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
>
> $$\psi_i \mathrm{d}\xi_i = \delta w, \qquad (1.1)$$
>
> 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

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

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

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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

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

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

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

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

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

☺

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

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

Where electric and magnetic work are presents along with the one given by the stress σ and strain ε. 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.

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

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

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

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

Also, in this case the tensor is symmetric since ε and σ 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 $\mathbf{q}$ 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 $\mathbf{q} = \mathbf{q}'$.

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[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 **p** entries are non-zero we have electrocaloric effect, and with it also **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** Θ becomes important. In particular one can call **i-tensors** the ones that are invariant under Θ and **c-tensors** the others we will have that the magnetic field is inside the latter, having

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

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

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

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

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

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

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

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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
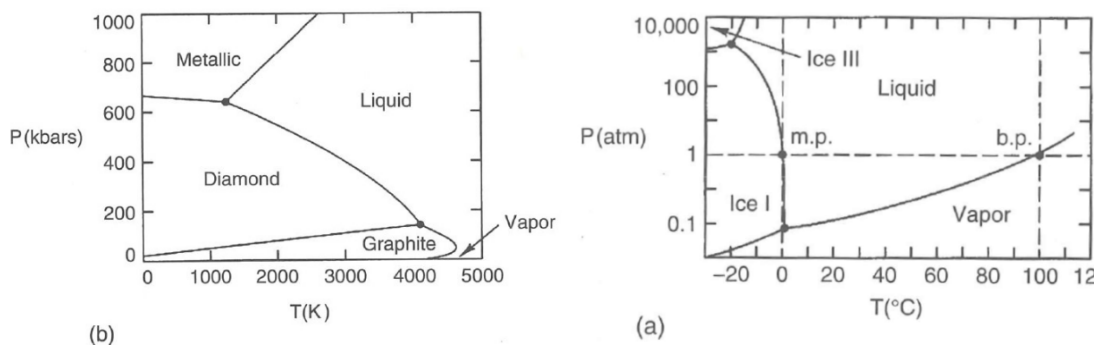

Figure 1.2: Phase diagrams of simple unary systems: Carbon(a) and Water(b). Both are reported in a P vs T graph, where we can clearly see the triple points and the coexistence lines.

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:
> $$T^\alpha = T^\beta, \qquad\qquad P^\alpha = P^\beta, \qquad\qquad \mu^\alpha = \mu^\beta. \qquad (1.18)$$

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

$$U^\alpha + U^\beta = const, \qquad\qquad V^\alpha + V^\beta = const, \qquad\qquad N^\alpha + N^\beta = const. \qquad (1.19)$$

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

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

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

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

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

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

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

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

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

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

particular one, the **Gibbs free energy** G. The reasons for it are several, for example one can see from its differential how taking the Gibbs energy per number of mole, $\overline{G}$, 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

$$d\mu = -SdT + VdP. \tag{1.24}$$

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

$$d\mu \leq -SdT + VdP. \tag{1.25}$$

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

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

As a last remark it could be interesting to understand how the values of μ can be computed inside a system, in particular using experimental results. The idea is starting from the differential Eq. (1.24)
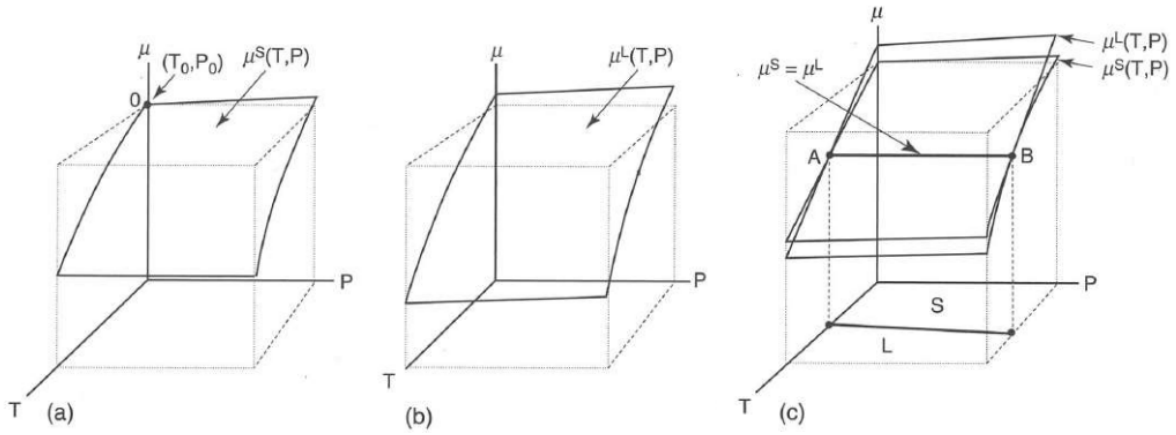
Figure 1.3: Graphical raprezentation of the chemical potential for a solid phase(a), liquid phase(b) and the superposition of the two to see which one prevails on the other for the equilibrium phase(c). It's possible to see how in the part of the phase diagram where $\mu^S = \mu^L$ a coexistence line appear.

