\frac{\mathrm{d}f}{\mathrm{d}X_2}, \tag{1.57}$$

[4] Keep in mind that this happens only because we have decied 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.

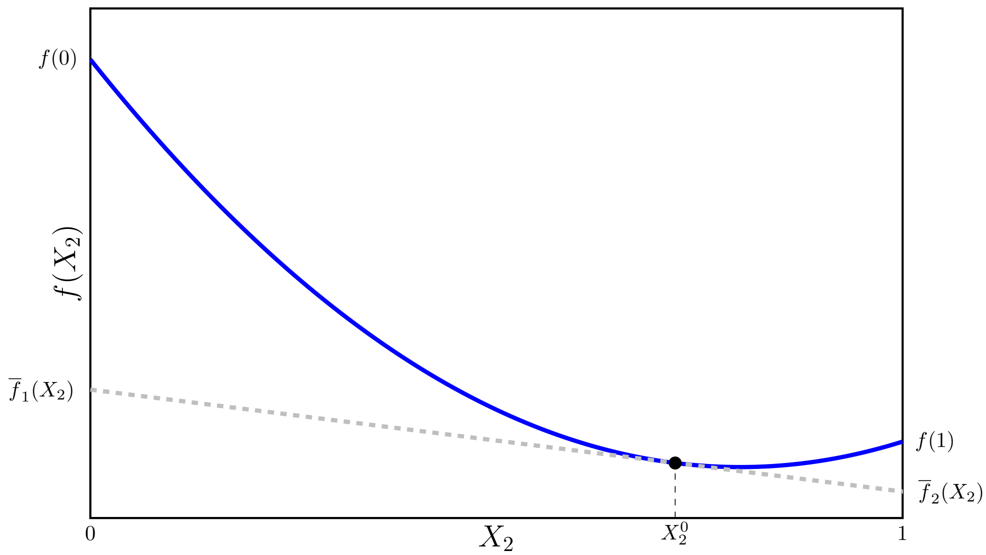


Figure 1.5: Illustration of the graphical method to compute the PMPs of a binary system in the case of a simple physical quantity. It's possible to see how the method basically select one point X_2^0 and then draw the tangent to f in that point finding the PMPs as the intercepts with the $X_2 = 0$ and $X_2 = 1$ 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 $\overline{f}_1$ 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 $\overline{f}_i$ 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

$$\Delta f_{mix} = \sum_i \overline{f}_i X_i - \sum_i f_i^\circ X_i = \sum_i \Delta \overline{f}_i X_i, \tag{1.58}$$

where f_i° represent $\overline{f}_i$ 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** $\Delta\overline{f}_i$. 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

$$\sum_i \mathrm{d}\left(\Delta \overline{f}_i\right) X_i = 0. \tag{1.59}$$

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

$$\mathrm{d}(\Delta f_{mix}) = \mathrm{d}\overline{f}_i X_i + \overline{f}_i \mathrm{d}X_i - \mathrm{d}f_i^\circ - f_i^\circ \mathrm{d}X_i = \Delta \overline{f}_i \mathrm{d}X_i. \tag{1.60}$$

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

$$\mathrm{d}(\Delta f_{mix}) = \Delta \overline{f}_i \mathrm{d}X_i. \tag{1.61}$$

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

$$\mathrm{d}(\Delta f_{mix}) = \mathrm{d}\left(\Delta \overline{f}_i\right) X_i + \Delta \overline{f}_i \mathrm{d}X_i, \tag{1.62}$$

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

$$\Delta \overline{H}_1 = \Delta H_{mix} - \frac{\mathrm{d}(\Delta H_{mix})}{\mathrm{d}X_2} X_2, \tag{1.63}$$

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

$$\Delta \overline{H}_1 = aX_2^2, \qquad \Delta \overline{H}_2 = aX_1^2. \tag{1.64}$$

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

$$\Delta \overline{H}_1 = \int_0^{X_1} \frac{X_1'}{(X_1' - 1)} 2a(X_1' - 1)\mathrm{d}X_1' = aX_1^2. \tag{1.65}$$

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

$$\Delta\mu_i = \mu_i - \mu_i^\circ = RT \ln a_i. \tag{1.66}$$

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

$$\Delta\overline{S}_i = -\left.\frac{\partial\Delta\mu_i}{\partial T}\right|_{n_k,P} = -R\ln X_i, \qquad \Delta\overline{V}_i = \left.\frac{\partial\Delta\mu_i}{\partial P}\right|_{n_k,T} = 0. \tag{1.67}$$

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

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

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

$$a_i = \gamma_i X_i. \tag{1.69}$$

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

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

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

$$\sum_i \mathrm{d}(\ln\gamma_i)\, X_i = 0. \tag{1.71}$$

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

$$\lim_{X_i\to 0} a_i = \gamma_i^\circ X_i. \tag{1.72}$$

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, $X_2 \to 0$, the solvent, $X_1 \to 1$ shows ideal behavior with $\gamma_1 \to 1$, 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.

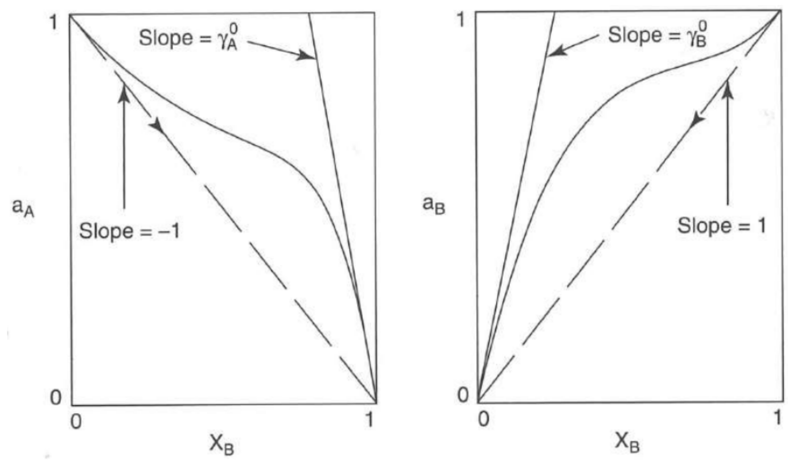


Figure 1.6: Illustration of the activity inside a binary system composed by the phases a and b, showing the expected behaviors of ideality in the diluted case.

