

# Phase Field Modelling

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## 0.1 Solution Models

In this section, we will talk about a particular model for understanding the thermodynamics of alloy systems. This model is known as regular solution model.

Everybody knows that nickel, copper and silver are metals which crystallize in the cubic crystal structures, specifically, the face centred cubic system. Zinc, for example, crystallizes in the hexagonal crystal structure.

Taking two crystals, for example nickel and copper, and putting them together, they actually form a solid solution.

About more than 100 years ago, people understood that complicated things can happen if different types of atoms are put together and wide variety of things can be seen; for instance, nickel and copper form what is known as an isomorphous system, so it is completely immiscible both in the solid state and in the liquid state. Copper and silver, for example, form what is known as an eutectic system. Nickel and aluminium form a lots of altered structures, instead aluminium and zinc phase separate.

The regular solution model, which will be discussed, is one of the models to understand what happens when taken different types of atoms and put them together. The base for this model is the Gibbs free energy. At constant temperature and constant pressure, in those systems, it is possible to understand the equilibrium as one which minimises the Gibbs free energy. The Gibbs free energy is written as follows:

$$G = H - TS \tag{1}$$

In condensed systems (solids and liquids), it is a good approximation consider the enthalpy the same as the internal energy; in other words, the  $pV$  term is neglected and it is possible to write:

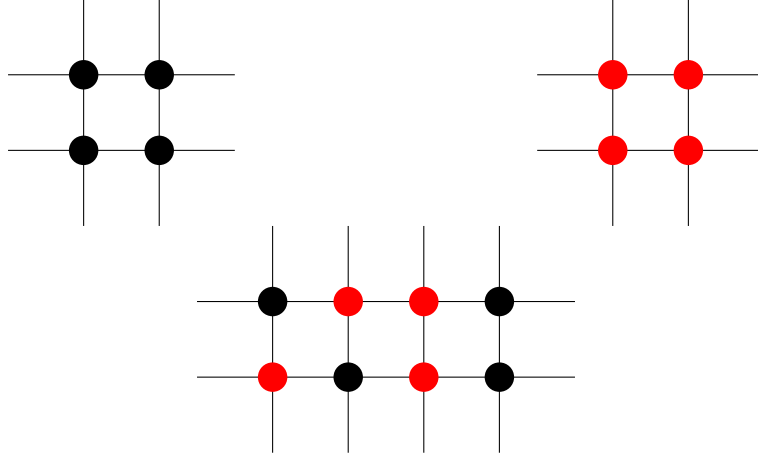
$$G \simeq U - TS \tag{2}$$

Supposing to have a system which consists of two different type of atoms,  $A$  and  $B$ . One of the simplest model which can be think of, is to understand what happen when putting together  $A$  and  $B$  type of atoms and considering a solid, so a binary alloy at normal atmosphere pressure.

The most basic thermodynamic model which can be built, is known as Ideals Solution and before talk about it, the free energy of mixing should be defined.

Assume to have some  $A$  type of atoms (black) and  $B$  type of atoms (red) and there will be a certain free energy associated with them in the initial configuration. After, suppose to bring them together and to have, for example, a configuration like in the picture, which will have a certain free energy. The difference between the free energy of the configuration and the free energy of the two initial condition separated, is known as the free energy of mixing:

$$\Delta G^{Mix} = \Delta U^{Mix} - T\Delta S^{Mix} \quad (3)$$



There are several different ways by which this mixing can happen at atomistic level and, depending on whichever is the one which is going to give the maximum reduction in the  $\Delta G^{Mix}$  to be negative and as larger as possible in modulus, that will be the one that would be preferred out of them.

In the case of ideal solution, it is assumed that the quantity  $\Delta U^{Mix}$  is equal to zero.

Another assumption is made; in majority of the cases for these kind of alloy models, the only contribution of entropy comes from the configurational entropy:

$$\Delta S^{Mix} = \Delta S^{Mix,Config.}$$

The configurational entropy is given by Boltzmann's entropy formula:

$$S = k \ln(\omega) \quad (4)$$

Where  $\omega$  is the number of possible configurations (microstates) in which is possible to distribute  $N_A$  number of  $A$  atoms and  $N_B$  number of  $B$  atoms on a lattice of size  $N = N_A + N_B$ . If it is not possible to distinguish the  $N_A$  and the  $N_B$  type of atoms (all  $N_A$  are equal and all  $N_B$  are equal), the following expression is valid:

$$\omega = \frac{N!}{N_A! N_B!} \quad (5)$$

Initially, the initial configuration entropy is zero, because there are only atoms of type  $A$  and  $B$  and  $\omega = 1$ , which implies 0 entropy.

$$\Delta S^{Mix,Config.} = k \ln\left(\frac{N!}{N_A! N_B!}\right) \quad (6)$$

For large values of  $N$ , it is possible to use the sterling approximation:

$$\ln(N!) = N \ln(N) - N \quad (7)$$

$$\begin{aligned} \Delta S^{Mix,Config.} &= k \left[ \ln(N!) - \ln(N_A!) - \ln(N_B!) \right] \\ &= k \left[ N \ln(N) - N - N_A \ln(N_A) + N_A - N_B \ln(N_B) + N_B \right] \\ &= k \left[ (N_A + N_B) \ln(N) - N_A \ln(N_A) - N_B \ln(N_B) \right] \\ &= -k \left[ -N_A \ln(N) - N_B \ln(N) + N_A \ln(N_A) + N_B \ln(N_B) \right] \\ &= -k \left[ N_A \ln\left(\frac{N_A}{N}\right) + N_B \ln\left(\frac{N_B}{N}\right) \right] \\ &= -k \left[ N_A \ln(X_A) + N_B \ln(X_B) \right] \\ &= -kN \left[ \frac{N_A}{N} \ln(X_A) + \frac{N_B}{N} \ln(X_B) \right] \\ &= -kN \left[ X_A \ln(X_A) + X_B \ln(X_B) \right] \end{aligned} \quad (8)$$

Where  $X_A$  and  $X_B$  are the atomic fraction of  $A$  and  $B$  respectively

$$\Delta G^{Mix} = -T \Delta S^{Mix} = kTN \left[ X_A \ln(X_A) + X_B \ln(X_B) \right] \quad (9)$$

If  $N = N_{Avog.}$ , it is possible to write the equation for one mole of substance ( $n = 1$ )

$$\Delta G^{Mix} = TR \left[ X_A \ln(X_A) + X_B \ln(X_B) \right] \quad (10)$$

$T$  and  $R$  are positive quantities, instead logarithm of some fraction (number less than 1) is a negative number and totally  $\Delta G^{Mix} < 0$ .

There is a reason why it is called ideal solution, because it will always mix very homogeneous, because the perfect mixing randomly arrange the  $A$  and  $B$  atoms on the given lattice. It is also ideal solution in another sense. The system it is not able to distinguish between  $A$  type of atoms and the  $B$  type of atoms, and this is why the internal energy of mixing is 0.

The next model, is slightly more complicated than the ideal solution. In the case of what is known as a regular solution model, It is assumed that  $\Delta S^{Mix}$  is still given only by the configurational entropy and what is more, the expression that was derived by assuming that the  $A$  and  $B$  atoms are randomly distributed, that approximation is also valid and the same expression that was derived in the ideal solution is used. In addition, let's assume that

$\Delta H^{Mix}$ , which was assumed to be zero in the ideal solution case, is not equal to 0 but it is still a small number  $\Delta H^{Mix} \ll 1$ .

$\Delta H^{Mix}$  is related to the differences in bond energies ( $AA, BB, AB$ ). At higher temperature the entropy term is dominant and at very lower temperature the enthalpy term is dominant.

$$\Delta H^{Mix} = \Omega X_A X_B = \Omega(1 - X_B)X_B \quad (11)$$

Where  $\Omega$  is known as the regular solution parameter

$$\Omega = N_{Avog} \zeta \epsilon \quad (12)$$

Where  $\zeta$  is the number of nearest neighbours in the crystal structure

$$\epsilon = E_{AB} - \frac{1}{2}(E_{AA} + E_{BB}) \quad (13)$$

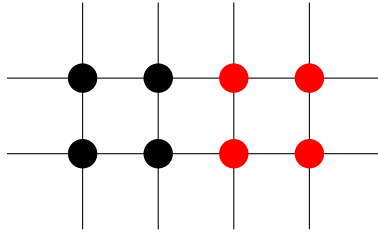
this one represents the difference in the bond energies. Let consider two  $AA$  and  $BB$  bounds, break them and make  $AB$  bounds and  $\epsilon$  calculates what is the difference in energies. If  $\epsilon > 0$  this means that  $AB$  bonds have higher energy instead if  $\epsilon < 0$  this means that the average of  $AA$  plus  $BB$  bonds have higher energy

$$\Delta G^{Mix} = \Omega X_B(1 - X_B) + TR \left[ X_B \ln(X_B) + (1 - X_B) \ln(1 - X_B) \right] \quad (14)$$

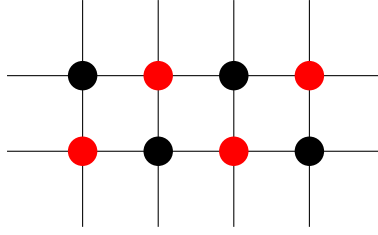
$$\Delta G^{Mix} = \Omega X_A(1 - X_A) + TR \left[ X_A \ln(X_A) + (1 - X_A) \ln(1 - X_A) \right] \quad (15)$$

This is valid because  $X_A + X_B = 1$ . Most of the times, the first expression is used.