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

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

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

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

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

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

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

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

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

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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

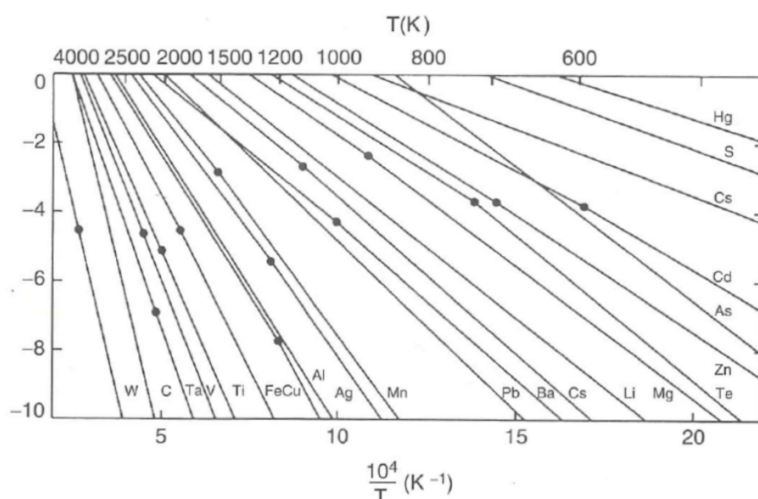$$\frac{\mathrm{d}P}{P} = \frac{\Delta H}{R}\frac{\mathrm{d}T}{T^2}, \tag{1.36}$$

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 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 gas.

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

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

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

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

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 $\mathbf{n} \to \lambda\mathbf{n}$, 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

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

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

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

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

$$df = \overline{f}_1 dX_1 + \overline{f}_2 dX_2, \tag{1.54}$$

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

$$\frac{df}{dX_2} = \overline{f}_2 - \overline{f}_1, \tag{1.55}$$

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

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

---

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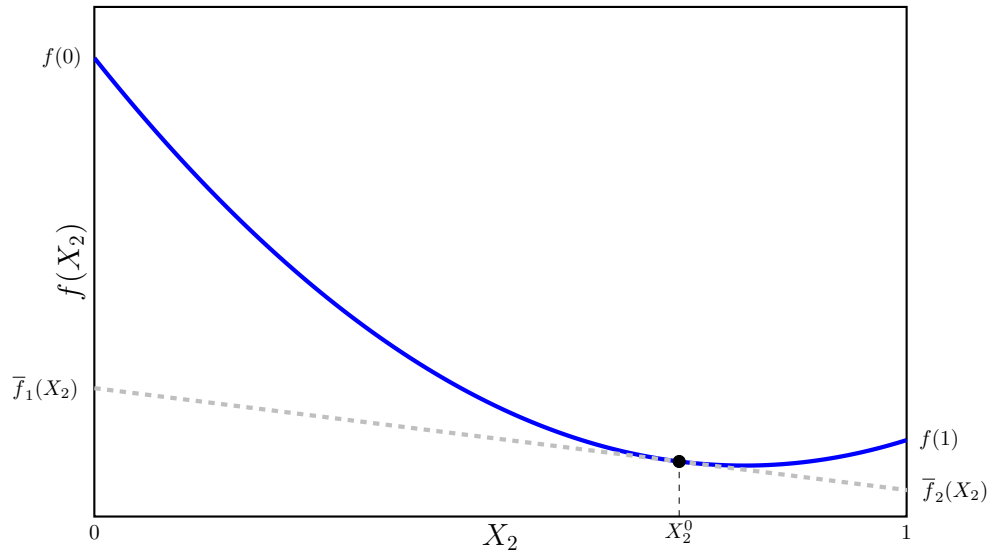
Figure 1.5: Illustration of the graphical method to compute the PMPs of a binary system in the case of a simple physical quantity. It's possible to see how the method basically select one point X_2^0 and then draw the tangent to f in that point finding the PMPs as the intercepts with the $X_2 = 0$ and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