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

$$\Delta S_{mix} = -RX_i \ln X_i. \tag{1.73}$$

2. The enthalpy of mixing is different from zero

$$\Delta H_{mix} = \Delta H^{[}_{mix} xs] \neq 0. \tag{1.74}$$

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

$$\frac{\partial \Delta H^{xs}_{mix}}{\partial T} = \frac{\partial \Delta G^{xs}_{mix} - T\Delta S^{xs}_{mix}}{\partial T} = \frac{\partial \Delta G^{xs}_{mix}}{\partial T} = -\Delta S^{xs}_{mix} = 0, \tag{1.75}$$

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

$$\Delta \mu_i^{xs} = \Delta \overline{H}_i, \tag{1.76}$$

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

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

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

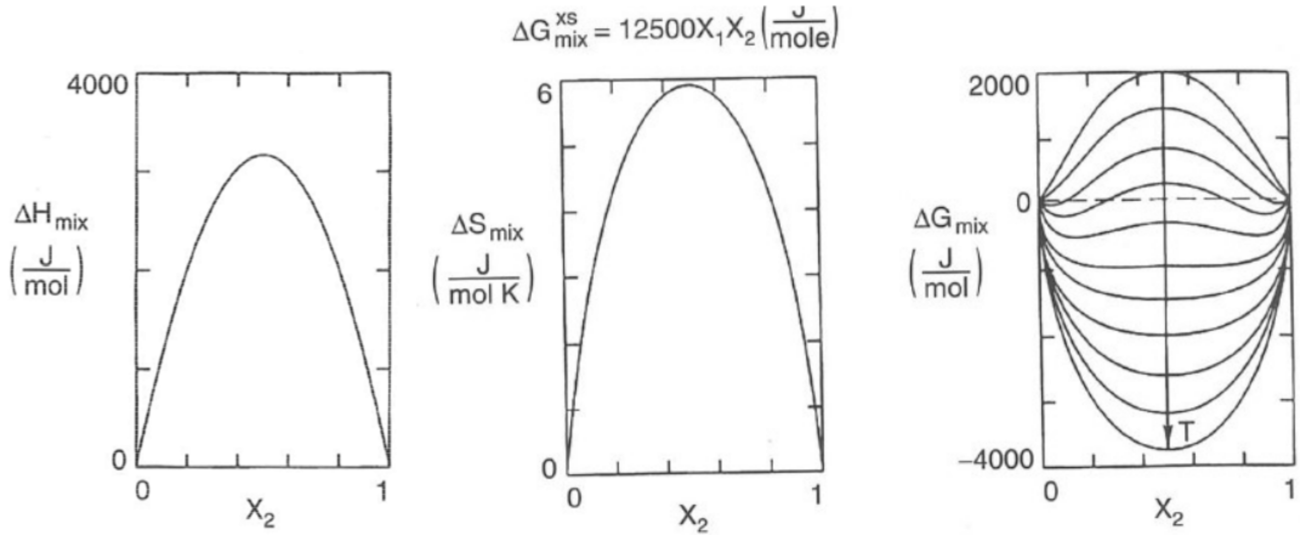


Figure 1.7: Computed values of mixing properties for the simple system given by the mixing enthalpy aX_1X_2. It's possible to see how only the mixing free energy has a temperature dependence, and it's interesting that for some values of T a curve with two global minima is obtained.

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

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

This result also shows how $\lim_{X_i \to 1} \gamma_i$ 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-**

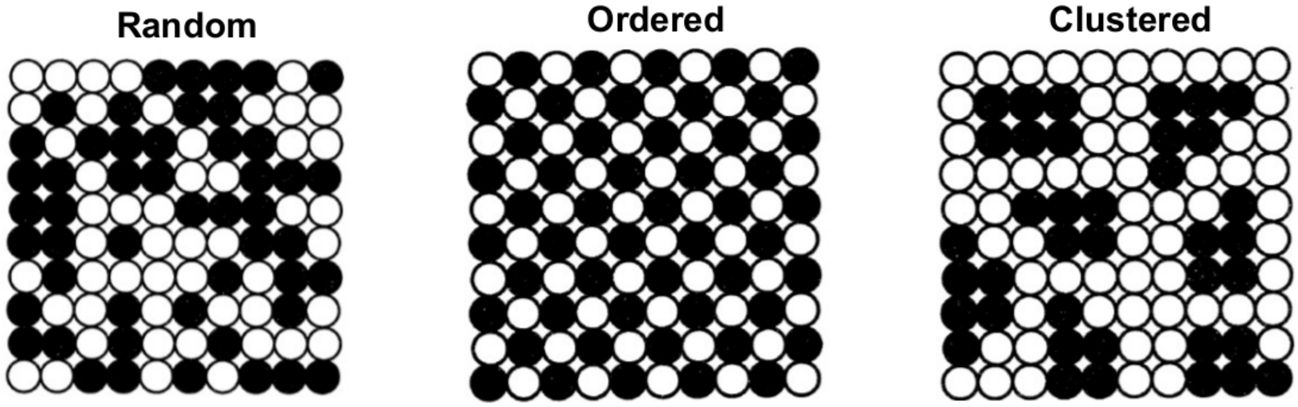


Figure 1.8: Illustration of the three possible type of distributions of the atoms inside a binary system, with the possibility of randomly placed atoms, ordered structure creating a known lattice and clustered systems.

chemical model, meaning that we will focus on the bonds that can be generated between nearest neighbors 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

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

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

$$0 \le X_i \le 1, \qquad -\frac{1}{2} \le \eta \le \frac{1}{2}. \tag{1.80}$$

Also, using some further mathematical consideration one can find out how $\eta \le \min(X_B, X_A)$. 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^i to be averages we can write $X_B^j = N_B^j/N = P(B, j)$ having

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

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

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

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

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

$$N_{BB} = \frac{NZ}{2} X_B^\alpha X_B^\beta = \frac{NZ}{2} \left[X_B^2 - \eta^2 \right], \tag{1.84}$$

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

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

$$U = N_{AA} E_{AA} + N_{BB} E_{BB} + N_{AB} E_{AB}. \tag{1.86}$$

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

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

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

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

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

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}. \tag{1.89}$$

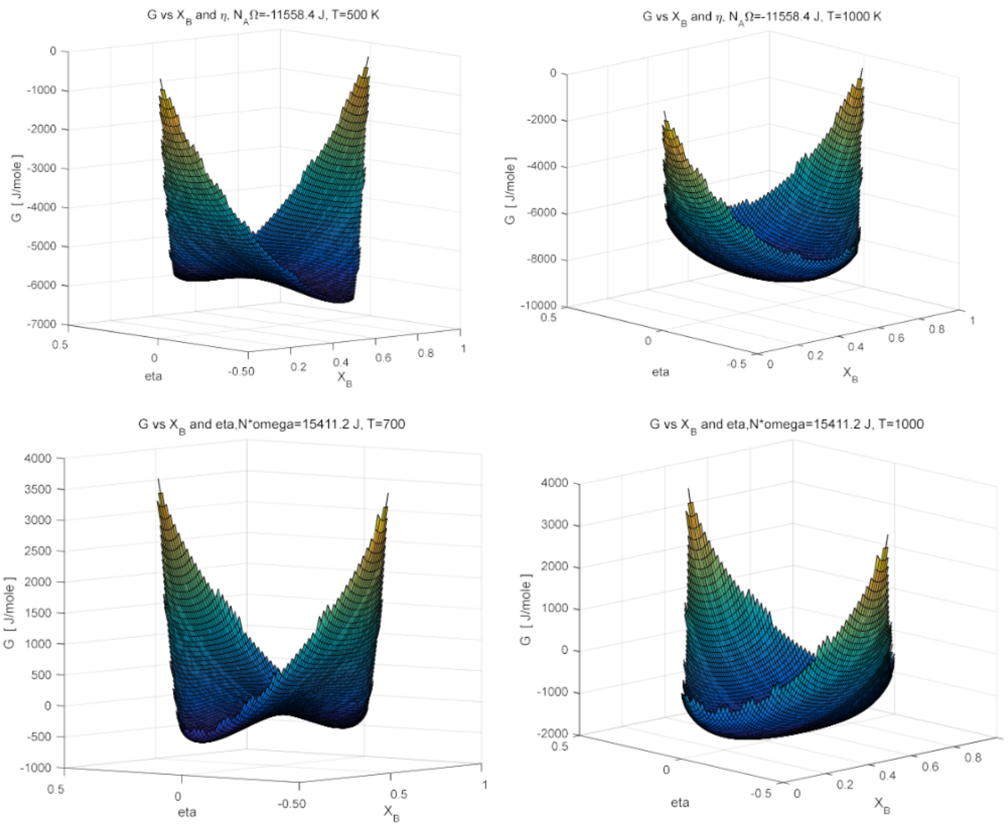


Figure 1.9: Graphical visualization of the ΔG_{mix} inside a binary system for different values of interaction parameter and temperature. In the top row negative Ω are plotted, while positive ones are shown in the bottom row.