Let as assume to stay at absolute temperature ( $T = 0K$ ), so there is no configurational entropy. The system behaviour is completely determined by the regular solution parameter. Suppose to have  $AA$  and  $BB$  bonds, brake them and make  $AB$  bonds and and seeing that  $AB$  bounds is going to be very expensive in terms of energy, then the system will prefer to have  $AA$  and  $BB$  bonds and form a phase separate configuration (or immiscible configuration) like in the picture



On the other hand, suppose making  $AA$  and  $BB$  bonds is very expensive in terms of energy and if it brakes them making  $AB$  bonds is cheaper, then the configuration is assisted to have just  $AB$  bonds like in the picture and is called ordered crystal structure



At any temperature above the absolute, the entropy is always trying to make the system goes to a more random configuration, and It prefers neither of the previous two because them are too ordered from entropy point of view.

The models that will be talk about in this course, are basically models meant to study this kind of phase separation by specific mechanisms known as spinodal decomposition.

Basically, all phase will models, can be taught of as models of built from these 2 basic components: model one which is known as Cahn-Hilliard model which was returned to explain the phase separation behaviour through a specific mechanism and another model which is known as Allen-Cahn model which was returned to describe the ordering behaviour.

### 0.1.1 Proof of regular solution parameter

The total energy of the system is:

$$E = p_{AB}E_{AB} + p_{AA}E_{AA} + p_{BB}E_{BB} \quad (16)$$

Where  $p_{AB}, p_{AA}, p_{BB}$  are the probability (total number of bonds) to find the  $AB, AA, BB$  bonds in the lattice.

The total number of  $A$  bonds is  $N_A\zeta$  and should be equal to:

$$N_A\zeta = p_{AB} + 2p_{AA} \Rightarrow p_{AA} = \frac{N_A\zeta}{2} - \frac{p_{AB}}{2} \quad (17)$$

the same can be done for  $B$

$$N_B\zeta = p_{AB} + 2p_{BB} \Rightarrow p_{BB} = \frac{N_B\zeta}{2} - \frac{p_{AB}}{2} \quad (18)$$

The total energy becomes:

$$\begin{aligned} E &= p_{AB}E_{AB} + \left(\frac{N_A\zeta}{2} - \frac{p_{AB}}{2}\right)E_{AA} + \left(\frac{N_B\zeta}{2} - \frac{p_{AB}}{2}\right)E_{BB} \\ &= p_{AB}\left(E_{AB} - \frac{E_{AA} + E_{BB}}{2}\right) + \frac{N_A\zeta}{2}E_{AA} + \frac{N_B\zeta}{2}E_{BB} \end{aligned} \quad (19)$$

$$\Delta E = E - \frac{N_A\zeta}{2}E_{AA} - \frac{N_B\zeta}{2}E_{BB} = p_{AB}\left(E_{AB} - \frac{E_{AA} + E_{BB}}{2}\right) \quad (20)$$

where the probability that any given pair of site will actually have a bond  $AB$  is:

$$p_{AB} = (X_A X_B + X_B X_A) \frac{N_{Avog} \zeta}{2} = 2X_A X_B \frac{N_{Avog} \zeta}{2} \quad (21)$$

the same can be done for  $AA$  and  $BB$ :

$$p_{AA} = X_A^2 \quad p_{BB} = X_B^2 \quad (22)$$

Finally, the following is obtained:

$$\Delta E = X_A X_B N_{Avog} \zeta \left( E_{AB} - \frac{E_{AA} + E_{BB}}{2} \right) \quad (23)$$

## 0.2 G vs X Diagrams

The plot of the  $\Delta H^{Mix}$  as function of the composition  $X_B$  is a parabola centered at  $X_B = 0.5$  in which is concave for  $\Omega > 0$  and convex for  $\Omega < 0$ .

The plot of the  $T\Delta S^{Mix}$  as function of the composition  $X_B$  is like a parabola centered at  $X_B = 0.5$  and is always convex (negative).

An interesting thing can happen when the temperature is not very high and  $\Omega > 0$ . In this case,  $\Delta G^{Mix}$  can be seen that the entropy term is dominant at the corners of the diagram but then the  $\Delta H^{Mix}$  becomes dominant in the middle of the diagram and the plot is the following (green curve). This kind of system is known as phase separating systems as was discussed previously because  $\Omega > 0$ .

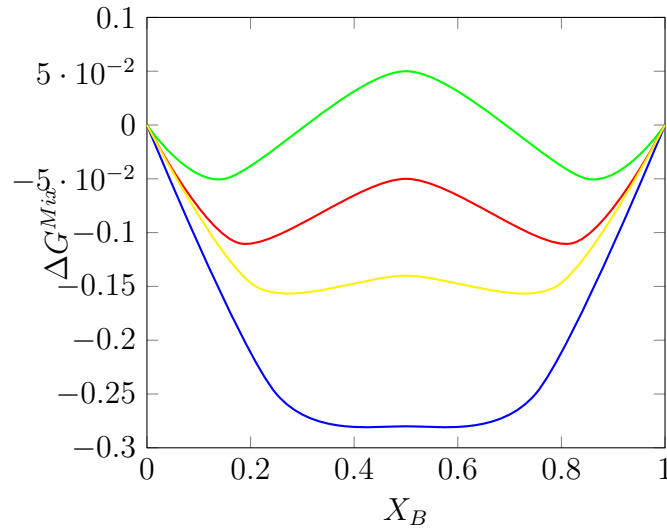


Figure 1: Gibbs free energy of binary mixtures as a function of the composition at constant pressure and temperature. The green curve is at low temperature, instead red, yellow and blue are curves in which the temperature is increasing

### 0.3 Phase Diagrams

If one wants to know the free energy of the mix itself  $G$ , it is calculated in this way:

$$G = X_B G_B + (1 - X_B) G_A + \Omega X_B (1 - X_B) + TR \left[ X_B \ln(X_B) + (1 - X_B) \ln(1 - X_B) \right] \quad (24)$$

The first two terms added are just a straight line and the plot becomes:

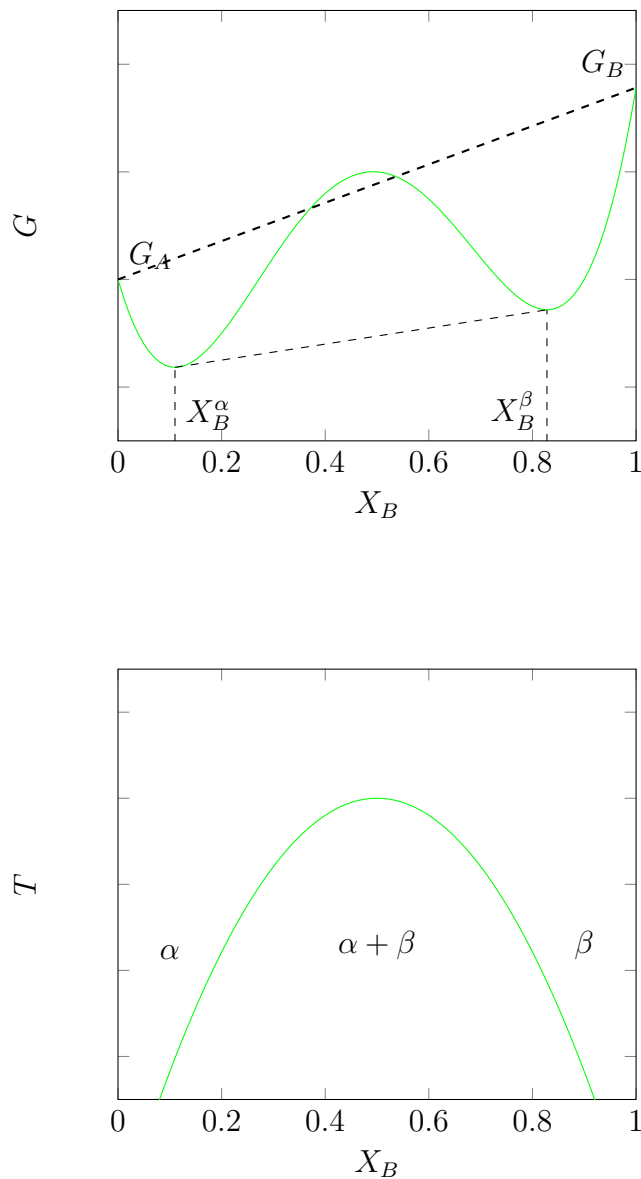


Figure 2: The green curve is for low temperature and the blue curve is for high temperature. The intersection with the left vertical axis is  $G_A$  instead the other one is  $G_B$



These type of curves in the first plot are called composition free energy diagrams.

It is possible to plot what are the phases that would exist in a system at every temperature and such diagrams are called phase diagrams or equilibrium diagrams as shown in the second picture.

The points in which the common tangent touch the free energy curve are called  $X_B^\alpha$  and  $X_B^\beta$ . As can be seen, inside the parabola of the second plot, there is an in-miscible solution composed of  $\alpha + \beta$ . The complete mixing in that region is not possible because the free energy increases.