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> **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 $\Delta H_{mix} = a X_1 X_2$. 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
>
> $$\Delta \overline{H}_1 = a X_2^2, \qquad\qquad \Delta \overline{H}_2 = a X_1^2. \tag{1.64}$$
>
> 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
>
> $$\Delta \overline{H}_1 = \int_0^{X_1} \frac{X_1'}{(X_1' - 1)} 2a(X_1' - 1)\mathrm{d}X_1' = a X_1^2. \tag{1.65}$$

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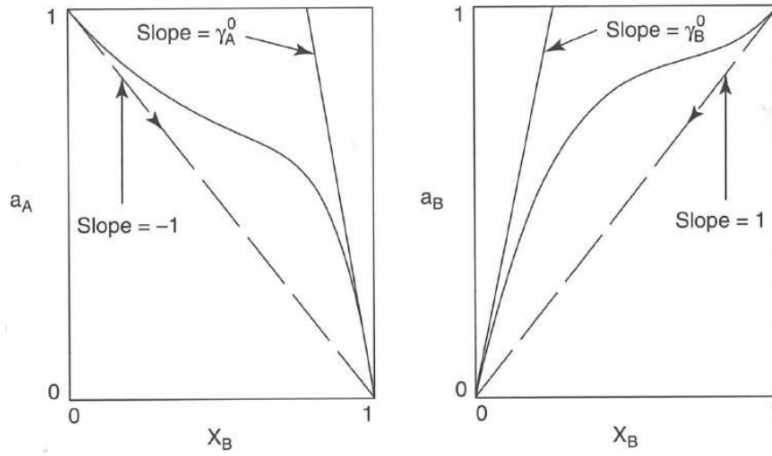
Figure 1.6: Illustration of the activity inside a binary system composed by the phases a and b, showing the expected behaviors of ideality in the diluted case.

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.

<div>

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

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

</div>

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

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

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.

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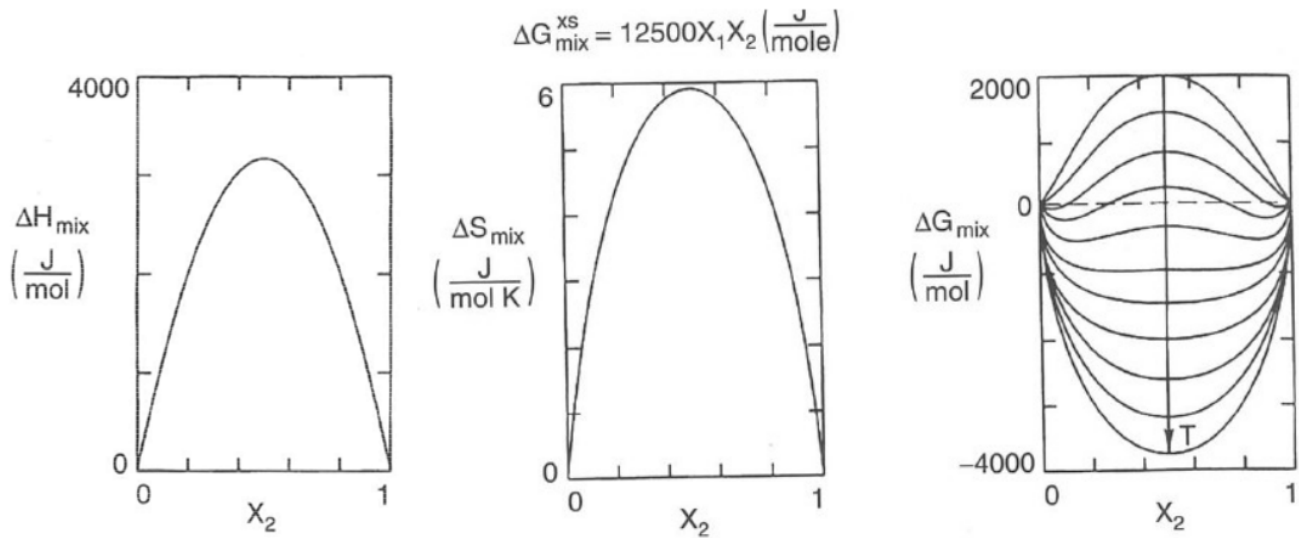$$\Delta G^{xs}_{mix} = 12500 X_1 X_2 \left(\frac{J}{mole}\right)$$

Figure 1.7: Computed values of mixing properties for the simple system given by the mixing enthalpy $a X_1 X_2$. 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.