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

$$\Delta H_{mix} = \Delta U_{mix} + P\Delta V_{mix} \approx N\Omega\left(X_A X_B + \eta^2\right). \tag{1.90}$$

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**

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

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

$$\Delta G_{mix} = N\Omega\left(X_A X_B + \eta^2\right) + \frac{k_B T N}{2}\sum_{i=A,B}\left[(X_i+\eta)\ln(X_i+\eta) + (X_i-\eta)\ln(X_i-\eta)\right]. \tag{1.92}$$

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	$\pm$ 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

$$\Delta G_{mix} = N\Omega X_A X_B + RT\left(X_A \ln X_A + X_B \ln X_B\right) = \Delta H_{mix} - T\Delta S^{id}_{mix}. \tag{1.93}$$

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

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

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

$$K_B T^C = -2\Omega X_A X_B, \qquad T^C_{max} = -\frac{\Omega}{2k_B}, \qquad \frac{T^C}{T^C_{max}} = 4X_A X_B. \tag{1.95}$$

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

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

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

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

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

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

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

$$k_B T^s = 2\Omega X_A X_B, \qquad T^s_{max} = \frac{\Omega}{2k_B}, \tag{1.99}$$

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 sad, 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 with 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

$$T^\alpha = T^\beta, \qquad P^\alpha = P^\beta, \qquad \mu_i^\alpha = \mu_i^\beta. \tag{1.100}$$

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

$$\mathrm{d}U' = \sum_{\nu=1}^{p}\left(T^\nu \mathrm{d}S'^\nu - P^\nu \mathrm{d}V'^\nu + \sum_{i=1}^{c}\mu_i^\nu \mathrm{d}n_i^\nu\right). \tag{1.101}$$

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

$$\sum_\nu \mathrm{d}U'^\nu = 0, \qquad \sum_\nu \mathrm{d}V'^\nu = 0, \qquad \sum_\nu \mathrm{d}n_i^\nu = 0, \tag{1.102}$$

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

$$f = c - P + 2. \tag{1.103}$$

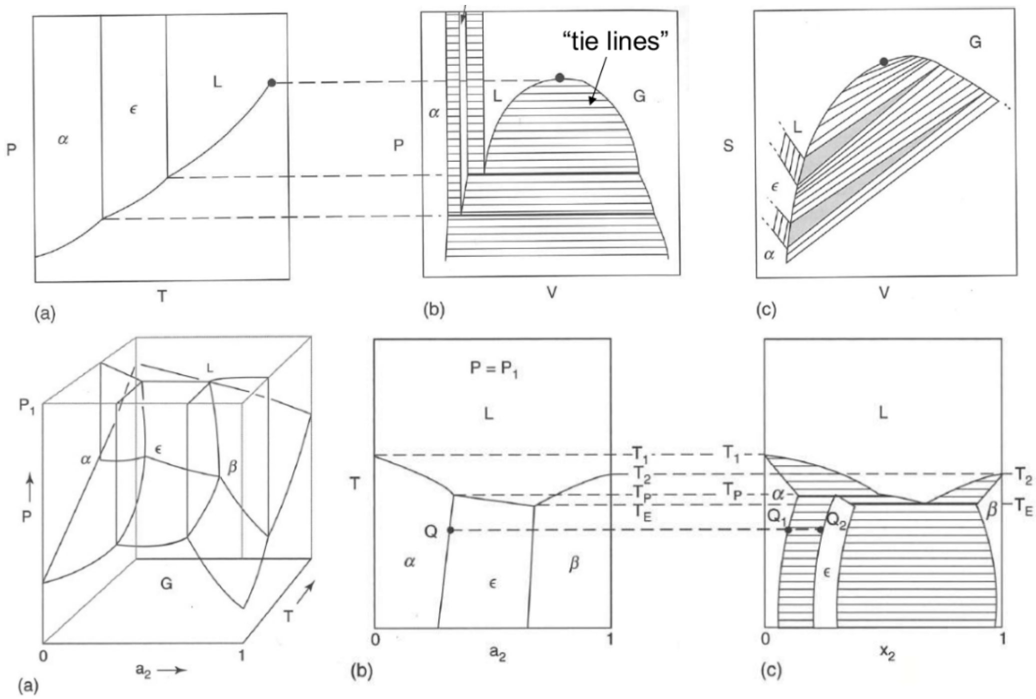


Figure 1.10: Examples of phase diagrams in different phase space for a two component, top, and a three component system, bottom. It's possible to see how the Gibbs' phase rule is respected perfectly in the T vs P phase space while modifications due to more freedom in the parameters are present in the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

$$\sum_i X_i^j = 1, \qquad \forall j \in \{1, \ldots, p\}. \tag{1.104}$$

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

$$f = 2 + (c-1)p - c(p-1) = c - p + 2, \tag{1.105}$$

as expected. 😃

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 $c+2$.

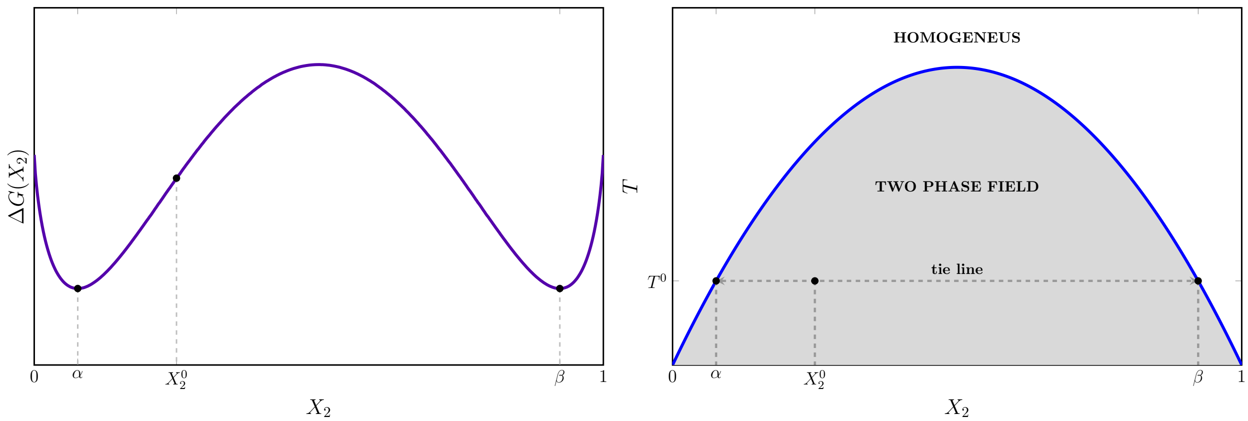


Figure 1.11: Illustration of a two phase system with miscibility gap, showing so a two phase field inside the phase diagram under the curve that describes the critical temperature of the system after which we have a homogeneous disordered phase.