## 0.4 Chemical Potential

Let's take a system with constant pressure and temperature and let there be some  $N_A$  and  $N_B$  atoms. Suppose to add  $dn_A$  number of atoms to the system, the question is what happen to the total free energy.

The number of atoms of  $A$  added is very small such that  $X_A$  and also  $X_B$  do not change.

This is not the molar free energy and It will be distinguished with an accent on top:

$$dG' = \mu_A dn_A \quad (25)$$

Where  $\mu_A$  is the partial molar free energy of  $A$  in the particular system or also called chemical potential.

$$\mu_A = \left( \frac{\partial G'}{\partial n_A} \right)_{T,p,n_B} \quad (26)$$

Let consider a case in which one mole of atoms is added to the system but keeping the same alloy composition. The chemical potential is not changing and in this case the molar free energy is:

$$dG' = \mu_A dn_A + \mu_B dn_B \quad (27)$$

Now dividing everything by  $n_A + n_B$

$$\frac{dG'}{n_A + n_B} = \mu_A \frac{dn_A}{n_A + n_B} + \mu_B \frac{dn_B}{n_A + n_B} \quad (28)$$

$$dG = \mu_A dX_A + \mu_B dX_B \quad (29)$$

$$\frac{dG}{dX_B} = \mu_A \frac{dX_A}{dX_B} + \mu_B = -\mu_A + \mu_B \quad (30)$$

$$G = \mu_A X_A + \mu_B X_B \quad (31)$$

From here is possible to find:

$$\mu_B = \frac{G - \mu_A X_A}{X_B} \quad (32)$$

and substituting inside (30) is possible to find:

$$\mu_A = G - X_B \frac{dG}{dX_B} \quad (33)$$

Let consider a free energy vs composition diagram as below with the curve in red

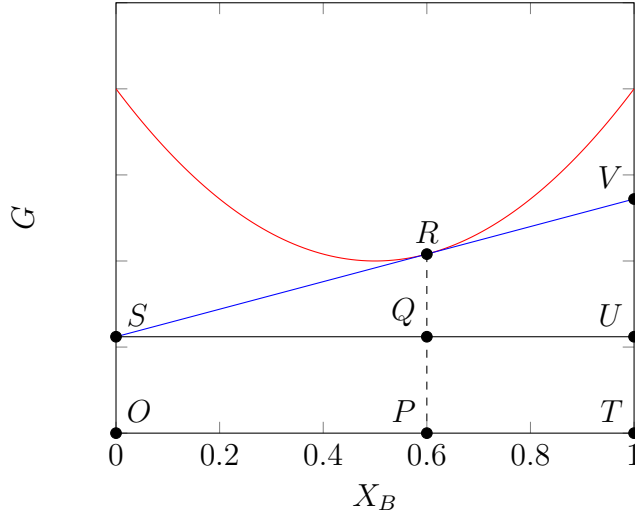


Figure 3

Let's choose a point  $R$  that it is the generic alloy composition on the graph, and send a common tangent to it (blue line) which will intersect the  $G$  axis in two points  $S$  and  $V$ . We had defined  $\mu_A$  in (33) and for this graph becomes:

$$\mu_A = PR - X_B \frac{RQ}{SQ} = PR - X_B \frac{RQ}{X_B} = PR - RQ = PQ = OS \quad (34)$$

Geometrically,  $\mu_A$  is the point in which the common tangent intersects the pure  $A$  axis. From (30) It is possible to calculate  $\mu_B$ :

$$\mu_B = OS + \frac{UV}{US} = OS + \frac{UV}{1} = OS + UV = TV \quad (35)$$

Geometrically,  $\mu_B$  is the point in which the common tangent intersects the pure  $B$  axis.

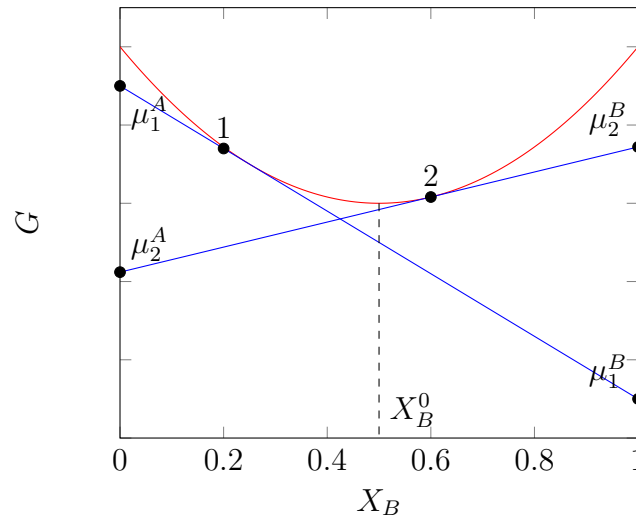
## 0.5 Diffusion and Chemical potential

The equilibrium structure that the system would get, is given by thermodynamics. We are also interested in knowing the kinetics in the sense that how long is it going to take, for the system, to reach the equilibrium.

In all the cases that we are going to discuss, which is mostly solid-solid phase transformations, then it depends on diffusion because diffusion is the one that controls the rates far as the kinetics is concerned.

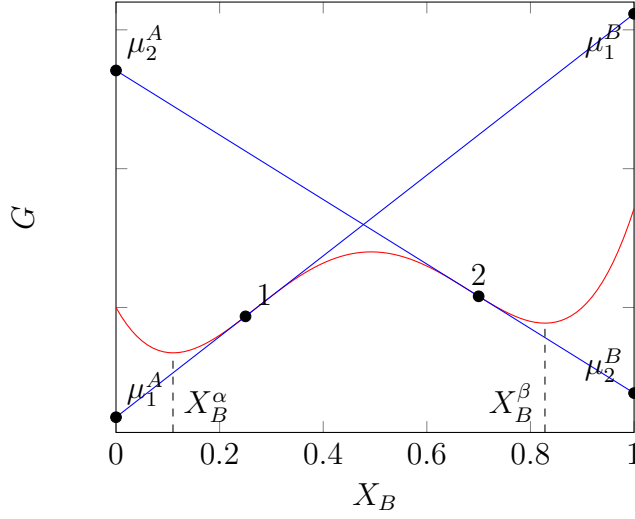
The definition of chemical potential says that is the quantity which decides in which way the atoms will move.

Let's consider two plot of free energy vs composition curves and let two alloys chosen called 1 and 2 at concentration  $X_B^1 = 0.2$  and  $X_B^2 = 0.6$  respectively.



As can be seen, the chemical potential for  $A$  in 1 is higher than in 2 and the chemical potential for  $B$  in 2 is higher than in 1.

If we weld the two alloy composition together and we keep it at high enough temperature where diffusion can take place, since that the chemical potential for  $B$  in 2 is higher than the chemical potential for  $B$  in 1, then the  $B$  atoms are going to go from 2 to 1. Similarly, because the chemical potential for  $A$  in 1 is higher than the chemical potential for  $A$  in 2, the  $A$  atoms are going to go from 1 to 2. At the end, after long time, the over all composition is going to reach the homogeneous composition  $X_B^0$ . Regions rich in  $A$  give out  $A$  atoms to regions poor of  $A$  and the same for  $B$ , so that the overall alloy gets to the same composition.



The chemical potential for  $B$  in 2 is lower than the chemical potential for  $B$  in 1, then the  $B$  atoms are going to go from 1 to 2. Similarly, because the chemical potential for  $A$  in 1 is lower than the chemical potential for  $A$  in 2, the  $A$  atoms are going to go from 2 to 1. At the end, there will get a mechanical mixture with two phases, the  $A$  rich phase  $X_B^\alpha$  and the  $B$  rich phase  $X_B^\beta$ .

## 0.6 Fick's law

The Fick's first law says that the flux of atoms is proportional to the concentration gradients by the diffusivity constant. The atomic fluxing should be in such a way to minimize the concentration gradient, and so there will be a negative sine:

$$\mathbf{J} = -D\nabla C \quad (36)$$

There should be respected also the law of conservation of mass that is the following:

$$\frac{\partial C}{\partial t} = -\nabla \cdot \mathbf{J} \quad (37)$$

Substitution (36) into (37) we get the Fick's seconds law:

$$\frac{\partial C}{\partial t} = D\nabla^2 C \quad (38)$$

This equation describes very well the behavior in which the free energy vs composition curves is that with homogeneous composition at the end of the diffusion but does not work in the case of mechanical mixture behavior but will work only if the diffusivity constant becomes

negative.

There is an explanation of why the diffusivity suddenly changes sign. We know that systems evolve in such a way that the free energies are getting minimized. The free energy minimization is the same thing as chemical potential becoming equal in two systems where atomic fluxes are allowed. The Fick's first law is modified to this one:

$$\mathbf{J} = -M\nabla\mu \quad (39)$$

Where  $M$  is called mobility that is always positive.

## 0.7 Spinoidal decomposition

The following plot is valid if the  $\alpha$  and  $\beta$  have the same crystal structure and the only difference is in the composition and there is a phase separation. Spinoidal line (black dashed curve) is obtained when the second derivative of the free energy with respect to  $X_B$  is equal to 0. This spinodal can be visualized inside the phase diagram and separates the metastable region from the unstable region. Points inside the spinodal are unstable points instead of points outside but, at the same time inside the miscibility gap, are metastable points.