Example 1.3.3

To make an example of where the relation Eq. (1.77) can be really useful. Basically the simplest model possible for a regular solution posses as excess enthalpy the quantity $H^{xs}_{mix} = a X_1 X_2$, that we have already studied, and we know have $\Delta \overline{H}_i = a X_i^2$, so

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

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

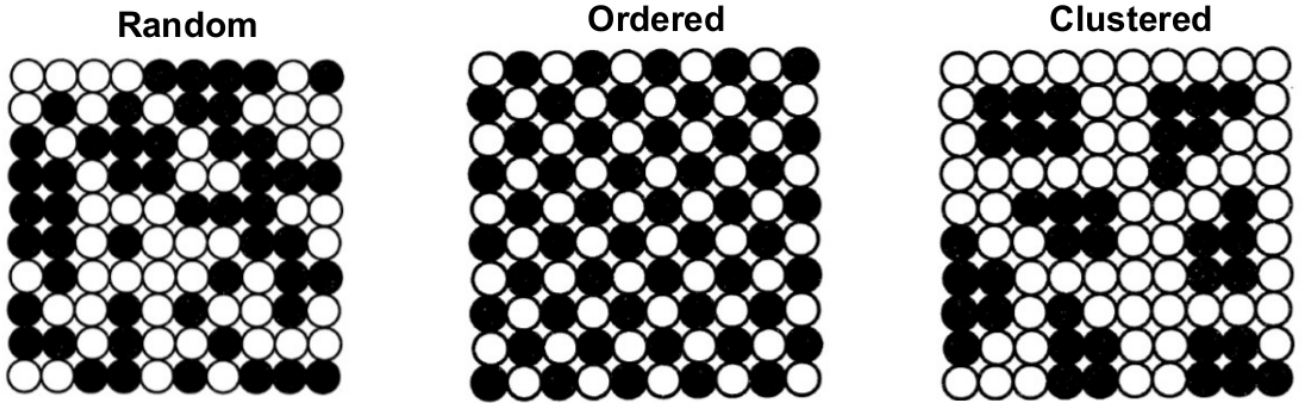**Random**   **Ordered**   **Clustered**

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.

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-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

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

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

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

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

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

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.

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

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

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

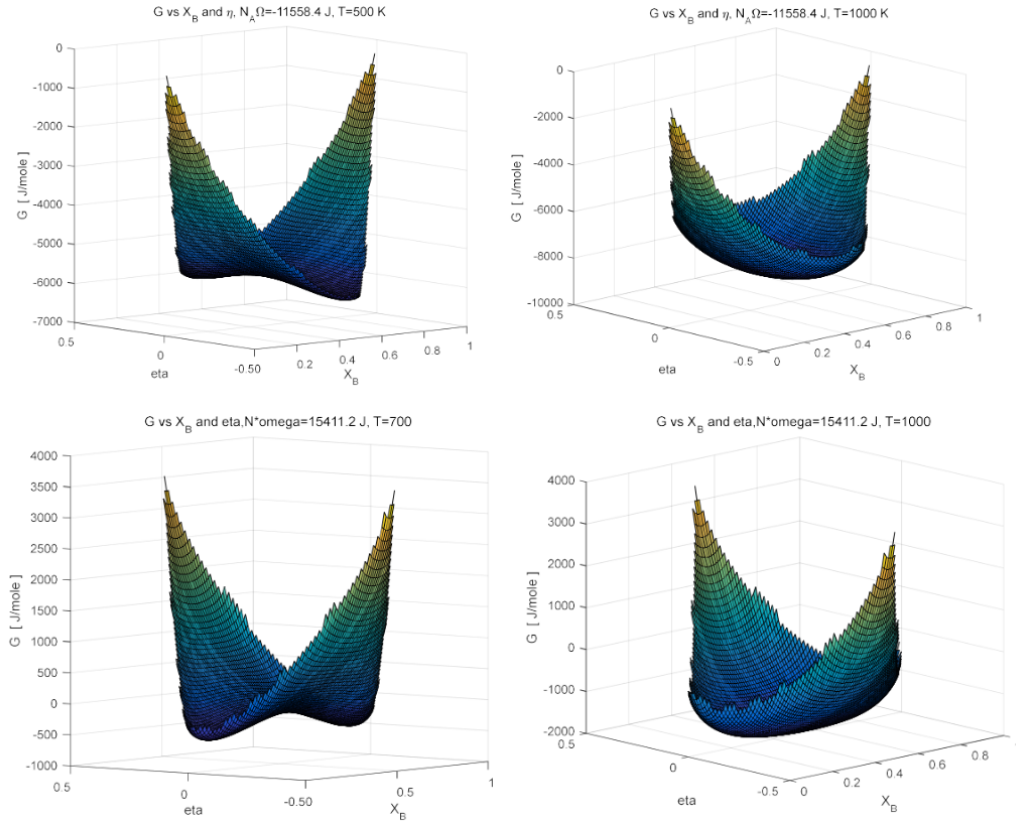$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}. \tag{1.89}$$