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.

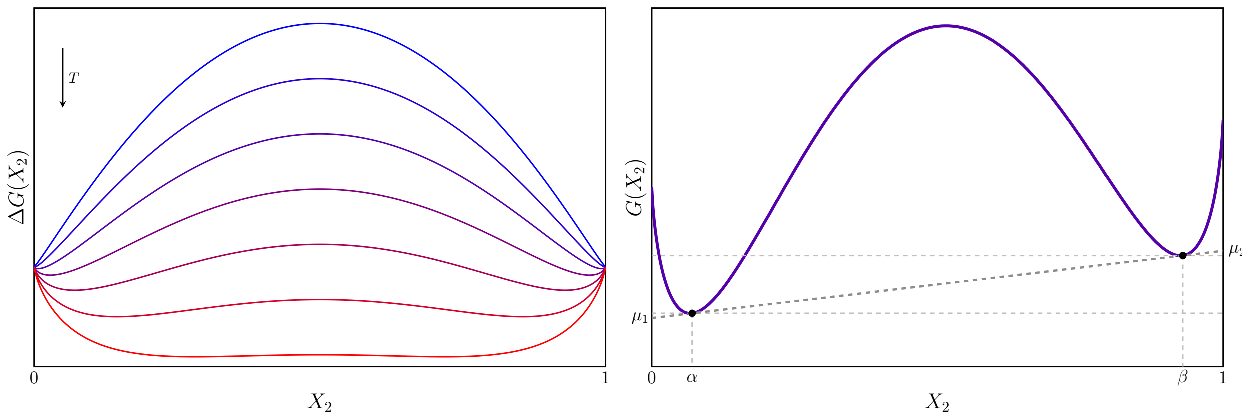


Figure 1.12: Representation of the mixing free energy at different temperatures on the left, and of the form of the normal free energy written as $G = \Delta G + \mu_2^0 X_2$ assuming $\mu_1^0 = 0$ on the left. It's possible to notice how the final form of G is asymmetric.

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

$$a_\alpha + a_\beta = 1, \qquad a_\alpha X_2^\alpha + a_\beta X_2^\beta = X_2^0, \tag{1.106}$$

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

$$a_\alpha = \frac{X_2^\beta - X_2^0}{X_2^\beta - X_2^\alpha}, \qquad a_\beta = \frac{X_2^0 - X_2^\alpha}{X_2^\beta - X_2^\alpha} \tag{1.107}$$

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

$$G = \Delta G + \sum_i \mu_i^0 X_i, \tag{1.108}$$

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

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

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 con 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

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

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

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.

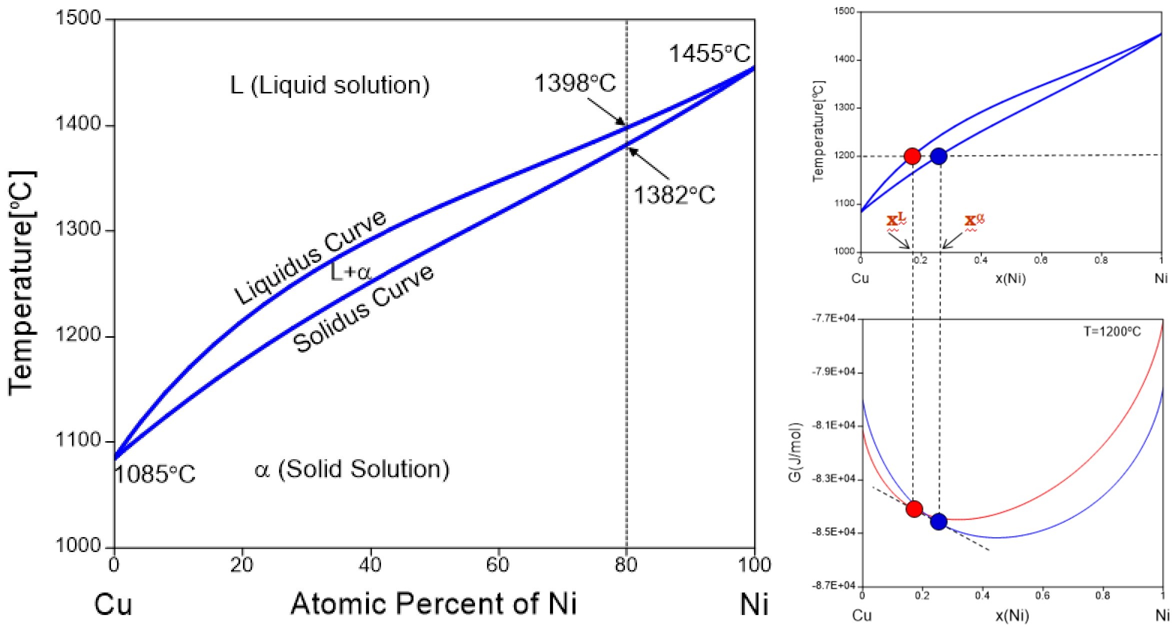


Figure 1.13: Phase diagram of Cu – Ni system on the left, with double tangent construction of it on the right for a certain fixed temperature reported on the image.

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

$$X < \gamma, \text{ homogeneous}; \qquad X > \gamma, \text{ heterogeneous}. \tag{1.112}$$

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 ceCu-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

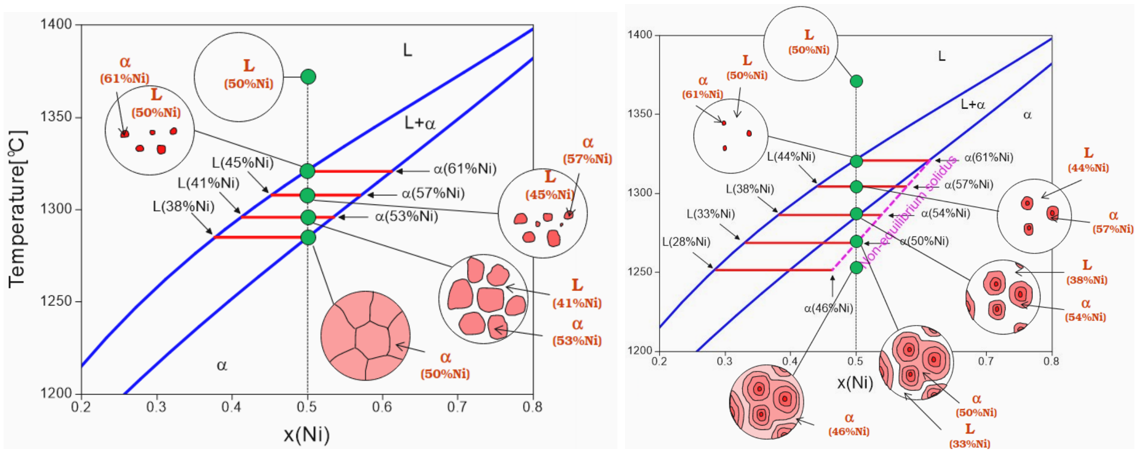


Figure 1.14: Illustration of the cooling of the system from the liquid phase to the solid one using a slow process, on the left, and a quick one where system as no time to reach equilibrium at every step, on the right.

describes the behaviors of the single elements. Therefore, giving us the values of the melting points of Cu and Ni being at $1085\,°\mathrm{C}$ and $1455\,°\mathrm{C}$ 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,