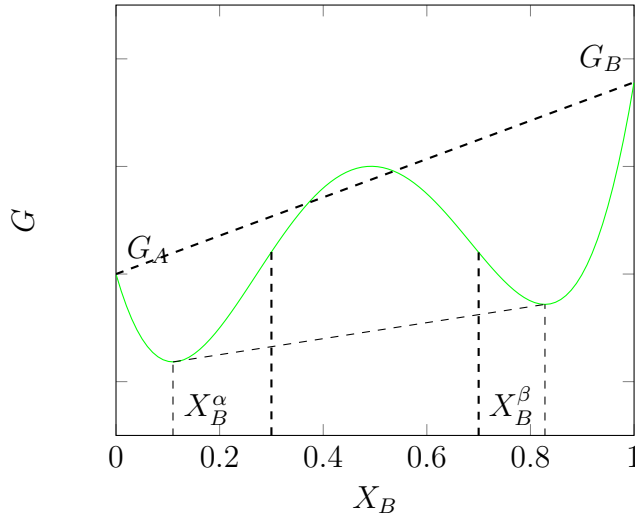


Figure 4

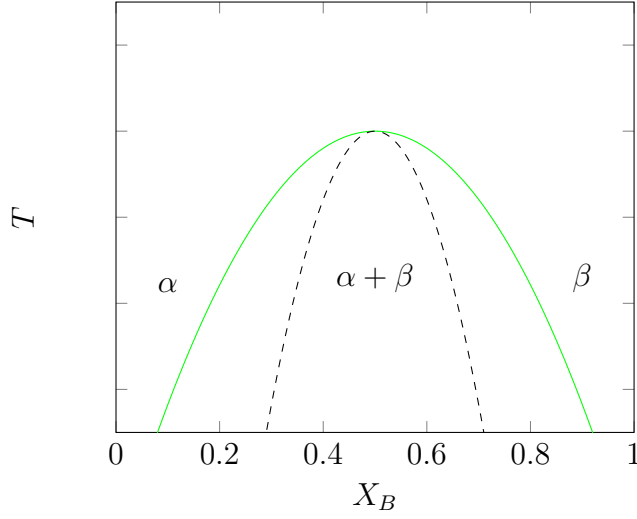


Figure 5

Looking at the free energy vs composition diagram, the stable point is the point in which there is the absolute minimum free energy. The metastable point instead is a stable point but is a relative minimum of free energy. The unstable point is the maximum of the free energy.

Consider the plot of a generic thermodynamic property, that will be identified by  $Y$ , vs composition. Choosing a particular solution (large amount of material) at composition  $X_B^0$  and starting from this one we want to produce a small region which has composition  $X_B'$ . The amount of  $X_B'$  produced is so small that the solution composition remains at  $X_B^0$ . Since that we are dealing with closed systems, from the composition  $X_B^0$  and when we add or remove  $A$  and  $B$  atoms from that composition, we will have changes in the property which are known as partial molar properties associated with this small production.

The partial molar property is given by sending the tangent to the point at  $X_B^0$  composition and intersecting the pure  $A$  and  $B$  axis. Let's call  $\bar{Y}_1(X_B^0)$  the partial molar property at pure  $A$  and  $\bar{Y}_2(X_B^0)$  the partial molar property at pure  $B$ .

The change in property  $Y$  for transferring  $X_B'$  moles of component 2 from material of composition  $X_B^0$  to a material of composition  $X_B'$  is:

$$\Delta Y^a = X_B' \left[ \bar{Y}_2(X_B') - \bar{Y}_2(X_B^0) \right] \quad (40)$$

The change in property  $Y$  for transferring  $(1 - X_B')$  moles of component 1 from material of composition  $X_B^0$  to a material of composition  $X_B'$  is:

$$\Delta Y^b = (1 - X_B') \left[ \bar{Y}_1(X_B') - \bar{Y}_1(X_B^0) \right] \quad (41)$$

The total change in the property associated with producing material of composition  $X_B'$  from

a solution of composition  $X_B^0$  is basically the addition of these two terms:

$$\begin{aligned}\Delta Y &= \Delta Y^a + \Delta Y^b = X'_B \left[ \bar{Y}_2(X'_B) - \bar{Y}_2(X_B^0) \right] + (1 - X'_B) \left[ \bar{Y}_1(X'_B) - \bar{Y}_1(X_B^0) \right] \\ &= X'_B \bar{Y}_2(X'_B) + (1 - X'_B) \bar{Y}_1(X'_B) - X_B^0 \bar{Y}_2(X_B^0) - (1 - X_B^0) \bar{Y}_1(X_B^0) + \\ &\quad + (X_B^0 - X'_B) \left[ \bar{Y}_2(X_B^0) - \bar{Y}_1(X'_B) \right]\end{aligned}\tag{42}$$

$$\Delta Y = Y(c') - Y(c_0) - (X'_B - X_B^0) \left( \frac{dY}{dX_B} \right)_{X_B^0}\tag{43}$$

where  $c = X_B$  is the composition.

Assuming that  $c' - c_0 = \delta c$  (very small), is possible to do a Taylor series expansion to get the property  $Y$  at some composition  $c'$ :

$$Y(c') = Y(c_0) + \delta c Y'(c_0) + \frac{1}{2}(\delta c)^2 Y''(c_0) + \dots\tag{44}$$

$$Y(c') - Y(c_0) - \delta c Y'(c_0) = \frac{1}{2}(\delta c)^2 Y''(c_0) + \dots\tag{45}$$

Comparing (45) and (43) yields:

$$\Delta Y = \frac{1}{2}(\delta c)^2 Y''(c_0) + \dots\tag{46}$$

$$\Delta Y \simeq \frac{1}{2}(\delta c)^2 Y''(c_0) + O(\delta c^3)\tag{47}$$

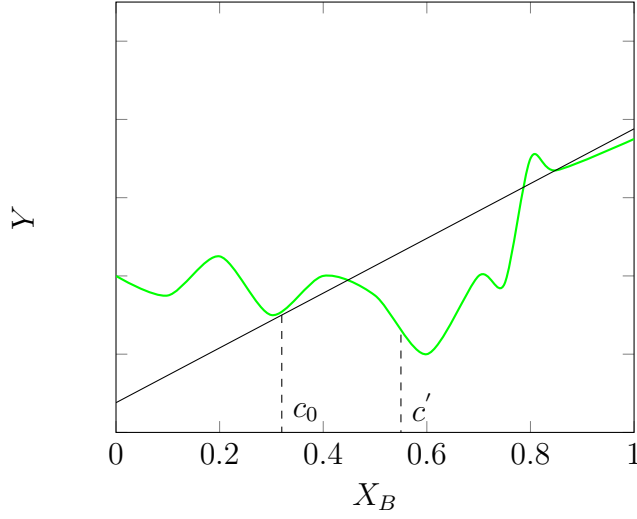
For example, considering the free energy:

$$\Delta G \simeq \frac{1}{2}(\delta c)^2 G''(c_0)\tag{48}$$

The sign of the change in free energy is given by the sign of  $G''(c_0)$ .

If  $G''(c_0) < 0 \Rightarrow \Delta G < 0$  and so the system is unstable because by producing the small amount of second phase which has composition  $c'$ , the system will reduce its free energy and so it is going to spontaneously do that.

If  $G''(c_0) > 0 \Rightarrow \Delta G > 0$  and so the system is metastable because to produce the small amount of second phase, the system must overcome the barrier of free energy.



The vertical distance of  $Y(c')$  from the straight line is  $\Delta Y$ . For all the points below the tangent to  $Y(c_0)$  (straight line),  $\Delta Y < 0$ .

## 0.8 Solution of classical diffusion equation

We want to solve the following differential equation:

$$\frac{\partial c}{\partial t} = D \nabla^2 c \quad (49)$$

In 1-D becomes:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (50)$$

Assuming that the solution of this equation is something of this type:

$$c - c_0 = A(\beta, t) \exp(i\beta x) \quad (51)$$

where  $\beta = \frac{2\pi}{\lambda}$  with  $\lambda$  the wave length and  $A$  is the amplitude of the wave. Substituting the solution inside the differential equation we get:

$$\frac{dA(\beta, t)}{dt} \exp(i\beta x) = -D A(\beta, t) \beta^2 \exp(i\beta x) \quad (52)$$

The two exponential goes away and so we end up with a ordinary differential equation:

$$\frac{dA(\beta, t)}{dt} = -D A(\beta, t) \beta^2 \quad (53)$$

The solution can be achieved by separating the variables:



$$\frac{dA(\beta, t)}{A} = -D\beta^2 dt \quad (54)$$

$$\ln(A) = -D\beta^2 t + k \quad (55)$$

$$A = A_0 \exp(-D\beta^2 t) \quad (56)$$

## 0.9 Diffusivity and Mobility

The flux expression for atoms of component 1 is the following:

$$J_1 = -N_V(1-c)v_1 \frac{\partial \mu_1}{\partial x} \quad (57)$$

where  $N_V$  is the number of atoms per mole,  $(1-c)$  composition of the atoms 1 because  $c$  is the composition of atoms 2,  $v_1$  the velocity of atoms of component 1 under unit potential gradient and  $\mu_1$  is the chemical potential per atom.