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,

25

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

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

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

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

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

> **Note**
>
> *The Gibbs free energy of mixing in Eq. (1.92) is fairly general and interesting, for example we can see easily how in the case of a disordered system, $\eta = 0$, Eq. (1.92) becomes the free energy of a regular solution*
>
> $$\Delta G_{mix} = N\Omega X_A X_B + RT\left(X_A \ln X_A + X_B \ln X_B\right) = \Delta H_{mix} - T\Delta S_{mix}^{id}. \qquad (1.93)$$
>
> *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

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

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

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

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 $\forall i \in \{0, \ldots, c\}$ components
>
> $$T^\alpha = T^\beta, \qquad\qquad P^\alpha = P^\beta, \qquad\qquad \mu_i^\alpha = \mu_i^\beta. \qquad (1.100)$$

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

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

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

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

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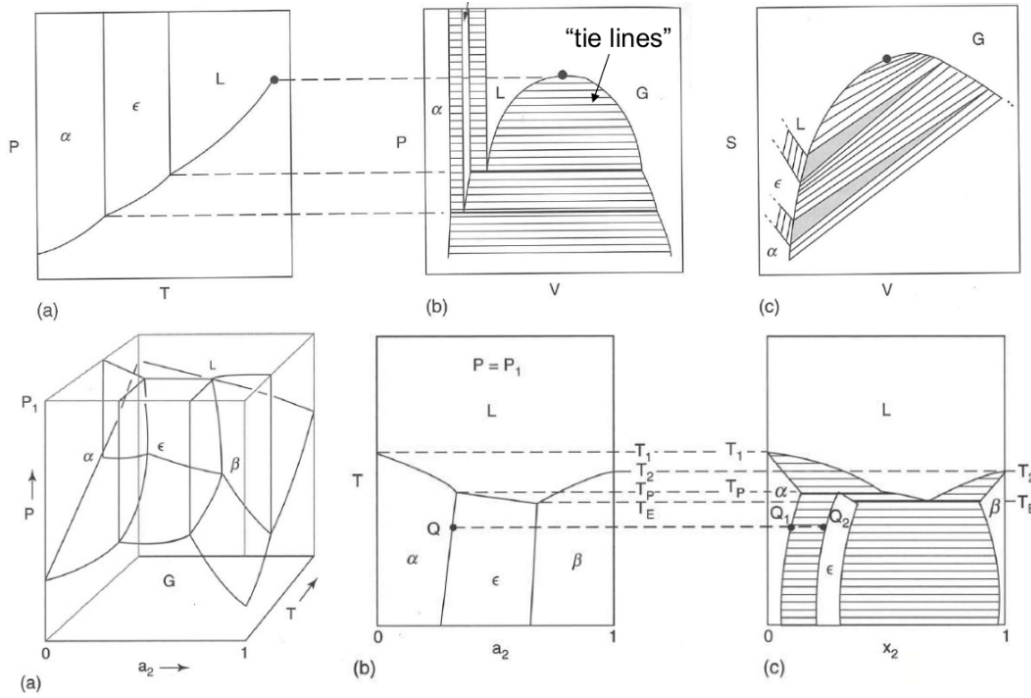> $$f = c - P + 2. \qquad (1.103)$$

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 a 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