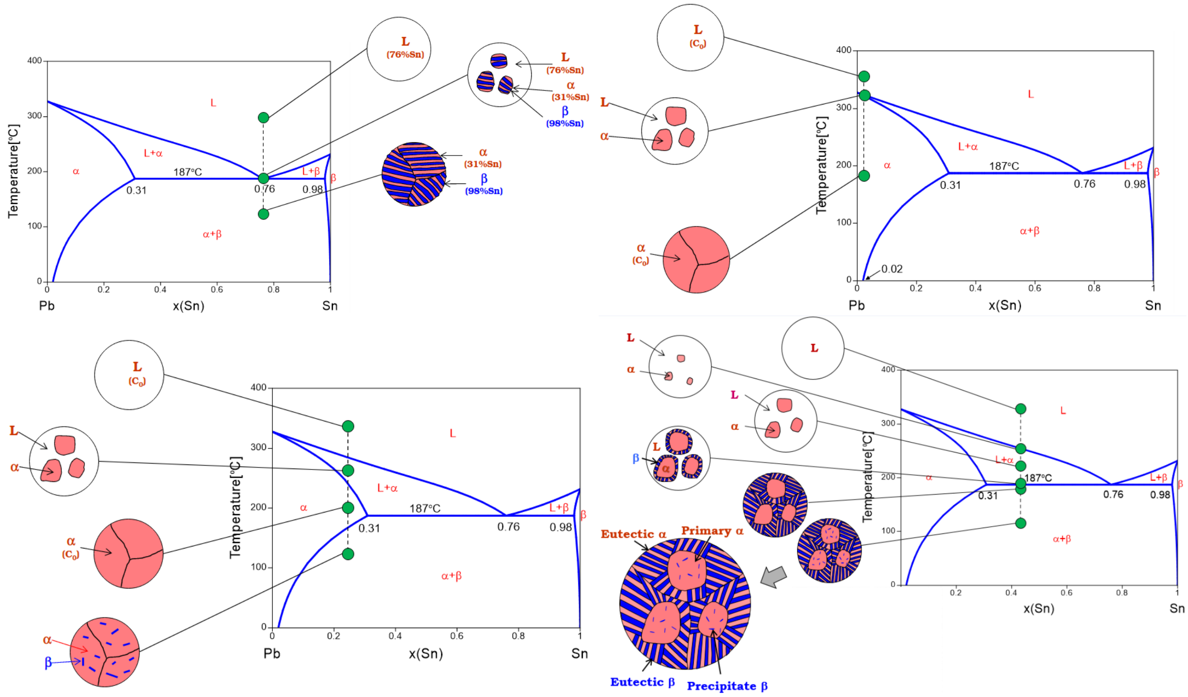


Figure 1.15: Illustration of the cooling of a Eutectic system in different points of the phase diagram, looking at positions near the eutectic point and away from it.

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

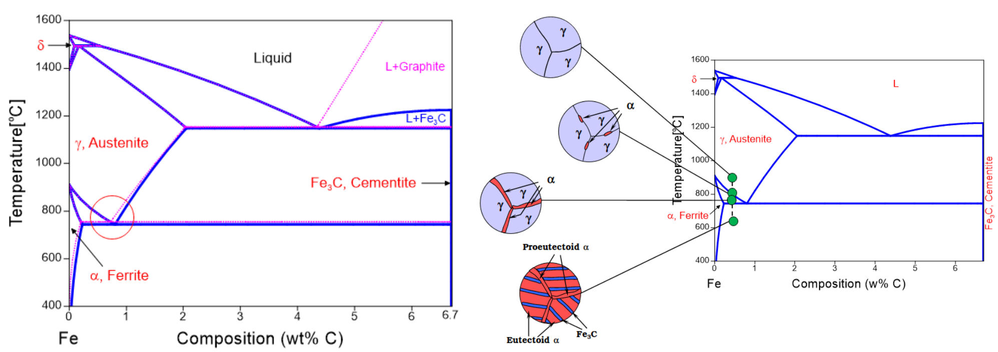
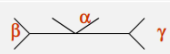
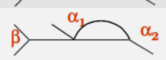


Figure 1.16: Phase diagram of Iron-Carbon system expressed in weight percentage of Carbon. On the left the phase diagram is shown along with the real equilibrium theoretical one in pink, the difference from equilibrium are present since the mixture is in reality a metastable state that take a long time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

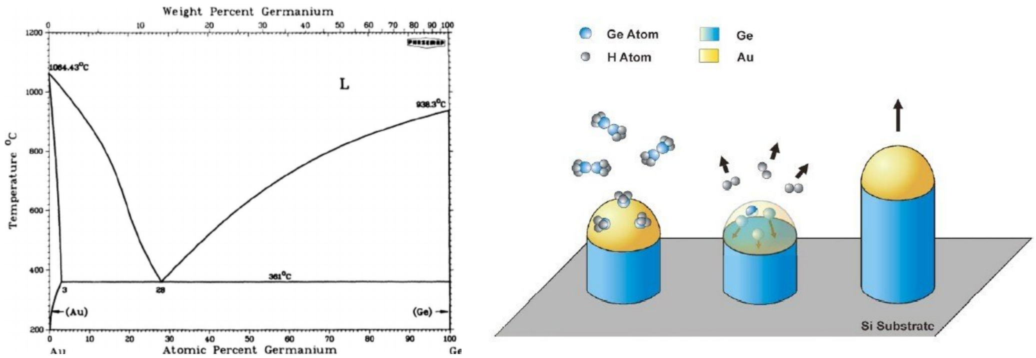


Figure 1.17: Phase diagram of Ge – Au mixture showing how the two elements are immiscible at normal temperature with a eutectic point at 28% of Germanium, on the left. Visualization of the Ge nanowire growth, on the right.

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 cleaver 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

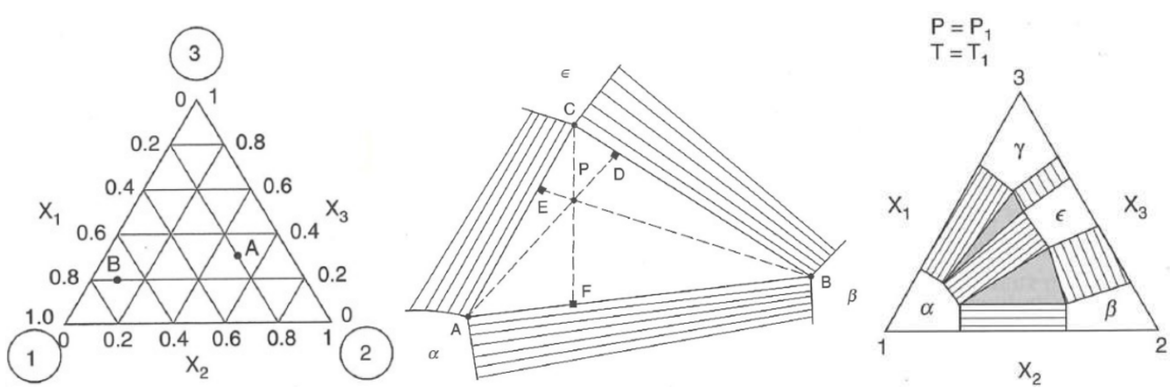


Figure 1.18: From the left: Gibbs triangle representation of the ternary systems' phase space, example of the lever rule in a three phase field portion of the phase space, and example of a ternary phase diagram.