The same can be done for the component 2:

$$J_2 = -N_V c v_2 \frac{\partial \mu_2}{\partial x} \quad (58)$$

We know that spontaneously diffusion happens to minimize free energy and the correct quantity which represents the minimization is basically the chemical potential. The right way to representing the atomic flux is to connect them to the chemical potential gradient. We are going to define the flux with respect to a particular frame of reference, a reference plane called Matano interface which is a moving plane defined in such a way the total atomic flux across this plane is zero.

We know that the first Fick's law is written for atoms of type  $B$  and now we want to connect the diffusivity with the mobility that comes from the chemical potential gradient.

The flux of atoms of type 2 with respect to matano interface is the following:

$$\begin{aligned} J &= J_2 - c(J_1 + J_2) = -N_V c v_2 \frac{\partial \mu_2}{\partial x} + c N_V (1-c) v_1 \frac{\partial \mu_1}{\partial x} + c N_V c v_2 \frac{\partial \mu_2}{\partial x} \\ &= -N_V c \left[ v_2 \frac{\partial \mu_2}{\partial x} - c v_2 \frac{\partial \mu_2}{\partial x} - (1-c) v_1 \frac{\partial \mu_1}{\partial x} \right] \\ &= -N_V c (1-c) \left[ v_2 \frac{\partial \mu_2}{\partial x} - v_1 \frac{\partial \mu_1}{\partial x} \right] \\ &= -N_V c (1-c) [(1-c)v_2 + c v_1] \left[ \frac{\partial \mu_2}{\partial x} - \frac{\partial \mu_1}{\partial x} \right] + (v_2 - v_1) \left[ c \frac{\partial \mu_2}{\partial x} + (1-c) \frac{\partial \mu_1}{\partial x} \right] \end{aligned} \quad (59)$$

From the Bibbs-Duhen relationship, the last bracket is equal to 0 because we are at constant pressure and temperature and we left with:

$$J = -N_V M \left[ \frac{\partial \mu_2}{\partial x} - \frac{\partial \mu_1}{\partial x} \right] \quad (60)$$

Where the mobility is defines as:

$$M = c(1 - c) [(1 - c)v_2 + cv_1] \quad (61)$$

We know that:

$$N_V(\mu_2 - \mu_1) = \frac{\partial G}{\partial c} \quad (62)$$

and the flux becomes:

$$J = -M \frac{\partial}{\partial x} \left( \frac{\partial G}{\partial c} \right) = -M \frac{\partial^2 G}{\partial c^2} \frac{\partial c}{\partial x} = -MG'' \frac{\partial c}{\partial x} \quad (63)$$

We know from mass conservation:

$$\frac{\partial c}{\partial t} = -\frac{1}{N_V} \frac{\partial J}{\partial x} \quad (64)$$

and placing (63) into (64) yields:

$$\frac{\partial c}{\partial t} = \frac{1}{N_V} \frac{\partial}{\partial x} \left( MG'' \frac{\partial c}{\partial x} \right) \quad (65)$$

Assuming that  $M$  and  $G''$  constants, then:

$$\frac{\partial c}{\partial t} = \frac{M}{N_V} G'' \frac{\partial^2 c}{\partial x^2} \quad (66)$$

An comparing this equation with the first Fick's law we get:

$$D = \frac{M}{N_V} G'' \quad (67)$$

Spinodal region is the region in which  $G'' < 0$  and since that mobility is always positive, the diffusivity becomes negative.

## 0.10 Failure of classical diffusion equation

We know that

$$A = A_0 \exp\left(-\frac{M}{N_V} G'' \beta^2 t\right) \quad (68)$$

$$A = A_0 \exp(R(\beta)t) \quad (69)$$

where  $R(\beta) = -\frac{M}{N_V} G'' \beta^2$ .

$R(\beta) < 0 \Rightarrow G'' > 0$  and in this case the exponential is decreasing, which means that the amplitude of the wave, for any  $\beta$ , as times goes by is going to decrease and everything becomes homogeneous. This equation tell that there should not be any nucleation, because nucleation meas heterogeneity, there has to be some regions where the composition becomes some particular value. Nucleation happens because compositional fluctuations which are result of thermal fluctuation and this physics is not incorporated in this analysis. The solution of the equation that was derived shows that the solution is going toward homogenization. Different instead is the case of  $R(\beta) > 0 \Rightarrow G'' < 0$  in which any concentration fluctuation is grow for all  $\beta$ .

We are saying that in case of spinodal  $G'' < 0$  ( $\Omega > 0$  that means  $AA, BB$  bonds are preferred over  $AB$  bonds), which means  $R(\beta) > 0$ , which means any wave lenght that we are going to introduce is going to grow.

If suppose we have an homogeneous solution and we introduce a small fluctuation, that is going to grow as function of time. This growth is irrespective of what the  $\beta$  value is. If  $\beta$  becomes larger and larger or the same if  $\lambda$  becomes smaller and smaller, than growth is really fast because it's exponentially growing. The  $\lambda$  cannot be arbitrarily small because we are looking at crystalline structures, so  $A$  and  $B$  atoms are going to be sitting on a lattices anf there is a limit to the wavelength that can be achieved (not smaller than the distance between  $A$  and  $B$  atoms).

Here we have a contradiction with the solution the the classical diffusion equation because because does not explain the phase separation phenomena, but says to have a ordered solution, even if we change the sign of the diffusivity.

## 0.11 Non-classical diffusion equation

The interface related free energy is missing inside the classical diffusion equation. There is a lower limit to how fine can this phase separation be and we know from experimentally that is of the order of  $\lambda = 100\text{\AA}$ .

This equation is known as Cahn-Hilliard eq. :

$$\frac{\partial c}{\partial t} = \frac{M}{N_V} \left[ G'' \frac{\partial^2 c}{\partial x^2} - 2K \frac{\partial^4 c}{\partial x^4} \right] \quad (70)$$

where  $K$  is called gradient energy coefficient.

This equation is derived by incorporating into the thermodynamics, the information of the energy associated with interface and that makes the free energy no longer a function of composition but a functional of composition.

## 0.12 Ideal solution using MATLAB

In all numerical computation, it is always got to have non-denationalized equation. The ideal solution becomes:

$$\frac{\Delta G}{RT} = [X \ln(X) + (1 - X) \ln(1 - X)] \quad (71)$$

Here is shown the MATLAB code:

```
X=0.001:0.001:0.999;
DeltaG=X.*log(X) + (1.-X).*log(1.-X)

plot(X,DeltaG)
xlabel('X')
ylabel('\Delta G/(RT)')

DG300=DeltaG.*300.*8.314
DG600=DeltaG.*600.*8.314

plot(X,DG300, X,DG600)
legend({'T=300 K', 'T=600 K'}, 'Location', 'southwest')
xlabel('X')
ylabel('\Delta G')
```

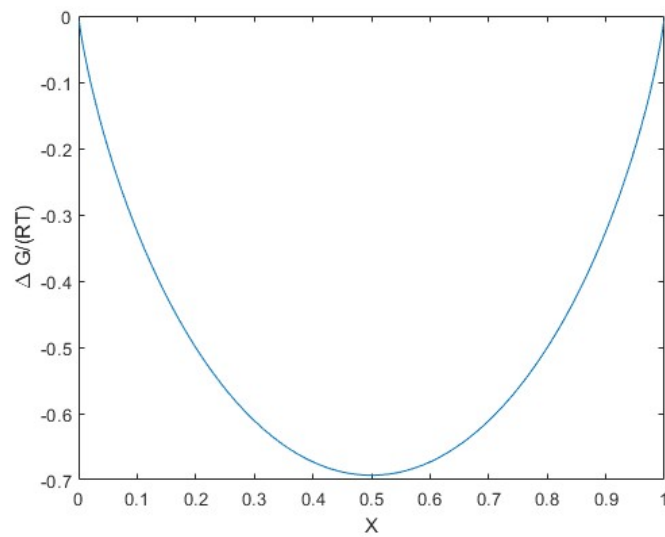


Figure 6: Plot of the dimensionless free energy vs composition

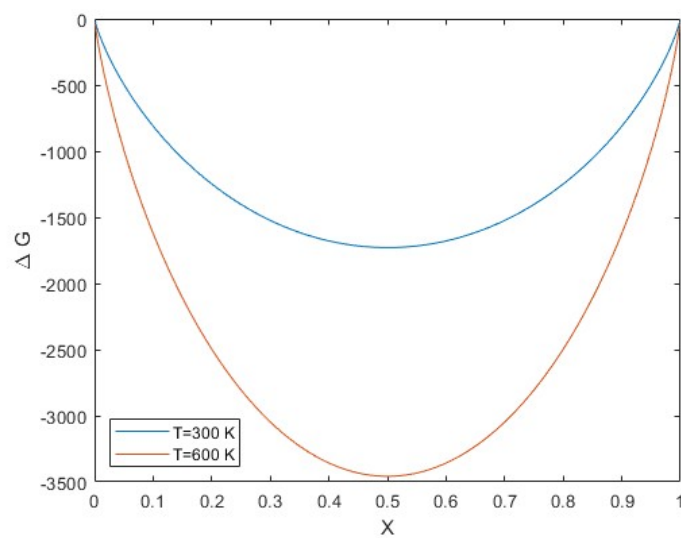


Figure 7: Plot of the free energy vs composition at  $T = 300K$  and  $T = 600K$

### 0.13 Regular solution using MATLAB

The dimensionless Regular solution equation is:

$$\begin{aligned}\frac{\Delta G}{RT} &= \frac{\Omega}{RT}X(1-X) + [X\ln(X) + (1-X)\ln(1-X)] \\ DG &= \alpha X(1-X) + [X\ln(X) + (1-X)\ln(1-X)] = DH + DS\end{aligned}\tag{72}$$