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

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

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

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 $c + 2$.
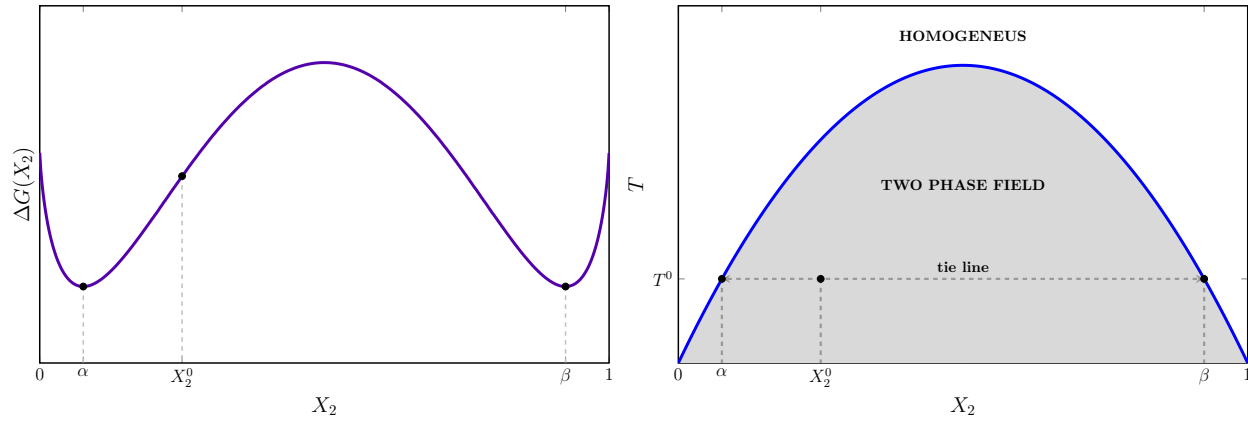
Figure 1.11: Illustration of a two phase system with miscibility gap, showing so a two phase field inside the phase diagram under the curve that describes the critical temperature of the system after which we have a homogeneous disordered phase.

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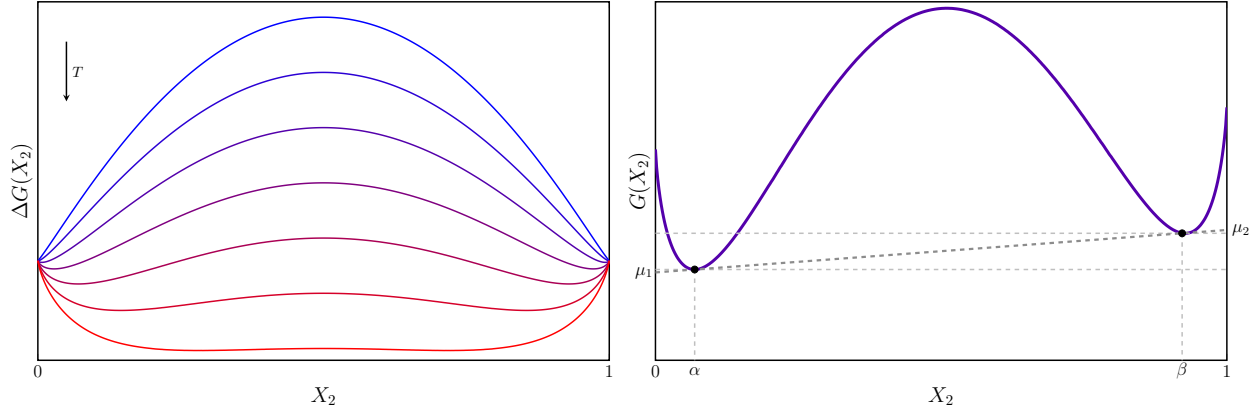
Figure 1.12: Representation of the mixing free energy at different temperatures on the left, and of the form of the normal free energy written as $G = \Delta G + \mu_2^0 X_2$ assuming $\mu_1^0 = 0$ on the left. It's possible to notice how the final form of G is asymmetric.

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

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

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

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

In this way we can understand how much total volume of the system the two phases will take for themselves.

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

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

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 creating a variation of the chemical potentials respect to the one that we would expect from the **tangent construction** that we have discussed before. In fact, by taking the tangents in the two minima we would have that the chemical potentials obtained $\mu_i(X_2^\alpha)$ and $\mu_i(X_2^\beta)$ would be at different height and so have different values, while equilibrium conditions needed them to be equal. We can overcome this problem in a simple way, using the so-called **Double tangent construction**, where basically you construct a line connecting the two minima and the intercepts on the y-axis will give the μ_1 on the left and μ_2 on the right. Really simple and intuitive, even if we haven't demonstrated it mathematically, that allow us to find out μ also in this type of systems.