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

$$a_\alpha = PD/AD, \qquad a_\beta = PE/BE, \qquad a_\epsilon = PF/CF, \tag{1.113}$$

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 sad 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

$$\frac{\mathrm{d}S_1}{\mathrm{d}t} = -\frac{I_Q}{T+\Delta T}, \qquad \frac{\mathrm{d}S_2}{\mathrm{d}t} = \frac{I_Q}{T}. \tag{2.1}$$

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

$$\frac{\mathrm{d}S}{\mathrm{d}t} \approx \frac{I_Q}{T}\frac{\Delta T}{T} > 0, \tag{2.2}$$

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 Jaul effect, in fact, generates entropy since we have

$$P = \Delta V I_q, \qquad \frac{\mathrm{d}S}{\mathrm{d}t} = \frac{P}{T} = \frac{\Delta V}{T} I_q. \tag{2.3}$$

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

$$T\mathrm{d}s = \mathrm{d}u - \psi_i \mathrm{d}\xi_i, \tag{2.4}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\mathrm{d}u = \delta Q + \psi_i \mathrm{d}\xi_i, \qquad \mathbf{J}_u = \mathbf{J}_Q + \psi_i \mathbf{J}_i, \tag{2.12}$$

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

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

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

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

$$\begin{aligned}
&\text{Heat}, && \mathbf{J}_Q, && -\frac{\mathbf{\nabla}T}{T}, && \mathbf{J}_Q = -\kappa\mathbf{\nabla}T; && (2.14)\\
&\text{Charge}, && \mathbf{J}_q, && -\mathbf{\nabla}\phi, && \mathbf{J}_q = -\rho^{-1}\mathbf{\nabla}\phi; && (2.15)\\
&\text{Matter}, && \mathbf{J}_i, && -\mathbf{\nabla}\mu, && \mathbf{J}_i = -c_i M_i \mathbf{\nabla}\mu. && (2.16)
\end{aligned}$$

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

$$\dot{\sigma} \geq 0. \tag{2.17}$$

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

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

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 it's driving force but all of them give a contribution, having in general

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

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

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

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

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

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

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

$$\mathcal{L}_{\alpha\beta} = \mathcal{L}_{\beta\alpha}. \tag{2.22}$$

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

$$\frac{\partial J_\alpha}{\partial F_\beta} = \frac{\partial J_\beta}{\partial F_\alpha}, \tag{2.23}$$

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 presen,t 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

$$k_{\alpha\beta} = k_{\beta\alpha}. \tag{2.24}$$

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

$$\beta_{ij} = \beta'_{ji}. \tag{2.25}$$

$\mathbf{D}_i$ 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

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

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

$$\nabla\phi = -S\nabla T, \qquad S = \frac{\rho\beta}{T}. \tag{2.27}$$

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

$$\mathbf{J}_Q = \Pi\mathbf{J}_q, \qquad \Pi = \beta'\rho, \tag{2.28}$$

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

$$\Pi_{ij} = TS_{ij}, \tag{2.29}$$

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

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

Where, we can understand that the constant in front gives out the order of magnitude for the value of S, which is $k_B/e \approx 87\,\mu\mathrm{V/K}$. 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

$$S \approx \frac{\sigma_n S_n + \sigma_p S_p}{\sigma_n + \sigma_p}. \tag{2.31}$$

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

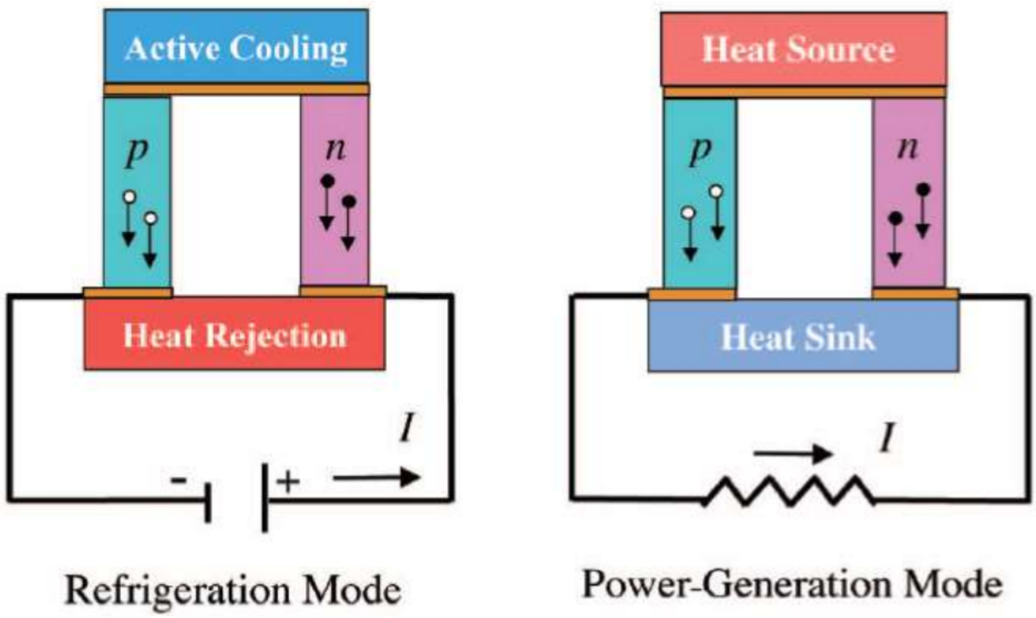


Figure 2.1: Diagram of a Peltier thermoelectric couple made of an n-type and a p-type thermoelectric material. Refrigeration and power generation modes are possible, depending on the configuration.

spacecraft engineering where Radioisotope Thermoelectric Generators(RTG) are widely used. Such devices bring a lot of advantages in genera, 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

$$ZT \equiv \frac{S^2 \sigma T}{\kappa}, \tag{2.32}$$

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

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

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

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

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 $\eta \longrightarrow \eta_c$ for $ZT \longrightarrow \infty$. Therefore, we are looking for materials that posses 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 greate electrical one. Still this is not so easy to achive 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**

$$\kappa = \kappa_E + \kappa_P, \qquad \kappa_E = L\sigma T, \tag{2.35}$$

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

$$\kappa_P = \frac{1}{3} v_s C \lambda_P, \tag{2.36}$$

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 $0.25\,\mathrm{W m^{-1} K^{-1}}$. 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 $160\,\mathrm{\mu V K^{-1}}$. 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.

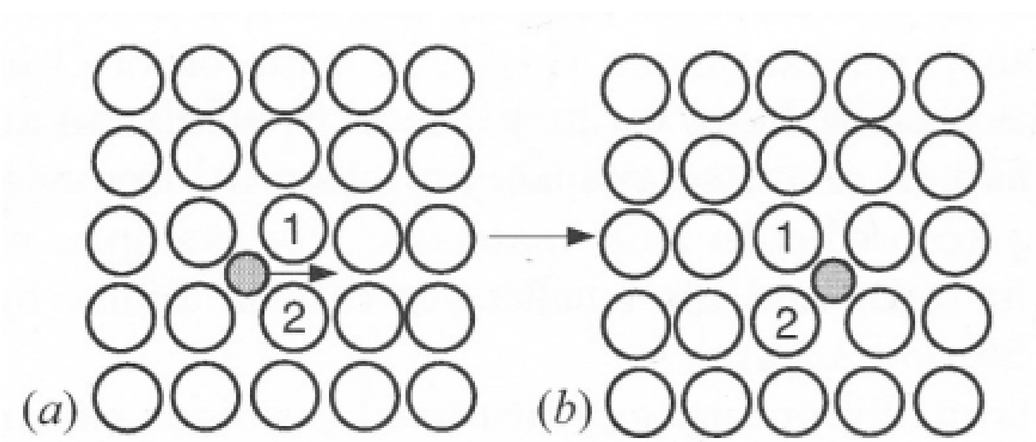


Figure 2.2: Example of diffusion of an interstitial atom inside a general simple lattice.