There is a critical point when  $\alpha = 2$  in which the system phase separates because develops two symmetric minima with a maxima in the middle 0.5.

```
function y = G(X,a)
y=a.*X.*(1.-X) + X.*log(X) + (1.-X).*log(1.-X);
end

clear all
clc

hold on;
X=0.001:0.001:0.999;

a=1.0; %inicialization of alpha
for i=1:4
    a=a+1;
    plot(X,G(X,a));
end

hold off
legend show
legend({'\alpha=1','\alpha=2','\alpha=3','\alpha=4'})

xlabel('X')
ylabel('DG')
```

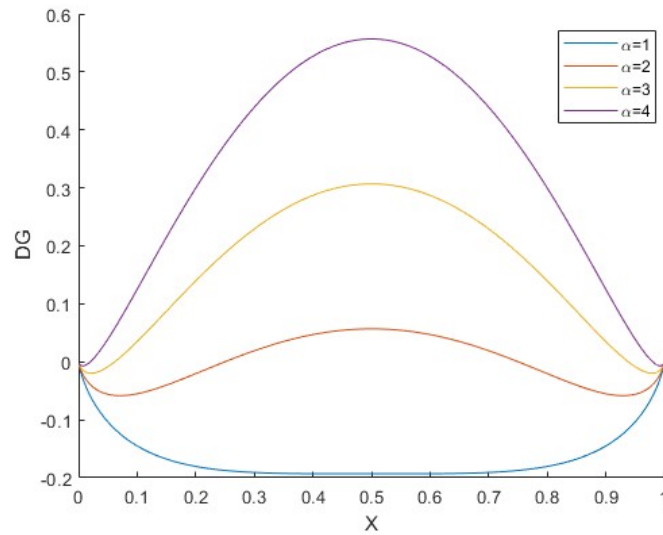


Figure 8: Plot of the dimensionless free energy vs composition at different  $\alpha$

## 0.14 Construction of phase diagram using MATLAB

```
function y = G(a,X)
y=a.*X.*(1.-X) + X.*log(X) + (1.-X).*log(1.-X);
end

clear all
clc

X=0.001:0.001:0.999;

a(1)=2.0; %inizialization of alpha
for i=1:400
    c(i)=fminbnd(@(X) G(a(i),X),0.001,0.499,optimset('TolX',1.e-12));
    d(i)=fminbnd(@(X) G(a(i),X),0.501,0.999,optimset('TolX',1.e-12));
    a(i+1)=a(i)+0.01;
    %plot(X,G(X,a));
end

for i=1:400
    b(i)=a(i);
end
```

```

plot(c,1./b,"red");

hold on;

plot(d,1./b,"red");

xlabel('X')
ylabel('R T/\Omega')

```

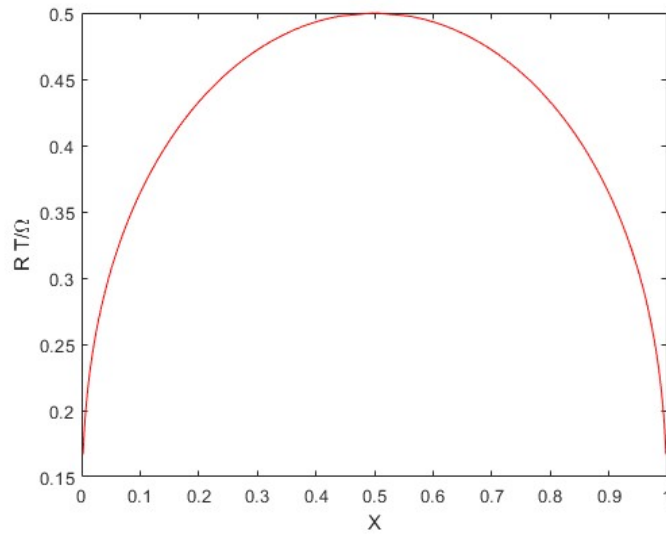


Figure 9: Plot of the phase diagram

### 0.15 Plotting spinoidal line on MATLAB

$$DG' = \alpha - 2\alpha X + \ln\left(\frac{X}{1-X}\right) \quad (73)$$

$$DG'' = -2\alpha + \frac{1}{X} + \frac{1}{1-X} \quad (74)$$

```

function y = G(a,X)
y=a.*X.*(1.-X) + X.*log(X) + (1.-X).*log(1.-X);
end

```



```

function z = Gpp(a,X)
z=-2*a + 1./X + 1./(1.-X);
end

clear all
clc

X=0.001:0.001:0.999;
a(1)=2.0; %inizialization of alpha
for i=1:400
    c(i)=fminbnd(@(X) G(a(i),X),0.001,0.499,optimset('TolX',1.e-12));
    d(i)=fminbnd(@(X) G(a(i),X),0.501,0.999,optimset('TolX',1.e-12));
    a(i+1)=a(i)+0.01;
    %plot(X,G(X,a));
end

for i=1:400
    b(i)=a(i);
end

plot(c,1./b,"red");

hold on;

plot(d,1./b,"red");

xlabel('X')
ylabel('R T/\Omega')

hold on;

X=0.001:0.001:0.999;

a(1)=2.01; %inizialization of alpha

X0=[0.0001;0.5001];
X1=[0.4999;0.9999];

for i=1:400
    f(i)=fzero(@(X) Gpp(a(i),X),X0);

```

```

g(i)=fzero(@(X) Gpp(a(i),X),X1);

a(i+1)=a(i)+0.01;

end

for i=1:400
    b(i)=a(i);
end

plot(f,1./b,"blue");

hold on;

plot(g,1./b,"blue");

xlabel('X')
ylabel('R T/\Omega')

```

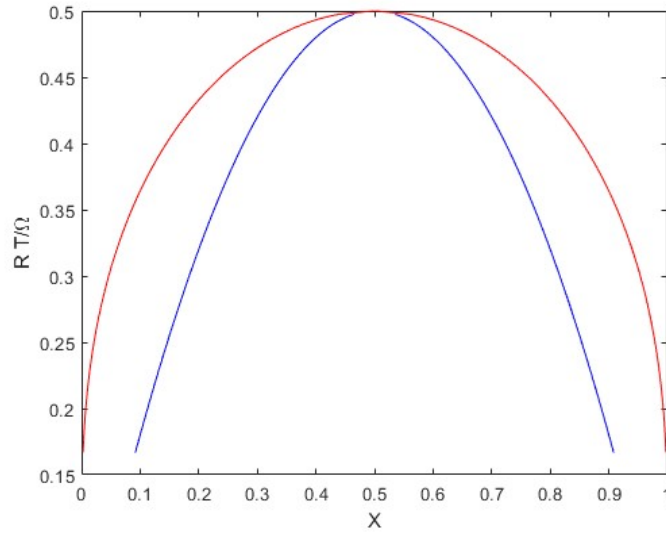


Figure 10: Plot of the phase diagram with spinodal

## 0.16 Non-dimensionalization of diffusion equation

The Fick's seconds law is:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (75)$$

The quantities that must be dimensionalized are  $t = [T]$ ,  $D = [L^2 T^{-1}]$  and  $x = [L]$ . Time and length are the only basic dimensional quantities that we have and so we have to define a characteristic time and a characteristic length.

$\tau$  and  $L_0$  are the characteristic time and length choose. The equation becomes:

$$\frac{1}{\tau} \frac{\partial c}{\partial(t/\tau)} = \frac{D}{L_0^2} \frac{\partial^2 c}{\partial(x/L_0)^2} \quad (76)$$

$$\frac{\partial c}{\partial t^*} = D^* \frac{\partial^2 c}{\partial x^{*2}} \quad (77)$$

where  $D^* = \frac{D\tau}{L_0^2}$ ,  $t^* = \frac{t}{\tau}$  and  $x^* = \frac{x}{L_0}$ .

## 0.17 Diffusion equation: Analytical solution

The following non-dimensional partial differential equation must be solved (for simplicity we remove the asterisk):

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (78)$$

It is important to know the boundary conditions. For example we chose  $c(0, t) = 0$  and  $c(L, t) = 0$ .

The other condition is the initial condition, for example we chose  $c(x, 0) = f(x)$ . The function assumed must respect also the boundary conditions, that is  $f(0) = f(L) = 0$ .

The idea for solving this equation analytically, is to reduce the partial differential equation to some ordinary differential equations.

We assume that the position part and the time part are two different functions, and the solution is a combination of these two functions:

$$c(x, t) = F(x)G(t) \quad (79)$$

and substituting inside the partial differential equation, yields:

$$\frac{\partial(F G)}{\partial t} = D \frac{\partial^2(F G)}{\partial x^2} \quad (80)$$

$$F \frac{\partial G}{\partial t} = D G \frac{\partial^2 F}{\partial x^2} \quad (81)$$

$$\frac{\dot{G}}{D G} = \frac{1}{F} F'' \quad (82)$$

Since that we have that a function of only position (on the right) is equal to a function of only time (on the left), the only possibility is that is equal to a constant that we call  $-p^2$ .