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

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

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

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

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

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

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

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

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

$$\nabla \mu_i = \frac{k_B T}{c_i} \nabla c_i. \tag{2.41}$$

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

$$D_i = k_B T M_i, \tag{2.42}$$

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

Substitutional diffusion

To be able to model the flux of a certain atomic spicy 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

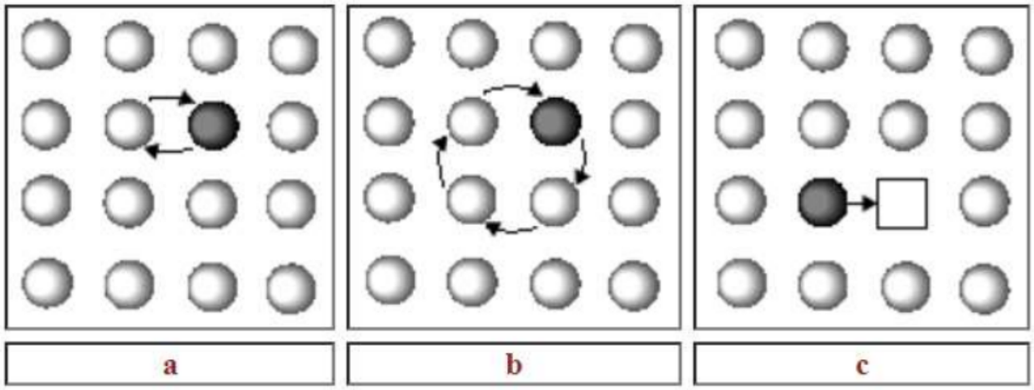


Figure 2.3: Representation of the three main possible diffusion mechanism, in order: direct exchange, cyclic exchange, and vacancy diffusion.

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 spicy 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 constrains 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

$$\mathbf{J}_A + \mathbf{J}_B = 0. \tag{2.43}$$

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 $785\,^\circ\mathrm{C}$ 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 spicy 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

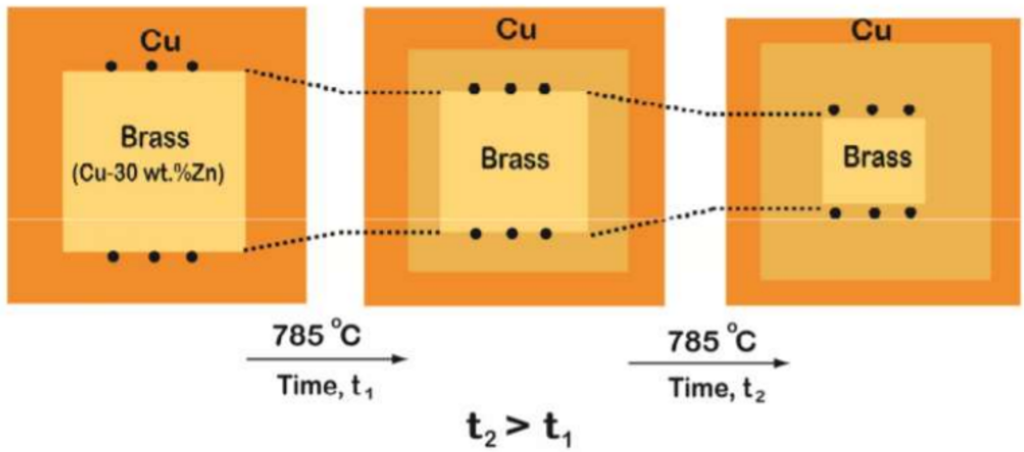


Figure 2.4: Results of the Kirkendall experiment showing how the Brass core becomes smaller due to different values of the fluxes for the two different atomic species.

so that fluxes relation would be

$$\mathbf{J}_A + \mathbf{J}_B + \mathbf{J}_V = 0, \tag{2.44}$$

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 sad 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:

$$\sum_{i=1}^{c+1} \mathrm{d}N_i = 0. \tag{2.45}$$

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

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

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 con be use as a reference for the others. Basically, we can select a component j and use Eq. (2.45) to rewrite it's differential using the others, so that

$$\mathrm{d}N_j = -\sum_{i \neq j} \mathrm{d}N_i, \tag{2.47}$$

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

$$G = \sum_{i=1}^{c+1} \mu_i \mathrm{d}N_i = \sum_{i \neq j} \left(\mu_i - \mu_j\right) \mathrm{d}N_i. \tag{2.48}$$

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 $\mathrm{d}N_i$ quantities, and so the fluxes, can be rescaled in terms of a component. Meaning that we can simply write the driving forces using the realtion

$$\mathbf{F} = -\nabla \left(\mu_i - \mu_j\right), \tag{2.49}$$

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

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

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

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

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. 😁

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

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

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

$$c_1 \mathrm{d}\mu_1 + c_2 \mathrm{d}\mu_2 = 0, \qquad \mathrm{d}\mu_1 = -\frac{c_2}{c_1}\mathrm{d}\mu_2, \tag{2.53}$$

where $\mathrm{d}\mu_V = 0$ 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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\mathbf{v}_C^V = (D_1 - D_2)\,\overline{V}_1 \boldsymbol{\nabla} c_1. \tag{2.61}$$

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

$$\tilde{D} = c_1 \overline{V}_1 D_2 + c_2 \overline{V}_2 D_1. \tag{2.62}$$

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

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

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

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

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

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

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 difrattometry 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 $0.65\,\mathrm{eV}$.

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

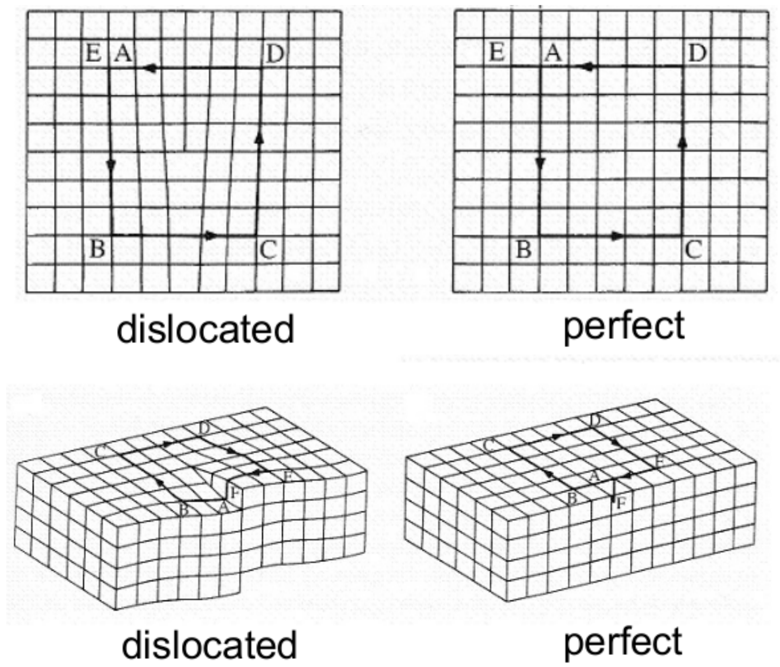


Figure 2.5: Construction of Burger's vectors in two different types of dislocations: edge dislocations on top, and screw one on the bottom.

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, **destroing 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**

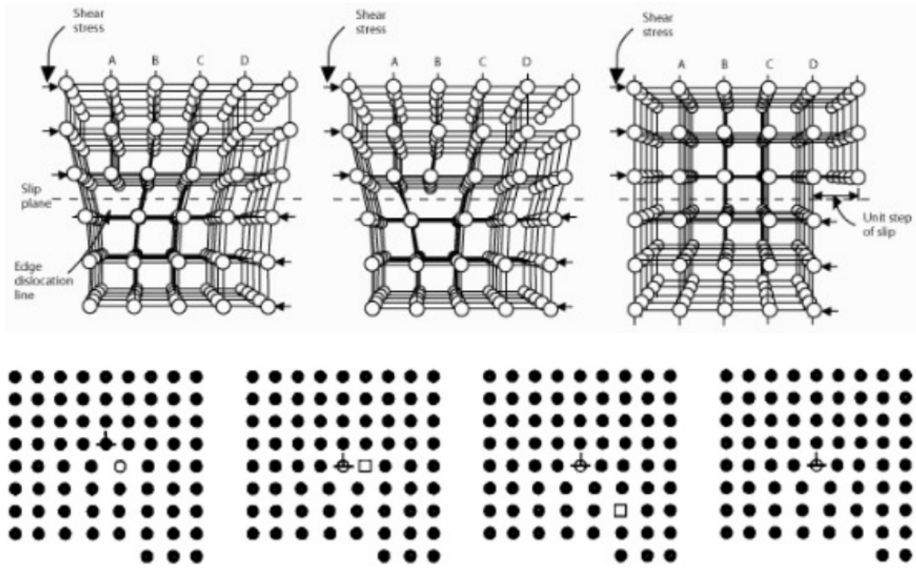


Figure 2.6: Graphical representation of the two types of dislocations movements: glide movement on top, climb movement on the bottom. In particular, the climb movement bring the dislocation down in this case.

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

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

where $\Delta \overline{V}_i$ is the local variation of the volume occupied by the i-th spicy 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

$$\Phi_i = \mu_i + \Delta \overline{V}_i P, \tag{2.67}$$

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

$$\Phi_i = \mu_i + q_i \phi. \tag{2.68}$$

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

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i. \tag{2.69}$$

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

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

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

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

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

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

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

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 $c_i(x, t \longrightarrow 0) = n_i \delta(x)$ than the following function is the solution

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

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

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

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

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

Where d is the dimensionality of the system, and we can see how the Dirac delta form for $t \to 0$ 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

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

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

$$\ln c_i = const. - \frac{x^2}{4D_i t}, \tag{2.77}$$

meaning that by making a linear fit in a lnc_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

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

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 it's value will take the form of

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

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

$$\left\langle R^2(t)\right\rangle = \Gamma t \left\langle r^2\right\rangle, \tag{2.80}$$

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 though 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
>
> $$D = \frac{\Gamma \left\langle r^2\right\rangle f}{2d}, \qquad f = 1 + \frac{2\Pi(t)}{\Gamma t \left\langle r^2\right\rangle}, \tag{2.81}$$
>
> 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

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

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

$$D = \frac{\Gamma \left\langle r^2\right\rangle f}{2d}, \tag{2.83}$$

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:

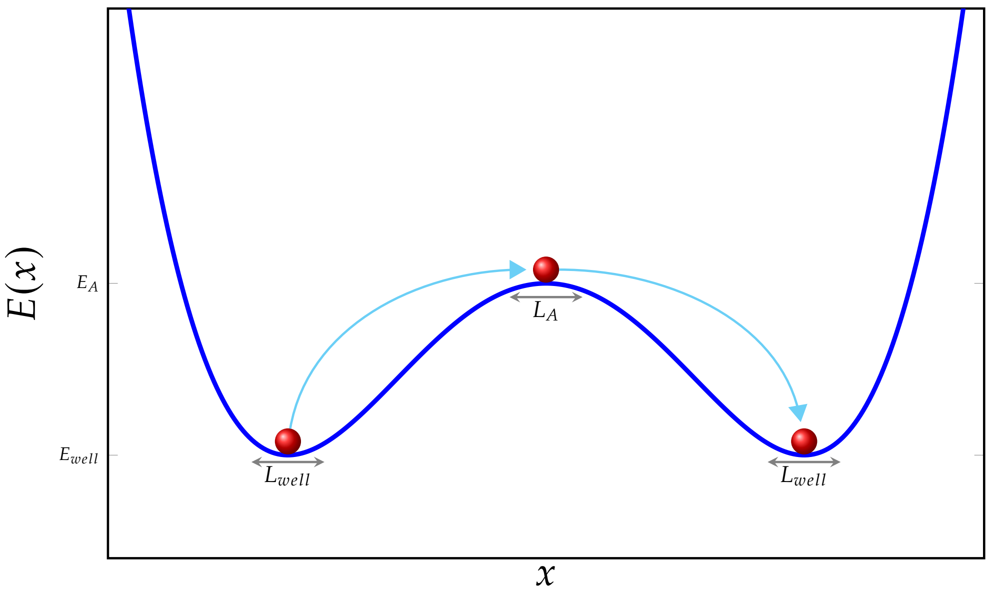


Figure 2.7: Representation of the energy landscape of a possible system under study in the context of thermally activated processes. Where the path followed by the atom is in 1D and is described by the directions of the arrows.

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

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

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

$$\tau_{cross} = \frac{L_A}{\langle v \rangle}, \qquad \langle v \rangle = \frac{\int_{\mathbb{R}^+} v e^{-\frac{mv^2}{2k_B T}} \mathrm{d}v}{\int_{\mathbb{R}^+} e^{-\frac{mv^2}{2k_B T}} \mathrm{d}v} = \sqrt{\frac{2\pi m}{k_B T}}, \tag{2.85}$$

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

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

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 that 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

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

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

$$\Gamma' = \frac{P_A}{\tau_{cross}} = \frac{Z_A}{Z_{well}} \frac{1}{\tau_{cross}} = \nu e^{-\frac{E^m}{k_B T}}, \tag{2.88}$$

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

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

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

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

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 $\left\langle r^2 \right\rangle = a^2/2$. 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

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

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

$$\Gamma_A = \Gamma_V \frac{N_V}{N_T} = \Gamma_V X_V. \tag{2.92}$$

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

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

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 $D_A^0 \approx 0.1 - 1.0\,\mathrm{cm^2 s^{-1}}$, in good agreement with the typical values of $a \approx 3\,\text{Å}$, $\nu \approx 1 \times 10^{13}\,\mathrm{s^{-1}}$ 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

$$n_1^r R_1 + n_2^r R_2 + \cdots + n_N^r R_N \rightleftharpoons n_1^p P_1 + n_2^p P_2 + \cdots + n_M^p P_M, \tag{2.94}$$

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

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

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

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

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

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

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

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

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 found 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 tusk 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 $\mathrm{X_S}^{\mathrm{C}}$, 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 defects 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.