We have obtained two ordinary differential equations:

$$\frac{1}{F}F'' = -p^2 \Rightarrow F'' + p^2F = 0 \quad (83)$$

$$\frac{\dot{G}}{DG} = -p^2 \Rightarrow \dot{G} + p^2DG = 0 \quad (84)$$

The solution of the first ordinary differential equation is assumed to be something like:

$$F(x) = A\cos(px) + B\sin(px) \quad (85)$$

Since that  $c(0, t) = 0 \Rightarrow F(0)G(t) = 0$ , but we cannot assume the  $G(t) = 0$  that is the trivial solution but must be  $F(0) = 0$ . The same for the second boundary condition,  $c(L, t) = 0 \Rightarrow F(L)G(t) = 0$  that must be  $F(L) = 0$ .

$$F(0) = A = 0 \quad (86)$$

$$F(L) = B\sin(pL) = 0 \quad (87)$$

but we do not want the trivial solution  $B = 0$  and so  $\sin(pL) = 0 \Rightarrow pL = n\pi \Rightarrow p = \frac{n\pi}{L}$  with  $n = 1, 2, \dots$

The solution for the position dependent part is:

$$F_n(x) = B_n \sin\left(\frac{n\pi x}{L}\right) \quad n = 1, 2, \dots \quad (88)$$

Substituting the  $p^2$  inside the second ordinary differential equation yields:

$$\dot{G} + \frac{n^2\pi^2x^2}{L^2}DG = 0 \quad (89)$$

Let's call  $\lambda_n = \frac{n^2\pi^2x^2}{L^2}D$  and so

$$\dot{G} + \lambda_n^2 G = 0 \quad (90)$$

where the solution is:

$$G_n(t) = k_n \exp(-\lambda_n^2 t) \quad n = 1, 2, \dots \quad (91)$$

The total solution is:

$$c_n(x, t) = k_n \exp(-\lambda_n^2 t) B_n \sin\left(\frac{n\pi x}{L}\right) \quad (92)$$

$$c_n(x, t) = A_n \exp(-\lambda_n^2 t) \sin\left(\frac{n\pi x}{L}\right) \quad (93)$$

$$c(x, t) = \sum_{n=1}^{\infty} c_n(x, t) = \sum_{n=1}^{\infty} A_n \exp(-\lambda_n^2 t) \sin\left(\frac{n\pi x}{L}\right) \quad (94)$$

$$c(x, 0) = f(x) = \sum_{n=1}^{\infty} c_n(x, 0) = \sum_{n=1}^{\infty} A_n \sin\left(\frac{n\pi x}{L}\right) \quad (95)$$

Multiplying both sides by  $\sin\left(\frac{n\pi x}{L}\right)$  and integrating yields:

$$A_n = \frac{2}{L} \int_0^L f(x) \sin\left(\frac{n\pi x}{L}\right) dx \quad (96)$$

## 0.18 Diffusion equation: Error function solution

In this case, the rod is considered very long (infinitely large).

Let's define a parameter which ranges from 0 to 1:

$$\eta = \frac{c - c_i}{c_0 - c_i} \quad (97)$$

Where  $c_0$  is the concentration at  $x = 0$  and  $c_i$  is the concentration in the rest of the domain. Let's define a characteristic time  $t_0$  and a characteristic length  $L$  and typically correspond to the length of the domain itself.

Let's define  $\frac{x}{L} = \zeta$  and  $\frac{t}{t_0} = \tau$ .

The dimensionless diffusion equation is:

$$\frac{\partial \eta}{\partial \tau} = \frac{D t_0}{L^2} \frac{\partial^2 \eta}{\partial \zeta^2} \quad (98)$$

We want to chose  $t_0$  in such a way the dimensionless diffusivity is 1, and so  $t_0 = \frac{L^2}{D}$ . The equation becomes:

$$\frac{\partial \eta}{\partial \tau} = \frac{\partial^2 \eta}{\partial \zeta^2} \quad (99)$$

with initial conditions that  $\eta = 0$  at  $\tau = 0$  for  $0 < \zeta \leq 1$  and boundary condition  $\eta = 1$  at  $\tau > 0$  for  $\zeta = 0$ . Since that the system is infinite, it is not needed the other boundary condition. We assume that the solution is a function of only:

$$\eta = f\left(\frac{\zeta}{\sqrt{\tau}}\right) = f\left(\frac{x}{\sqrt{D t}}\right) \quad (100)$$

where  $\frac{x}{\sqrt{D t}}$  is a dimensionless quantity and  $x = \sqrt{D t}$  is called diffusion distance (distance over which the diffusion takes place).

Define  $y = \frac{\zeta}{\sqrt{\tau}}$  and  $\frac{d\eta}{dy} = p$ .

$$\frac{\partial \eta}{\partial \tau} = \frac{\partial \eta}{\partial y} \frac{\partial y}{\partial \tau} \quad (101)$$

$$\frac{\partial y}{\partial \tau} = -\frac{1}{2} \frac{\zeta}{\tau \sqrt{\tau}} = -\frac{y}{2\tau} \quad (102)$$

$$\frac{\partial \eta}{\partial \tau} = -\left(\frac{\partial \eta}{\partial y}\right)_\zeta \frac{y}{2\tau} \quad (103)$$

$$\frac{\partial^2 \eta}{\partial \zeta^2} = \frac{\partial}{\partial \zeta} \frac{\partial \eta}{\partial \zeta} = \frac{\partial}{\partial \zeta} \left( \frac{\partial \eta}{\partial y} \frac{\partial y}{\partial \tau} \right) = \frac{\partial}{\partial \zeta} \left( \frac{\partial \eta}{\partial y} \frac{1}{\sqrt{\tau}} \right) = \frac{1}{\sqrt{\tau}} \frac{\partial}{\partial \zeta} \frac{\partial \eta}{\partial y} = \frac{1}{\sqrt{\tau}} \frac{\partial}{\partial y} \frac{\partial \eta}{\partial y} \frac{\partial y}{\partial \zeta} = \frac{1}{\tau} \left( \frac{\partial^2 \eta}{\partial y^2} \right)_{\tau} \quad (104)$$

The equation becomes the following ordinary differential equation:

$$-\frac{d\eta}{dy} \frac{y}{2\tau} = \frac{1}{\tau} \frac{d^2 \eta}{dy^2} \Rightarrow \frac{dp}{dy} = -\frac{y p}{2} \quad (105)$$

Integrating this equation, the solution is:

$$\ln(p) = -\frac{y^2}{4} + \ln(A) \Rightarrow p = A \exp\left(-\frac{y^2}{4}\right) = \frac{d\eta}{dy} \Rightarrow \eta = \int A \exp\left(-\frac{y^2}{4}\right) dy \quad (106)$$

$$c(x, t) = c_i + (c_0 - c_i) \int A \exp\left(-\frac{y^2}{4}\right) dy \quad (107)$$

## 0.19 Finite difference method

Suppose to have the domain and discretize it. Each discrete part is of length  $\Delta x$  and so the number of pieces is  $n = \frac{L}{\Delta x}$ . Also the time should be discretized by  $\Delta t$ .

The first derivative in time at the  $i$ -th position, is approximated as:

$$\left( \frac{\partial c}{\partial t} \right)_i \simeq \frac{c_i^{t+\Delta t} - c_i^t}{\Delta t} \quad (108)$$

The first derivative in position at time  $t$ , using central difference, is approximated as:

$$\frac{\partial c}{\partial x} = \left( \frac{c_{i+1}^t - c_{i-1}^t}{2\Delta x} \right) \quad (109)$$

The second derivative in position at time  $t$  (explicit way) is:

$$\frac{\partial^2 c}{\partial x^2} \simeq \frac{1}{(\Delta x)^2} (c_{i-1}^t + c_{i+1}^t - 2c_i^t) \quad (110)$$

The diffusion equation becomes:

$$\frac{c_i^{t+\Delta t} - c_i^t}{\Delta t} = \frac{D}{(\Delta x)^2} (c_{i-1}^t + c_{i+1}^t - 2c_i^t) \quad (111)$$

At any position  $i$ , the composition at the future time  $\Delta t$  is:

$$c_i^{t+\Delta t} = c_i^t (1 - 2\alpha) + \alpha (c_{i-1}^t + c_{i+1}^t) \quad (112)$$

where  $\alpha = \frac{D \Delta t}{(\Delta x)^2}$ . This type of approach is called explicit. We need two boundary conditions: at  $i = 0$  what is  $c_{i-1}$  and at  $i = n$  what is  $c_{i+1}$ . There are three type of boundary conditions.

The Dirichlet BC's in which at  $i = 0$  and at  $i = n$  we give the composition itself  $c_0$ . Neumann BC's in which at  $i = 0$  and at  $i = n$  we give  $\frac{\partial c}{\partial x} = k$ . Robin BC's which is a linear combination of the previous two. The second derivative in position at time  $t + \Delta t$  (implicit way) is:

$$\frac{\partial^2 c}{\partial x^2} \simeq \frac{1}{(\Delta x)^2} (c_{i-1}^{t+\Delta t} + c_{i+1}^{t+\Delta t} - 2c_i^{t+\Delta t}) \quad (113)$$

and we end by:

$$c_i^{t+\Delta t} (1 + 2\alpha) + \alpha [c_{i-1}^{t+\Delta t} + c_{i+1}^{t+\Delta t}] = c_i^t \quad (114)$$

A shorter way to write the same equation is in matrix form:

$$\begin{bmatrix} 1+2\alpha & -\alpha & 0 & 0 & 0 & \dots & 0 \\ -\alpha & 1+2\alpha & -\alpha & 0 & 0 & \dots & 0 \\ 0 & -\alpha & 1+2\alpha & -\alpha & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \dots & -\alpha & 1+2\alpha \end{bmatrix} \begin{bmatrix} c_1^{t+\Delta t} \\ c_2^{t+\Delta t} \\ c_3^{t+\Delta t} \\ \vdots \\ c_n^{t+\Delta t} \end{bmatrix} = \begin{bmatrix} c_1^t \\ c_2^t \\ c_3^t \\ \vdots \\ c_n^t \end{bmatrix}$$

where the matrix must be inverted and the solution is obtained.

## 0.20 1-D Diffusion equation in MATLAB

Solve the diffusion equation in explicit way in which the diffusion can take place only the axial  $x$  direction. The BC's are:  $c(0, t) = 1$  and no flux at  $x = L$ , which means  $(\frac{\partial c}{\partial x})_{x=L} = 0$ . The initial condition is  $c(x, 0) = 0$  for  $x > 0$ .

We have that from the first BC:

$$c_{i=1}(t) = 1 \quad \forall t \quad (115)$$

and for the second BC:

$$\left( \frac{\partial c}{\partial x} \right)_{i=n} = \left( \frac{c_{n+1} - c_{n-1}}{2\Delta x} \right) = 0 \Rightarrow c_{n+1} = c_{n-1} \quad \forall t \quad (116)$$

from which:

$$c_n^{t+\Delta t} = c_n^t (1 - 2\alpha) + 2\alpha c_{n-1}^t \quad (117)$$

```

clf
clear all

delt = 0.1;
delx = 0.5;
D = 1.0;

alpha = D*delt/(delx*delx);

%define a vector with 101 rows and 1 columns initialized with 0
c = zeros(101,1);

c(1) = 1.0;

plot(c);

ax = gca;

set(ax,"linewidth",2.0);
axis("square");

hold on;

for k=1:20
    for j=1:500
        for i=2:100
            c(i) = c(i)*(1-2*alpha) + alpha*(c(i-1)+c(i+1));
        end

        c(101) = c(i)*(1-2*alpha) + 2*alpha*c(i-1);

    end

    plot(c)
end

```



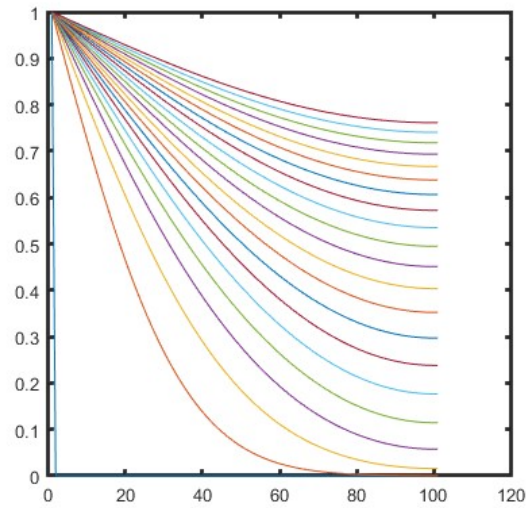


Figure 11

Since that the flux at  $x = L$  is equal to 0, the particles cannot exit and so remains there and the concentration will grow up until it will reach the value 1.

We want to solve the same problem but using the implicit scheme. The first row and column of the matrix and also the first value of the two vectors would not be considered. Since that the flux is 0 at position  $x = L$ , the  $(n, n - 1)$  position of the matrix should be equal to  $-2\alpha$ .

```
clf
clear all

delt = 0.1;
delx = 0.5;
D = 1.0;
N = 101; %dimension of the vectors

alpha = D*delt/(delx*delx);

%define a vector with 101 rows and 1 columns initialized with 0
c = zeros(N,1);

c(1) = 1.0;
for j=1:N
    cold(j,1) = c(j,1);
end

plot(c);
```

```

ax = gca;
set(ax,"linewidth",2.0);
axis("square");

hold on;

A = zeros(N,N);
A(1,1) = 1.0;

for j=2:N
    A(j,j) = 1+2*alpha;
end

for j=2:N-1
    A(j,j-1) = -alpha;
end

A(N,N-1) = -2*alpha;

for j=3:N
    A(j-1,j) = -alpha;
end

for k=1:20
    for j=1:500
        c = inv(A)*cold; %inverting the matrix
        for i=1:N
            cold(i) = c(i);
        end
    end
    plot(c)
end

```

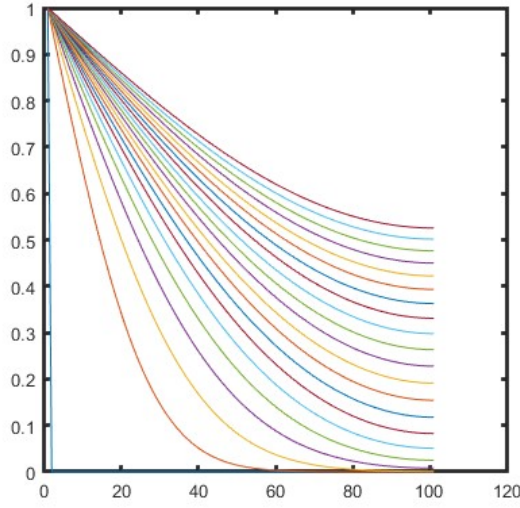


Figure 12

## 0.21 Spectral technique

Another way to reduce a partial differential equation to an ordinary differential equation is the use of Fourier transforms.

For the case of diffusion equation we want to apply the Fourier transform to the function  $c(\mathbf{x}, t)$ . The first Fourier transform is what takes times domain and transform into frequency domain but in this case we are interested. In material science, we are interested to takes from the space to the Fourier space (also called reciprocal space). We are talking about special Fourier transform in which we go from  $\mathbf{x}$  to  $\mathbf{k}$  which is the wave vector space:

$$\tilde{c} = c(\mathbf{k}, t) = A \int_{-\infty}^{\infty} c(\mathbf{x}, t) \exp(i \mathbf{k} \cdot \mathbf{x}) d\mathbf{x} \quad (118)$$

Applying the Fourier transform to the diffusion equation yields:

$$\frac{\partial \tilde{c}}{\partial t} = D \frac{\partial^2 \tilde{c}}{\partial x^2} \Rightarrow \frac{\partial}{\partial t} \int_{-\infty}^{\infty} c(\mathbf{x}, t) \exp(i \mathbf{k} \cdot \mathbf{x}) d\mathbf{x} = D \frac{\partial^2}{\partial x^2} \int_{-\infty}^{\infty} c(\mathbf{x}, t) \exp(i \mathbf{k} \cdot \mathbf{x}) d\mathbf{x} \quad (119)$$

Putting the derivative inside the integral we obtain the ODE:

$$\frac{d\tilde{c}}{dt} = -Dk^2 \tilde{c} \quad (120)$$

The Fast Fourier Transform algorithm (FFT) is a Discrete Fourier Transform (DFT) and is an implicit method (because the right hand side is calculated at the future time). Applying

to the PDE, the equation becomes:

$$\frac{\tilde{c}^{t+\Delta t} - \tilde{c}^t}{\Delta t} = -Dk^2\tilde{c}^{t+\Delta t} \quad (121)$$

$$\tilde{c}^{t+\Delta t} = \frac{\tilde{c}^t}{1 + Dk^2\Delta t} \quad (122)$$

This method is very stable because there are not restrictions on the size of  $\Delta t$ . This method automatically assumes a periodic boundary condition.

```
clf
clear all

N = 128;
D = 1.0;
delt = 1.0;

c = zeros(N,1);
M = 2; %2 waves

for j=1:N
    c(j,1) = 0.5*(1+sin(2*pi*M*j/N));
end

plot(c);
ax = gca;
set(ax,"linewidth",2.0);
axis("square");

hold on;

halfN = N/2;

delk = 2*pi/N;

for k = 1:20

    for m = 1:500
        ctilde = fft(c);

        for i=1:N
```

```

    if(i<halfN) k = i*delk;
    end

    if(i>=halfN) k = (i-N)*delk;
    end

    ctilde(i,1) = ctilde(i,1)/(1+D*k*k*delt);
    end

end
c = real(ifft(ctilde));

plot(c);

end

```

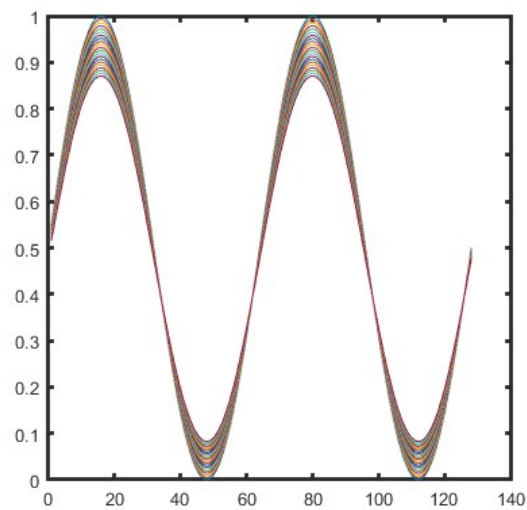


Figure 13